A Study on Skin/Core Optimization in Co-injection Molding of Biopolyester Blends

By

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ABSTRACT

A Study on Skin/Core Optimization in Co-injection Molding of Biopolyester Blends

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This research is a two part study investigating the effectiveness of blending and co-injection molding as solutions for providing performance rounded polymers with increased biocontent. The polymer industry relies heavily on petroleum for the production of its products which in coming years is expected to rise in price and demand for. In an effort to sustain the increasing demands for polymers in the future, effective and viable polymers produced from renewable feed-stocks must be used as a replacement. Currently the opportunity to use bio-based polymers is limited as they often fail to match the properties of their petroleum based counterparts. Introducing bio-based content into industrial productions can be achieved by blending poly(trimethylene terephthalate) containing 37% bio-content with 100% petroleum based poly(butylenes terephthalate). The first part of this study focused on optimizing the processing parameters for injection molding of the PTT/PBT blend through the statistical Taguchi analysis on the mechanical properties. The second part of this study focused on improving the brittleness of the PTT/PBT blend. Co-injection molding technique was used to encase the PTT/PBT blend in a tough outer coating of biodegradable poly(butylenes succinate) and poly(butylenes adiapatate terephthalate). Examination of skin and core blends under both mechanical and imaging analysis show adequate compatibility for future development. These techniques led to the successful increment of bio-content into conventional applications without affecting the cost or performance of pure petroleum based polymers.
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ABBREVIATIONS

( + ) - Indicates a polymer formulation with an additive or fiber. PP + GF is a composite of polypropylene and glass fiber

( / ) – indicates a blend between two polymers. PTT/PBT is a polymer blend between poly(trimethylene terephthalate) and poly(butylene terephthalate)

( | ) – indicates a co-injection formulation where the left side of the line is the skin material, and the right side of the line is the core material. For example (PP/PS|PP+ miscanthus) is a blend of polypropylene and polystyrene as the skin, and a composite of polypropylene and miscanthus as the core.

PTT – poly(trimethylene terephthalate)

PBT – poly(butylene terephthalate)

PP – polypropylene

PS – polystyrene

SEBS – styrene ethylene butadiene styrene

PA 6 – polyamide, nylon 6

ANOVA – analysis of variance

PMMA - poly(methyl methacrylate)

ABS - acrylonitrile butadiene styrene

HDPE – high density polyethylene

DOE – design of experiments

T_m - melting temperature

T_g - glass transition temperature

DSC – differential scanning calorimeter

HDT - heat deflection temperature
1. Introduction

The history of mankind has always been closely identified by the materials of its particular age. The progression of civilizations can be derived entirely from the material resources available used for creating objects and innovations synonymous with the times. A popular argument that has been voiced from many historians including Stephen Sass author of *The Substance of Civilization: Materials and Human History from the Stone Age to the Age of Silicon*,\(^1\) is that from the Paleolithic fashioning of stone chip axes to the immaculately forged steel samurai swords it can be easily argued that materials provide the definition of a civilization through its cultural, political, and economical landscape.\(^1\) The stone age, iron age, copper age, and steel age have all been periods in man's desire to create and produce have been largely influenced by the materials available, even artists have favored materials in various eras, from marble and stone, to precious gems and gold. Fast forward to the current age in which a multitude of highly developed materials have come into the existence of everyday lives. Lightweight aluminum increases the safety of our cars while reducing the weight. High modulus carbon composites create airplanes with tough outer shells, and hockey sticks with superior snapping action. While historical functions of materials are being redefined with the development of specialized nano-materials and self-healing concretes. Of all the materials being used today none have being more defining of the current era than polymers. The definition of polymers is best described by its root words from Greek origins. Polymer is composed of two root words, poly or ‘polus’ meaning many, and mer, or “meros” which means “parts”. Thus the definition of polymer is simple many combinations of single repeating parts or units which form together to produce chains of macromolecules. The overall shape of this macromolecular chain can vary in size depending on the fabrication process for the polymer (known as polymerization) and the type of feed stock used. The variation in feed stocks and polymerization are determinants for the overall properties of the polymer including toughness, viscoelasticity, crystallization, and strength.

Polymers can be broadly separated into two different types, thermoplastic and thermosets.\(^2\) Thermosets are resins which when exposed to an external source of energy like heat or UV radiation, undergo extreme chemical cross linkage which lock the macromolecular chains
together. Under this sequence of cross linkage thermosets cannot be reused as they will burn before returning to a viscous state of flow under the application of heat. Thermoplastics are polymers which can be easily reheated and remolded without incurring a significant level of degradation. Many popular thermoplastics such as polypropylene, polyethylene, poly (vinyl chloride), and polycarbonate are being used to produce cheap mass produced products, of which could be largely linked to the defining ethos of materialism for our time. An unequivocal amount of thermoplastics are currently in demand, in 2010 the world polymer demand was equal to 196 Million metric tons. A recent report states in 2010 roughly 191 million barrels of petroleum were used in the United States to make 90% of all polymer products, while another 412 billion cubic feet of natural gas was used in making the remaining 10%. The onset of a global economy based on consumption of commercial goods has led to serious repercussions in dealing with the cheaply manufactured products, which inevitably end up polluting our oceans, lands, and atmosphere with improper disposal or burning of plastics. As it has been historically argued in the increasing demand for fossil fuels will soon surpass the supply, in what is known as a “peak production”. In a new twist many economists are now predicting that the demand for conventional crude oil will decline while energy sources from plant based sources and unconventional liquids (oil sands, natural gas, and oil shale) will rise in demand due to three major causes. The first being advancements in technology, increased political mandates, and customer demand. It is predicted that the historically low price for oil will experience an exponential growth.

The answer to this foreboding threat incurred by the dependency of fossil fuels is the emergence of what has been dubbed the “third industrial revolution” by the famous author Jeremy Rifkin. A new era of materials and manufacturing have been considered as a substitute for the unsustainable consumption of fossil fuels and, this revolution has also been titled as the bio-economy. The bio-economy seeks to replace the current economy by creating a market for products which are sourced from renewable “green” content. This new economy seeks to maintain the current need for energy, chemicals, and materials by sourcing the environment. A successful establishment of this new bio-economy will address the problems incurring for a more sustainable future. One in which future generations will have no fear in the lack of ability to power the current infrastructure which dominates our economic landscape today. This thesis is a
small attempt to bring the current crude oil dependent polymer industry towards a greener and more sustainable future.

2. Literature Review

2.1 Biopolymers

Biopolymers, bioplastics, and ‘green’ polymers, are all variations of a certain group of polymers which separate themselves from conventional plastics by the sources of their feed stocks. Biopolymers gain their feed stock from renewable resources. These resources can have origins ranging from agricultural, bacterial, food scraps, and even sewage.\(^6\)\(^9\) NatureWorks Poly (lactic acid) has been one of the most successful companies in producing a useful polymer which is cost competitive and produced in large enough quantities for industrial applications. PLA is largely derived from corn at a rate of 140,000 tonne-per-year in a single manufacturing facility.\(^7\) This is however only a small victory, in comparison 8.4 million tons of polypropylene is produced in the U.S. each year. Bioplastics are seeing some of the largest market growth with projections of gaining a world production share of 3% in 2020 compared to the currently estimated 1.5% of the world production share.\(^11\) Biopolymers are currently being explored for their potential to relieve pressures on the environment which is being taxed by the use of petroleum. Oil resources have a particular stigma attached to their sourcing and disposal methods. As explained in the introduction conventionally sourced polymers are produced from carbon sources that have been withheld in the earth’s crust. Uses of these fossil fuels have only two eventual endings. The first is to be disposed of in a landfill, an ending that is particularly bad for the environment due to diminishing land availability, and the pollution of the landscape, particularly in the oceans. The second means of disposal for conventional plastics is through incineration. This method releases carbon dioxide, which is a greenhouse gas responsible for atmospheric warming, in addition to other chemicals such as chlorine and nitric oxide which deplete the ozone layer. The benefit of polymers sourced from renewable resources is that the carbon that is depleted at the end of its life time will have been previously absorbed from the environment during the production or growth of the feed stock. Many biopolymers are also biodegradable. This biodegradability is a
large marketing point of the biopolymer industry. It should be noted that while biopolymers are synonymous with biodegradability, not all biopolymers are biodegradable. Likewise not all biodegradable polymers are biobased. Under this ethos biopolymers have been marketed as environmentally friendly materials. Other reasons for utilizing biopolymers are the eventual exceeding costs of oil and petroleum resources will catapult the use of bio resources as they become more economical to use.

In a better effort to control biomaterial claims the United States government and recently began implementing with the ASTM certification program for USDA voluntary biobased product labeling program, known as the USDA BioPreferred® program. This is a governmental program in which companies can voluntarily submit a product to be audited for meeting specifications for a product with adequate bio content. Upon meeting the required conditions, based on the product, the company can then use the USDA certified biobased product label. Amongst the growing trend in biopolymers there are also a growing number of critics. The arguments against biopolymers are often linked to the food vs. fuel debate, a concern that increasing demand for biofuels or biopolymers will raise the cost for food. In a later chapter of this thesis the possibility of sourcing agricultural feed stocks from wastes produced after harvesting are considered as an answer to concerns with sustainable sourcing of biomaterials. For this thesis we define biopolymers as being either fully or partially sourced from renewable resources.

2.2 Amorphous and Crystalline Polymers

As hinted in the introduction polymers are formed by macromolecular chains. Polymers can be considered to have two states of molecular orientation, amorphous and crystalline. Amorphous phase has no structural or positional order on the molecular scale. Much like the building blocks of proteins with quaternary structure, polymers also undergo molecular folding to produce highly structured, three-dimensional shapes. Polymers can be based on the presence of the two opposing phases present in the polymer, the nomenclature for determining the polymer based on phase is given in terms of total percentage of crystalline phase. Amorphous polymers have 0% degree of crystallization while a crystalline polymer is defined as having greater than 90% degree of crystallinity. Polymers between the two extremes are classified as semicrystalline polymers.
(containing both crystalline and amorphous regions in the same sample). The semicrystalline case can be pictured according to the "fringed micelle" model. Hermann et al.\textsuperscript{12} first conceived this model in 1930 to explain the structure of gelatin, while the model was later more fully expanded by Flory.\textsuperscript{13-15} Below is a two-dimensional representation, which shows the molecular chains entering and removing through crystalline and amorphous phases.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fringed_micelle.png}
\caption{Fringed micelle model displaying a semi crystalline polymer with chains in crystal structures (parallel lines) and amorphous structure (random lines)}
\end{figure}

Transformation from amorphous to crystalline form occurs in the polymer at specific points known as nucleation sites. Nucleation sites are the specific points at which the transformation occurs, usually due to local deformations or stress areas which shock the free amorphous chains into forming a structured crystal. The process from nucleation to growth is a defining moment of the polymer and has a direct involvement in the overall morphology. To consider these morphologies the lamellar model is used. While the micelle model has been presented earlier, it is often less used to describe the crystallization of semi-crystalline materials due to certain limitations is describing morphology phenomenon such as spherulites.\textsuperscript{12} The lamellar model is similar to the micelle model but different in the idea of that there are sheets of folded chains called “lamella” to represent the crystalline form, while the amorphous form is simply called the inter-lamellar region which can link together separate crystal sheets as seen in Figure 2.
A lamellar model that was initially proposed by Flory was the random reentry model.\textsuperscript{14} Growth of the lamella plates have been extensively modeled by many researchers although none so popular as the Lauritzen-Hoffman secondary nucleation theory\textsuperscript{16} and its various alternatives\textsuperscript{17-19} The entirety of the mathematical concepts is beyond the need for this thesis, rather, it should be known that the model extends the explanation of the folded lamella structure as a falling dominos effect in which a single “stem” or fold is straightened out and aligned from the twisted amorphous agglomerate and consequently undergoes a loss in entropy ($\Delta S$). This in turn sets of a stepwise reaction where each linear “stem” produced in the lamellar plane forces two more stems to form in alignment adjacent to the original “stem”.

### 2.3 Growth Rate and Regime Kinetics

With the understanding that lamellar layers are created through the deposition of stems, it can be understood that the rate of crystallization or growth is defined by the rate of which aligned stems
are folded into the crystalline form. This is formally known as the substrate nucleation rate. The growth rate of a crystal is defined by the substrate nucleation rate, and the substrate completion rate, which is an expression of the total length of the polymer chain and the lamellar thickness. For a better understanding consider that the growth of the crystalline structure in a semi-crystalline polymer can be split into three regimes which are largely defined by the temperature at which crystallization is taking place. In regime I the implemented nucleus grows fast enough that no other nucleation sites can take hold. For regime II the rates of nucleation and the growth of the nucleated sites are relatively similar, thus new crystals are being formed along with other crystals being allowed to grow. Regime III is a nucleation dominated process in which nucleation occurs at such a fast rate that previous crystals are unable to propagate. The practical use of crystallization rates in semi-crystalline polymer molding has a large application. Products which undergo regime I crystallization often undergo warping after coming out of the mold due to inter-molecular stress arising from the rigid formations occurring due to high crystalline forms. Alternatively semi-crystalline polymers which experience regime III nucleation will experience post-mold crystallization (post mold shrinkage). This is due to the large amounts of amorphous phase which is often left caught in between the many nucleated crystals. This amorphous phase can sometime spontaneously crystallize. In doing do the more ordered structure reduces its original volume causing the product to shrink and often cause warping from the arising stresses.

### 2.4 Spherulites

Spherulites are three dimensional molecular structures which are arranged in specific orientations. They are easily seen in polarized optical microscopy and often display radial fibrils stemming from a central nucleus. Depending on the crystallization temperature there can be a variety of spherulite morphologies that are producible from a single polymer. Fibrils consist of lamellae radiating outward with the chain folding direction being transverse to the growth direction, as displayed in Figure 3.
Figure 3: Spherulite structure of radiating lamella which varies from amorphous and crystalline structure. Adapted from\textsuperscript{18} with permission of The Royal Society of Chemistry.

On the basis of birefringence, the spherulites are commonly divided into two categories. (a) Negatively birefringent: These are the most prevalent types of spherulites present in polymeric materials and are characterized by their refractive index along the transverse direction being greater than along the growth direction.\textsuperscript{18} This optical character is due to the chain direction on an average being in transverse direction, this being a result of chain disposition within a lamella and lamellar arrangement within a spherulite. (b) Positively birefringent: These types of spherulites are observed when the refractive index along the radial direction exceeds that along the transverse direction.\textsuperscript{18}

It has been traditionally thought that smaller spherulitic sizes result in better impact strength and higher elongation to break. However, experimental studies supporting such conclusions continue
to be scarce. Sharples\textsuperscript{20} observed that the yield stress in nylon 6, 6 samples increased by 30\% as the spherulitic size was decreased from 50 microns to 3 microns. Kargin et al.\textsuperscript{21} demonstrated over a wide range of spherulitic sizes that the mechanical properties deteriorated by 2-3 times whereas the elongation to break decreased from 500\% to 25\% as the spherulitic sizes were increased. Way et al.\textsuperscript{22} showed that the yield stress of isotactic polypropylene goes through a maximum and then drops precipitously as the average spherulitic size was increased.

Semicrystalline polymers are easy to process due to having distinct melting temperatures (T\textsubscript{m}) in which the crystalline phases are relieved and the chain mobility increases allowing the polymer to act as a liquid form which can be used to fill cavities such as molds. Amorphous polymers do not contain a T\textsubscript{m}, but are rather defined by softening as the temperature is raised above the polymers glass transition temperature (T\textsubscript{g}). T\textsubscript{g} is an indication of the temperature in which a polymer begins to become more mobile, or lose its relative brittleness and hardness like glass. All polymers have a T\textsubscript{g} and different polymers are used either above or below the T\textsubscript{g}, which is usually defined by the proximity of the polymers T\textsubscript{g} to room temperature. Hard polymers such as polystyrene polypropylene have and T\textsubscript{g}’s ranging from 360-410 °C.\textsuperscript{23} Softer polymers such as natural rubber have glass transition temperatures below -75 °C.

\textbf{2.5 Injection Molding}

The injection molding process was first initialized in 1872 but gathered increasing popularity during the course of the Second World War through the need for cheap mass produced products.\textsuperscript{24} The injection molding unit has two separate sections, an injection unit and a clamping unit as seen in Figure 4. The injection unit consists of a large screw set that can be modified for specific purposes. The most common process for injection molding requires a screw set, which rotates in a contained space known as a barrel. The barrel has heating elements attached to it which allows for added polymer to reach a molten state. Much of the heat transferred to the polymer is created through shear friction caused by the rotation of the screws. The barrel often consists of various heating zones which can be set to required temperatures. Polymer is supplied through a feed zone, an access hole through the barrel to the screws. The polymer is usually fed into the barrel by a hopper. For large scale injection molding platforms hoppers can become
large storage silos which deliver a continuous feed of polymer to individual molding machines via a vacuum assisted tube. In a process known as metering raw material is introduced into the barrel by the rotation of the screws. Upon entering the barrel the polymer undergoes a rapid exposure to high heat and shear forces which overcome the polymers melting point. Once the polymer has fully melted and enough of it has been fed into the barrel, the injection process begins. The melted polymer is forced out of the nozzle of the barrel via rotation of the screws passing through a runner and fills a mold in the clamping unit.

