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ANALYSIS OF CORRELATION BETWEEN MOLECULAR WEIGHT DISTRIBUTION
AND MELT FLOW INDEX OF POLYETHYLENE AND POLYPROPYLE BLENDS

by
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A THESIS

Submitted to the graduate faculty of The University of Alabama at Birmingham,
in partial fulfillment of the requirements for the degree of
Master of Science

BIRMINGHAM, ALABAMA

2023

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2023

ANALYSIS OF CORRELATION BETWEEN MOLECULAR WEIGHT DISTRIBUTION AND MELT FLOW INDEX OF POLYETHYLENE AND POLYPROPYLE BLENDS

ETHAN STONECIPHER

MATERIALS ENGINEERING

ABSTRACT

Recycling of plastics is one of the biggest challenges facing the earth in the 21st century due to the environmental impact they have on the waste stream. One of the biggest challenges in the recycling of these materials are their incompatibility; therefore, the segregation of waste in order to repurpose them back into something useful for a second life is an important barrier to overcome. This study expands on work done in literature to correlate rheological properties of linear virgin plastics to their \overline{M}_w , which is useful in deducing some mechanical behaviors of the material. The benefit being the impact on industries to run cost-effective and reliable measurements using a Melt Flow Indexer to roughly determine the ratio of HDPE/PP blends if a rough estimate for \overline{M}_w is provided. Otherwise, a \overline{M}_w can be deduced with a reasonable estimate of the blend of HDPE/PP in the waste stream. This paper employs techniques such as differential scanning calorimetry, thermogravimetric analysis, melt flow indexing, and gel-permeation chromatography to investigate thermal, rheological, and mechanical properties of various blends of both virgin and post-consumer HDPE and PP over five heat histories. The introduction of blends of virgin materials expands on the literature, and post-consumer plastics provide a real-world example of how this relation holds with every day post-consumer plastics such as milk jugs, coffee jars, plastic pottery, and detergent bottles. The results show that the correlation established in literature holds for the virgin materials; however, the post-consumer plastics did not favor this relationship and was more accurately predicted using the raw data plotted against one another. This is an interesting discovery and leads to the investigation of exactly what properties affect this correlation, and if there is a predictable curve depending on the presence of additives or the spread in MFI or \overline{M}_w properties.

Keywords: Polyethylene, Polypropylene, Molecular Weight, Melt Flow Index

DEDICATION

I would like to dedicate this thesis to my grandmother and to my wife, who both provided financial and emotional stability for me throughout this entire process. From providing housing, meals, a place to call home, and a shoulder to lean on, I honestly would not have been able to do this without the two.

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Many thanks to my undergraduate peers, Zach Newman and Khaleed Blocker, whom I trusted whole heartedly to keep an eye on the processing and kept this research going along. Their company during the late nights and early mornings to push through the processing of this research will forever be valued. Additionally, my graduate peers and mentors Carlos Angulo and Daniel Lerew, whose experience and insights through coursework, experimental design, and general approaches on both my personal and professional life have been immensely appreciated.

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LIST OF ABBREVIATIONS

DSC: Differential Scanning Calorimetry

GPC: Gel Permeation Chromatography

HDPE: High Density Polyethylene

MFI: Melt Flow Index

PDI: Polydispersity Index

PP: Polypropylene

TGA: Thermogravimetric Analysis

\overline{M}_w : Weight average molecular weight

\overline{M}_n : Number average molecular weight

r100/0: Recycled 100% HDPE 0% PP

r75/25: Recycled 75% HDPE 25% PP

r50/50: Recycled 50% HDPE 50% PP

r25/75: Recycled 25% HDPE 75% PP

r0/100: Recycled 0% HDPE 100% PP

v100/0: Virgin 100% HDPE 0% PP

v75/25: Virgin 75% HDPE 25% PP

v50/50: Virgin 50% HDPE 50% PP

v25/75: Virgin 25% HDPE 75% PP

v0/100: Virgin 0% HDPE 100% PP

1.0 INTRODUCTION

1.1 Polymers and Their Environmental Impact

Polymeric materials have had a broad impact on many fields of science and engineering throughout the 20th and into the 21st century. With the freedom to synthesize new material, humanity has not been limited to only natural resources for its needs; however, this has come at the cost of a new waste management issue. It is currently more cost effective to create new material in favor of repurposing, or recycling, used polymers into some new use cases. There is a wide consensus across the globe that one of the biggest threats to the world in the 21st century is climate change, [1], [2] and a significant contributor to this is the issue of plastic waste [3], [1] [1] [4]. According to the sources cited, an estimated 300 million tons of plastic are produced each year, and about half of that is only intended to be used one time before discarded. This leads to landfills being full and requires expanding onto wildlife's territory to dump waste. This disturbs the local ecosystems and is leading to a debate in the scientific community about whether the earth is experiencing its 6th mass extinction event [5], [6]. One of the most used consumer plastics is polyethylene terephthalate (PET), which sees applications in single-use water/drink bottles, food storage, and polyester in its fiber form for clothing [7]. In addition to PET, high-density polyethylene (HDPE) and polypropylene (PP) are also among the most used post-consumer plastics. Together, these polymers are used in consumer goods such as grocery bags, plastic straws, soda packs, water bottles,

packaging materials and coffee “K-Cups.” Altogether these materials are only designed to be used once before being discarded, which raises the pressing question: “What can we do to extend the life of the plastics in order to reduce the rate at which we waste?”

1.2 Recycling Polymers

A significant roadblock in the recycling of these post-consumer plastics is the segregation of different recycle numbers, which separates the plastics based on their chemical structure (Figure 1). Some are similar in chemical composition; in that they share a common backbone of carbon bonds with varying hydrogen bonds attached, such as Polyethylene (recycle #2) and Polypropylene (recycle #5). Contrasting this, PET has a carbon backbone with a benzene ring and varying oxygen bonds [8].

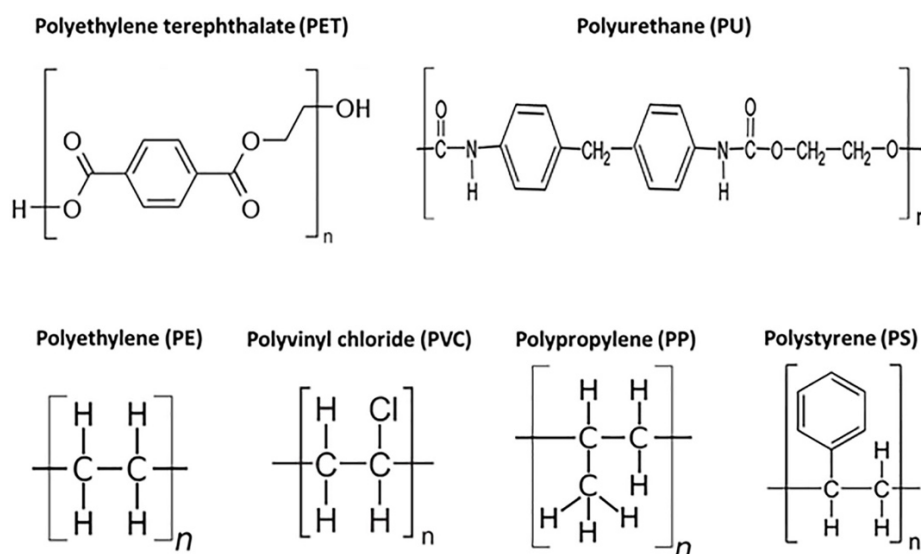


Figure 1. The chemical structure of post-consumer plastics.

Due to their varying chemical structure, most of the above polymers are immiscible [8], [9]. Therefore, it is necessary to segregate many of the polymers during the recycling process. Moreover, there are several challenges in recycling post-consumer plastics that are unrelated to the chemical structure of the polymer. Cleaning food waste and unwanted oils from containers is a necessary endeavor [10] and can get quite

complicated on large scales [11]. Anecdotally, a challenge to this research is related to the labeling techniques used in industry. Companies that use the same polymer have their own stickers made from paper or unlabeled plastic and these should be removed to reduce contamination. After stickers are taken from their product, there is still an issue with adhesive residue if the label is not printed directly onto the container. This means that the best solution is for individuals to clean the waste from their used plastic containers after use [12].

If polymers are similar enough in chemical structure, they should be exempt from the segregation barrier in the recycling process. Polyolefins are hydrocarbons with at least one double bond [13], and since polyethylene and polypropylene are both polyolefins, they are capable of being mixed and blended into one material [14], [15]. Even if not totally miscible in their microstructure, they have similar enough composition to mix and have useful properties. Authors such as Alfred Rudin and Phillip Choi argue that if one is unable to tell if they are miscible, there is not much point in discussing if they are truly miscible on the microscopic scale [16]. Polyolefins are blended together for commercial use in packaging [17], automotive bumpers [18], cable insulation [19] and other cases where thermoplastic or rubber properties are desired. Therefore, characterizing the behavior of a blend between HDPE and PP should prove useful in the recycling issue facing the globe.

Extensive research characterizing both virgin and recycled HDPE and PP exists in literature. Thermal characterization includes primarily differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), [20] - [21]. Rheological properties are explored via melt flow indexers [22], [23], while mechanical behavior is explored via

tensile testing, flexural testing, and Izod impact testing [24] - [25]. Each of these gives useful information about material behavior and performance under stressed conditions during application. These tests are convenient ways to understand how a polymer will behave at certain temperatures, or under specific loading conditions, but none of these tests yield too much information outside of their specified goal.

Therefore, the motivation of this study is to investigate an approach to correlate rheology with mechanical behavior, as it would be a cost-effective tool in industry by saving the initial investment of several machines and the time to operate them into one test that takes only several minutes to complete: the melt flow indexer. The melt flow indexer is already a common method of testing for intrinsic viscosity, shear rate, and the melt flow index in plastic producing industries. In order to understand how to correlate results from a melt flow indexer to mechanical behaviors, a discussion is required on how the molecular weight distribution of polymers influences certain mechanical properties.

1.3 Molecular Weight Distribution

The molecular weight distribution (MWD) of a polymer is one of the determining factors of that polymer's mechanical and rheological properties, which in turn influences the performance and processability. Processability is one of the most important considerations of a polymer, as this is what makes something synthesized in a lab a useful commodity, and the MWD of the polymer is indicative of how it will behave. In general, higher molecular weight polymers tend to exhibit higher tensile strength, elastic modulus, and brittleness; while lower molecular weight polymers tend to be more ductile with lower tensile strength and elastic modulus [26]. This is because there is less energy stored in the structural packing of low molecular weight polymers, so it required less energy to

fail under load. Moreover, there is more room for the polymer chains to move around and become stretched; therefore, they will tend to have a longer elastic region on their stress-strain curves [27].

There are several ways to discuss the MWD of a polymer, but the two most common are the number average molecular weight (\overline{M}_n) and the weight average molecular weight (\overline{M}_w). The \overline{M}_n is the average number of molecular chains in a given volume and is defined by the summation of the fraction of molecules with some specified molecular weight. If instead of considering the size of molecular chains, one considers the weight of each chain, then the \overline{M}_w is obtained. Both can be formulated as follows:

$$\overline{M}_n = \frac{\sum x_i M_i}{\sum x_i}$$

$$\overline{M}_w = \frac{\sum x_i M_i^2}{\sum x_i M_i}$$

Where x_i is the fraction of molecules with molecular weight M_i .

Another useful measurement of the MWD is the polydispersity index (PDI). This is the ratio of $\overline{M}_w/\overline{M}_n$ and gives insight to the breadth of the MWD. While the values for \overline{M}_n and \overline{M}_w are indicative of the distribution of the polymer chains, the description of the MWD is not complete without describing the deviation of the averages. A monodisperse polymer (a polymer whose \overline{M}_n is equal to \overline{M}_w) will have a PDI of 1.0, but it is a theoretical limit instead of a practical one. Therefore, many instruments measuring the MWD calibrate to polystyrene whose PDI is 1.04 and provides a sharp peak of a distribution. Conversely, polymers that may have varying degrees of molecular weights, either through branching or mixing, may exhibit broader peaks with higher PDIs.

The technique used in this study for measuring the MWD is called gel permeation chromatography (GPC), which has also been referred to as size exclusion chromatography (SEC). This is a separation process wherein a dissolved polymer is filtered through columns filled with porous gel beads. Those polymer chains that are longer will pass by the gel beads, while those with shorter chains gets caught up in the pores and are later flushed out of the columns via the solvent. What is produced is a curve plotting molecular weight versus elution volume, which can be thought of as the amount of time the polymer spent in the columns, where the longer chains are the first to pass through, so they make up the left-hand side of a MWD curve, while the shortest chains spend more time in the columns and are on the far-right hand side [28]. Figure 2 [29] illustrates this method of separation in the column where large molecular chains are filtered first, and the smaller molecules are flushed out with solvent.

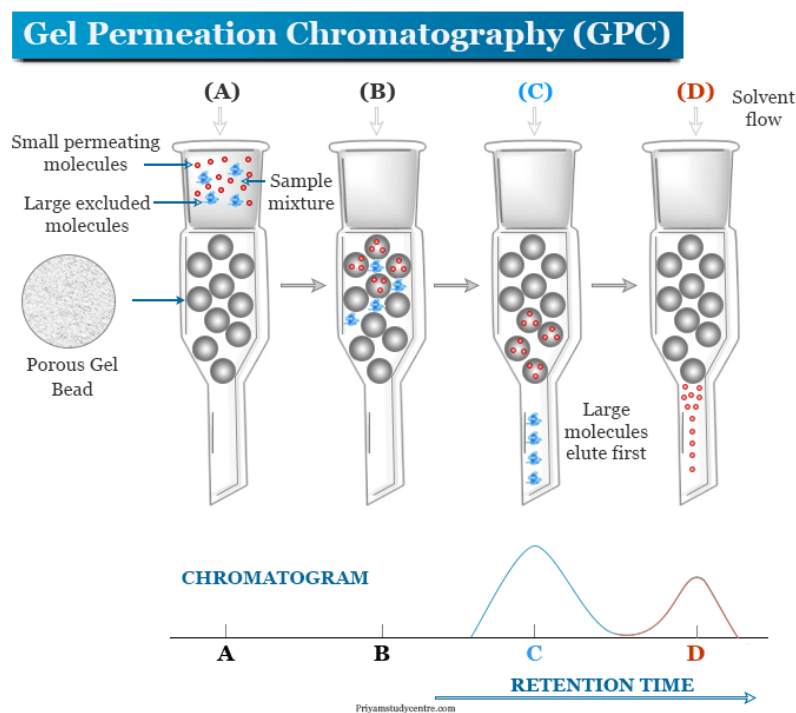


Figure 2: Illustration of GPC Separation Technique

Figure 3 is a representative sample from this research of a typical GPC graph. The sample is a virgin polypropylene sample that was run intermittently as a reference to ensure GPC results were consistent.

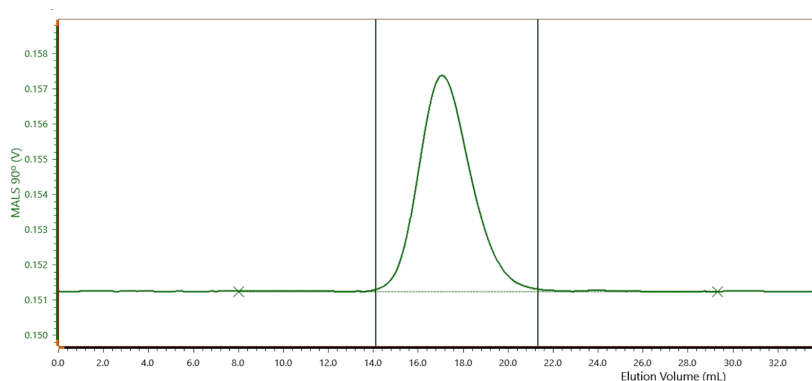


Figure 3: Representative sample of typical GPC curve.

More techniques have been developed to measure the MWD during a GPC test, including viscometers and multi-angle light scattering instruments which the polymer solution also passes through and gives readings on the MWD. This is useful to confirm the results given by the three columns which contains gel beads. While the viscometer relies on rheology to determine the MWD, the light scattering is the most empirical form of measuring the \overline{M}_n and \overline{M}_w by shining a laser at the solution and measuring the diffraction from up to 17 different angles.

1.4 Melt Flow Index

The melt flow index (MFI) of a polymer is a measure of how much material will flow through a die over a given amount of time. The standard units are given in grams per 10-minutes (g/10min), but other readings on the melt volume rate (cc/10min), shear rate (1/sec), and viscosity (pascal sec) are also useful information. The setup consists of a vertical thermally insulated cylinder that fits a removable die. The die is placed in the cylinder and allowed to come to the desired temperature, which should be determined by

ASTM D1238-10 *Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer*, and the material is placed in the cylinder followed by a piston and load with some known weight. The piston and weight apply some calculable stress on the molten material which is forced through the die, and the machine measures how much material flows through the die over some distance. A diagram of this process is shown in Figure 4. Calculations are then made about the MFI and other properties. It should be noted that these calculations require known geometries of the cylinder, die, piston weight, weight, and the material's density [30]. The specifications used in this research can be found in the experimental section of this document, but all are in line with ASTM D1238-10.

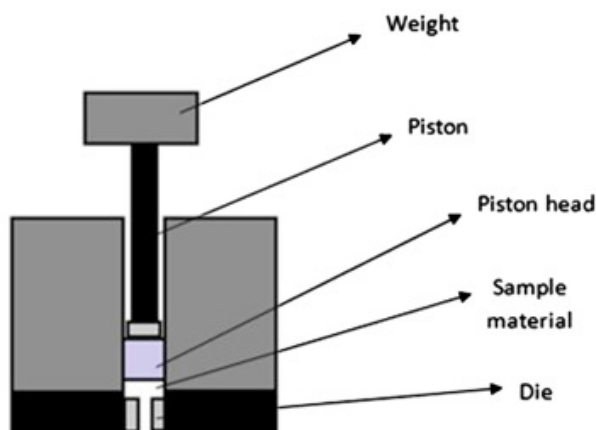


Figure 4. A diagram of the experimental design for general melt flow indexer.

1.5 Thermogravimetric Analysis

TGA is a technique that measures the mass of a material as a function of both temperature and time. The sample material is placed on a scale capable of measuring hundredths of milligrams, so it needs a stable environment as to not be affected by external drafts/winds. A sample is held in an inert atmosphere and subjected to temperatures as high as 1,200°C under a ramp of up to 40°C/min, while the machine

measures the mass and plots the weight loss as a percentage on the y-axis versus the temperature (or time) on the x-axis.

1.6 Differential Scanning Calorimetry

DSC is an abbreviation for both the technique used to analyze (calorimetry) and the machine used to do the analysis (calorimeter). The technique measures the heat flow rate differential between the sample pan and a reference pan, where the pans are hermetically sealed and typically made of aluminum [31]. Both pans are supplied with equal and linear rates of heating and cooling via a heater, while the temperature difference is kept constant using a heat sink and heat resistor [32]. The samples sit on a temperature sensor and in the case of any temperature deviation, either by endothermic or exothermic reactions, the heat supply is increased or decreased appropriately to the sample pan to keep the temperature differential constant. The environment is controlled using an inert gas flowing through the cell, and throughout this work nitrogen was the gas purge of choice.

1.7 Literature Review

While the MFI is only a rheological measure, several studies have been done to correlate this value to other properties [22], [33], [34] with varying degrees of success. Some of the pioneers in expanding the implications of MFI tests from strictly quality control to relating other factors include Shenoy et. al. in 1986 [22], who conducted a meta-analysis on MFI correlations done up to that point. The authors thoroughly discussed the ways in which MFI for virgin polymers can relate to properties such as tensile strength, ultimate elongation, tenacity, elastic modulus, flexural stress, impact strength, brittle temperature, tear strength, environmental stress cracking, gloss, and

clarity. They made the case that MFI tests can be useful in the synthesis, processing, and application stages of a polymer's life and should be expanded into more than a quality control measure of processability. While this analysis is of value, there is a burden of correlating every polymeric structure with each of these physical properties under specific conditions of the MFI experimental setup. For example, the relationship between MFI and tear strength will differ between polybutadienes and polyethylene; moreover, the relationship may vary with the load and temperature chosen for the MFI test.

A few years after Shenoy's publication, Alfred Rudin and his team investigated the relationship between MFI and the MWD of various linear virgin polymers including polystyrene, polypropylene, linear low-density polyethylene, and high-density polyethylene [33]. The authors walk us through a discussion starting with Poiseuille's equation for the flow of a material through an orifice, and arrive at a relationship between the \overline{M}_w and MFI, which is given in the equation below:

$$\frac{1}{MFI} = G \overline{M}_w^x$$

where G is a constant determined by both the geometry of the melt flow indexer and inherent polymer properties, while x is determined experimentally. While the Mark-Houwink relationship was established in the late 1930s [35], which related the intrinsic viscosity and the molecular weight of a polymer, Rudin illustrated several specific curves of $\overline{M}_w^x \times 10^y$ vs MFI^{-1} where $3.4 \leq x \leq 3.7$ and $-15 \leq y \leq -18$ and demonstrated the linear relationships between the two with varying degrees of correlation coefficients. An example of one such relationship from this paper is shown in Figure 5 for HDPE. The results were satisfactory, but the scope was quite limited to linear polymers with similar PDIs and processing histories.

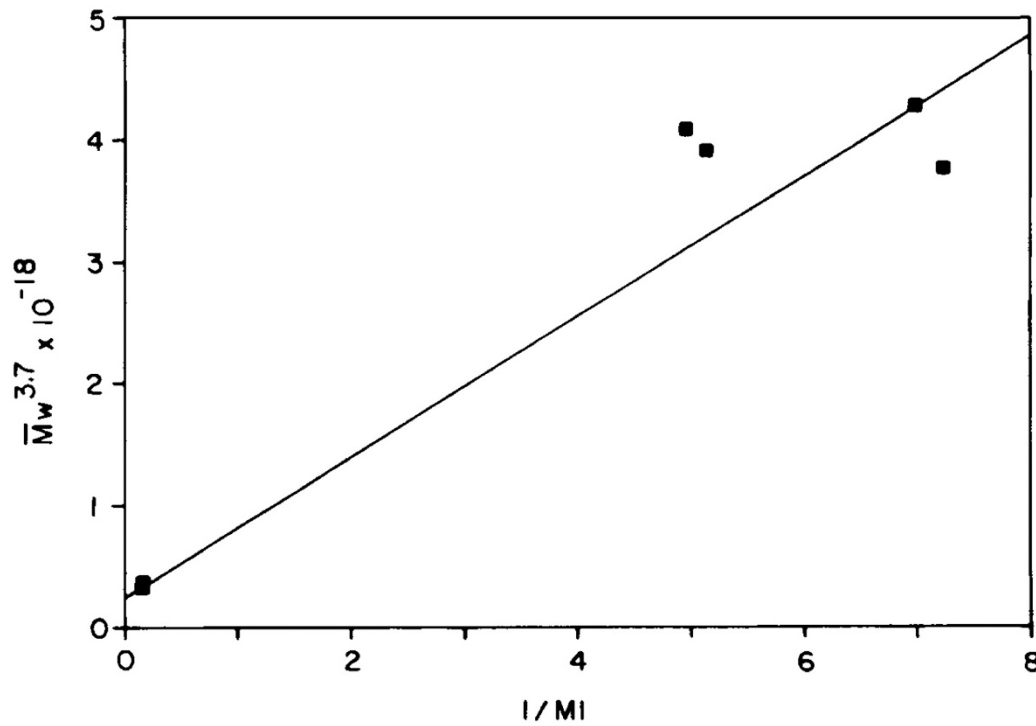


Figure 5. Rudin's $M_w^{3.7}$ vs $1/MFI$ of HDPE.