Figure 4: Schematic of a typical injection molding machine with a clamping mold and single hopper delivering polymers into the feed zone.

When the melt hits the cool walls of the mold it begins to solidify. With enough cooling time the mold is parted and the newly molded part is removed from the mold cavity. There are many different variations and setups that can be obtained from this basic design. Engineers and molding technicians are required to manipulate certain processing parameters that can affect the successful molding of a part. One of the first considerations is shear rate which is given by Equation 1.  

Equation 1.
$SR = \frac{D \times N}{h}$

Where $SR$ is shear rate (sec$^{-1}$), $D$ is screw diameter, $N$ is screw rotation rate, and $h$ is depth of channel. Shear rate is an important property in regards to the degradation of the polymer melt. Since each polymer is different in structure and bonding there is a specific critical shear rate. This critical rate occurs when the polymer has absorbed too much energy and begins to degrade within the barrel. As equation 1 suggests, once a screw size is chosen, screw rotation rate becomes the only variable in the shear rate. However mixing time and temperature of the barrel also take dominating roles in the transfer of energy to the polymer.

Another important aspect of the injection molding machine is the clamping unit. The clamping unit or molding unit has the simple purpose of clamping the two sides of a cavity mold together during the melt transfer process. The ability to hold the two sides of the mold together and resist the forces of the incoming polymer melt is how injection molding machines are classified. As an example a 77 ton injection molding machine indicates that there is 77 tons of clamping force that can be exerted by the machine. However injection molding covers a vast number of products with the smallest machine using a shot weight of 300 mg and large scale applications involving the molding of a sail boat hull with a part weight of 20 kg. One of the largest clamping forces ever produced boasts 100 000 kN produced by a company called Billion.$^{26}$

There are generally two types of molding units, firstly is the toggle type, in which the clamping ability is produced by mechanical leverage which locks the mold into place as seen in Figure (5.a). Secondly, is the hydraulic mold which is simply two sides of the mold held in place by hydraulically powered sliders that open and close the mold plates as seen in Figure (5.b).
These are important variables in the selection of proper molding machines as a set amount of force is required to hold the two mold sides together. Hydraulic clamping forces the mold together with the help of oil compression and can be variably changed as the injection sequence occurs. Hydraulics provide much better control over the clamping pressure compared to the toggle clamp, which only has one setting of clamping power. In addition setting the magnitude of clamping power for a toggle unit is difficult to adjust. Proper setting of clamping power is an important factor in the proper injection molding process. A lack of clamping force will allow the injected polymer to escape from the mold cavity. Providing too much clamping force can potentially damaging the mold. However it is advised that the choice of a proper molding machine should be delegated by the shot size and not the clamping force. Listed below is a table outlining the type of machine to the shot weight.

Figure 5: (a) Mold closing of toggle type clamping unit. (b) Mold closing of hydraulic unit
There is a combination of various parameters which have an effect on the injection molding of polymer parts. Proper analyses on all of these variables are almost impossible to cover and are specific to individual cases. It is however much agreed throughout literature that the main processing parameters can be simplified to those that fall under the domain of temperature, pressure, time, and mold design.

Temperature effects are largely characterized by the melt temperature and mold temperature. Melt temperature is the temperature of the polymer as it is being mixed in the barrel of the injection unit. This temperature is regulated from the heating elements and shear forces created from within the barrel. The engineer must take care in selecting the right melt temperature for the polymer being injected. Polymers become less viscous as they heat up, in general a polymer with low viscosity will become easier to mold resulting in faster molding cycle times, which increases part production. Too high of a temperature can result in polymer degradation along with increased energy costs to heat the barrel. Mold temperature is another aspect of temperature effects on injection molding. Once a polymer melt is injected into the mold it immediately begins to cool down and freeze into a solid shape. Manipulation on the mold surface temperature provides a direct implication on the polymer’s rate of solidification. This is a requisite for large molds that require the polymer melt to cover large areas before solidifying. The cooling rate for a polymer melt has a definitive effect on the final mechanical properties of the molded shape as discussed in the literature review on crystallization kinetics.
Pressure plays an important role in the injection molding process for much of the same reasons as temperature, specifically in relation the rate of cooling and filling of the mold. During the injection process there are two types of pressure. The first pressure effect is initial pressure, which is the force that is used to push the polymer melt through the nozzle and into the mold. In an industrial setting the molding engineer attempts to utilize the highest available pressure from their respected machinery with the lowest injection time to transfer the melt. This ensures the smallest cycle time, which has an economical benefit, and ensures that the melt solidifies evenly, rather than over a prolonged time period due to a lagging supply of material. The second pressure effect is known as holding pressure. This is the pressure used to hold the material in the mold after the injection of the melt is completed and is cooling in the mold. This pressure ensures the polymer will hold the shape of the mold.

Injection time is also a critical parameter for the formation of a properly molded sample. Again in a similar fashion to the temperature, injection speed can play a dominating role in the cooling effects of the polymer. A fast injection time is desired, however, too fast of an injection time will result in a poorly filled mold. A slow injection time will allow the initial melt to solidify before the mold is fully filled, resulting in a non-uniform product. Holding time is the time that the polymer is left to cool in the mold. A proper holding time ensures that the polymer is fully solidified before being released from the mold. Each polymer has a specific temperature at which is can be released without risking deformation to that part. This is known as the heat deflection temperature (HDT). Materials with high HDTs are valued for their ability to decrease the cycle times by requiring less time within the mold to solidify.

Mold design is the last of the parameters and can be subdivided into specific geometries of the mold. Runners are conduits channels used within the mold to transfer the polymer melt evenly across the mold cavities. Longer runner lengths can cause the incoming polymer to cool down, disrupting the flow of the polymer melt. To overcome problems with longer runners hot runners can be used. These are runners with heating elements that allow for a higher temperature inside the runner than the rest of the mold. This in turn reduces the heat loss as the polymer melt is transferred from the injection sprue to the mold cavity.
2.6 Co-Injection Molding

Co-Injection molding found its beginnings from as a solution stemming from a process that was patented by DOW Chemicals in 1962 for structural foam molding.\textsuperscript{28} This method was the initial application of gas assisted injection molding and is now known as the high pressure process. These structural foam parts have good flexural stiffness, low warping, and good weight reduction. However these structural foamed parts lack the finished surface that is seen in conventionally injected parts. In many cases discoloration of the part also occurred. A method was required in which foamed polymers or resins could be utilized without undergoing the detrimental surface properties that came with it. A successful solution to this problem was presented in the form of co-injection molding in which two separate materials are combined to produce a sandwich structure in which the outer layer or skin is an unfoamed product that encapsulates a foamed core thus producing a solid surface that resembles a product with no foamed material at all.\textsuperscript{29, 30}

Co-injection molding or sandwich molding was originally patented in 1972 and 1973 by Garner and Oxley who worked for ICI.\textsuperscript{31-33} As previously explained its original intention was to encapsulate foamed cores with a solid outer layer. Under this process two separate polymer or polymeric materials are injected into the same mold cavity in such a way that one material takes the form of the skin while the other material fills the center of the mold. The ability of co-injection molding to produce layered polymer structures leads largely with the phenomenon of parabolic flow front. Figure 6 displays a parabolic flow front occurring from the advancement of polymer through a rectangular mold cavity.
Figure 6: Parabolic flow front with displayed velocity gradients on mold front and walls. Reprinted from Structural hierarchy developed in co-injection molded polystyrene/polypropylene parts, 40(11), Kadota M, Cakmaka M, Hamada H. Polymer, pg 3119 – 3145, Copyright 1999, with permission from Elsevier.

The parabolic flow front is largely created due to viscosity differences in the polymer from the center of the mold to the mold wall. As the polymer moves farther away from the core of the melt and towards the mold wall it begins to cool down, an effect that occurs due to the temperature differences between the polymer melt and the mold wall. In this case the viscosity is subjected to an increasing viscosity profile as the polymer moves closer to the wall, in response the velocity profile of the polymer decreases towards the mold wall. When this occurs a channel is created for the melt polymer that has yet to cool down from wall contact. This channel continues to deliver the polymer to the front of the polymer flow. The polymer emitted from this channel mimics the flow of a fountain such that the emerging polymer is pushed to the outside by continuous flowing polymer behind it. Co-injection takes advantage of this channel which is created from the initially injected polymer by injecting a second polymer. The second polymer continues the flow and replaces the first polymer in the channel. At this time there is already an establishment of the first polymer which has solidified at the wall. The second polymer travels through the established channel and continues to push material to the flow front as seen in Figure 7. If the proper selection of volume between the two polymers is achieved the second polymer will push the remainder of the first polymer all the way to the end of the mold. In some cases after the second polymer has finished its cycle one last injection of the first material is used to close up the gate end of the sample resulting in a full enclosure on the molded part.
Figure 7: Two phase parabolic flow fronts displaying separate velocity gradients. Reprinted from Structural hierarchy developed in co-injection molded polystyrene/polypropylene parts, 40(11), Kadota M, Cakmaka M, Hamada H. Polymer, pg 3119 – 3145, Copyright 1999, with permission from Elsevier.34

Gomes et al.35 display the different steps of mold filling through the use of pressure sensors embedded into the mold. They describe the process in the following which is visually displayed in Figure 8. Pressure profiles were measured in the mold cavity. (1) Initially the skin melt is injected into the cavity. (2) After a certain amount of skin has been injected the core material replaces the incoming polymer stream. Pressure rises as the skin melt is pushed to the ends of the mold cavity. (3) Eventually the entire mold will be filled while extra pressure is added from the incoming polymer stream to start the compression stage. The entire sample is compressed, polymer melt is packed and pressure rises as maximum pressure is reached. (4) Holding pressure stage begins, and solidification takes place. (5) As the polymer cools it undergoes thermal contraction, which causes the pressure to drop. The extent of this shrinkage is critical to the performance of co-injected samples. If the skin and core materials undergo different extends of crystallization debonding can occur. Post molding shrinkage was seen in co-injected samples of (PP|PS) and (PP + styrene-b-ethylene-co-butylene-b-styrene(SEBS)|PP), this post shrinkage was not seen with the addition of nano-clay in PP.35
Figure 8: Steps for mold filling during co-injection molding

There are a number of different methods used for a successful co-injection process, and is usually varied through the use of specific machines or set ups. The first method is simply labeled as the single channel technique as seen in Figure 9. For this setup two separate injection units are used, they can be placed side to side or horizontally and vertically. Skin material resides in one unit while the core material resides in the other. Looking at Figure 9 we can see that each injection unit is connected to an adjustable valve. This valve switches from skin to core allowing for the sequential injection process to take place. After a specified amount of skin material is first injected into the mold the valve will switch and allow the second unit to inject the core material into the mold, pushing the first material both down and along the mold cavity walls. The use of this machine is often limited to simple shapes as many defects can occur while switching the valve over from unit 1 to unit 2. This switchover often produces defects in the skin as a result. Another major problem related to this set up is the loss of mold cavity pressure which has been researched by Gomes et al. and related to mold shrinkage of the core material. To
solve these problems the Battenfeld co-injection molding process was developed.\textsuperscript{34, 37} In this particular setup each material is delivered to the mold gate via individual channels. This allows for simultaneous injection in a single molding cycle ensuring that a moving flow front is maintained throughout the entire cycle.

![Diagram of single channel co-injection molding setup](image)

*Figure 9: Schematic of single channel co-injection molding setup with two separate injection units*

This method becomes increasingly complex and in turn requires multiple experimental trials which often hinder its use in a fast paced industrial setting. A third set up is the mono-sandwich technique which was produced by Ferromatik Milakron, a German injection molding developer.\textsuperscript{38} In this setup the separate materials are layered into a single injection unit. This is done through the use of a hot runner which transports skin material from a side extruder to the front of the injection unit. When enough skin material is delivered to the front the injection unit begins to push the core material into the mold. The skin material which was delivered to the front is now pushed into the mold from the core material. In doing so ensures that there is no loss of pressure during a switchover period and removes blemishes commonly seen from the switchover time in single channel molding. Co-injection has only recently been gaining more attention. In the past only a handful of companies manufactured co-injection equipment, which created a both a lack of machinery and high initial costs. Under these constraints co-injection molding for cost...
saving purposes has been limited. Currently there is more competition for co-injection machines which is expected to lower the cost of equipment to a more affordable level.\textsuperscript{39}

In an effort to reduce the costs of obtaining a co-injection molding machine Joel Thomson has produced the twin shot, which consists of only a simple modification of the screws used in a typical single injection unit. In this case a solid screw has been placed into a larger hollow screw with the idea that each screw holds a separate polymer. The benefit of this set up is that it requires only one barrel and no elaborate timing mechanism to switch the melts over. It is limited to simple geometries as well only one melt temperature can be used for both the skin and core melt.\textsuperscript{40} Furthermore the lack of similar screw exposures between the polymers inside the screw to outside the screw could result in different shear rates, which could provide some limitations on the polymers available for co-injecting. Other new trends have been presented at conferences and trade shows that focus on improving the use of co-injection machines. In 2012 an innovative tooling design created by Husky\textsuperscript{®} and Mold-Masters focused on producing multi component injections through the use of hot runners with valves that are built in the mold. Hot runners are a unique addition to complex or large mold shapes in which channels with in the mold block that are used to supply material to the mold cavity are heated. Co-injection is achieved by direct sensing of the melt pressure and temperature within the hot runner. New gate (valve) developments for the hot runners has allowed for a plethora of multi component formulations, some gates can store up to 32 recipes and 200 events.\textsuperscript{41} Companies such as Incoe Corp.\textsuperscript{42} have produced hot runner gates which are controlled though hydraulics for fast and accurate gate time closures. This has been marketed as a fast colour changing tool that has “precisely timed gradual pin actuation” which removes any major drops in pressure during changeover periods.\textsuperscript{43}

While the origins of the co-injection process have roots as an effective solution for foam molding, the novel idea of a producing sandwich parts has not been limited to foam enclosures. The sandwich injection molding technique has been fully utilized by designers and engineers since its inoculation to produce parts that would be unachievable coming from a homogeneously single injected part. Proper selection of the skin material can influence the polymers ability to interact with its surroundings. Surface properties such as color, texture, hardness, thermal and
chemical resistance all stem from the skin material. Alternatively the core material often remains hidden while constituting the overall strength of the part, along with being an ingenious way to incorporate recycled, foamed or other less than desirable materials into a final product without limiting the products final look or use. Material combinations that are typical can include soft or unfilled skin/hard or foamed core, for automotive door handles, gear lever and body panels. Unfilled skin/core with conductive filler for electromagnetic shielding in computer housings. Virgin skin/recycled core for garden furniture and storage buckets. Other general combinations include skin/reinforced core, reinforced skin/core, and flexible skin/ stiff core. More recently the co-injection method has been explored as a possibility of increasing total bio-content in a part with non-contemporary bio-based fillers and bio-based polymers.

Understanding how to produce optimal co-injected parts through sandwich molding requires control over the flow fronts of the injected polymers. This can be done through varying skin/core volume fractions, processing conditions, and rheological properties. For a better understanding on how to control the outcomes there has been a significant amount of research performed on varying processing parameters to determine their effect on the final product. Processing parameters that are most commonly studied include, core/skin volume ratio, core/skin melt temperatures, injection speed, and mold temperatures. These processing parameters have been cited as having the most significant effect in controlling the core/skin distribution in a part. The following sections explain the effect that each parameter has on the sandwich molding of a part.

2.7. Co-Injection Parameters

2.7.1. Core/Skin Ratio

The volumetric difference between two polymers produces the largest effect on the sample outcome through variations on the flow front of the injected polymers. An insignificant amount of core will develop a sample that has no core amount with the inability to distribute itself uniformly throughout the mold resulting in an unsatisfactory part. Alternatively when the volume of skin material being injected is too low the core material will push through the skin material
before reaching the end of the mold. The core polymer then begins to dominate the flow front and finish filling the rest of the mold.\textsuperscript{50} In this case the part can no longer be considered a sandwich injected part. Acceptable ratios of core to skin volumes have been found to range from 65\% to 75\% core content in simple axial parts. This number is reduced depending on material compatibility and mold shape complexity.\textsuperscript{51} Gomes et al.\textsuperscript{35} optimized skin core volume ratios with mold flow analysis. Viscosities were obtained from rheology of PP and PS for data entry into the mold flow model. The model was used to test a variation of skin/core volume ratios returning 55\% skin (PS) and 45\% core (PP) as the optimal result.