One step to further test the results of the above work is to expand this correlation of MFI to \overline{M}_w with recycled plastics, as they will have been in contact with various additives and foreign particulates not synthesized in the lab. Authors E. E. Ferg & L. L. Bolo investigated the effect of varying mass loads on MFI tests to the relationship above and reported results consistent with literature [34]. Namely, the 3.4 power discussed in Rudin's paper was confirmed here with recycled polypropylene recovered from Pb-acid batteries. They obtained the value from taking the slope of a least squares linear fit of $\ln(1/MFI)$ versus $\ln(\overline{M}_w)$ from various melt flow indices and the average \overline{M}_w . Ferg and Bolo did argue that perhaps a linear correlation was not useful for all samples. They noted that the spread in MFI values for Rudin's work included those values with less than 1g/10min, so a linear trend will intercept the y-axis at the origin. However, the data for

Ferg and Bolo had the lowest MFI of 4 g/10min, so extrapolating a linear fit would yield a y-intercept of roughly 26,000 g/mol. This physically means that a polymer with \overline{M}_w of 26,000 g/mol would have exactly zero flow, but this theoretical boundary is not satisfactory with real life experimentation, so the authors chose to model the MFI vs \overline{M}_w with a power function instead, whose results are illustrated in Figure 6.

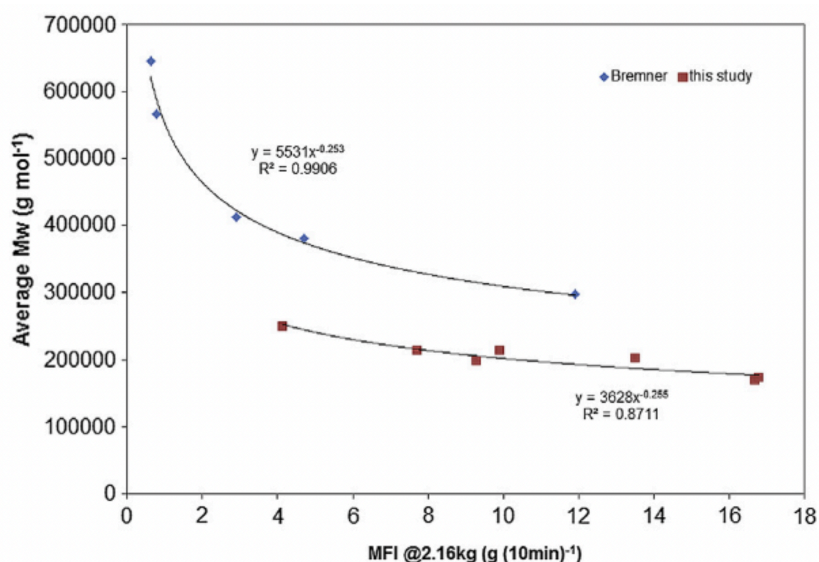


Figure 6. Rudin's results of M_w vs MFI with power function (blue) versus Bolo's results with power function (red).

Lastly, some discussion is to be had about mixing rules for these polymer blends. While the correlation of the MFI vs \overline{M}_w shows promising results, rules of mixing can be used to describe the ratio of polymer blends without the discussion of mechanical properties. Centeno et. al. showed through a meta-analysis that standard mixing rules may have high error and can be adjusted to more accurately reflect the mixing of petroleum [36]. Moreover, relevant literature in describing mixing rules for immiscible polymer blends were explored by Grizzuti Nino, et. al [37]. These both are relevant in their discussion of mixing rules for various properties of polymer blends such as

viscosity and molecular weight. Simple mixing rules can be described as the summation of the products of each component's weight or volume fraction with the respective component's property. For example, a simple mixing rule for viscosity can be seen below.

$$\eta_{Blend}^n = \phi_A \eta_A^n + (1 - \phi_A) \eta_B^n$$

The Greek symbol *eta* is the viscosity of the blend, *phi* is the volume fraction of the respective component, and *n* is experimentally derived. It is important to note that the densities of materials in this study are both similar enough that weight fractions are considered in place of volume fractions.

2.0 PROCESSING AND TESTING PROCEDURES

2.1 Material Selection

The virgin materials for this project were manufactured by Amoco (polypropylene) and PolyOne (high density polyethylene), while the post-consumer (recycled) plastics collected consists of milk cartons, coffee containers, sour cream bottles, plant pots, among various other household items. Both the virgin and post-consumer plastics were separated and blended by weight % according to Table 1 to a sum total of 2.3 kilograms.

Table 1. Ratios of HDPE to PP studied in this paper.

Label	100/0	75/25	50/50	25/75	0/100
Ratio (by weight %)	100% HDPE + 0% PP	75% HDPE + 25% PP	50% HDPE + 50% PP	25% HDPE + 75% PP	0% HDPE + 100% PP

Nomenclature in this study follows the “Label” row in Table 1 with information to describe whether the material is virgin (v) or recycled (r) in addition to a numerical value that represents how many times the material was processed via the twin screw. A blend of 75% virgin HDPE and 25% virgin PP passed through the twin screw once would be denoted as “v75/25 (1),” while a blend consisting of 25% post-consumer HDPE and 75% post-consumer PP through the twin screw 4 times would be “r25/75 (4).” It should be noted that either end of this spectrum contains 0% of HDPE or PP; nevertheless, they

will be referred to as a “blend” when the material is discussed. For clarity: the word “*blend*” will refer to the ratio by weight percent of HDPE to PP, “*material*” will refer to a specific blend at a certain heat history, and “*sample*” will refer to the material used in a single test. The reader may also refer the “List of Abbreviations” section for a complete list of the nomenclature. The post-consumer plastics were hand washed with dish soap before they were chopped using an industrial grade granulator and filtered through 3/8” circular holes. Both the virgin and recycled material were then measured by weight and thoroughly mixed according to Table 1 in a large plastic bag before being placed into a hopper.

2.2 Processing

Attached to the hopper is a *PowerPulse* motor by Syntron® that vibrates the material down a channel and into the mouth of a *Leistritz MICRO-18 35D* twin screw. The twin screw consists of two thin screws that co-rotate (both counterclockwise offset by exactly 1/2 screw length), which allows for shearing forces to break down and mix the material being fed, while pushing said material down the length of the screw through seven different heating zones. These temperature zones are set to ensure that the material will melt shortly after entering the first zone of the twin screw; therefore, vary slightly for each blend (Table 2). If the plastic does not melt fully, a thorough mixing will not occur, in addition to the possibility of the twin-screw seizing up due to an overload on the motor that drives the two screws. An illustration of the components for the twin screw is exhibited in Figure 8 in the context of showing the entire experimental setup. Table 2 shows the general temperature gradient for the blends of polymers used in this study. It

should be noted that small changes in the parameters needed adjustment over time as the processability of the material varied between virgin/recycled and between heat histories.

Table 2. General temperature gradient for each blend.

Material	Temperature (°C)							Speed (RPM)
	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	
100/0	140	145	150	155	155	155	160	90
75/25	145	150	155	160	165	165	165	90
50/50	150	155	160	160	165	165	170	90
25/75	160	165	170	170	175	175	175	90
0/100	165	165	170	170	175	175	175	90

Once the material leaves the die at the end of Zone 7, which has a diameter of 2 mm, it will then drop into a water bath approximately 1.5 meters long and pulled into a *Versa Caterpillar Puller* model *DSP-418*. This consists of two 48” belts that contact one another to pull the filament down its length and is then collected on a spool. By the time the polymer reaches the caterpillar puller, it has been solidified due to the cooling bath, so there is little effect on the integrity of the filament’s diameter at this point. A schematic of the extruder process can be found in Figure 7.

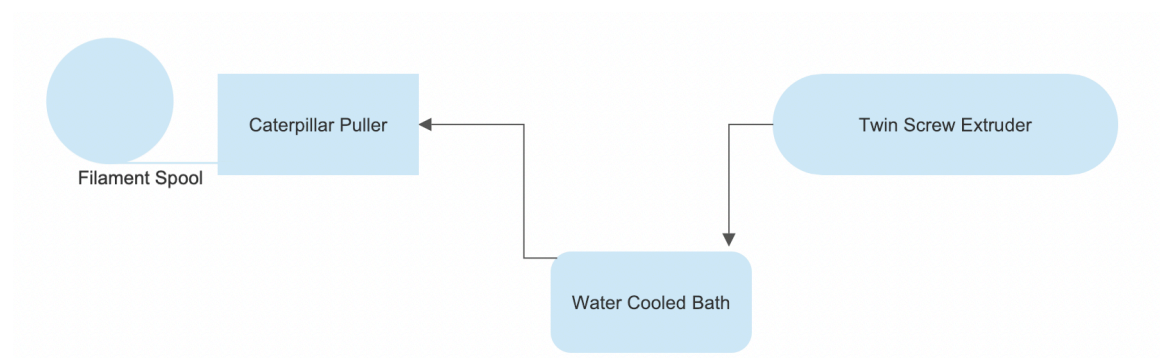


Figure 7. Schematic of the extruder process.

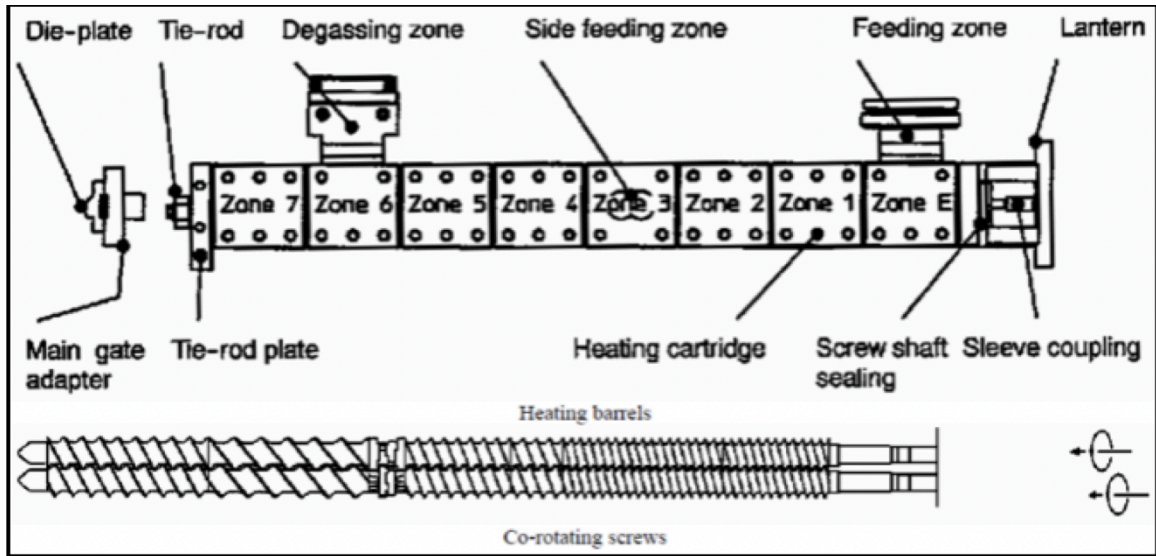


Figure 8. Diagram of the Leistritz MICRO-18 35D twin screw.

Once 2.3 kilograms of material is collected on a spool, it is then moved and set up on a second puller designed at the University of Alabama of Birmingham's (UAB) *Material Processing and Application Development Center* (MPAD), which is made of two rotating cylinders stacked vertically on one another. The filament passes through these cylinders and feed the material directly into a *Killion Business Group* model DSC-80DAC chopper that is capable of spinning blades at up to 700rpm to produce pellets that are 2-5 mm in length. The chopping process is vacuum assisted by attaching a hose to a 3D printed adapter that leads to a shop vacuum. The shop vacuum is tediously cleaned between chopping different blends, and a fine mesh water filter is attached to prevent any cross-contamination. A diagram of this process is shown in Figure 9. After the pellets are removed from the vacuum, 225 grams is removed for testing/characterizing, while the rest repeats this cycle until five passes through the twin screw is achieved.

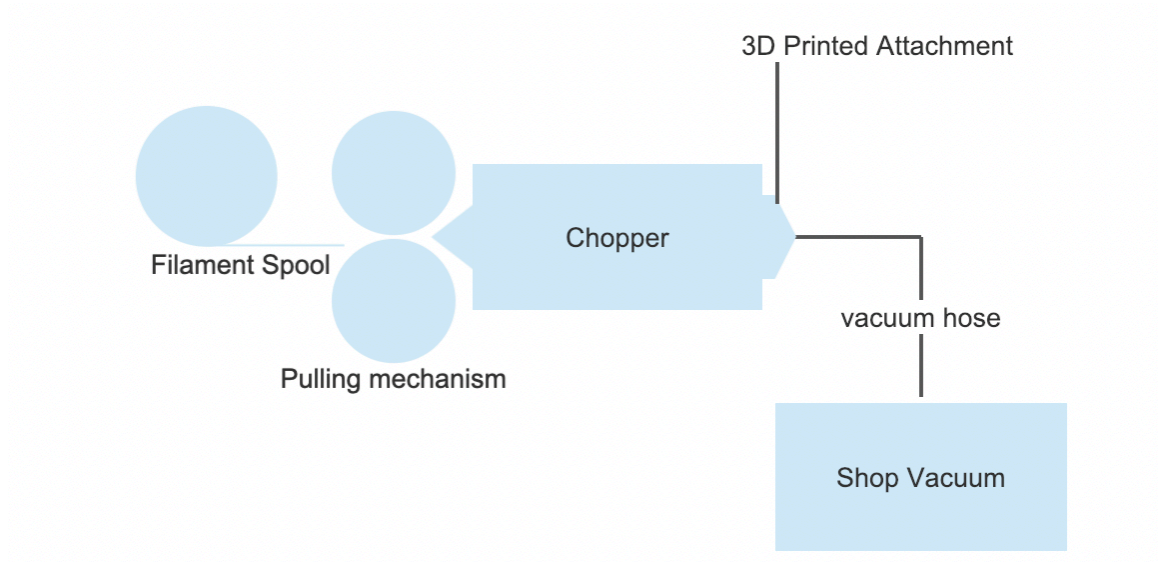


Figure 9. Schematic for chopping the filament into pellets.

3.0 CHARACTERIZATION OF MATERIAL

3.1 Thermogravimetric Analysis (TGA)

The TGA data for this project was collected using *TA's Discovery Series TGA550* following ASTM Standard E1131-20 *Standard Test Method for Compositional Analysis by Thermogravimetry*. Results from the TGA are useful as they serve as a reference to the heat histories of polymers as they go through many heating processes. TGA will give insight to see if degradation of the material occurs at varying onset temperatures, declines at varying rates, or see if there are any inorganic materials in the post-consumer mix. Inorganic materials will be identified if the weight loss % is <99% of the original sample weight. All these gives insight to the limits of these materials after so many processes. Each material saw a heat ramp of 20 °C/min up to 600 °C, where the test was ended.

TGA results for virgin samples lost over 99% (Table 3) of their initial mass on an average, indicating that no inorganic material which may degrade after 600°C was present.

Table 3 Weight loss percent of each virgin blend across heat history (1-5).

Heat History	1	2	3	4	5	
Material	Weight Loss Percent (%)					Average (%)
v100/0	98.7	98.4	99.5	99.7	99.8	99.2
v75/25	99.8	99.7	99.7	99.8	100.0	99.8
v50/50	99.5	99.7	100.0	99.8	99.8	99.8
v25/75	99.5	99.7	99.8	99.8	99.6	99.7
v0/100	99.7	99.6	99.9	99.8	99.8	99.8

In addition to weight loss percent, the onset temperature of degradation was also recorded (Table 4), and no significant change in degradation was observed for neat virgin polypropylene or any blend of the two. The addition of PP to HDPE had no observable effect on the onset degradation temperature, which agree with sources in literature [38], [39], [40]. A two-factor ANOVA test was run on the v100/0 blend to determine if there was any statistical significance between this blend and the others containing PP and found that there was a statistical difference between v100/0 and the rest of the group. This suggests that there was more variation in the initial virgin samples that polypropylene helped reduce. The onset degradation temperature fell in line with those observed in the rest of the materials, so it is likely that some chain scission occurred for the vHDPE and was sorted out by the 5th reprocessing history. As will be discussed later, there was no effect on the \overline{M}_w , so there are likely some competing mechanisms at play.

Table 4. Onset degradation temperature (°C) of each virgin blend across heat histories.

Heat History	1	2	3	4	5	
Material	Onset Degradation Temperature (°C)					Average (°C)
v100/0	399.0	389.9	367.9	447.8	449.0	410.7
v75/25	436.8	436.0	434.8	436.1	437.8	436.3
v50/50	424.5	438.0	432.1	433.4	431.4	431.9
v25/75	427.1	437.0	428.6	426.9	434.0	430.7
v0/100	423.3	430.0	428.2	426.3	425.6	426.7

Figures 10 and 11 are a graphical representation of the data in Table 4, which was provided by the TA's software. The rate of weight loss was similar in between the 1st and 5th heat history of each sample. The 50/50 blend is representative of the rest of the tests.

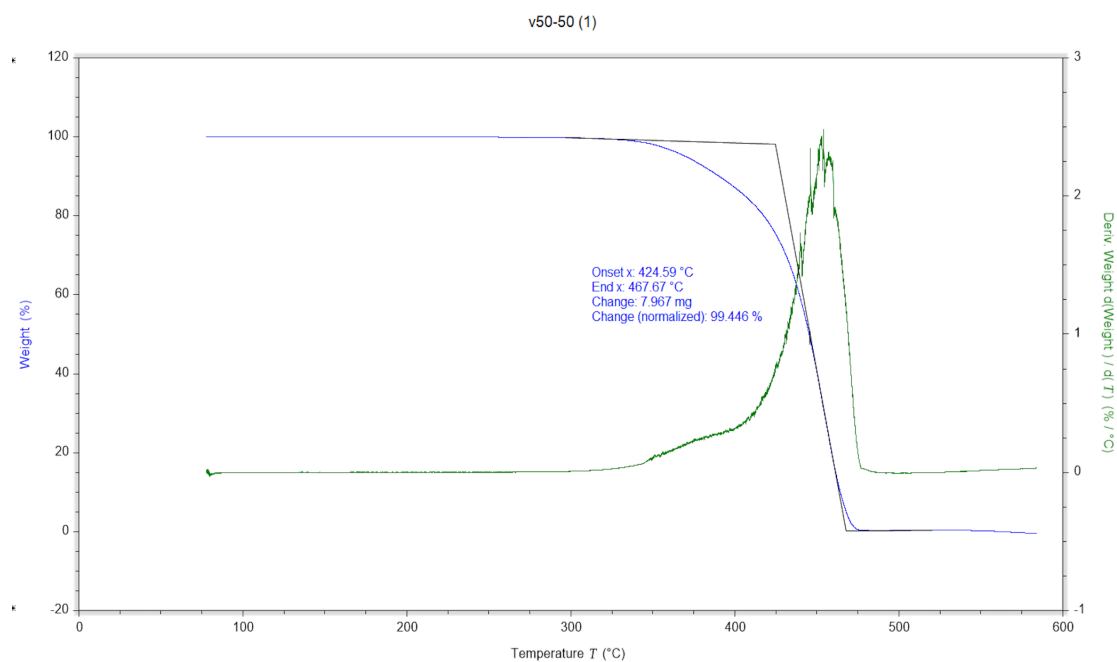


Figure 10. TGA of Virgin 50/50 Blend 1st heat history.

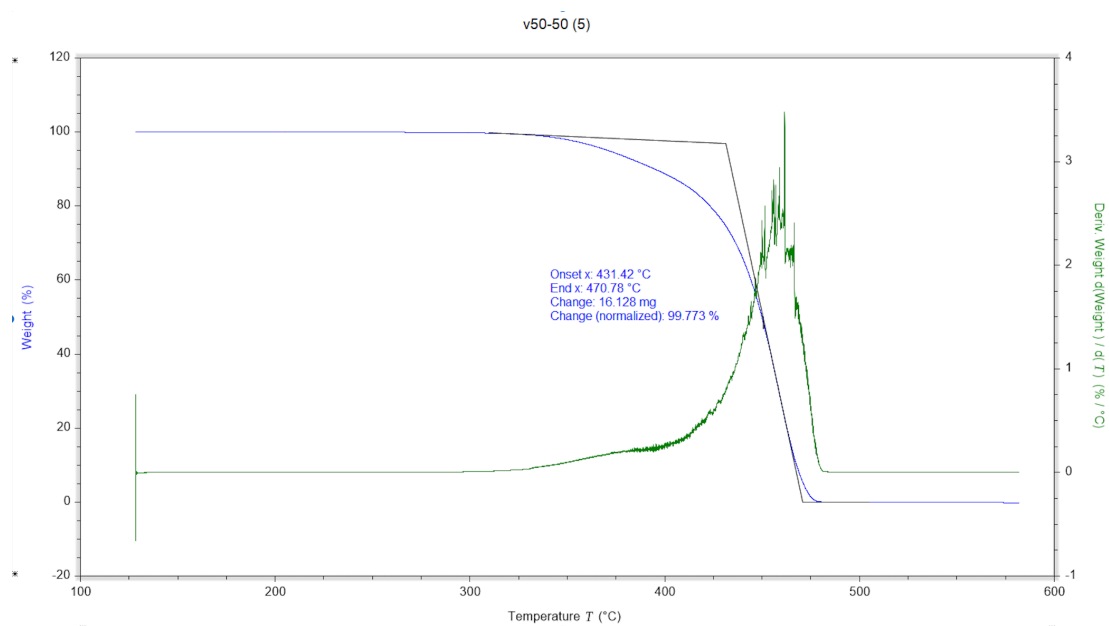


Figure 11. TGA of Virgin 50/50 Blend 5th heat history.

The post-consumer polymer had varying TGA results, indicating that some inorganic material may have been present, especially in the polypropylene collected for this study. Table 5 shows the data of weight loss percentage for each recycled blend of material. The HDPE had a weight loss of nearly 100% while the polypropylene observed just shy of 94% of its original weight loss. When the blends are plotted against average weight loss, as they are in Figure 12, a linear trend ($R^2=0.9966$) appears as PP is mixed with HDPE. It is common to introduce plasticizers in industry for ease of processing and for food packaging [41], [42]; therefore, given the sources of polypropylene collection, this is not unexpected. One reason that plasticizers may not be common in the HDPE in this study could simply be the nature of commodities stored in HDPE. Largely collected by milk jugs, which is not exposed to the elevated temperatures that cause polymers to break down and contaminate food, plasticizers have little added benefit to the samples collected for this study.