### 2.7.2. Material Viscosity Ratios

The viscosity ratio between the core and skin material has been widely regarded as a defining trait of successful co-injected parts. To obtain proper mold filling it is recommended that the viscosity of the core material is higher than the skin viscosity. In this case the more viscous core can effectively push the remaining skin material to the end of the mold without breaking through and disrupting the skins encapsulation.\textsuperscript{51-53} Previous studies have shown that the viscosity ratio $\eta_{\text{core}}/\eta_{\text{skin}}$ should be between 0.5 and 5.\textsuperscript{34} Other sources have cited that optimal ratio between viscosities ranges between 0.8 and 1.8.\textsuperscript{49} Young et al.\textsuperscript{50} report that greater skin uniformity occurs when the ratio of zero shear viscosities is between 1.5 and 2.0. The authors Young et al.\textsuperscript{50} compare multiple polymer pairings for co-injection under varying viscosity ratios as they deviate from an optimal value. Viscosity ratios which are lower than the optimal value lead to a breakthrough of core material, whereas a higher viscosity leads to poor mold filling. In the case of the lower ratios the skin material has a higher viscosity than the core. The lower viscosity of the core means the cores ability to evenly translate the pressure exerted from the injection of the core into the skin material is lost. Core material having a lower viscosity will accumulate and break through weaker points of the skins encapsulation, causing the heterogeneity of the layers to be lost and forcing the sandwich injected part to be scrapped. Alternatively a large viscosity ratio is related to the core viscosity being much higher than the skins. Under these circumstances the ability of the skin material to contain the core material as its being injected is lost. Too low of a skin viscosity translates into an inability to contain the core material. Having no ability to resist the pressure from the incoming core polymer melt the majority of the skin material is pushed to the end of the mold, resulting in a non-uniformly distributed part in which most of the core is
situated around the gate and the skin material is at the end furthest away from the gate. Watanbe et al. investigated the dependency of core breakthrough on viscosity. They concluded that when the $\eta_{core}/\eta_{skin}$ ratio was high the core material was able to penetrate further through the sample but breakthrough occurred very close to the gate. When the viscosity ratio was at an intermediate value good material distribution and uniformity occurred.

### 2.7.3. Core/Skin Melt Temperature

Changing the melt or barrel temperatures of the polymers are a secondary effect. This variance has a great deal of effect on the rheological or viscous properties of the materials. The extent of this effect is governed by the temperature sensitivity of the material for both viscosity and thermal expansion. Changing skin, core, or both polymer melt temperatures can be relayed as a change in the $\eta_{core}/\eta_{skin}$ viscosity ratio. As explained before the effectiveness of core temperature on skin/core distribution during the co-injection process is a popular topic. Selden recorded the changes in skin core distribution based on a fractional factorial statistical design with polyamide (PA 6) as the skin, and PBT + 20% glass fiber as the core. An ANOVA of the data returned core temperature as one of three processing parameters that had a significant effect on skin/core distribution with a two levels of variation 240 °C and 255 °C. Selden indicates that increasing core temperature has a positive effect on the skin thickness. For a further indication on the significance of core temperature on the core/skin distribution Selden compares the difference between skin thicknesses of samples at close to the gate and furthest away from the gate. The highest reported core temperature minimizes the difference in skin thickness between the two selected areas relative to the gate distance. This was attributed to a lowering of the core/skin viscosity ratio thus allowing the skin to become more resilient to the pressures applied by the core melt flow. Under these circumstances less skin is displaced near the gate and becomes more evenly distributed as the core melt flow continues its way through the mold cavity. Similar results were obtained by Vangosa with his study on variations of processing parameters on the co-injection of poly(methyl methacrylate) (PMMA) as the skin and acrylonitrile butadiene styrene (ABS) as the core (PMMA|ABS) for a basin shaped cavity. Core temperature along with skin temperature was varied from 220 °C to 240 °C, with a 230 °C center point in the DOE. Like Selden it was reported that increasing the core temperature produces a positive correlation on the skin thickness. Gomes et al. reports the variation of core temperature of co-injected
Variations of the co-injected materials are made by adding compatibilizers to the skin material. In this case Gomes et al.\textsuperscript{35} reports the effects of core melt temperature variation on (PP|PS), (PP|PS+styrene-ethylyne-butadiene-styrene (SEBS)) and (PP|PS+EVA). Melt temperature was varied 210, 230 and 250 °C for each composition. Each temperature produced a viscosity ratio of 1.4, 1.13, and 0.98 respectively, all within suggested range. Ratio of the skin to core area is presented from cross sections taken close to the gate. In this case skin content near the gate is reduced as the core temperature increases. By increasing core temperature (thus decreasing viscosity ratio) the flow front of the core material penetrates further into the mold with a higher velocity. Gomes et al.\textsuperscript{35} continues to comment on this trend indicating that the lower the core/skin ratio, the poorer distribution of the core inside the skin. As in similarly reported literature increasing the core temperature improves upon skin and core uniformity. T. Nagaoka et al.\textsuperscript{54} co-injected (PP|PP) with a focus on varying core melt temperature. The skin PP temperature was kept constant while the core varied 180, 230 and 270 °C. In relation to mechanical testing the melt core temperature had a significant effect on the properties along with injection speed. A higher core melt temperature led to increased tensile strength while the flexural strength decreased as the heat was raised. Watanabe et al.\textsuperscript{53} reported also that by increasing the melt temperature the skins flow front becomes increasingly easier to push, naturally due to the decreased viscosity of the core, which in turn allows for a greater amount of core material to be incorporated into the part. Watanabe et al.\textsuperscript{53} used SEM imaging to show that the orientation of the core skin material becomes increasingly parallel with the flow direction. This fact coupled with the observation that the skin is becoming thinner with increased core melt temperature leads to the conclusion that as the core melt temperature increases the skin flow front experiences a greater push causing a “drawing” effect on the skin thereby providing greater chance for deformations to occur.

**2.7.4. Numerical Interpretation on Viscosity Relation to Temperatures for two Phase Flow**

Young et al.\textsuperscript{50} present a hydrodynamic interpretation of two phase flow in molds using lubrication Hele-Shaw Flow Theory.\textsuperscript{55,57} Under this model the two melt flow phases 1 and 2 are pictured to flow side by side while both filling the mold cavity. Mean velocity of each phase is explained as a Newtownian fluid.
Where $\bar{u}$ is the mean velocity, $H$ is the distance from the center of the fluid layer to the wall such that $2H$ is the thickness of the fluid layer, $\eta$ is the fluid viscosity, and $\nabla p$ is the pressure gradient experienced by the fluid, fluid, being the molten polymer. At the interface the pressures and pressure gradients are equal.

$$p_1 = p_1 \quad \nabla p_1 = \nabla p_2$$

Thus at any interface position,

$$\eta_1 \bar{u}_1 = \eta_2 \bar{u}_2 \quad (4)$$

$$\frac{\bar{u}_2}{\bar{u}_1} = \frac{\eta_1}{\eta_2} \quad (5)$$

From this relation we can conclude that when $\eta_2 > \eta_1$ the more viscous polymer melt (2) will move slower than the less viscous melt (1). If the core melt viscosity ($\eta_2$) becomes increasing more viscous than the skin, $\eta_2 \gg \eta_1$ than the core material will have a low velocity and undergo low core penetration. Young et al.\textsuperscript{51} perform the same relation for non-Newtonian fluids.

$$\bar{u}_1 = -\frac{2n_1}{2n_1 + 1} \frac{(H/2)^{n_1+1}}{k_1^{1/n_1}} |-\nabla p| \frac{1-n_1}{n_1} \nabla p \quad (6)$$

$$\bar{u}_2 = -\frac{2n_2}{2n_2 + 1} \frac{(H/2)^{n_2+1}}{k_2^{1/n_2}} |-\nabla p| \frac{1-n_2}{n_2} \nabla p \quad (7)$$
Again equalizing the pressures and pressure gradients at the interface when $n_1 = n_2$ the non-Newtownian relation becomes

$$\frac{\dot{\gamma}_2}{\dot{\gamma}_1} = \left(\frac{K_1}{K_2}\right)^{\frac{1}{n}} \tag{8}$$

Where $K$ is the flow consistency index (Pa*s$^n$), and relates to viscosity (or stress) at a shear rate of $1s^{-1}$ and $n$ is the flow behavior index which is a measure on the extent of how far removed the fluid is from a state of acting as a Newtonian fluid (dimensionless). This allows us to present the same conclusions drawn from the Newtonian relation. Throne$^{57}$ reports using the co-extrusion relation for sandwich molding for a similar prediction that break through can occur when the skin material has a higher viscosity than the core material. This relation becomes problematic when we consider that the material to first hit the mold wall undergoes the greatest degree of cooling. In this case it will increase its viscosity due to having the largest amount of time in contact with the cool wall. The extent of this cooling is largely dependent on the skin material’s activation energy of viscous flow.$^{50}$ Young et al.$^{50}$ studied the application of PS as a skin material to conclude increasing mold temperature decreased the skins viscosity thus increasing its velocity and minimizing breakout. Likewise when the mold temperature was increased with HDPE as the skin its viscosity became too low and allowed the core PS to break out. Kunyu at al.$^{48}$ performed co-injection of a bio-composite co-injection of (PBS/PBAT|PHBV+ miscanthus) over three different mold temperature 35, 45, and 55 $^{\circ}$C. Lowering the mold to 35 $^{\circ}$C caused the skin to cool too quickly producing core breakthrough. At the high end of the mold temperature spectrum poor material uniformity was present. Increased mold temperature decreased the skins viscosity too much allowing the skin to be swept away by the shear forces of the income core melt flow. The researchers reported an optimal value of 45 $^{\circ}$C for producing samples with minimal defects in material uniformity. The effective temperature gradient between the skin and core layers has a clear impact on the material distribution and uniformity and thus the mechanical properties of the final part.$^{55}$
2.7.5. Mold Temperature

In a similar account on the significance of melt temperatures Young et al.\textsuperscript{50} reported that variances amongst mold temperatures can also have an important role on the core/skin distribution of a co-injected part. Young et al.\textsuperscript{50} molded co-injected samples in a mold type developed by Dee\textsuperscript{5}, White\textsuperscript{57}, and Oda et al.\textsuperscript{58} in which two aluminum clamping blocks with thick glass windows (1/2x2x4\textquotedbl") and an internal plate of various thickness and shapes was used, they reported variations of mold temperature at 120, 150 and 180 °C. The effect of this change is displayed with the co-injection (PS|HDPE). When PS was injected first, increasing the mold temperature led to reduced core penetration. Oppositely when HDPE was injected first, increasing mold temperature led to core breakout. This information is a key understanding that the effect of mold temperature is dependent on the materials used in conjunction. Young et al.\textsuperscript{50} performed the injection process with two different machines. Firstly a ¾ inch Barbender screw extruder and ram injection molding machine for separate delivery of melt into the mold. Secondly was a mono-injection method with polymers layered in the barrel of an Instron capillary rheometer for sequential injection. They report that the use of these machines is unable to replicate the shear forces that would be produced from larger industrial machines. With this in mind they report the effect of viscous dissipation rates. Viscous dissipation is the conversion of kinetic energy (fluid flowing) to internal energy (heating up the fluid) due to viscosity.\textsuperscript{59} Young et al.\textsuperscript{50} report the following equations in reference to viscous dissipation $\varphi$ where $\eta$ is the fluid viscosity, $\gamma$ is the shear rate, $x$ is the direction of flow and $y$ is the direction of shear.\textsuperscript{50}

\begin{equation}
\varphi = \eta \gamma^2 = \frac{\sigma_{xy}^2}{\eta}
\end{equation}

While the adiabatic rate of heat transfer is

\begin{equation}
\rho c \Delta T_{adiabatic} = \frac{(\sigma_{xy})^2_w}{\eta} \left( \frac{\gamma}{H} \right)^2 t_{res}
\end{equation}
Where $\rho$ is fluid density, $c$ is specific heat capacity, $\Delta T_{\text{adiabatic}}$ is the temperature change within fluid as an adiabatic process, $\eta$ is the fluid(or polymer) viscosity, $\sigma$ is stress, $x$ is stress in the direction of flow, $y$ is stress in the direction of shear, $H$ is the characteristic length in direction of velocity gradient, and $t_{\text{ref}}$ is the reference temperature. These equations state that there are different effects of the viscous dissipation depending on the viscosity of the melt and the temperature gradient that it experiences in a specified xy plane. Under these equations low viscosity provides an understanding on the effect of heat dissipation on skin/core distribution, specifically on the contact between the skin and cold mold wall.

With the above equations in mind it is beneficial to view the discussion from Young et al.\textsuperscript{50} on viscous dissipation heating as a predominate effect on the distribution of materials, especially near the mold wall. If there is a large temperature difference, such as the melt polymer in contact with the cold mold wall, there will be a larger viscosity gradient. Heat generated from the melt will be maintained in the core and viscosity differences minimized. Should the lower viscosity material become the skin material and undergo a large temperature gradient from contact with the mold wall it will decrease its temperature past that of the core melt and the viscosity difference will become larger. Thus controlling the temperature difference between the skin melt and mold wall can have a significant effect on the core/skin distribution.

\textbf{2.7.6. Injection Speed}

Having briefly discussed the possibility of injection speed to switch the modes of heat transfer during co-injection based on shear and injection force rates we shall consider studies in which injection speed is sufficiently high enough to produce shear forces. During the injection of the first material (skin injection) velocity has an indirect effect on the skins viscosity due to its ability to control the solidification of the skin as it comes into contact with the cold mold wall. A high injection velocity gives the skin less time to solidify against the mold wall, meaning more of the skin melt is pushed towards the end of the mold cavity during the second injection cycle.\textsuperscript{60} In his design of experiments (DOE) study on (PA 6|PBT + 20% Glass Fiber) Selden\textsuperscript{49} indicates that injection velocity has a significant effect on variations of skin/core distribution. Increasing injection speed resulted in a 13% thicker skin at the middle of the mold, with an increase in the difference of skin thicknesses between the end of the mold and the beginning of the mold.
Obtaining an optimal distribution of skin material through the entire length of the mold required a lower injection speed. In this case it can be assumed that when comparing to an optimal injection speed an increased injection speed will continue to force more skin to the end of the mold, while too slow of an injection speed will ensure all of the skin solidifies close to the gate, forcing the core to fill the rest of the mold. In a study of (PP|PP) T. Nagaoka et al.\textsuperscript{55} varied injection speeds and determined that the significance of injection speed is dependent on the skin/core material combination, additionally, injection speed provided a much greater effect in sequential injection process over a single injection sandwich process (layered, mono-injection). This is likely due to the switch over period that occurs during sequential sandwich molding.\textsuperscript{55} Increasing the injection speed of sequentially injected (PP|PP) increased the ratio of core area. Watanabe et al.\textsuperscript{52} investigated variations of injection speed on both skin and core materials. The authors report that core material injection speed affected the core penetration length while skin injection speed had no effect.

### 2.7.7. Interactions of Parameters

Having discussed the wide variety of effects that occur while changing processing parameters for co-injection, one can become easily overwhelmed. Not only does each parameter have a considerable effect on the physical process of skin/core distribution but they fail to maintain independence from the other parameters. For example increasing the mold temperature ensures that heat dissipation in minimized as the temperature and viscosity gradients between the cold mold wall and the first material is reduced. Likewise an increase in the injection speed will reduce the filling time, also minimizing the heat dissipation and ensuring that more skin material travels to the end of the mold cavity. By changing both of these parameters one could consider the potential for a “super effect” occurring based on the heat dissipation from the skin to the mold. T. Nagaoka et al.\textsuperscript{54} report an interesting interaction between injection speed and core melt temperature on core area ratio of co-injected (PP|PP) The effect of core temperature on the core cross sectional area was limited by the injection speed. At low speeds there was a slight increase in the core area as the melt shifted from 180 °C to 230 °C, but was reduced at 270 °C, while at high injection speeds the cross sectional area was decreased going from 180 to 230 °C, and increased at 270 °C. In the same paper Nagaoka et al.\textsuperscript{54} indicate that varying mold temperature also produces different effects in combination with varying core melt temperature. Such
troubling interactions are endless and without proper consideration could render the understanding of two materials under co-injection impossible.

2.7.8. Effects of Mold Type

A large determinant of the skin/core vol. ratio is the mold geometry. Much of the reported literature for experimental co-injection trials is done on a simple rectangular mold with either a center plate gate\(^3\) or a lateral gate\(^4\) while even fewer papers report co-injection results with complex shapes.\(^5\) This research reports co-injection data from samples molded in a complex three pronged geometry as seen in Figure 10

![Figure 10: Three pronged mold design used in the co-injection study](image)

For this reason there is an inability to fully encapsulate all three of the sample shapes. By focusing on fully encapsulating the tensile bar the flexural, and impact bars are left unfilled by the core, alternatively, by allowing the core to fully penetrate the flexural and impact samples the tensile bar experienced extensive core breakthrough. This problem was also experienced by Kunyu et al.\(^4\) Due to the nature of this research the skin/core ratio was chosen to allow for a full
usage of all the samples. This was done by allowing the tensile sample to experience a restricted amount of core break, such that it did not extend into the narrow section of the sample. By ensuring that the narrow section was fully encapsulated it could thus be assumed that the area under testing would be providing a proper representation of the tensile effects. Watanabe et al. recorded the flow behavior of the core melt and occurrence of the breakthrough phenomenon in sandwich injection as influenced by mold cavity thickness. It was discovered that by increasing the thickness of the mold cavity the occurrence of breakthrough was reduced while the core penetration length increased.

2.7.9. Polymer to Polymer Bonding / Adhesion

Three common problems that molders encounter while trying to achieve high quality parts include incomplete filling, breakthrough of one or more components, and insufficient chemical or mechanical bonding. As previously discussed, filling and breakthrough of the two phases is largely dictated by processing conditions such as melt temperatures and injection speed. Some of the common parameters related to detrimental bonding are time and temperature. Specifically that the timing of the material injections and the temperature of the first material as it joins together with the second material. If the first material undergoes to much cooling as it comes into contact with the mold and also the core material the bonding interaction suffers. Alternatively the skin material must have underwent some degree of cooling before coming into contact with the core material or it will become too easily displaced under the second flow front. Timing can affect bonding, such that it is a secondary factor in the cooling of the skin material. If the second material is injected to soon, the skin material will have a low viscosity and become easily compressed allowing the second material to encase over it.

Before processing conditions are applied a proper material selection must be performed to ensure the end product has proper adhesion between the skin and core layers. Additives, fibers, fillers, and pigments all have an effect on the adhesive ability of polymers. Fibers in the skin material have been known to induce mechanical interlocking with the second material. While fillers that hold lots of moisture can often be detrimental to the interfacial bonding. To avoid these problems hydrophilic materials should be adequately dried before processing.
2.8. Statistical Optimization

Much of the optimization techniques used for polymer processing are variations of statistical optimization methods. Since there are many different types of processing parameters such as melt temperature, mold temperature, injection speed, and so on changing the levels of these parameters can often result in hundreds and thousands of different possible combinations of processing values. Statistical methods are utilized to reduce the total number of experiments in such a way that the use of statistical analysis can extract all the required information from overlapping interactions of the processing parameters. The use of statistical methods is heavily used in the polymer industry and research for these reasons. This thesis utilizes two major statistical methods for optimization and mapping of processing effects. These two methods are classified as the factorial analysis and Taguchi statistical analysis. Both methods are dependent on creating a respective design of experiments. The design of experiments is an underlying experimental design step in all research programs requiring.

Creating the design of experiments (DOE) is often a meticulous process, text books provide basic DOEs but any modifications and customizing entails a proper understanding of the statistical process. This however, can be overcome by the use of certain computer software. Designing a proper DOE will ensure that each experiment has a purpose in our overall understanding of the research topic. To do this a required output of the statistical design must be indicated. In most cases the output is a quantitative response which is recorded as a result of a particular experiment.

When deciding upon the proper output variables, factors, and levels for producing an effective DOE the researcher should base their values on previous findings or understandings of the process. In doing so the experimenter negates the potential risk of producing experiments which produce poor unusable results, ranges that are outside of the equipments ability, or even damaging the equipment. If no attention is paid beforehand the research might end up with experiments that are unreasonable, dangerous, which would be removed from the statistical design. 63
2.8.1. Factorial and Fractional Factorial Designs

Factorial and fractional factorial designs are possibly the more popular method and require research on two or more independent variables. The benefit of a factorial design is its ability to study varied factors simultaneously instead of one at a time. In this way factorial designs can comment on the interaction effect that occurs between two or more variables. Interaction effects arise when a variable is seen to change under the effect of varying another variable, as previously discussed in the co-injection discussion. To recap it is possible that raising the temperature of a polymer melt will vary the effect that injection speed has on the final part. Such that higher melt temperatures lower the viscosity of the polymer and thus with increasing injection speed violent turbulent flow could occur when at lower temperatures the turbulence is not as profound during mold filling. In this situation it can be said that there is an interaction effect between the melt temperature and injection speed. Factorial analysis allows the researcher to test if these interactions are actually occurring.

Fractional factorial designs differ from complete factorial designs in such that they reduce the total required experiments which are required to gather a proper statistical understanding of the main variable effects and their interactions. Oppositely full factorial designs produce studies with maximum precision due to all possible combinations of the levels being tested. This however can become cumbersome and costly when the total number of runs becomes too large. In this case it becomes more efficient to use a fractional factorial design. As an example consider a $2^5$ fractional factorial design ($2^5$ reads as five variables or processing parameters each with two levels, for a total of 32 possible combinations). Under the computer software the user can be prompted to opt for the $1/2$ factorial design in which the required number of experiments drops to 16. A $1/2$ factorial $2^5$ study can estimate the impact of all main effects and two-factor interactions, under the assumption that interactions that contain three or more factors are insignificant. This particular design would be described as having a resolution V. The larger the number of primary variables, the greater is the degree of fractionation that is possible. There are 6 possible resolutions varying from I to VI were I is in effective experiment that cannot distinguish the difference between levels of one factor, to VI Which can estimate the main effects of variables with up to four levels of interactions between main effects. The most frequently used fractional factorials are for situations in which all variable are at two conditions (or levels).
2.8.2. The Taguchi Method

Genichi Taguchi produced his optimizing methods while working for a phone company in Japan. His method has since then been considered an important part of experimentation for industrial product design, development, and evaluation. The Taguchi method promotes running low-resolution, minimal run orthogonal arrays. These orthogonal arrays along with Taguchi analysis are a family of experimental designs derived from standard fractional factorial plans. The purpose of the Taguchi method is greatly used to identify process conditions which produce the most consistent outputs, or those having the greatest ability to resist variability in the processing due to noise from processing parameters, environmental noise, and conditions in which the product is to be used. Taguchi begins to separate from the factorial methods by focusing on controlling variability in the noise through a proper selection of primary variables. The control of this noise is done with ‘blocking’ in the experimental design. Blocking is a method in which certain experiments are grouped together due to a similarity compared amongst each other to reduce variability in the experimental design. Standard blocking techniques assume that there are no interactions between the primary variables and the noise variables, and thus cannot address the reduction of noise variation through controlling the primary variables. Taguchi methods main focus is blocking primary and noise variables to define the lowest amount of noise in a process. However, other methods which are utilized in this research, are also performed by the Taguchi Method. In this research we use Taguchi’s method of combining the mean output (impact strength) along with the variability of the impact strength (standard deviation) into one response variable known as the “signal to noise” variable. This signal to noise ratio can be modified to indicate which processing variables give a “maximum is best”, “closest to target is best”, or “smallest is best” output.

2.9 Problem Statement

The current industry of conventional plastics or polymers which are derived entirely from petroleum feedstock is an extensive and ever growing industry. Problems with this industry have arisen during future outlooks which deem it as non-sustainable. In an effort to deviate from this trend bioplastics have been gathering increased interest. Unfortunately, the widespread use of biopolymers has been hindered by either costs or inability to match current petroleum based
polymers. This research aims at increasing the bio-content used in industry by showcasing possible methods of optimized injection molding of polymer blends and the co-injection of those blends. The first blend to be optimized through a Taguchi method is poly(trimethylene terephthalate) and poly(butylene terephthalate), (PTT/PBT 70/30 wt.%). PTT is partially biobased polymer which is similar to PBT but is more costly. Blending will reduce costs while incorporating a level of bio content. The co-injection of the PTT/PBT blend with another blend of poly(butylene succinate) and poly(butylene adiapatate-co-terephthalate) (PBS/PBAT 60/40 wt.%) address the concept of using advanced injection molding techniques to utilize biocontent.

2.10 Objectives and Hypotheses

In an effort to reduce the industries dependency on petroleum the main theme of this research revolves around increasing biocontent in polymers through the manipulation of molding conditions and selection of materials. Optimization of the molding conditions and material selections are produced by statistical methods. The aforementioned techniques are to be used in optimizing a blend of partially bio-based poly(trimethylene – terephthalate) (PTT) with fully petro based poly(butylenes – terephthalate) to improve biobased content and maintain the highest mechanical properties of the blend. Optimization of the blend will be evaluated based on mechanical, thermal, and morphological properties. The final outcome of this blend is used in the advanced method of co-injection molding to overcome the inherent brittleness of the aliphatic polyester blend.

2.9.1 Objective 1

The first objective of this research is to research the blending ability between PTT which is partially bio-based but more expensive than PBT, which is fully petroleum based and used extensively in automotive and electronic applications. An effort will be made to obtain the best available processing conditions that improve upon the impact strength of the blend, which is a poor characteristic of both pure polymers. This includes the utilization of the Taguchi method for the optimization of the processing parameters. Similar polyesters have been previously cited as acting as miscible polymers when in reality they are only intermixed on a fine scale, which
allows the blend to act as a single polymer. Taguchi methods have been extensively used for optimization in the polymer industry.

2.9.2 Objective 2

To improve the low impact strength of the PTT/PBT blends research on the co-injection process will attempt to encase this brittle blend with a tough outer layer of biodegradable PBS/PBAT. Proper adhesion between the two blends can achieve good co-injection compatibility which will transfer the key characteristic properties of each blend into one uniformly acting polymer. Factorial analysis will be used in an effort to map the relations between the co-injected properties and the processing conditions. It is expected that if the proper compatibility is achieved the impact strength will increase compared to pure PTT/PBT while the flexural and tensile strengths will increase in relation to the PBS/PBAT values, and proper co-injection will be achieved from the information gathered from the fractional factorial analysis.
2.11 References


[38] Jaroschek C. "Lower production costs by multicomponent injection moulding techniques", Kaut. Gummi Kunststoffe 1994; 47: 672


[56] Richardson S. Hele Shaw flows with a free boundary produced by the injection of fluid into a narrow channel. J Fluid Mech 1972; 56


Note: The following chapters 3 and 4 are divided into two manuscripts both of which revolve around maximizing the use of bio-content through the optimization of injection molding processes. This is a direct effort to show that there are simple solutions to improving bio-materials which occur through proper diligence of the molding engineer.

3. Manuscript - 1

The following paper is a fully published article in the Journal of International Polymer Processing under the publisher Hanser. With their kind permission this article appears in this work unedited from the original report. In this chapter the feasibility of blending Poly (Butylene Terephthalate) with Poly (trimethylene terephthalate) is explored. This paper provides important information regarding the ability to blend two materials together by only improving molding conditions alone. Furthermore it provides the groundwork and inspiration for the second part of this thesis.

**Use of the Taguchi Method for Optimization of Poly (Butylene Terephthalate) and Poly (Trimethylene Terephthalate) Blends through Injection Molding**  
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3.1 Introduction

Polymer blending is a method of mixing different polymers in the hopes of creating a new polymer with certain desired properties.\(^1\) Blended components are chosen with the goal of producing a polymer with an optimum balance in mechanical properties. The method of blending is generally direct, easy, and cost effective. New focus has been placed on producing bioplastic blends to create effective materials which reduce petroleum consumption, whether they are fully or partially biobased.\(^2\) In the past decade or so many researchers have explored the blending capabilities of the polyesters poly (ethylene terephthalate), poly (butylene terephthalate) (PBT), and poly (trimethylene terephthalate) (PTT) with more focus on binary blends between PBT and PET, or PBT/PC and PET/PC.\(^3\) - \(^8\) More recently DuPont was able to synthesize PTT through a less expensive pathway, thus lowering the cost of the polymer and sparking research interests in blends with either PTT and PBT \(^9\), \(^10\) or ternary blends of PTT, PBT, and PET.\(^11\), \(^12\) Many properties of PTT are between those of poly (ethylene terephthalate) (PET) and PBT. Its mechanical properties are comparable with that of PET, whereas its processing characteristics are similar to that of PBT. DuPont’s Sorona® can contain up to 37% renewable resourced content. Thermal behaviour and crystallization kinetics of PTT has been thoroughly investigated by Chuah (2004)\(^13\), Guijuan et al. (2006)\(^14\), Hong et al. (2002)\(^15\), and Lui at al. (2005)\(^16\). Its glass-transition temperature \((T_g)\) is in the range of 42-75\(^{0}\)C, depending on the thermal history.\(^17\) It has a melting temperature around 228\(^{0}\)C which is very close to that of PBT (roughly 225 \(^{0}\)C).

Injection molding is one of the most highly used processing methods and accounts for 32% of the plastic consumed in the world.\(^18\) Crystallization rates of semicrystalline polymers are an important characteristic in the industrial application of injection molding. Short molding cycle times are often required when molding semi-crystalline polymers. Chuah (2004)\(^13\), investigated the crystallization rates of PBT and PTT and found that PBT has the highest crystallization rate, at an order of magnitude faster than PTT. PBT’s faster crystallization rate allows for wide use in injection molding processes.\(^17\) For this study, a blend of 30 wt.% PBT and 70 wt.% PTT was created to produce a new fast crystallizing polymer blend that would integrate a degree of biobased resources in injection molding applications. Blending the two materials keeps the costs of PTT down by augmenting a percentage of the material with the cheaper and more widely used
PBT. In doing so the demand for PTT will rise and production costs will fall, allowing for pure PTT applications in the future which would increase usage of renewably resourced content. The Taguchi method is used to determine the most optimal set of processing conditions, as well as provide some statistical insight into the significance of the mold temperature on mechanical properties.

The process engineer Dr. Taguchi of Nippon Telephones and Telegraph Company created a quality engineering method commonly known as the Taguchi method. This method produces a Design of Experiments (DOE) based on orthogonal arrays in such a way that allows for the study of many parameters simultaneously using a reduced number of experiments. Results are based on the mean output values of the quality characteristic at each parameter level (e.g. Young’s modulus or tensile strength) before performing main effect analysis. Analysis of variance test (ANOVA) is then used to determine which of the studied parameters is statistically significant. It is then possible to predict the optimum parameters based on the obtained main effects from Signal to Noise ratio (S/N) and ANOVA analysis. S/N ratio can be defined in three separate criteria: the nominal the better, the smaller the better, and the larger the better. A larger S/N number means that the signal (characteristic value) is much larger than the noise (average of the characteristic values), thus for our comparisons the “larger the better” criteria will be utilized. The larger the better S/N formula is displayed in Equation 11.

\[ S_{N_t} = -10 \log_{10} \left[ \frac{1}{n} \sum_{i=1}^{n} \left( \frac{1}{y_i} \right)^2 \right] \]  

(11)

### 3.2 Experimental

#### 3.2.1 Materials

For this study, PBT was supplied by Ticona in Florence, Kentucky under the trade name Celanex® grade 2000-3. PTT was supplied by DuPont in Delaware, USA under the trade name Sorona®. For all samples PTT and PBT where dried in a convection oven for at least 4 hours at 80°C before processing.
3.2.2 Taguchi Method

The impact strengths are to be used as the characteristic values for the definition of optimization in the Taguchi analysis, as it was seen to be one of PTT’s major deterring properties along with having the highest sensitivity to change processing parameters as observed from the initial trials. As described in the previous section, the S/N ratio was performed with “the larger the better” criteria as shown in Equation 1. These S/N values are used to rank the best level for each processing parameter. The determined levels are then used to predict the optimized impact strength value.

3.2.3 Processing

Blended samples were extruded from a Lab-Scale Twin Screw Extruder with two vertical 150mm long screws and an L/D of 18, before being injected into a DSM Xplore 15 cc Micro compounder, into standard mold shapes for testing. A series of pre-experimental trials where performed before establishing the final blend composition to ensure that an appropriate composition was selected. The choice of the PTT/PBT (70/30 wt.%) blend was selected in order to maintain high biobased content while achieving optimal results. For all samples created, the barrel temperature was 250 °C, the screw speed was 150 RPM, and the processing or dwell time of the materials inside the barrel was 3 minutes. The next series of parameters were selected to be the variables in the DOE and included: mold temperature (70, 80, 90, 100 °C), injection pressure (2, 3, 4, 5 PSI), holding pressure (2, 3, 4, 5 PSI), injection time (6 and 8 seconds), and holding time (6 and 8 seconds). These ranges were selected from the series of pre-trials conducted before the DOE was carried out. The four levels of the first three parameters and two levels of the last two parameters are displayed in Table 2. The appropriate DOE was selected to be a L_{16} (4^3 X 2^2) orthogonal array (OA) with 5 columns and 16 rows. Table 3: Taguchi DOE for Processing Parameters shows the DOE where each row represents an experiment. The columns indicate the combination of different parameter levels utilized for the experiment.
Table 2: DOE Parameters and Their Respected Levels

<table>
<thead>
<tr>
<th>Factor</th>
<th>Parameter</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>Mold Temp</td>
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<td>90</td>
<td>100</td>
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<td>B</td>
<td>Injection Pressure</td>
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<td>4</td>
<td>5</td>
</tr>
<tr>
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<td>Holding Pressure</td>
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<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>Injection Time</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Holding Time</td>
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Table 3: Taguchi DOE for Processing Parameters

<table>
<thead>
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<th>Experiment NO.</th>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>Experiment NO.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>8</td>
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<td>8</td>
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<td>100</td>
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<td>2</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

3.4 Characterization

3.4.1 Mechanical properties

Notch Izod impact strength was recorded with a Testing Machine Inc. according to ASTM D-256, using a minimum of 6 samples, each with a rectangular shape.
3.4.2 Dynamic Mechanical Analysis (DMA)

Heat deflection temperature values were determined using a DMAQ800 from TA Instruments with a temperature range of 35 °C to 150 °C with a heating rate of 2 °C/min. Three rectangular (64 x 13 x 3mm) samples were tested for each trial.