Table 5. Weight loss percent (%) of recycled blend across heat history.

Heat History	1	2	3	4	5	Average
r100/0	98.8	99.1	99.2	99.0	99.2	99.1
r75/25	97.9	98.1	98.0	98.0	98.2	98.0
r50/50	96.5	96.4	96.5	96.6	96.5	96.5
r25/75	94.9	95.1	95.1	95.0	95.3	95.1
r0/100	93.3	93.7	93.6	93.6	93.8	93.6

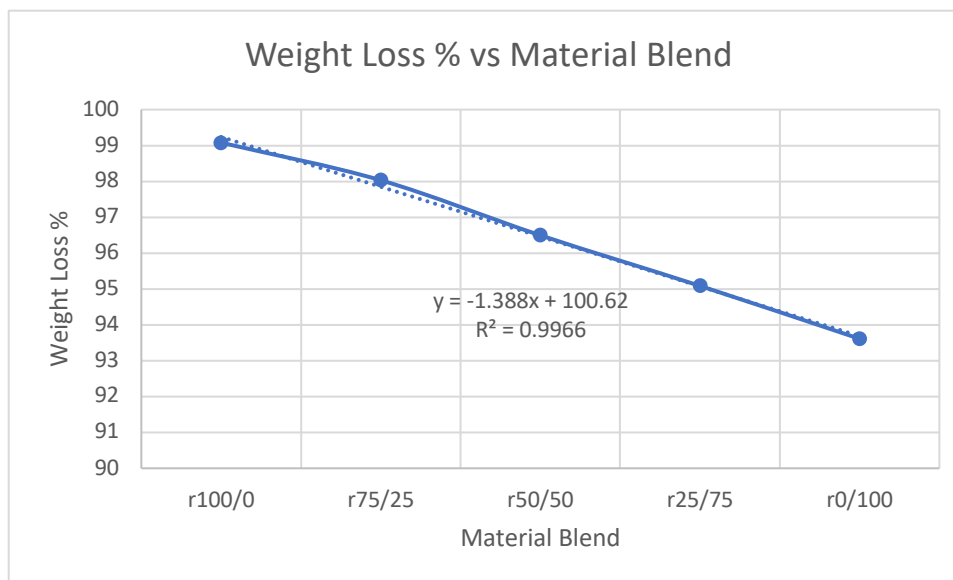


Figure 12. The weight loss percent of post-consumer blends.

The onset of degradation temperature for the recycled material is shown below in Table 6, and seems to have a significant change of nearly 20°C once PP is blended with HDPE. Since this disagrees with the literature discussed in the virgin counterpart, this also indicates that some additive was introduced to the PPs that were collected for the study.

Table 6. Onset degradation temperature (°C) of recycled blend across heat history.

Heat History	1	2	3	4	5	Average
r100/0	450.5	446.8	460.0	450.9	450.2	451.7
r75/25	440.2	451.9	416.4	445.9	445.3	439.9
r50/50	434.8	442.4	417.5	417.7	439.0	430.3
r25/75	428.7	434.9	427.5	437.3	439.4	433.5
r0/100	433.5	429.0	428.7	431.2	433.0	431.1

Figures 13 and 14 below are representative TGA samples from the r50/50 blend at both the first and fifth heat history. The onset degradation temperature does not differ significantly, and both saw a weight loss percent of 96.5% before reaching 500°C.

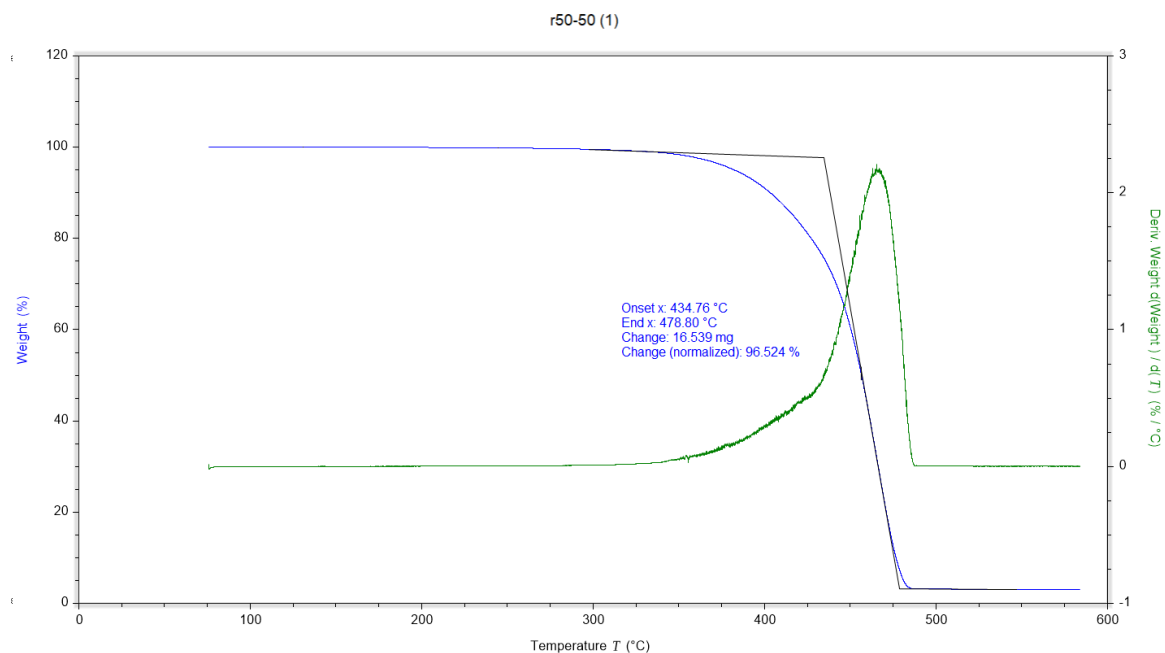


Figure 13. TGA of Recycled 50/50 Blend 1st heat history.

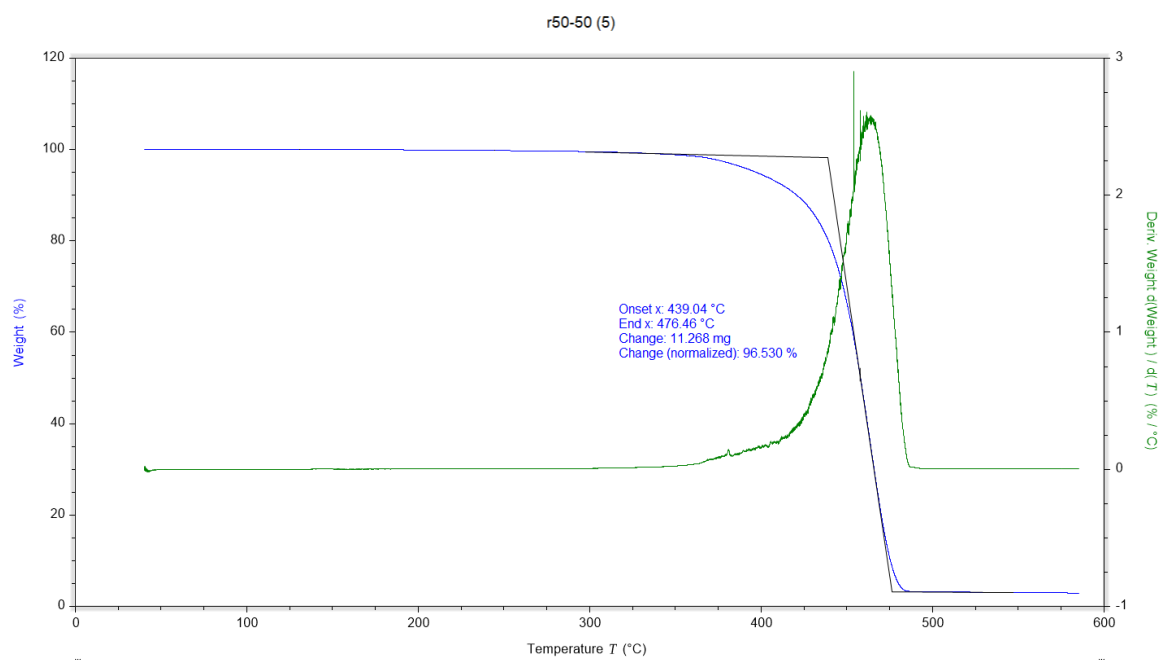


Figure 14. TGA of Recycled 50/50 Blend 5th heat history.

3.2 DSC

DSC data was collected from *TA's Discovery Series 2500* following ASTM Standard E793-06 *Standard Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry*. DSC is useful to obtain information about the melting temperature (T_m), recrystallization temperature, and the heat energy (enthalpy or heat of fusion) needed to melt the polymer during increasing heat, as well as the enthalpy taken to recrystallize the polymer chains upon cooling. When polymer chains are heated during processing, the molecular bonds break down and allow the material to flow in a viscoelastic manner. Upon cooling, the chains are allowed to realign themselves into their crystalline backbone or repeating structure. If given enough time, the chains will settle into thermodynamic equilibrium, but if cooled too quickly, the material could settle into a higher energetic state. Many cycles of heating and cooling may affect their ability to bond back the way they first were. Therefore, it is useful to make note of the properties to give insight to the polymer's limits once they are repurposed for consumer use. To achieve this analysis, a heat-cool-heat test was performed where heating ramps are 10 °C/min up to 200 °C, 5 °C/min down to 50 °C, and 10 °C/min back up to 200 °C respectively. The differing in cooling versus heating ramps is intentional so as to allow the polymer chains to find their thermodynamic equilibrium, instead of settling into some higher energetic state.

Something to note regarding trends in DSC results is the linear trend in the required energy to melt both HDPE and PP as one polymer is introduced to the other. Other research conducted also found a decrease in enthalpy upon the blending of

HDPE and PP when compared to their component values [40]. Analysis of the heat of fusion (χ) was done by considering the ratio of ideal mass normalized enthalpy values to DSC calculated enthalpy values. The ideal value for the mass normalized enthalpy was obtained from a report by TA Instruments [43]. Table 7 shows the average enthalpy of each blend of polymer at all 5 stages of known heat history.

Table 7. Average Enthalpy Values of Virgin Blends for 5 Heat Histories.

Material	HDPE Enthalpy (J/g)	PP Enthalpy (J/g)	χ_{HDPE}	χ_{PP}
v100/0	148.5	0.0	50.7	0.0
v75/25	108.5	17.2	37.1	8.3
v50/50	68.4	36.3	23.3	17.6
v25/75	30.3	53.7	10.3	25.9
v0/100	0.0	80.7	0.0	39.0

When enthalpy and heat of fusion are plotted against the material blend, as in Figure 15 below, both show a convincing linear correlation.