3.4.3 Differential Scanning Calorimeter (DSC)

Measurements were taken from a Q100 DSC from TA Instruments with Tzero Aluminum pans. First run melt crystallization curves of the blended materials were recorded from a temperature range of 0 °C to 250 °C at 5 °C/min. Three samples weighing 7.00 (+/- 0.01) mg were taken from samples created from each of the different mold temperatures. For the non-isothermal melt crystallization exotherms, samples were quickly heated to 250 °C at 40 °C/min and held there for five min before being cooled to 0 °C at varying rates (5, 10, 20, and 30 °C/min). Three samples weighing 7 (+/- 0.01) mg were taken from molded specimens.

3.4.4 Polarized Light Microscopy (PLM)

The radial growth of the PTT/PBT blend spherulites was observed using a Nikon Eclipse LV100DA-U microscope with hot stage. PLM micrographs were taken to observe the crystallization under thermal conditions similar to molding. Measurements were performed on a small fragment of polymer, inserted between two microscope cover glasses, and heated to 250 °C for 3 minutes on a hotplate (where the melt was squeezed into a film through a small pressure applied to the upper glass). The slide was then quickly transferred to the microscopes hotplate which was heated to a specific temperature of 70, 80, 90, or 100 °C.

3.4.5 Atomic Force Microscopy (AFM)

AFM images were obtained with a BRUKER SPM multimode 8. Probes with resonant frequency of 300 kHz and spring constants of 40 N/m where used for tapping mode in air to obtain phase images. Scan frequency was 0.501 Hz at 256 samples per line.
3.3 Results and Discussion

3.3.1 Taguchi results

The impact strengths of each experiment from the DOE are recorded in Table 4. The mean S/N ratios for each processing parameter and level are displayed in Figure 11. It is observed in Figure 1 that mold temperature has the largest effect on the impact strength, which has been reported in literature by Zhang\textsuperscript{13}.

<table>
<thead>
<tr>
<th>Experiment NO.</th>
<th>Notched Impact Strength (J/m)</th>
<th>Experiment NO.</th>
<th>Notched Impact Strength (J/m)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>15.76 (2.4)</td>
<td>9</td>
<td>25.8 (2.5)</td>
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<tr>
<td>2</td>
<td>15.84 (4.3)</td>
<td>10</td>
<td>26.7 (2.8)</td>
</tr>
<tr>
<td>3</td>
<td>15.73 (1)</td>
<td>11</td>
<td>26 (2.3)</td>
</tr>
<tr>
<td>4</td>
<td>17.16 (2.1)</td>
<td>12</td>
<td>22.9 (1.6)</td>
</tr>
<tr>
<td>5</td>
<td>24 (6.8)</td>
<td>13</td>
<td>15.6 (1.6)</td>
</tr>
<tr>
<td>6</td>
<td>13.5 (1.5)</td>
<td>14</td>
<td>14.4 (2.7)</td>
</tr>
<tr>
<td>7</td>
<td>20.8 (1.25)</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>19.4 (5.5)</td>
<td>16</td>
<td>14</td>
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</table>

Results of the ANOVA analysis are shown in Table 5 and indicate the only significant processing parameter is mold temperature at a p-value of 4.6%. All other parameters failed statistical significance. The optimized parameters were found to be a mold temperature of 90 °C, injection pressure of 4 PSI, holding pressure of 3 PSI, injection time of 6 seconds, and a holding time of 8 seconds. These parameters were used to fabricate a final experiment of impact values. Using Minitab software, a prediction was run on the optimized results, which gave predicted impact strength of 31.67 with an S/N value of 30.897.
Figure 11: Taguchi’s signal to noise ratio of each processing parameter at the respected level
Table 5: ANOVA Results for the Significance of Processing Factors from Mean Impact Values

<table>
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<tr>
<th>Source</th>
<th>DF</th>
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<td>12.275</td>
<td>1.27</td>
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<tr>
<td>Holding Time</td>
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<td>0.81</td>
<td>0.420</td>
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</tbody>
</table>

The effectiveness of using the Taguchi method for optimizing PTT/PBT blend processing is shown in Table 6. Using the Taguchi method allows engineers to formulate prediction models which can be used to formulate samples with desired properties. While this research focuses on maximizing the output, a Taguchi analysis done with a S/N ratio of “nominal is best” criteria can be used to pinpoint specific requirements of molded samples. It can also be used with a “smaller the better” criteria if working on problems such as shrinkage or warpage reduction.

Table 6: Response Values of Impact Strength for the Optimized Parameter Selection Through Taguchi Analysis

<table>
<thead>
<tr>
<th></th>
<th>Predicted Value</th>
<th>Actual Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/N</td>
<td>30.8978</td>
<td>30.37</td>
</tr>
<tr>
<td>Mean</td>
<td>31.6683</td>
<td>33.09</td>
</tr>
<tr>
<td></td>
<td>(2.25)</td>
<td></td>
</tr>
</tbody>
</table>
3.3.2 Crystallization characterization

Much of the processing changes in the DOE are reflected by their effect on the crystallinity of the final sample. It is well known that the crystallinity has a pivotal role on the mechanical properties and is controlled by the crystallization rate. PTT, and more specifically PBT, have an extremely fast crystallization rate, and are used in fast cycle times. However the fast crystallization rates can lead to extreme mold shrinkage, producing warped surfaces. Oppositely, if the injection process minimizes the amount of mold crystallization, it will reduce the mold shrinkage but be prone to post-mold shrinkage or secondary crystallization. This is considered detrimental to the molded part as it causes deformations and mechanical loss from the extended reordering of the amorphous phase. Thus engineers must obtain a proper crystallization rate which balances between excessive mold shrinkage and excessive post-crystallization.

3.3.3 Non-isothermal Melt Crystallization behavior

The non-isothermal melt crystallization exotherms for PTT/PBT 70/30 wt.%) for corresponding cooling rates are shown in Figure 12. A single crystallization exotherm is indicative that both PBT and PTT crystallized within the same peak, however, it is known that both these both polymers crystallize without becoming co-crystals.14 With increasing cooling rate the exothermic trace is wider while the initial onset of crystallization temperature (Tc) is shifted down to lower temperatures, which is a general observation for both the pure and blended materials.6
Figure 12: Single melt crystallization exotherm curves of PTT/PBT (70/30 wt.%.) blend at different cooling rates. (a, b, c, d - 5, 10, 15, 20 °C/min)

The temperatures for the peaks of the melt crystallization exotherm curve of the blends at two different cooling rates are shown in Table 7. It is seen that as the cooling rate increases the peak temperature of the blend becomes higher than pure PTT, a result that has been previously reported by Supaphol et al.\textsuperscript{10}. At faster cooling rates, the disparity between crystallization rates for PBT and PTT is widened, increasing lag between crystallization mechanics. This observation of separated crystallization within the same general time frame has been reported in literature for PBT and PET blends.\textsuperscript{2,3}

\begin{table}[h]
\centering
\caption{Temperatures of the Peaks for Non-Isothermal Melt Crystallization Exotherms of PTT, PBT, and (PTT/PBT 70/30 wt.%) Blend}
\begin{tabular}{llll}
\hline
Cooling Rate (°C/min) & Exothermic Peak (°C) & \\
 & PTT & PBT & Blend \\
\hline
10 & 187 & 195.9 & 185 \\
30 & 150.6 & 184.5 & 169.3 \\
\hline
\end{tabular}
\end{table}
Crystallization rate disparity is greatly observed when a 30 °C mold temperature was used. Samples came out with a distinct skin and core like structure. In this case the disparity between the two crystallization rates was so large that PBT crystallized first, while PTT crystallized around the already solid PBT, thus creating a fully immiscible sample as seen in Figure 14(b).

*Figure 13:* Digital photo displaying differences in mold temperature on flexural bars. (a) Higher mold temperature (80 °C) produce visually homogeneous samples. (b) Low mold temperature (30 °C) cause shell core structure to occur.

### 3.3.2.3 First run Melt Crystallization Exotherms of samples with Molded Thermal History

Melting curves from the samples from the first trial of the PTT/PBT (70/30 wt.%) blend molded at different temperatures are shown in Figure 14. A single glass transition temperature can be noticed for each of the curves in the range of 40 to 46 °C which is taken as an indicator for miscibility in the amorphous chains. Depending on the temperature at which PTT is crystallized at, a possible production of multiple lamellae with different thickness can occur. It has been proposed that the production of thin lamella or thin crystals in the polymer lead to a three peak melting endotherm in PTT. The thin lamella are melted and recrystallized onto the thicker lamella depending on the extent of their crystallization.
Figure 14: First run endothermic curves of PTT/PBT (70/30 wt%) blends from different molding temperatures.

From Figure 14 it is evident that the recrystallization peak occurs in samples molded at 90 and 100 °C, and can be slightly seen in the lower mold temperatures. The enthalpy of the recrystallization and melt crystallization curves are calculated and reported in table 8.

Table 8: Latent Heat of Enthalpy for DSC Melt Curves from Different Mold Samples

<table>
<thead>
<tr>
<th>Mold temp. °C</th>
<th>Recrystallization $\Delta H_C$</th>
<th>Melting $\Delta H_C$</th>
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</thead>
<tbody>
<tr>
<td>70</td>
<td>1.596</td>
<td>62.58</td>
</tr>
<tr>
<td>80</td>
<td>0.3108</td>
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<tr>
<td>90</td>
<td>2.624</td>
<td>53.27</td>
</tr>
<tr>
<td>100</td>
<td>3.609</td>
<td>54.03</td>
</tr>
</tbody>
</table>
It has been reported that during DSC scanning, the melting and recrystallization of the first peak occurs as the same time, thus it is hard to obtain an accurate magnitude of crystallization from the exothermic melt peak. It is interesting to note that the melt enthalpy decreases with increasing mold temperature. This is an opposite response to that of many other polymers such as PLA and PTT in which a higher mold temperature produces a larger degree of crystallization.

To explain the observed phenomenon of increasing crystallization with decreasing mold temperature, it is helpful to consider the miscibility criteria set forward by Woo and Kuo. The researchers explored the miscibility of a ternary blend of PBT, PTT, and poly (ethylene terephthalate) (PET). They dismiss that a ternary, or binary blend of homologous polymers each sharing the same functional groups require transesterfercation to act as a miscible blend. They report that the ternary blend showed all the typical requirements of a miscible blend (single T_g and single cold crystallization exotherm), but contained multiple melting peaks. The authors related these signs of miscibility to the individual polymers being mixed on a very fine scale such that any two separate chains from differing polymers could be interwoven into a single chain segment with a single T_g as they reacted to external heat. The interwoven chains could react to the temperature changes and would reorganize at the same time, leading to a single cold crystallization temperature.

As described in Section 3.2.1, we consider that the two polymers are actually crystallizing separately but within the same time. It is proposed that at higher temperatures, PTT and PBT are in the free amorphous state for longer. This would mean that the chains of PTT and PBT are floating towards their respective nucleation sites at the same time, causing additional interlocking of chains and effectively reducing the crystallization rates of each polymer. Retardation of PTT crystallization has previously been reported with the addition of amorphous poly (ether imide) PEI and PET/PBT blends. The researchers attribute the retardation for similar reasons, notably a higher melt viscosity from PEI content, which slows the PTT chains from fusing to the crystals thus lowering the crystallization growth rate. Additionally there is a larger temperature gradient experienced by the dominating PTT polymer. This could allow for the formation of different lamellae sizes, thus increasing the recrystallization peak as seen in figure 15. Furthermore Wu and Woo have indicated that as the thinner lamella crystals become more ordered, they are less likely to undergo recrystallization. Therefore, a lesser recrystallization peak is a possible indication of greater crystal perfection in
smaller lamellae. Alternatively, at lower melt temperatures, the onset $T_c$ of PBT is greater than PTT, thus the PBT chains are free to move to their respective nucleation sites without any hindrance from nucleating PTT sites. This allows for a more complete crystal formation for both polymers.

### 3.3.3 Polarized Optical Microscopy (POM)

POM images were taken of the PTT/PBT (70/30 wt.%) blend isothermally at the mold temperatures used in the DOE, the resulting images are shown in Figure 16. From Figure 16 a distinct parallel to regime III nucleation. In this regime nucleation dominates all processes, as can be seen from the numerous amounts of non-banded spherulites. The high number of nucleuses interferes with crystal growth and leads to a distorted lamellae. It is evident that the mold temperature has an effect on the morphology of the polymer. Samples that were held at temperatures 70 °C and 80 °C had smaller spherulite diameters while those held at 90 °C and 100 °C contained larger diameters. The biggest correlation however, is most noticeable for the two higher holding temperatures. In Figure 16 (c, d) a dominant phase of relatively large spherulites showing a slightly distinctive maltase cross pattern is coupled with spherulites that are much smaller in diameter. When comparing these images to the DSC curves presented in Figure 4, we can deduce a possible relation of the presence of these smaller spherulites to the thinner lamellae forming the multiple melting peaks seen in the melt DSC curves. More information is needed to fully understand this potential relationship.
Figure 15: POM images taken of PTT/PBT (70/30 wt.%) blend isothermally at the mold temperatures used in the DOE. (a) 70 °C mold temperature. (b) 80 °C mold temperature (c) 90 °C mold temperature, (d) 100 °C mold temperature.

3.3.4 Atomic Force Microscopy (AFM)

The nanoscale morphology of the PTT and PBT blends was analyzed using an Atomic Force Microscopy. Phase imaging is a function of tapping mode, in which a cantilever with a small tip is oscillated as it moves over the surface of a sample. As the tip oscillates it intermittently interacts with the surface. Phase contrast arises from close monitoring of the oscillating tip. The tip is set to oscillate at a set amplitude. When the tip comes into contact with a surface its amplitude will change. This change in amplitude is a result of the tip interacting with the surface. The energy dissipated in this contact period depends on a number of factors including viscoelasticity, adhesion, and contact area. Aside from these phase imaging also provides topographical information, thus requiring any interpretations of phase imaging to be performed
on flat surfaces.\textsuperscript{28} Phase imaging has been previously used to record the ring banding phenomenon in PTT.\textsuperscript{29} Ring banding has said to be caused by periodic lamella twisting during spherulite growth due to unbalanced stress on the lamella surface.\textsuperscript{30} Figure 17 displays a 10 x 10 \( \mu \text{m}^2 \) scan size of a phase image taken from pure PTT. The morphology is rather smooth, and contains a flat-on lamellae growth as reported previously for non-banded PTT.\textsuperscript{29} Figure 18 displays a 10 x 10 \( \mu \text{m}^2 \) scan size of a phase image taken from the PTT/PBT blend molded at 70 \( \degree \text{C} \). It can be seen that an extensive banding pattern exists. We compare these results to the banding reported by Chuang et al.\textsuperscript{29} and note some differences. Firstly, the width of the banded lines for our blend is roughly 1 \( \mu \text{m} \), much smaller than the \(~20 \mu \text{m} \) rings reported by the literature. It has been previously reported that in polymer blends band spacing is usually decreased.\textsuperscript{31, 32}\textsuperscript{31, 32} Alternatively Chen et al.\textsuperscript{33} reported an increase in band spacing of PTT with increased crystallization temperature. It was initially hypothesized that the different polymers, PTT and PBT, could be distinguished under AFM phase image under the expectation that PTT would contain larger spherulites with a distinctive ring banding size in comparison to the PBT component of the blend. This was met with difficulty as the researchers lacked the ability to produce a flat enough surface for imaging. Cyrofracturing the samples enabled for very small localized imaging, but were met with difficulties when attempting to expand the scan size due to the unevenness of the sample. This led to poor imaging and increased topological information in the phase image. Future work is required for this analysis in which a flat surface will enable larger scan sizes to be utilized. This will give better information on overall spherulite morphologies, which could provide the images for distinguishing between PTT and PBT components within the blend.
Figure 16: 10 x 10 μm² scan size of a phase image taken from pure PTT

Figure 17: 10 x 10 μm² scan size of a phase image taken from the PTT/PBT blend molded at 70 °C

3.3.5 Heat Deflection

The heat deflection temperature (HDT) for each experiment set is shown in table 9. It can be seen that there is a higher deflection temperature for the samples formed in the 90 °C mold range when compared to the other mold temperatures, with the optimized HDT as the highest temperature. Often an increased HDT is an indication of increased crystallinity due to highly ordered structure of a crystal requiring more energy to move the chains. As indicated in section 3.2.3, the crystallinity is largest for samples molded at 70 °C. However, the HDTs for the lower mold temperatures are between 77 and 84 °C which is the lowest HDT reported amongst all
samples. A possible reason for this outcome is that the recrystallization peaks in the melting endotherms.

<table>
<thead>
<tr>
<th>Table 9: HDT Values for each Experiment from the DOE</th>
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<tbody>
<tr>
<td>Experiment</td>
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<tr>
<td>------------</td>
</tr>
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</table>

3.4 Conclusion

PTT/PBT blends were produced on a mini-scale injection molding machine. The Taguchi method was used to design a series of experiments in an effort to optimize parameter values of PTT/PBT blend processing. It was found though ANOVA that the variance of the mold temperature produced the most significant effects on the impact strength of the polymer blends. The Taguchi method was used to obtain a set of optimal processing parameter levels, the results are in good agreement with the data analyzed. This research shows that statistical models such as the Taguchi analysis are strong tools for molding engineering applications. It was found that the other mechanical properties had no changes when processed under the different experimental trials; however, HDT and degree of crystallization were altered. From DSC analysis it is evident that higher mold temperatures influences the ability of PBT to hinder the crystallization rate of PTT, leading to lesser formed crystals which are viewed as recrystallization and multiple melt peaks in the PTT/PBT blend with higher mold temperatures. POM images confirm the presence of lesser perfected crystals, which are possibly linked to the recrystallization peaks found in samples molded at higher temperatures. From phase images of the AFM machine there visible banding. A presence of spherulite banding can lead to a possible distinguishing between PTT and PBT components, however surface preparation for this analysis was not available. Further work
is required in this area. Injection molding engineers should be aware of the potential retardation of crystal growth in PTT due to the PBT amorphous melt phase. This knowledge allows for more control over mold shrinkage and post crystallization in PTT parts.

3.5 Acknowledgements

Authors are thankful to the financial support of highly qualified personnel (HQP) Scholarship from the Ontario Ministry of Agriculture, Food the Ministry of Rural Affairs (OMAF and MRA), Ontario, Canada and Natural Sciences and Engineering Research Council (NSERC)- NCE - AUTO21, Canada.
3.6 References


[30] Lotz B, Cheng S Z D. A critical assessment of unbalanced surface stresses as the mechanical origin of twisting and scrolling of polymer crystals, Polymer, 2005; 46(3), 577-610,


4. Manuscript 2

This second manuscript is currently seeking publication. It overviews the challenges and outcomes that came with using a co-injection set up with (PTT/PBT |PBS/PBAT). This chapter is an extension of the research done in chapter 3 as an effort to resolve the poor impact properties of the inherently brittle PTT/PBT blend. To overcome this brittleness the authors explore the method of co-injection molding. This research maintains the overall goal of this research by analyzing different ways of introducing bio-based materials into a viable product through the use of the PTT/PBT blend which was studied in the previous chapter. Additionally the bio-content of the co-injected part will see a major increase with the proposed production of bio-based PBS and PBAT, this topic is covered in greater detail in chapter 5. Use of co-injection molding for maintaining properties while increasing bio-content is a relatively new and novel idea that resonates with the overall goal of this research, which is to increase bio-content of polymeric products while maintaining desirable properties.
Submitted to the Journal of Applied Polymer Science

Study of the effect of processing conditions on the co-Injection of PBS/PBAT and PTT/PBT blends for parts with increased bio-content

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2 Department of Plant Agriculture, Bioproducts Discovery and Development Center (BDDC), University of Guelph, Guelph, Ontario, Canada N1G 2W1
4.1. Introduction

This work studies the effect of processing parameters on mechanical properties and material distribution of co-injected polymer blends within a complex mold shape. A partially bio-sourced blend of PTT/PBT was used for the core, with a tough biodegradable blend of PBS/PBAT for the skin. A ½ factorial design of experiments is used to identify significant processing parameters from skin and core melt temperatures, injection speed and pressure, and mold temperature. Interactions between the processing effects are considered, and the resulting statistical data produced accurate linear models indicating that the co-injection of the two blends can be controlled. Impact strength of the normally brittle PTT/PBT blend is shown to increase significantly with co-injection and variations in core to skin volume ratios to have a determining role in the overall impact strength. SEM images were taken of co-injected tensile samples with the PBS/PBAT skin dissolved displaying variations of mechanical interlocking occurring between the two blends.

Forecasts of depleted oil productions have prompted research into the field of bioplastics which are derived from renewable resources. The widespread use of biopolymers to fill the gap has, however, been hindered by a number of problems, the main concerns being both cost and performance.\textsuperscript{1} In an effort to resolve these issues bioplastics have been studied with a focus on fillers\textsuperscript{1,2}, reinforcements\textsuperscript{2,3}, or blending.\textsuperscript{4} Among the different solutions the advanced processing method such as co-injection molding (CIM) promises an effective way to resolve a number of the problems. Examining the processing parameters can provide a way to determine the effectiveness of using co-injection molding of a blend of poly(butylene terephthalate) and poly(trimethylene terephthalate) (PBT/PBT) as the core material with a blend of poly (butylene succinate) and poly (butylene adipate-co-terephthalate) (PBS/PBAT).

There are many variations of CIM but the basic concept utilizes more than one separate polymer components through sequential or continuous injection. The Co-Injection process was invented in the 1970 by Imperial Chemical Industries.\textsuperscript{5,6} Sandwich molding is one method of molding under the co-injection process, and is done with the sequential injection of the materials involved. The final result is a heterogeneous product composed of two separate layers, one core
layer and one encapsulating layer of skin material. Combining two materials in this fashion produces properties which are unrepeatable by a single homogeneous polymer blend. Strength and modulus’ result from core material properties, while impact strength, hardness, and other surface properties, are related to the skin material. Core material selection has historically been chosen to reduce costs through sourcing of recycled or cheaper polymers.\textsuperscript{7, 8} Furthermore the core can include reinforcements such as fibers or particles which have been known to improve upon the skin/core interface.\textsuperscript{9, 10}

Successful CIM of two different polymers is fundamental to the material compatibility. Materials must share similar thermal expansion and shrinkage or risk delamination at the polymer-polymer interface. The presence of interfacial bonding, through either chemical adhesion or mechanical interlocking of the two interfaces, also contributes to a successful CIM product.\textsuperscript{9} Appropriate material selection enables the proper distribution of the core within the skin material. Core distribution is highly dependent on the viscosities of the selected materials. It is generally accepted that the ratio of core to skin viscosity range from 0.5 to 5 for a successful co-injection of two separate materials.\textsuperscript{11-13} As documented by many researchers certain processing parameters including melt temperature, mold temperature, injection speeds, and injection pressure have a large effect on the viscosities of the materials and thus a direct impact on the core and skin distribution.\textsuperscript{7-16}

Much of the different material skin/core compatibility is focused on petroleum based polymers.\textsuperscript{17} As previously discussed increasing attention has been brought to the field of biopolymers in the recent forecasts of petroleum depletion and increasing greenhouse gas emission. With the hopes of improving bio-content usage, the core layer material choice is a blend of poly(butylene terephthalate) (PBT) and poly(trimethylene terephthalate) (PBT) at 30 and 70 wt.%. The PTT/PBT (70/30 wt.%) blend is used to keep costs lower while increasing bio-content for PBT applications by mixing it with PTT, which is sourced from bio-based 1,3-Propanediol and contains 37 wt.% of annually renewable plant-based content.\textsuperscript{18} This blend was found to be brittle and produce low impact strength. This paper proposes to increase the impact properties of the PTT/PBT blend by co-injecting it with a ductile blend of poly (butylene succinate) (PBS), and poly (butylene adipate-co-terephthalate) (PBAT). Poly(butylene succinate) (PBS) is a
biodegradable aliphatic polyester belonging to the poly(alkylene dicarboxylate) family, synthesized from succinic acid and with 1, 4-butanediol by two step process of esterfication and deglycolization. PBS has a relatively high melting temperature ~150 °C, excellent processing properties, and good thermal stability.\textsuperscript{19, 20} Pure PBS has is limited by its low impact strength.\textsuperscript{21} To overcome this problem researchers have focused on blending PBS with other aliphatic polyesters like poly(hydroxyl butyrate)\textsuperscript{22}, poly(ethylene oxide)\textsuperscript{23}, poly (butylenes terphathalte)\textsuperscript{24}, and poly(butlyene carbonate)\textsuperscript{25}. These blends with the exception of poly(butylenes carbonate) have a detrimental effect on the biodegradability of PBS. Poly(butylene adipate-co-terephthalate) (PBAT) is a well-known commercially popular biodegradable polymer. It is produced through the synthesis of 1, 4-butanediol, adipic acid and terephthalic acid. It has high elasticity, high elongation at break, resistance to wear, water, and oil, and has good processability\textsuperscript{26}. The compatibility of PBAT with PLA has been a highly researched blend.\textsuperscript{27, 28, 29} PBATs defining feature is its elongation property at 700% but contains relatively low tensile strength of 32 MPA.\textsuperscript{30}

Blending PBS, which has good tensile strength but low impact strength, with PBAT which has poor strength but excellent toughness, provides a potentially tough skin material for the CIM with the brittle PTT/PBT blend. Blends of PBS/PBAT where studied by Jacob et al.\textsuperscript{31} Formulations with a greater degree of PBS reported stronger tensile strengths, and crystallization percent, with a reduction in tensile elongation. PBS/PBAT blend was reported to be immiscible but produced a single T\textsubscript{g}, which was due the similar values of each polymers respective T\textsubscript{g}.\textsuperscript{31} Co-injection of PBS/PBAT as a tough biodegradable skin has been previously reported in a similar study done by co-workers, improving impact strength and tensile elongation of pure poly(hydroxybutyrate-co-valarate).\textsuperscript{32} The co-injection of PBS/PBAT skin is expected to increase the impact strength of the final product while maintaining a strong core from the PTT/PBT. The use of PBS/PBAT will soon further increase the biocontent of the entire co-injected formulation with the proposed release of PBS and PBAT produced from bio sourced 1,4 butanediol.\textsuperscript{34} This research aims at understanding the effects of varying the processing parameter on the properties of the co-injected samples with analysis from a fractional factorial design of experiments (DOE) as suggested by Selene R.\textsuperscript{8} and Vangosa F B.\textsuperscript{14}
4.2 Experimental Section

4.2.1 Materials

For this study PBT was supplied by Ticona in Florence, Kentucky under the trade name Celanex grade 2000-3. PTT was supplied by DuPont in Delaware, USA under the trade name Sorona. PBS (Biocosafe 2003) and PBAT Biocosafe – 2007) where both supplied by Xinfu from China. Extruded materials and neat polymers were dried overnight at 80°C before processing.

4.2.2 Processing Conditions

4.2.2.1 Extrusion

The PTT/PBT core and PBS/PBAT skin blends were prepared by a Leistritz co-rotating intermeshing twin screw extruder (MIC 27/aL-48) with a strand die. Pellets of PBT and PTT where hand mixed before processing at a 30/70 wt.% ratio respectively, similarly PBS and PBAT were also hand mixed at a ratio of 60/40 wt.%. The Leistritz extruder has 10 temperature zones along the extruder barrel, with an 11th temperature on the die. The temperature profile for the core PTT/PBT blend was, from feed to die, 230-235-240-240-240-240-240-240-235-230°C. For blending PBS/PBAT the temperature profile was 130-140-145-150-150-150-150-150-145-140°C, screw speed was kept at 112 RMP for both blends. The extruded strands where subsequently cooled in a water bath before being chopped into pellets for co-injection.

4.2.2.2 Molding

Testing samples were created from one mold with a geometry that combined type IV tensile, flexural and notched/un-notched Izod impact samples with dimensions based on ASTM standards, which are connected by runners from one gate entry. The molding was done in an ARBURG (Model No: 370 S &00-290/70, Germany) two unit injection molding machine, capable of both single and co-injection. Screw diameter in unit 1 was 35 mm with a temperature profile of 6 heating zones, while unit 2 screw diameters was 22 mm with 5 heating zones. Single injections were done using unit 1. The temperature profile for the single injection samples was 35-240-245-250-250-250 °C from feed to nozzle for PTT/PBT blends and 35-185-190-190-190-190 °C for PBS/PBAT. For the CIM core material was PTT/PBT with two different profiles depending on the experiment number; either 35-240-245-250-250-250 °C or 35-230-235-240-240-240 °C was used. The injection of the skin material of PBS/PBAT also had two different
profiles, depending on the experiment number. Either 35-155-160-160 °C or 35-185-190-190 °C was used. For the remainder of the paper the melt temperatures used during molding are denoted by the temperature used in the first zone of the barrel (240 – 250 °C for the core and 160 – 190 °C for the skin).

During CIM the skin blend was injected from unit 2 while the core was injected by unit 1. This allowed PTT/PBT, which has a higher processing temperature, to be injected by the larger barrel with a larger temperature profile. Skin to core volume ratio was chosen to be 60/40, it should be noted that this is not the expected ratio to be found in the molded samples. Due to the complex nature of the mold geometry there is a length of runners that must be accounted for in determining the amount of polymer accumulation in the final product. During the sequential injection molding a total of 28 cc is injected into the mold, thus 16.8 cc for skin and 11.2 cc for the core. The skin is injected first from unit 2 until 5 cc is left. The core material is then fully injected by unit 1 and then followed by the rest of the skin material. For the production of thinner impact samples a ratio of 40/60 vol.% skin to core was used. In this setup skin was injected first from unit 2 until 3cc was left. The core was then fully injected and followed up the remaining 3cc of skin polymer. Under this volume ratio the other testing specimens in the mold were unsuitable for testing due to core breakout.

4.2.2.3 Factorial Design
To map the effects of variations in processing parameters a one half factorial design with level IV resolution, 5 factors and 2 levels was implemented. This allows interaction effects between two parameters to be studied under the assumption that three-way interactions are of no importance. The five factors consisted of processing parameters that could be manipulated on the ARBURG and are presented in Table 10 with their respected levels. The one half factorial is displayed in table 11. To better understand the role PBS/PBAT has on improving impact strength a second set of impact samples were created to have increased core content with a thinner skin encasement. For these samples a volume ratio of (40/60) skin to core ratio was used with a processing set as displayed in table 12. All analysis was done with the software Minitab® 16.
Table 10: Processing Parameters and Respected Levels

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<th>Parameters</th>
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<th>High Level</th>
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<tr>
<td>Melt Temperature (Core)</td>
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<td>Injection Speed</td>
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Table 11: Co-injection 1/2 Factorial Design for PBS/PBAT and PTT/PBT

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<th></th>
<th>Melt Temp (°C) (skin)</th>
<th>Melt Temp (°C) (core)</th>
<th>Mold Temp (°C)</th>
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<td>50</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>190</td>
<td>250</td>
<td>50</td>
<td>750</td>
<td>20</td>
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<tr>
<td>6</td>
<td>190</td>
<td>240</td>
<td>50</td>
<td>750</td>
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<tr>
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<td>160</td>
<td>240</td>
<td>35</td>
<td>750</td>
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<td>750</td>
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<td>250</td>
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<td>750</td>
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<td>10</td>
<td>160</td>
<td>250</td>
<td>35</td>
<td>500</td>
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<tr>
<td>11</td>
<td>160</td>
<td>250</td>
<td>50</td>
<td>500</td>
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<td>12</td>
<td>190</td>
<td>250</td>
<td>35</td>
<td>750</td>
<td>10</td>
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<tr>
<td>13</td>
<td>160</td>
<td>250</td>
<td>50</td>
<td>750</td>
<td>10</td>
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<tr>
<td>14</td>
<td>190</td>
<td>250</td>
<td>50</td>
<td>500</td>
<td>10</td>
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<tr>
<td>15</td>
<td>190</td>
<td>240</td>
<td>35</td>
<td>750</td>
<td>20</td>
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<tr>
<td>16</td>
<td>190</td>
<td>250</td>
<td>35</td>
<td>500</td>
<td>20</td>
</tr>
</tbody>
</table>
Table 12: Processing Parameters for 40/60 Skin/Core Ratio Impact Samples

<table>
<thead>
<tr>
<th>Trial</th>
<th>Melt Temp (°C) (skin)</th>
<th>Melt Temp (°C) (core)</th>
<th>Mold Temp (°C)</th>
<th>Injection Pressure (PSI)</th>
<th>Injection Speed (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40/60 – 1</td>
<td>160</td>
<td>240</td>
<td>35</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>40/60 – 2</td>
<td>160</td>
<td>240</td>
<td>35</td>
<td>750</td>
<td>20</td>
</tr>
<tr>
<td>40/60 – 3</td>
<td>190</td>
<td>240</td>
<td>35</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>40/60 – 4</td>
<td>190</td>
<td>250</td>
<td>35</td>
<td>500</td>
<td>20</td>
</tr>
</tbody>
</table>

4.2.3 Testing Methodologies

Tensile and Flexural tests were conducted on an Instron testing machine (Model-3382) according to ASTM standards D638 and D790, respectively, taking the average of 5 samples. Notched impact strength was determined with a 5 ft-lb hammer on Testing Machine Inc (TMI 43-02) according to ASTM D256. For the testing of un-notched samples ASTM D256 was used with a 30 ft-lb hammer. Impact strength was taken as the average of 7 samples.