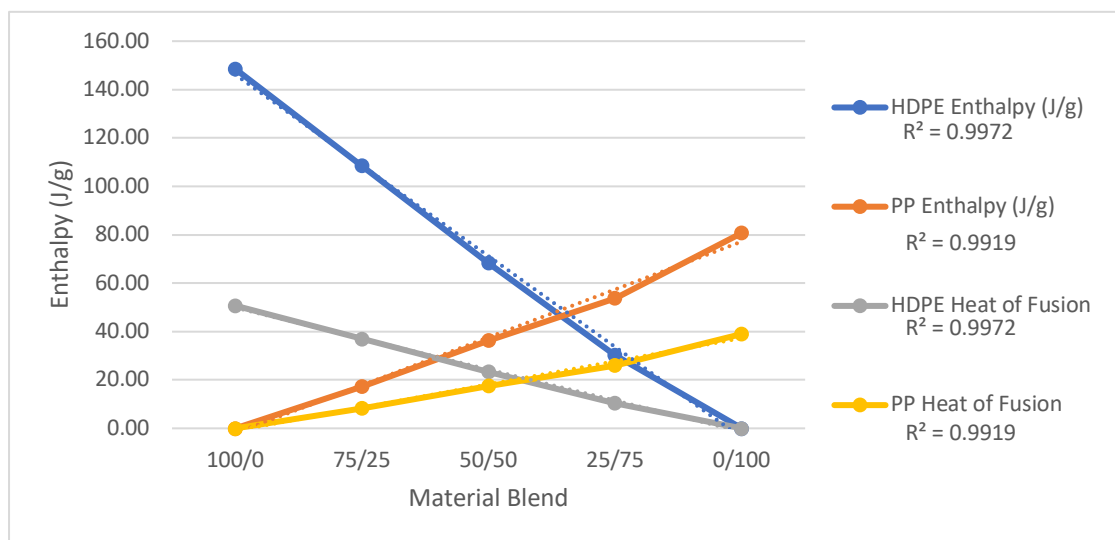


Figure 15. Scatterplot of linear trends in enthalpy and heat of fusion.

Other properties from DSC results were also consistent across the five simulated recycle iterations. The melting temperature of HDPE and PP remained clearly separate and consistent as shown in Table 8. The HDPE melt temperature maintained an average

of 129 °C while PP held steady at 165 °C. This varies slightly with results from Albano & Sanchez [40], who saw a 4°C shift from neat polymer to the blended counterpart. However, once the material was blended, they observed no change in T_m across the various ratios of blends.

Table 8. Summary of T_m of Each Virgin Material for Each Heat History.

Heat History	1		2		3		4		5		Average	
Material	Melting Temperature (°C)											
	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
v100/0	129.9	-	129.1	-	128.7	-	129.3	-	129.4	-	129.3	-
v75/25	129.2	165.2	129.4	165.4	129.5	165.9	129.5	165.5	129.4	165.7	129.4	165.5
v50/50	128.9	165.4	128.7	164.9	129.0	165.3	129.4	165.6	129.5	165.8	129.1	165.4
v25/75	128.9	165.3	129.3	165.8	128.9	165.4	129.0	165.6	128.9	165.1	129.0	165.4
v0/100	-	166.4	-	166.4	-	166.8	-	166.1	-	167.2	-	166.6

A decrease in enthalpy was observed upon the blending HDPE with PP, as compared to their respective component (100%) materials (see Table 7). Similarly, the heat of fusion for both HDPE and PP also decreased as the composition of each component decreased (see Table 7). This is likely due to an increase in enthalpy required to melt the more crystalline polymer [40], [44].

Despite a difference in enthalpy and percent crystallinity for both HDPE and PP as the composition of the material changed, no significant difference was found for each material for either property over the five heat histories (see Tables 9 and 10). This indicates consistency in the extrusion and cooling process used for each heat history. Moreover, the change in enthalpy between blends as one component was added to the other scaled linearly and can be expressed with the following rule of mixture:

$$H_{blend} = \omega_A H_A + (1 - \omega_A) H_B$$

Where H is the enthalpy, and ω is the weight fraction of the respective component. The linear nature of the mixing rule is evident without the use of exponents or operations and can be observed in Figure 15.

Table 9. Enthalpy of Virgin HPDE and PP in each material over the five heat histories.

Heat History	1		2		3		4		5		Average	
Material	Enthalpy (J/g)											
	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
v100/0	150.4	-	144.8	-	156.7	-	146.0	-	144.6	-	148.5	-
v75/25	104.8	16.1	108.6	17.9	109.6	16.8	112.3	17.6	11.0	16.8	109.3	17.0
v50/50	71.1	33.5	69.5	37.6	68.5	37.2	67.1	35.9	65.7	36.6	68.4	36.1
v25/75	31.4	53.8	28.8	52.4	29.9	55.9	30.9	49.3	30.5	55.3	30.3	53.3
v0/100	-	79.1	-	81.1	-	79.2	-	85.2	-	80.6	-	81.0

Table 10. Crystallinity (%) for Virgin HPDE and PP in each material over the five heat histories.

Heat History	1		2		3		4		5		Average	
Material	Crystallinity (%)*											
	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
v100/0	51.3	-	49.4	-	53.5	-	49.8	-	49.4	-	50.7	-
v75/25	35.8	7.7	37.1	8.6	37.4	8.1	38.3	8.5	37.9	8.1	37.1	8.3
v50/50	24.3	16.2	23.7	18.2	23.4	17.9	22.9	17.3	22.4	17.7	23.3	17.6
v25/75	10.7	25.9	9.8	25.3	10.2	27.0	10.6	23.8	10.4	26.7	10.3	25.9
v0/100	-	38.2	-	39.2	-	38.3	-	41.2	-	38.9	-	39.0

*The heat of fusion of 100% polymer crystallization for HDPE and PP used were 293 J/g and 207 J/g, respectively [43].

The DSC curves plotted by TA's software shows clear separations between the melting peaks. This illustrates the immiscibility of the polymer, as they are clearly melting in two distinct regions indicating boundaries of different structures and different temperatures required to break these crystalline structures down. Albano & Sanchez found similarly that melting peaks of HDPE and PP remained about 30°C separate from one another [45]. HDPE required at least 30 J/g more energy to completely melt than PP

at each stage of the recycle process and is represented by the endothermic reactions as shown in Figure 16. This is likely due to the more crystalline nature of HDPE when compared to PP. Together, Figures 16 and 17 shows that the DSC properties are largely unaffected by the 5 heat histories of passing through the twin-screw.

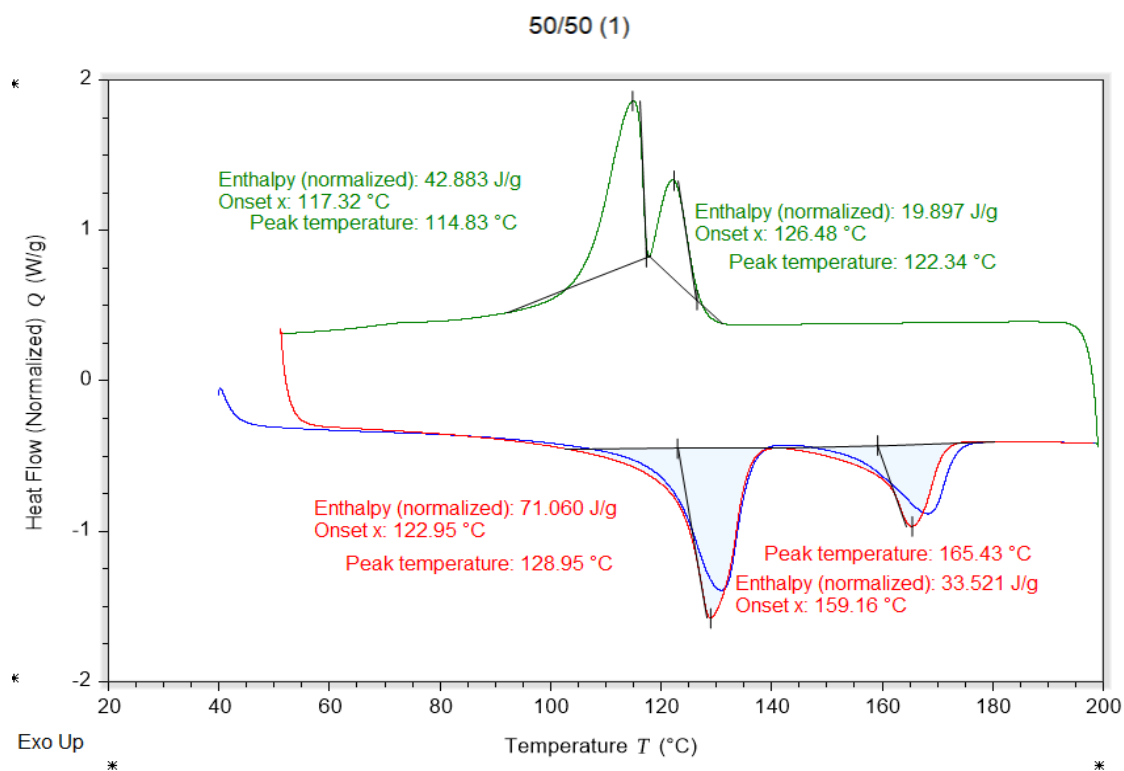


Figure 16. DSC of Virgin 50/50 Blend 1st heat history.

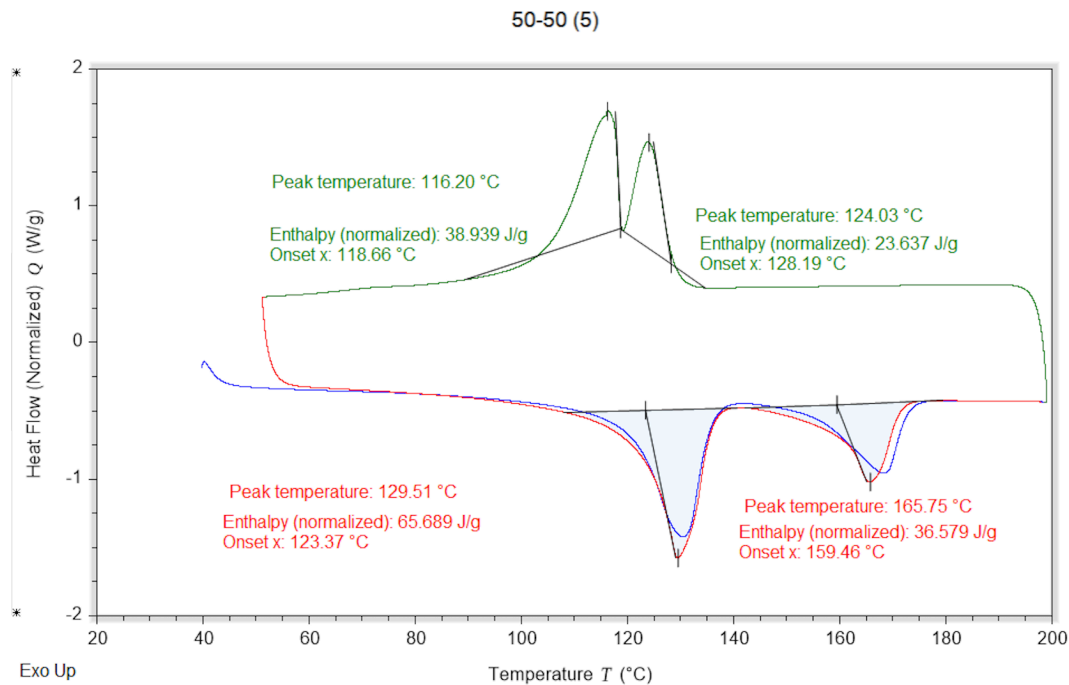


Figure 17. DSC of Virgin 50/50 Blend 5th heat history.

While the melting peaks remain distinct between the blends, the recrystallization peaks tend to merge. Figure 18 is the 25/75 and Figure 19 is the 75/25 blend. The recrystallization peaks for the 25/75 blend are nearly totally converged (Figure 18); the 75/25 peaks are even further separated from the 50/50 blend.

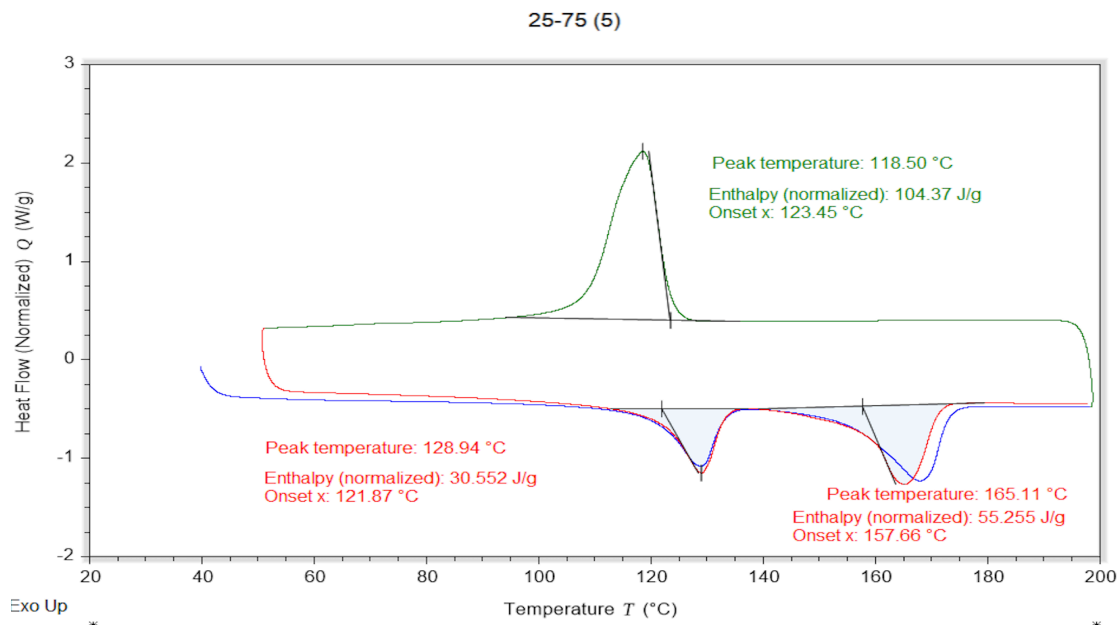


Figure 18. Representative DSC of Virgin 25/75 Blend.

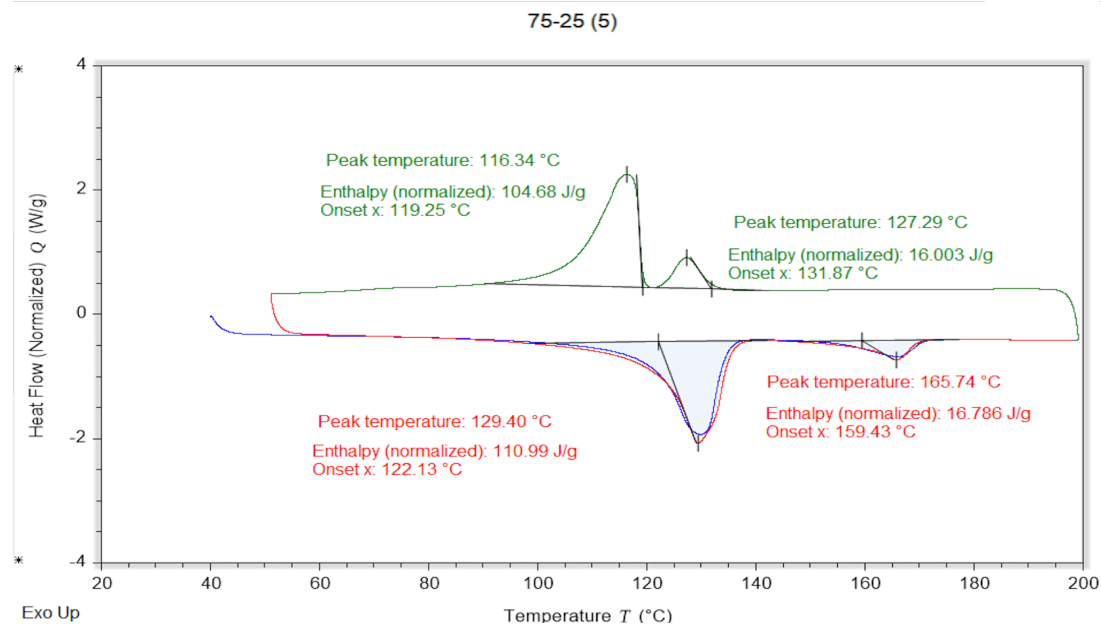


Figure 19. Representative DSC of Virgin 75/25 Blend.

The presence of PP in the blend correlates with both the overlap of these curves and their peak recrystallization temperatures. While both polymers have relatively simple chain structures, PP's monomer (C_3H_6) will tend to take up more space, and higher activation energy when compared to HDPE's monomer (C_2H_4). Therefore, PP will require more

time to reach a thermodynamic equilibrium in the presence of HDPE assuming equal cooling rates between the polymers. When there is more HDPE in the sample than PP, the PP monomers will settle in a higher thermodynamic equilibrium as it does not have the same volume to settle as it would be undisturbed. There is a similar trend in the HDPE but is less exacerbated due to its simple monomer requiring less volume to find this thermodynamic equilibrium, so the presence of a mixture affects the crystallization temperature of PP more than HDPE. In fact, HDPE acts a nucleating agent in PP, but this is not reciprocated. While HDPE affects the morphology of PP, it is not the other way around, which is why the crystallization temperature tends towards the HDPE. It should be noted that the crystallization temperature of pure PP (118 °C) is similar to pure HDPE (115 °C) since there is no competition to share the volume of space in the sample.

The heat of fusion (χ) and average enthalpy values for post-consumer material were also considered. The trends favor strongly with the recycled counterpart, meaning that each system's properties were unaffected by any post-consumer additives. With each stage and addition of one polymer to another, both the Enthalpy and % Crystallinity increased or decreased in a strongly linear fashion as recorded in Table 11 and shown in Figure 20.

Table 11. Average Enthalpy Values of Recycled Blends for 5 Heat Histories.

Material	rHDPE Enthalpy (J/g)	rPP Enthalpy (J/g)	rHDPE χ	rPP χ
r100/0	162.4	0.0	55.4	0.0
r75/25	122.2	9.0	41.7	4.4
r50/50	79.9	23.9	27.3	11.6
r25/75	37.6	38.6	12.8	18.7
r0/100	0.0	56.6	0.0	27.3

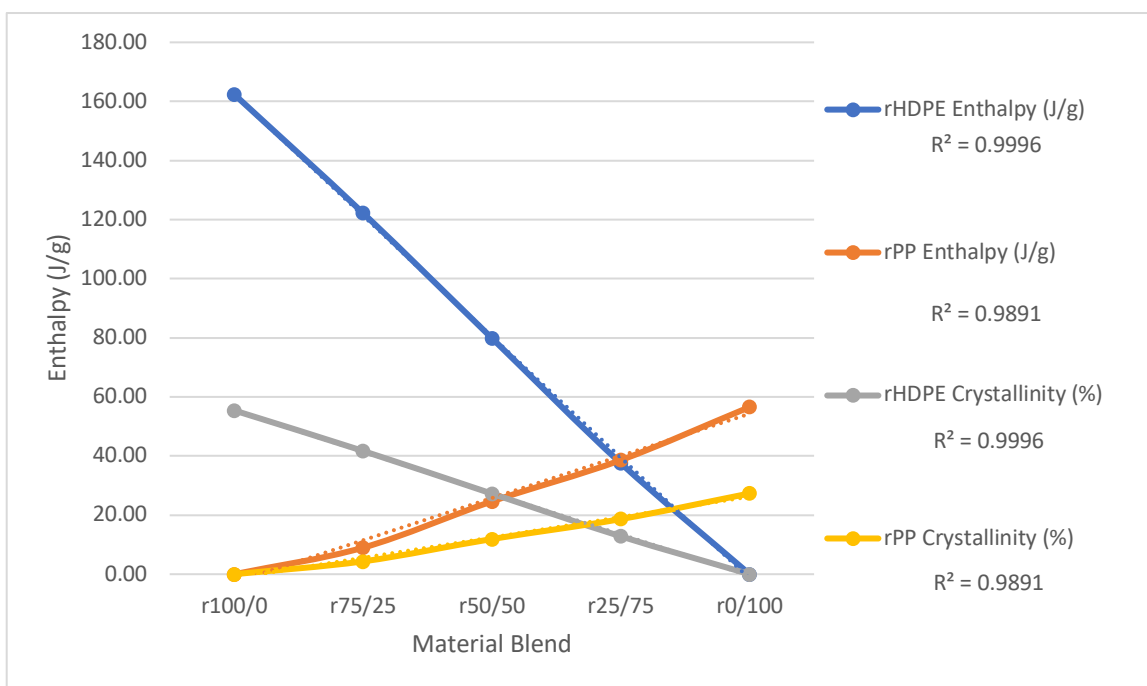


Figure 20. Scatterplot of linear trends in enthalpy and heat of fusion.

DSC results for the melting point of HDPE and PP were consistent across the 5 heat histories of the polymer. Melting temperatures were separate and distinct with the HDPE melting at an average of 133°C and PP at 164°C from the data in Table 12. It is worth noting that there is slightly more variation in the melting temperatures on the first

pass of HDPE when compared to the virgin material, but reasonable process stability is achieved after several iterations through the twin screw extruder. Additionally, the same mixing rule for virgin enthalpy values can be observed in Figure 20 and follow the same equation below:

$$H_{blend} = \omega_A H_A + (1 - \omega_A) H_B$$

Table 12. Summary of Tm of Each Recycled Material for Each Heat History.

Heat History	1		2		3		4		5	
	Melting Temperature (°C)									
Material	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
r100/0	134.2	-	133.2	-	133.2	-	133.1	-	133.6	-
r75/25	136.2	166.3	132.5	164.5	133.2	164.8	133.0	164.7	132.9	164.8
r50/50	132.3	163.5	131.9	163.0	132.2	163.6	132.3	163.4	132.4	163.4
r25/75	130.6	163.4	131.8	164.8	130.8	163.4	131.2	163.9	131.2	163.9
r0/100	-	164.1	-	164.2	-	164.4	-	163.7	-	163.6

The recycled material has a similar trend as the virgin material when observing the enthalpy and heat of fusion. As PP is added to the HDPE, both the enthalpy and % crystallinity values decrease which is noted in Table 13 and 14 respectively. Additionally, both values across the heat histories for each blend remain largely unaffected, which also indicates stable cooling in the processing of material.

Table 13. Enthalpy of Recycled HPDE and PP in Each Material over the Five Heat Histories.

Heat History	1		2		3		4		5		Average	
	Enthalpy (J/g)											
Material	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
r100/0	165.2	0.0	157.3	0.0	164.2	0.0	169.9	0.0	161.2	0.0	163.5	0.0
r75/25	103.2	6.4	127.9	9.1	126.4	9.8	130.5	9.9	127.4	9.7	123.1	9.0
r50/50	81.1	23.3	79.9	25.3	79.0	23.5	83.8	27.5	80.4	23.6	80.8	24.6
r25/75	37.0	40.0	36.0	36.3	37.5	39.4	40.3	38.7	39.8	38.7	38.1	38.6
r0/100	0	56.8	0.0	57.0	0.0	56.0	0.0	56.2	0.0	56.9	0.0	56.6

Table 14. Crystallinity (%) for Recycled HPDE and PP in Each Material over the Five Heat Histories.