4.2.4 Characterization Methodologies

Changes in core/skin ratios were recorded from area profiles of cross-sections of molded flexural samples. Cross sections were taken from the middle of flexural bars, and (+/-) 26mm from the middle. These are aligned with all three contact points of a 3 pt. bending test. An average was taken from three different flexural bars for each cross section. To calculate the area, cross sections cut from the sample with a blade were analyzed under an optical microscope equipped with measurement software. The change in area was calculated as the ratio of area change between the cross section closest to the injection gate, and the cross-section furthest away from the gate. The same method was used to characterize the skin thickness of the impact samples with cross sections taken from broken impact samples. The cross section was taken just under the break, and an average of the skin thickness on the notched side was taken from three cross sections.
4.3. Results and Discussion

As previously described the overall goal of this paper is to elucidate the behavior of the co-injection between both materials as a function of the processing parameters. Thus all mechanical data is paired with a statistical analysis to derive any possible trends that are occurring with the injection process.

4.3.1 ANOVA Analysis

Using a one half factorial design of experiments allowed for a statistical analysis between certain characteristics of the tested samples and the processing parameters used within each trial. Table 13 displays the P values returned from ANOVA analysis done on different responses from the trials, with the significant terms highlighted, with significance taken as $\alpha = 0.05$. To improve upon the significance weighting of the parameters some largely insignificant interactions were removed from the ANOVA model. Doing this removed accuracy in the prediction model but allowed for the significant parameters and interactions to have a greater contrast. Three of the explored responses deal directly with the mold filling and core/skin ratio in design (core penetration in a flexural sample, core/skin ratio reduction along the profile of the flexural sample, and skin thickness at the notch of impact sample) while the other three characteristic responses deal with the mechanical strengths of the samples (impact, flexural, and tensile strengths). When performing an analysis with interaction terms, the interaction P-values are more important than the main effect P-values due to the reasoning that if the interaction is significant than a change in both processing parameters will affect the response characteristic regardless of the main effect significance. Comparing the significant interaction it is noted that the interactions “melt(core)*injection pressure” and “melt(skin)*injection speed” are significant for all characteristic responses in which they are present. This information leads to the observation that as the temperature of the melts change they are increasingly impacted by the injection process is an indication that there is a temperature dependency on the final properties. In a previous factorial study on processing parameters, Selden\textsuperscript{8} reported that core melt temperature and injection velocity had statistically significant effects on the skin/core distribution of co-injected polyamide (PA-6) as the skin and poly (butylene terephthalate) (PBT) with 20% glass fiber as the core. Vangosa\textsuperscript{14} similarly reported core temperature, and the
interaction between core content and core injection rate as being statistically significant after a factorial analysis on co-injection processing parameters.

Table 13: ANOVA Analysis on DOE with Significant Terms Highlighted, and Removed Terms Asterisked.

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Core Penetration</th>
<th>Core Difference</th>
<th>Impact Skin Thickness</th>
<th>Impact</th>
<th>Tensile Strength</th>
<th>Flexural Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Effects</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0.057</td>
<td>0.049</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Melt(skin)</td>
<td>1</td>
<td>0.026</td>
<td>0.05</td>
<td>0.021</td>
<td>0.053</td>
<td>0.106</td>
<td>0.357</td>
</tr>
<tr>
<td>Melt(core)</td>
<td>1</td>
<td>0.591</td>
<td>0.026</td>
<td>0.04</td>
<td>0.122</td>
<td>0.131</td>
<td>0.574</td>
</tr>
<tr>
<td>Mold</td>
<td>1</td>
<td>0.009</td>
<td>0.028</td>
<td>0.187</td>
<td>0.05</td>
<td>0.075</td>
<td>0.022</td>
</tr>
<tr>
<td>injection pressure</td>
<td>1</td>
<td>0.942</td>
<td>0.294</td>
<td>0.204</td>
<td>0.121</td>
<td>0.983</td>
<td>0.731</td>
</tr>
<tr>
<td>injection speed</td>
<td>1</td>
<td>0.04</td>
<td>0.126</td>
<td>0.0149</td>
<td>0.027</td>
<td>0.042</td>
<td>0.776</td>
</tr>
<tr>
<td>2-Way Interactions</td>
<td>8</td>
<td>0.06</td>
<td>0.03</td>
<td>0.038</td>
<td>0.049</td>
<td>0.008</td>
<td>0.057</td>
</tr>
<tr>
<td>Melt(skin)*Melt(core)</td>
<td>1</td>
<td>0.06</td>
<td>*</td>
<td>0.087</td>
<td>*</td>
<td>0.016</td>
<td>*</td>
</tr>
<tr>
<td>Melt(skin)*Mold</td>
<td>1</td>
<td>0.048</td>
<td>*</td>
<td>0.063</td>
<td>0.092</td>
<td>*</td>
<td>0.066</td>
</tr>
<tr>
<td>Melt(skin)*injection pressure</td>
<td>1</td>
<td>0.033</td>
<td>0.085</td>
<td>*</td>
<td>0.039</td>
<td>0.002</td>
<td>*</td>
</tr>
<tr>
<td>Melt(skin)*injection speed</td>
<td>1</td>
<td>0.029</td>
<td>0.033</td>
<td>0.031</td>
<td>0.024</td>
<td>0.037</td>
<td>*</td>
</tr>
<tr>
<td>Melt(core)*Mold</td>
<td>1</td>
<td>0.063</td>
<td>0.095</td>
<td>*</td>
<td>0.026</td>
<td>0.096</td>
<td>0.096</td>
</tr>
<tr>
<td>Melt(core)*injection pressure</td>
<td>1</td>
<td>0.024</td>
<td>0.039</td>
<td>0.019</td>
<td>*</td>
<td>0.017</td>
<td>*</td>
</tr>
<tr>
<td>Melt(core)*injection speed</td>
<td>1</td>
<td>*</td>
<td>*</td>
<td>0.074</td>
<td>0.183</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Mold*injection pressure</td>
<td>1</td>
<td>0.08</td>
<td>*</td>
<td>0.049</td>
<td>0.15</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Mold*injection speed injection pressure</td>
<td>1</td>
<td>0.046</td>
<td>0.017</td>
<td>0.064</td>
<td>0.183</td>
<td>*</td>
<td>0.049</td>
</tr>
</tbody>
</table>

It should be noted that analyzing the full set of processing parameters on the final characteristics is largely linked to the mold shape, especially on a complex mold as used in this study. With the complexity of the mold it is important to report that the R squared value for the models derived by the ANOVA analysis provide a highly accurate model for the data points. Table 14 displays
the R squared along with the prediction R squared values for all response characteristics. R-squared prediction values are an indication of how accurate the model will be at predicting values that use processing parameters that are outside of the data set from which the model was created from. It can be noted that core penetration and tensile strength contained the highest R squared prediction values of 63% and 50%. This is generally a poor prediction value, thus while there is a good understanding of the co-injection process within the defined variables a limitation exists in terms of predicting the values from the ANOVA when using levels outside of the studied values.

Table 14: R-Squared and R-Squared Prediction Values for Statistical Models Based off of ANOVA of Factorial DOE

<table>
<thead>
<tr>
<th></th>
<th>R-Sq.</th>
<th>R-Sq.(pred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core Penetration</td>
<td>99.43</td>
<td>63.83</td>
</tr>
<tr>
<td>Core Difference</td>
<td>95.53</td>
<td>28.52</td>
</tr>
<tr>
<td>Impact Skin Thickness</td>
<td>97.51</td>
<td>29.08</td>
</tr>
<tr>
<td>Impact Strength</td>
<td>97.31</td>
<td>23.54</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>96.92</td>
<td>50.68</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>76.41</td>
<td>0</td>
</tr>
</tbody>
</table>

4.3.2 Notched Izod Impact

Impact strengths of the factorial DOE trials are displayed in Figure 18 along with the single injected PTT/PBT. It should be noted that the single injection of PBS/PBAT did not break under ASTM standards of any hammer size. The co-injected impact strengths which range from 450 to 95 are considerably higher than the single injection of PTT/PBT with a max value of 25. The increased impact strength as a result of PBS/PBAT encapsulation has been previously reported by Kuynu et al.\textsuperscript{20} Impact strengths are compared to the average outer wall thickness of the impact sample, as to determine whether the large increases in notched impact strengths are due to skin/core adhesion, or simple a thicker core. If a thicker skin envelopes the impact sample, upon notching the core will not be exposed to the hammer. In Figure 18 it can be seen that trial 2 produced the highest impact strength of the DOE experiments. Upon closer analysis of this result
is it obvious that standard deviation has a large magnitude. This is a good indication that the skin thickness at the notch was close to the thickness of the notch, thus some samples would have had a notch with no core exposed causing the impact strength to increase dramatically as crack propagation initializing in the core and spreading to the skin would be minimized. Notched testing was also done on the samples formed from an injection ratio of 40 vol.% skin and 60 vol.% core, producing samples with lower skin/core ratios (Higher core content). The final results are displayed in Figure 19, and indicate that samples with lower skin content will display smaller impact values. To better understand if there was a trend between the skin thickness on the notched side and the impact strength a Pearson correlation analysis was done. When considering the correlation between the factorial impact strengths and the skin thickness there was a poor correlation with a Pearson correlation of 0.110 and a $P$-Value = 0.685. When the results of the 60/40 trials impact strengths where added into the data set the correlation improved. Pearson correlation was 0.500 with a $P$-Value = 0.025, indicating that skin thickness has a positive correlation towards the co-injected impact strength and can be highly controlled by the skin/core ratios.
Figure 18: Impact Strengths of PTT/PBT and co-injected factorial DOE trials of PTT/PBT (40 vol.% with PBS/PBAT (60 vol.%). Refer to Table 11 for processing parameters of trials 1-16.

Figure 19: Notched impact strengths of co-injected PTT/PBT (70/30 wt.% [60 vol.% injected] with PBS/PBAT (60/40 wt.%) [40 vol.% injected]. Refer to Table 12 for processing parameters of trials 1-4.
4.3.3 Un-notched Izod Impact

By notching the impact samples a large defect is incurred along the continuity of the skin material. This in turn does not allow for a full understanding of the impact strength of the two dissimilar materials. To better understand the effect of co-injecting, un-notched impact samples are tested. For this test the impact processing method involving 60 vol.% PTT/PBT (70/30 wt.%) with 40 vol.% PBS/PBAT (60/40 wt.%) are used in an effort to test the thinnest possible skin layer. The samples failed to break under a 30 ft-lb hammer compared to pure PTT/PBT which shattered into many pieces under the 30 ft-lb hammer. From this data it can easily be said that the co-injection of PTT/PBT with PBS/PBAT helps offset the brittle nature of the PTT/PBT core.

4.3.4 Flexural Results

Flexural strength and modulus are presented in figure 20. Minimal variation in flexural results was recorded. Variation between trials was minimal with trial 10 at the highest 34.2 MPa and trial 4 at the lowest 26.28 MPa. The flexural modulus of the PBS/PBAT blend increased by 122% with the addition of PTT/PBT core. A 66% increase in flexural modulus with the addition of a high modulus core material has been previously reported with poly propylene as the skin and PP + 40% short glass fiber as the core, 33% increase with PA 6 as the skin and PBT as the core.
Figure 20: Flexural results of single injected PBS/PBAT, PTT/PBT, and co-injected factorial DOE trials of PTT/PBT (40 vol.%) with PBS/PBAT (60 vol.%). Refer to Table 11 for processing parameters of trials 1-16.

4.3.5 Tensile Results

Tensile strength, modulus and % of elongation at yield of the single injected PTT/PBT and the trials of the DOE are presented in figure 21. Tensile strengths contained the same level of variation seen in flexural strength similarly to flexural strength trial 10 had the highest at 35.7 MPa and trial 4 had the lowest at 27.0 MPa. Since tensile testing presents an axial load on the co-injected sample the young’s modulus is likely to be a closer average of the two separate components, as opposed to flexural modulus which has a stress gradient that increases as the material becomes further from the neutral axis. The most intriguing response was percent of elongation at yield which was subjected to significant variation within each separate trial. The variations are considered to be linked to interfacial adhesion of the co-injected samples. During
testing the tensile samples could be grouped into three different categories relating to their mode of failure.

Figure 21: Tensile results of single injection of PBS/PBAT, PTT/PBT, and co-injected factorial DOE trials of PTT/PBT (40 vol.%) with PBS/PBAT (60 vol.%). See table 11 for 1-16

Figure 22 displays the stress-strain curves of three most common modes of failure, some trials of the DOE displayed all three failure types within 5 samples. Failure mode 1 is shown to break at the end of the linear elongation with a % of elongation at yield > 3%. In this case the core material failed instantaneously with no necking visible. The skin material would often fully delaminate from the core and continue to be stretched. The second mode of failure contained the same linear elongation region but the core and skin maintained lamination before sudden core failure and delamination of the skin from the core. % elongation at yield for this type of failure ranged from 3 to 8%. The last mode of failure had the highest % of elongation at yield with values greater than 8%. In this case the core and skin stayed laminated while the core underwent extensive necking before failing and becoming delaminated from the skin. No trend was seen in
comparing tensile break modes to the processing parameters. It is thus proposed that the tensile failure mode must be an indication of randomly occurring mechanical interlocking between the polymer interfaces.

**Figure 22:** Three prominent modes of failure seen during tensile testing of co-injected factorial DOE trials. Failure mode 1 indicates lack of proper adhesion between PTT/PBT (70/30 wt.%) and PBS/PBAT (60/40%). Failure mode 2 indicates better adhesion between PTT/PBT and PBS/. Failure mode 3 indicates the highest level of adhesion. Core polymer PTT/PBT undergoes full plastic deformation before extensive necking.

### 4.3.6 SEM images

To observe the potential mechanical interlocking between the skin and core blends SEM pictures were taken on the surface of co-injected tensile samples. For each of the observed samples the PBS/PBAT skin was dissolved away. SEM pictures on the top surface of untested tensile
samples taken from trial 10 which reported the greatest % elongation at yield with minimal standard deviation. Both figure 23(a) and 23(c) indicate two different modes of mechanical interlocking. Along with deep cracks on the core surface, 23(a) contains large flakes of the PTT/PBT material seen on both the left and right side of the image. A larger magnification of the crack is displayed in 23(b) and indicates that skin/core interactions produces fine polymer strands which could indicate fine level interlocking. Figure 23(c) is another indication of extensive interlocking between the skin and core material. On the left side of 23(c) image it is evident that there is a large separation within the core material. This split within the core was visible with the naked eye. Figure 23(d) is a magnified section at the closing of the split displaying a rich texture of voids and extended fibers which suggest that the skin and core had achieved intense intermeshing. Figure 24 displays the surface of the PTT/PBT core material from tensile tested materials. In figure 24(a) the surface of a sample which underwent mode 1 failure is displayed. As expected the surface is relatively smooth with no indication of mechanical interlocking with PBS/PBAT. Figure 24(b) displays the surface of a sample that underwent mode 3 failure with extensive necking. In the wake of the dissolved skin a channel is visible on the surface of the skin, along with cracks and fibrous strands which suggest mechanical interlocking. While the processing parameter effects on the extent of skin/core interlocking are unknown it is considered that additional additives or fillers would regulate the mechanical interlocking and prove as useful modification in improving the % elongation at yield.
Figure 23: SEM images of surface of PTT/PBT core exposed by dissolving PBS/PBAT skin in chloroform. 6(a) surface at 100x magnification. 6(b) 1000x magnification of the outlined box in 6(a) displaying fibrous formations. 6(c) at 100x magnification shows a large split on the surface of the core material. 6(d) displays 1000X magnification of the area encased in the white rectangular box seen in 6(c), and displays the extensive formation of fibers and pockets.
4.4 Conclusion

This research investigated the feasibility and controllability of the co-injection a blend of PTT/PBT and PBS/PBAT in an effort to increase the scope of bio-polymer usage and add to the library of known compatible polymers for co-injection. The most promising effect was the increase in impact strength that was observed to increase with increasing skin (PBS/PBAT) thickness with values ranging from 56 to 450 J/m. Likewise samples with the thin skin profiles did not break in un-notched testing. Using a design of experiments for a factorial design allowed for a proper ANOVA analysis with interaction effects. The ANOVA results indicated that the interactions of melt(skin)*injection speed and melt(core*injection pressure) where prominent in most of the characteristic responses. This correlation indicates that a DOE is a good way to quickly map out the processing parameters effects on co-injection processability; however, it is largely dependent on mold shape. Three different modes of failure during the tensile testing is a possible indication of mechanical interlocking which improves adhesion as seen in SEM images. In this case there is the potential for an additives or filler to be used to increase the adhesion. This research indicates that the co-injection of PTT/PBT as a core material with PBS/PBAT as a skin material has a promising potential to be developed in to a final product with semi-biodegradable characteristics as well as contributing to a final material that improves upon the impact strength of pure PTT/PBT blends.

Figure 24: SEM images of co-injected PTT/PBT exposed by dissolving PBS/PBAT skin with chloroform after tensile testing. 7(a) displays the surface of core PTT/PBT of a tensile sample after undergoing failure mode 1. 7(b) displays the surface of core PTT/PBT of a tensile sample after undergoing failure mode 3.
4.5. Acknowledgments

Authors are thankful to the financial support of highly qualified personnel (HQP) Scholarship from the Ontario Ministry of Agriculture, Food and Ministry of Rural Affairs (OMAF and MRA), Ontario, Canada and Natural Sciences and Engineering Research Council (NSERC)-NCE-AUTO21, Canada.
4.6. References


5. Overview of Bioproducts and their sustainability with the Ontario agricultural market

In 2006 roughly 331 million barrels of liquid petroleum gases and natural gases were used to make plastics and resins in the United States, making up roughly 4.6% of the total U.S. petroleum consumption. In recent years the costs of petroleum has increased due to the threat of diminishing resources. This increase in costs has been initially felt by the common consumer in respects to automotive and energy applications. However a secondary impact is being felt in the polymer industry, as the increasing prices of petroleum has forced the price of polymers to rise in accordance. In a response to the increased price the Bioeconomy has been given a great deal of interest as a way to reduce industry dependence on petroleum. The bioeconomy can be defined as a revolution in getting industrial products of commercial value from biorenewable resources. The bio-economy has come in a response to the increasing energy demands of the expanding economies of the developing world. Thus the goal of utilizing the bioeconomy is to create an economically viable and sustainable use of biological resources to significantly reduce the environmental footprint associated with our energy systems. In this new economy there are three major categories, Biochemical, Bio-fuels/energy, and Biomaterials, all of which can come from the same biological sources. Biomaterials are a field of materials that are mainly derived from renewable resources, more specifically agricultural and bacterial resources. These materials are often heralded for their low environmental impact and sustainability. The increased costs of petroleum, research in biomaterials and consumer demand for “green” products has caused rapid growth in the biomaterials field. Biomaterials can be divided into two subsections, bio-polymers and bio-composites. Biopolymers synthesize agricultural feedstock or bacterial feedstock to produce a variety of pure and mixed polymers. The most popular include, poly(lactic acid) (PLA) which is based from corn and poly(hydroxyl alkanotates) (PHA’s), a family of polymers based from bacterial sources. Biocomposites are materials in which the polymer is reinforced with a type of fiber or particle. This enables the usage of many different types of agricultural biomass including jute, hemp, sisal, as well as waste products, such as soy stalks and distillers dry grain soulubles (DDGS) which is a by-product of the ethanol industry. The purpose of these
Biomasses can be to add strength and toughness to the polymer, or to act as cheap and light filler.

Biomaterials are usually forgotten in the biofuel-versus-food debate, but have a high potential to produce a lasting impact on the agricultural chain. In a 2009 article in *Bioplastics Magazine*, Carus and Piotrowski display the disparity between the biomaterials and biofuels demand by indicating that bioplastics now represent less than 0.1% of global cultivated land, compared to about 2% for biofuels, however, this percentage is expected to grow. Regardless of its small size the biomaterials sector has received criticism in the use of “food” crops on a basis of food source competition. These critics either argue that the sources are in direct competition with the biofuel industry. Such that in the case of biopolymers (particularly the corn based PLA) taking over conventional plastics could not be feasible due to the increased feedstock demand, in which government mandated ethanol production would have the majority of the feedstock. Other critics take the same stance as those opposed to the food vs. biofuel debate, in which there is a raised concern on the sustainability of the Bioeconomy while maintaining adequate food supplies. The feedstock pathways to final polymer form for the major polymers discussed in this thesis are displayed below in Figure 25. From Figure 25 it can be seen that all of the pathways stem from the production of glucose, which can be found all starch containing plants such as corn and wheat.
Sustainable development was first fully defined in the Bruntland Report\textsuperscript{7} as, “development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”\textsuperscript{7} The report further expands the idea of sustainability into three pillars, society, economy, and the environment. The following discussion will review the sustainability of Biomaterial production within Ontario, as the environmental sustainability of biomaterials is the largest selling point for many advocates.

As defined in the introduction of this thesis biopolymers can be 100\% renewably resourced as well as biodegradable. This allows for alternative polymers with reduced impact on the environment in comparison to conventional plastics made from petroleum sources, which must
ultimately be burned or placed in a landfill. The agricultural crop production in Ontario can be separated into two different groups, horticultural and field. For this analysis we are concerned only with field crops as they include winter/spring wheat, grain corn, soybeans oats, barley, hay, canola, and others. In 2010 Grain corn, and fodder corn brought in 7,747,400 and 4,472,400 tonnes respectively, making them the 1st and 3rd largest produced crop in Ontario. About 5.7% of global grain production and 10% of global vegetable oil production is used to make 85 billion and 15 billion liters of ethanol and biodiesel, respectively. The US numbers are 54 and 1.5 billion, requiring 5.0 billion bushels (40% of 2010 US corn production).

From a social standpoint the selling point of green alternatives has seen an increased use from commercially available products. The average consumer is more consciously aware of the environment and can be persuaded to buy certain products based on their environmental footprints. Oppositely, opinions have been voiced against biomaterials for different reasons. There is a fear that the widespread incorporation of biomaterials will be in direct competition with food production thereby reducing the amount of food available to the world, particularly those in third world countries. It is a common estimation that the world’s food supplies must increase 70% between 2000 and 2050, or 1.1% per year. Average Ontario production of grain corn, fodder corn, winter wheat, and soybeans has significantly increased as shown by Table 15. It can be seen that the compounded annual growth rates are much higher than 1.1%. By comparison the average world grain yield has increased by 1.5% per year from 1987 to 2007.

Table 15: Increase in Field Grain Productions from 2001 to 2010. Production Data from Ontario Census (CARG – Compound Annual Growth Rate).

<table>
<thead>
<tr>
<th>Field Grain</th>
<th>Production ('000 tonnes)</th>
<th>CAGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2001</strong></td>
<td><strong>2010</strong></td>
<td></td>
</tr>
<tr>
<td>Grain corn</td>
<td>5131</td>
<td>7747.4</td>
</tr>
<tr>
<td>Fodder corn</td>
<td>2993.7</td>
<td>4472.4</td>
</tr>
<tr>
<td>Wheat</td>
<td>1056</td>
<td>1763.6</td>
</tr>
<tr>
<td>Soybeans</td>
<td>1279.1</td>
<td>3048.1</td>
</tr>
</tbody>
</table>
These growths have put Ontario in a strong position to provide extra agricultural resources to industries other than the food chain. To further add to the security of food production new agricultural areas are seeing improved growth. This includes the revival of the eastern European agricultural economy, which before World War I, supplied Great Britain with most of its food. As well, growing powerhouses such as China and Brazil have begun to export much of their food. In spite of these growing production trends many in the plastics industry are unwilling to work with bioplastics. Many biocomposites can be produced from wastes materials of food crops, such as soy stalks, corn stover, and corn stalks. These are materials that can be used without any taxation to the food production levels. The total quantity of sustainably harvestable crop residue in Ontario is 3.12 million tonnes/year.\textsuperscript{11}

There are a total of 11 counties in Ontario which can provide the crop residues of 500,000 tons/year sustainably.\textsuperscript{11} The government of Ontario has already produced reports indicating the specific crop rotations required and indicating which are the highest yielding of waste materials. With the specific infrastructures already being considered there is increasing motives to create a sustainable biomaterials economy within Ontario, furthermore this is an economy that is run off of the Ontario agricultural sector. With the harvesting of wastes materials and incorporating those into the biomaterials farmers can increase the profits of their crops, and industries can reduce the costs of their final products.

The final and most important tier in the sustainability of biomaterials is the economy. As Biomaterials has recently been gaining strength in the past decade but has yet to live up to its potential. Current capacity the biomaterials can replace a mere 1 percent of plastics. However the growth rate of this market has been predicted to grow by a minimum of 17.7 percent per year, being driven by big corporations.\textsuperscript{12} Petroleum is used in a bewildering array of products and packaging, but fluctuations in oil prices make it difficult for companies to predict the cost of materials. Biobased fibers for textiles and acetate, used for things like pens and toothbrushes, dominate the biobased materials scene, accounting for 39 percent and 24 percent of the current $10.7 billion market.\textsuperscript{12} In a report by Lucintel, in 2012 the total global natural fiber composite materials market shipment roughly 200 thousand tonnes with a value of US $289.3 million and is expected to grow to US $531.3 million by 2016.\textsuperscript{13} Europe was the largest consumer of natural
fiber composites, with China and India rapidly increasing demand. In their report Lucintel predicts that there would be higher market fragmentation due to newly emerging economies. The future market will be highly competitive with innovative companies gaining the market share.

Currently there are a number of political mandates set by countries worldwide which specify the blending of ethanol into gasoline to reduce the consumption of gasoline. (Regulation 535/05 specifies that a minimum of 5% ethanol must be blended into gasoline being sold in Canada) Recently the effects of a drought were detrimental to the corn production forcing higher prices for corn. The increased price had an effect on the North American market as many products are linked with corn. Furthermore the increased price and lower supply has placed enormous pressure on the ethanol industry to meet demands for the ethanol mandate. Due to the failure of cellulosic ethanol the US mandated requirement for cellulosic ethanol in 2011 was recently scaled back from 250 million gallons to only 6.6 million to deal with this setback. Bioeconomy governmental mandates and strategies are a driving force in the development of bioeconomy technologies. Recently many investigations have been done by the Canadian government into the support of biomaterials with an emphasis on sustainability.

As it has been previously stated the problem lies in the unreliability of the market. The fear of food shortage has strong parallels to the 1970’s food crisis, a disaster which was avoided thanks to key players such as Norman Ernest Borlag, who through innovation and research increased the food output of farms. In the meantime governmental reports have suggested supporting new policies for biomaterial growth. The Ontario government has a great interest in seeing the biomaterials sector grow as it would provide extra income to farmers. The Canadian Agri-Food Policy Institute (CAPI) released a publication titled “Canada’s Agri-Food Destination: A New Strategic Approach.15 The reasoning for CAPIs proposal of strategic change comes from a “chronic unprofitability seen in the past 10 years as shown in figure 26. CAPI outlined a need for new governmental policies that focus on an encompassing agri-food system that connects the many agri-food players in the Canadian market into a structured and interwoven machine that is more efficient than the current value chain-based plan. These collaborative food systems would accelerate innovation and revive a struggling sector.
Figure 26: (Net farm income: Agriculture economic statistics, catalogue no 21-010-X; net government payments to the sector, after producer premiums: Direct payments to agricultural producers: agriculture economic statistics, catalogue no. 21-015-X, statistics Canada

CAPI proposes that it would be extremely beneficial if the biomaterials industry created more partnerships directly with farms, an idea that was also recommended by Sparling, et al. in their report of the Canadian Bioproducts Industry based on 2003 and 2006 census data. Both argue that much of the difficulties surrounding the use of agricultural biomass on bioproducts are through the shipment and transportation. As biomass has high volume to weight ratio, and increasing gas prices make shipping biomass expensive. It was reported that in 2006 10% of bioproduct firms used on site biomass, 28% was used off site within a 50km radius and 25% obtained their biomass from a 500km or greater radius. As a result sourcing and shipping become key determinant of the bioproduct industry. The solution in which both Oo and Lalange and the CAPI report suggest is an increased systematic approach to the bioproducts industry, this includes, local sourcing, materials from wastes products, and collaborative partnerships that would benefit both the farmers and the industry. A systems approach would
ensure that the byproduct of the farmer’s fields would be linked together with other farmers allowing them to meet with the demand of an industrial biomaterial product. CAPI also identifies biomaterials with another benefit to the agri-food chain, and that is sustainability. New demands from customers and increasing prices of the petroleum industry are forcing the food sector to look at ways of obtaining more sustainable practices. Historically by-products are used to enrich the soil, but certain products can give financial benefits.

It is evident that there are a number of challenges regarding to mass production of biomaterials. Public acceptance for greener materials is currently on the rise, but many are concerned with agricultural food supply. As it was previously discussed a 70% increase in food production between 2000 and 2050 must be created for a growing population. This places a large strain on world food supplies, but for Canada, specifically Ontario the required growth rate had been met. Further competition for agricultural biomass comes from the ethanol and biodiesel industry which are currently using around 40% of corn produced in the US. Biomaterials must find a sustainable way of existing if they are to be a viable option in the near future. The social and environmental aspects of biomaterials are the selling points, while the economic view is not as strongly supported as the other two. However there are many governmental proposals written by CAPI that have emphasized that biomaterials are a great asset into the systems approach as the industry can be created on the byproducts of many of the currently grown crops. In light of this new strategic demand a new bio based succinic acid production plant, which is the feedstock for PBS, has been under development in the chemical parks of Sarnia under a newly formed partnership between BioAmber and Mitsui & Co. This $125 million plant is expected to produce 50’000 metric tons of succinic acid by 2016. This new and growing sector represents an important chance to increase the product revenue of the Canadian agri-food chain, and can be feasibly done though continued agri-innovations and proper management of agricultural products.
5.1 References


6. Overall Conclusion and Future Recommendations

Each individual study was concluded in sections 3.4 and 4.4 respectively. This section serves as a summarization of the significance and scope of the project to date.

Research performed in the two manuscripts is an attempt to study various solutions to overcoming inherent problems that come with utilizing bio-content in polymeric materials. Partially bio-sourced PTT was blended with the fast crystallizing PBT in an effort to add some bio-content to the widely used polyester. Special consideration was placed on the effect of processing parameter on the blend. A design of experiments indicated that the mold temperature was the only significant processing parameter with respects to the blends impact strength. A Taguchi analysis was successfully used to optimize the impact strength of the PTT/PBT blend. Further investigations indicated that mold temperature was affecting the crystallization rates of the two polymers, particularly, hotter mold temperatures increased crystallization which in result lowered crystallinity. It was displayed that the PTT/PBT blends could effectively act as a miscible blend due to fine intermeshing of the two polymers, producing a polymer blend that acts like PBT while incorporating a level of bio-content.

The effectiveness of the PTT/PBT blend however was unable to overcome the inherent brittleness of pure PBT. In an effort to overcome the brittleness the PTT/PBT blend was used as a core material for co-injection with a tough blend of biodegradable PTT/PBT. The high degree of variability in co-injection with processing parameters was approached with a fractional factorial design of experiments. Execution of this DOE allowed for the ability to map the relative effects of processing parameters on the skin/core distribution and uniformity. The co-injection of (PTT/PBT | PBS/PBAT) successfully improved the poor impact strength of the single injection of PTT/PBT, while also improving upon the strength of the singly injected PBS/PBAT blend. A successful co-injection of a biodegradable skin with partially biobased core is a profound implication with the onset of newer and cheaper co-injection machine developments. This paper is to act as a stepping stone for further developments of co-injections with bio-based polymers, as well as a solution for increasing specific polymer properties with methods other than simple blending.
The research undertaken in this thesis began almost 4 years ago, since that time there have been a number of key advances in the materials being used for this research. When this research started PTT was the only biobased polymer available in the materials studied, at 37% biocontent. As previously discussed in chapter 5 all of the polymers used in this study can now be sourced from derivatives of glucose. The most notably commercially available bio-based PBT has been scheduled for production through a partnership of Toray and Genomatica for 2013. In light of this recent news the blend of PTT/PBT presented in this thesis will most likely have no implications for the future, however, the understanding of controlling the crystallization kinetics of PBT with a slower crystallizing polymer might prove useful in some applications. PBS and PBAT have also been reported to soon be produced by 100% biobased feedstocks which will substantially increase the biocontent of the co-injected formulation.

Biobased feedstocks which produce PTT, PBT, PBS, and PBAT are all derived from glucose monomers found in starch containing plants like corn and wheat. This has the potential to allow for a major development in the biopolymer and biomaterials field within Ontario, especially when considering the recommendations voiced by many economists who argue for localization between the biopolymer manufactures and the agricultural sources. This is seen as a solution in up keeping with agricultural demand while reducing infrastructure costs associated with transportation. The agricultural market in Ontario is also a prime candidate for an influx in biomaterial production due to their continuous growth rate, which will help augment some of the arguments voiced in the food vs. fuel debate.

In a further effort to improve both the bio-content and performance of the co-injected formulation bio-based additives such as biofibers, or biofillers should be investigated.