Heat History	1		2		3		4		5		Average	
	Crystallinity (%) *											
Material	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE	PP
r100/0	56.4	0.0	53.7	0.0	56.1	0.0	58.0	0.0	55.0	0.0	55.8	0.0
r75/25	35.2	3.1	43.6	4.4	43.1	4.7	44.5	4.8	43.5	4.7	42.0	4.4
r50/50	27.7	11.3	27.3	12.2	27.0	11.4	28.6	13.3	27.5	11.4	27.6	11.9
r25/75	12.6	19.3	12.3	17.6	12.8	19.0	13.8	18.7	13.6	18.7	13.0	18.6
r0/100	0.0	27.4	0.0	27.5	0.0	27.1	0.0	27.1	0.0	27.5	0.0	27.3

*The heat of fusion of 100% polymer crystallization for HDPE and PP used were 293 J/g and 207 J/g, respectively [43].

As noted in the virgin counterparts, the crystallization peaks in the recycled blends also have merged. These are shown in Figures 21 and 22 below.

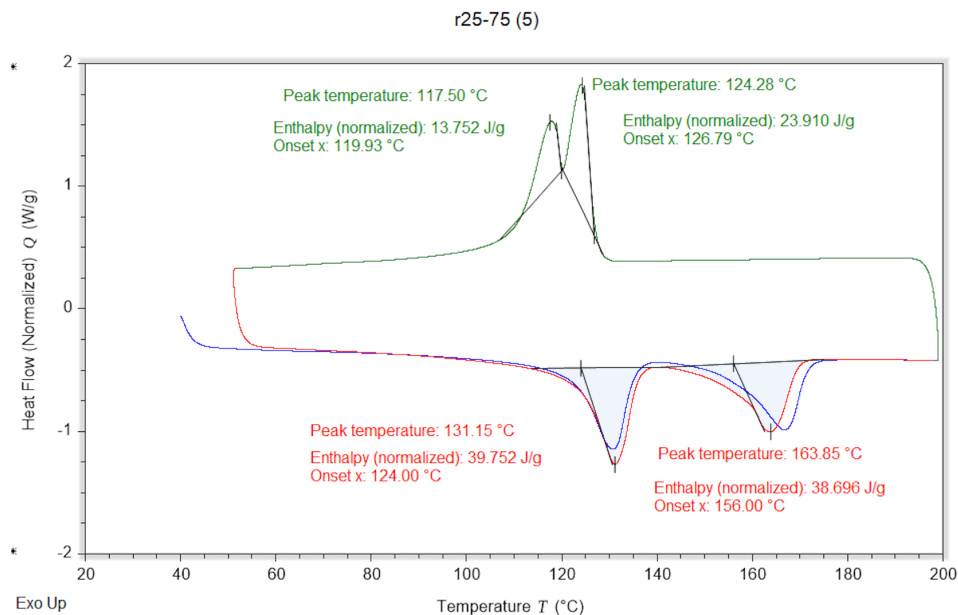


Figure 21: Representative DSC of Recycled 25/75 Blend.

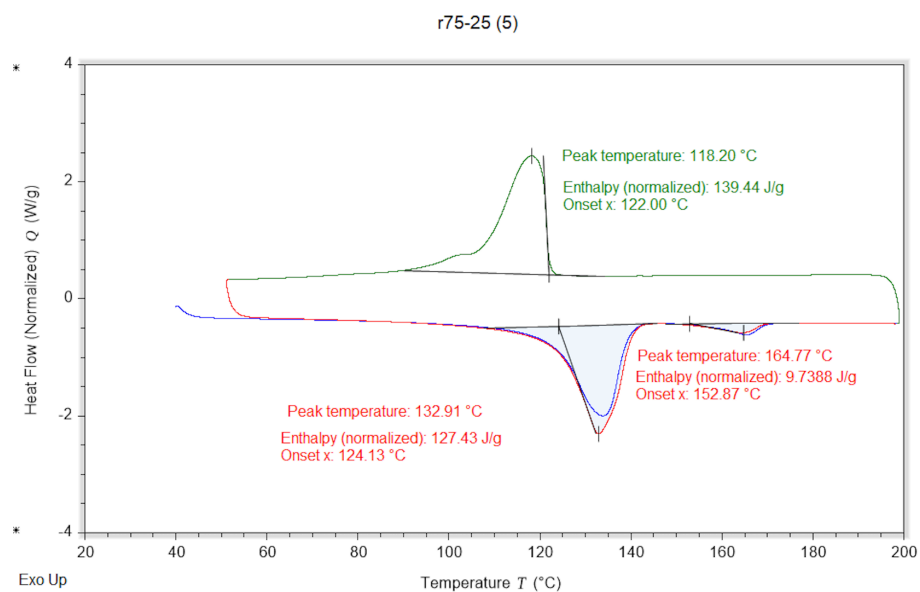


Figure 22: Representative DSC of Recycled 75/25 Blend.

These can be explained in a similar way as the virgin material. While the presence of additives and stabilizers in the post-consumer plastics have an effect on the shape of the peaks, the monomer structures are largely unchanged so the morphology between the blends behave similarly.

3.3 MFI

MFI analysis was obtained using Ray/Ran's Model 6 Advanced Melt Flow System following ASTM D1238-10 *Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer*. Around 4-6 grams of material was packed into a column heated to 210°C, and a weight of 2.16 kg was placed on top of the polymer which forced the material through a die with an orifice measuring 2 mm in diameter. The piston and die were placed in the heated bore for no less than 15 minutes to ensure they reached the testing temperature, and the material was allowed the 7-minute (± 30 seconds) pre heat period before every test. Upon completing a test, the system measured MFI, shear stress, shear rate, viscosity, and melt volume rate as discussed in the introduction section. Once the polymer was in the chamber for the designated pre-heat period, and the piston was within range, the test was initiated, and the machine measured 25 mm of the flowing material flowing through the die.

The average of these five samples is the representative data point in Table 15 shown below across each of the five heat histories.

Table 15. The Average of 5 MFI values of each virgin blend across the heat history.

Heat History	1	2	3	4	5	Average
v100/0	75.2	77.0	76.0	82.1	86.0	79.2
v75/25	50.2	50.2	47.9	49.7	48.6	49.3
v50/50	24.0	24.0	22.8	25.0	23.8	23.9
v25/75	8.1	7.9	7.6	7.9	7.8	7.9
v0/100	3.1	2.8	3.1	3.1	3.1	3.1

There was less variability in the data with the increase of PP to the blends. Additionally, the MFI shows a convincing parabolic decrease in MFI with the increase of PP in HDPE. These results agree with what is found in literature for lower MFI values [46], and Figure 23 shows the average MFI value of each sample for each material plotted against the blend. Broadly speaking, each of these blends show the same trend over the 5 simulated recycle periods. The neat HDPE samples here show a statistically significant difference across the reprocessing histories. This is another indication that was alluded to in the discussion of onset degradation temperature. These results indicate that some chain scission is occurring in the virgin HDPE samples, which would explain the increase in MFI over the processing history.

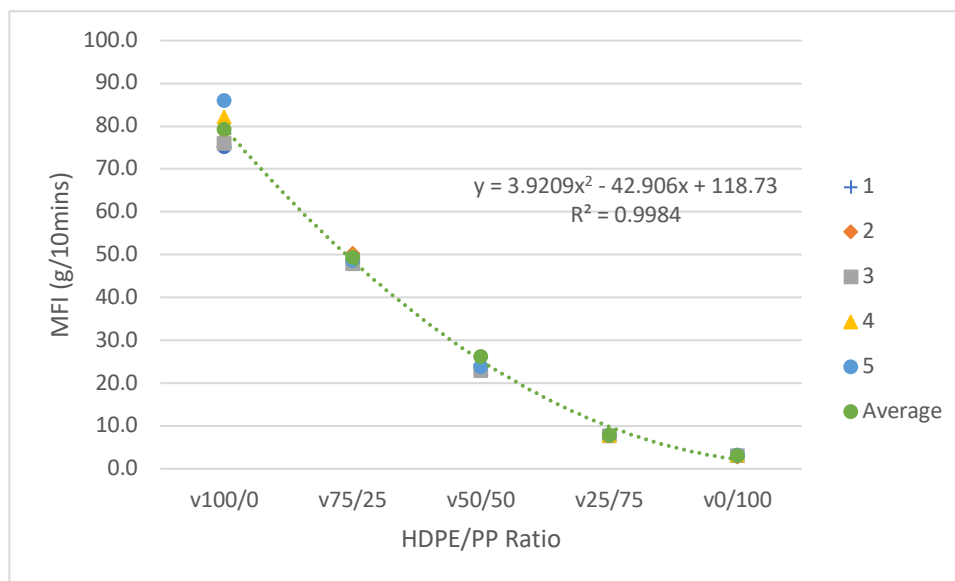


Figure 23. The average MFI values of the virgin blends at each heat history.

The neat polymers' MFI vary significantly from one another. HDPE's shows an average of 79.2 g/10 min while PP's is 3.1 g/10 min. If a smaller range of values were to be analyzed, perhaps a larger pool of data would need to be collected in order to have

sufficient sample size to determine if the blends are statistically significant from one another.

Moreover, the general mixing rule discussed previously can be modified to fit the curve above as:

$$MFI_{blend}^{1/2} = \omega_A MFI_A^{1/2} + (1 - \omega_A) MFI_B^{1/2}$$

Where ω_A is the weight fraction of component A and $(1 - \omega_A)$ is the weight fraction of component B. Mixing rules for blends of immiscible polyolefins such as HDPE and PP are useful indicators of “contaminants” in a blend of polymers, or a useful quality control measure for reliable mixing of these components.

Following the same standard test method as the virgin counterpart, an inverse relationship was observed when MFI values were obtained for post-consumer plastics. In this situation, most of the HDPE collected had a lower MFI than the PP. This varies from the virgin material, indicating the additives shown in the TGA results of the PP could have been used to decrease the viscosity of the material. The variability in the r0/100 was also less severe than the v100/0 counterpart. Table 16 records the data for the average of 5 data points across the five heat histories of recycled material.

Table 16. The Average of 5 melt flow values of each recycled blend across each heat history.

Heat History	1	2	3	4	5	Average
r100/0	2.4	2.4	2.4	2.4	2.4	2.4
r75/25	3.6	3.5	3.5	3.6	3.6	3.6
r50/50	8.3	8.4	8.9	8.8	8.5	8.6
r25/75	15.6	16.2	16.0	15.8	15.1	15.8
r0/100	29.7	28.4	29.3	27.6	29.1	28.8

There was also a strong natural log relationship as the higher MFI material (PP in this case) was added to the lower MFI material (HDPE in this case). The mixing rule that most accurately predicted MFI for the post-consumer plastics follows the relationship:

$$\ln MFI_{blend} = \ln MFI_A \omega_A + \ln (1 - \omega_A) MFI_B$$

This is similar to the virgin material and the literature discussed in that both are exponential trends. While there is not exactly a universal trend, the square root function did perform quite well on a correlation study in the post-consumer plastics. In-house testing with consistent raw materials can easily derive a mixing rule to suit the materials that are run in industry.

Where the virgin material had a significant shift in neat HDPE, the recycled counterpart did not. This could be due to additives and stabilizers that are stabilizing the melt flow of the recycled material. It is important to note that the “shape” of the curve changed from decreasing to increasing with the addition of rPP to rHDPE (See Figures 23 and 24 for a visual comparison) as an indication that MFI is not an inherent material property.

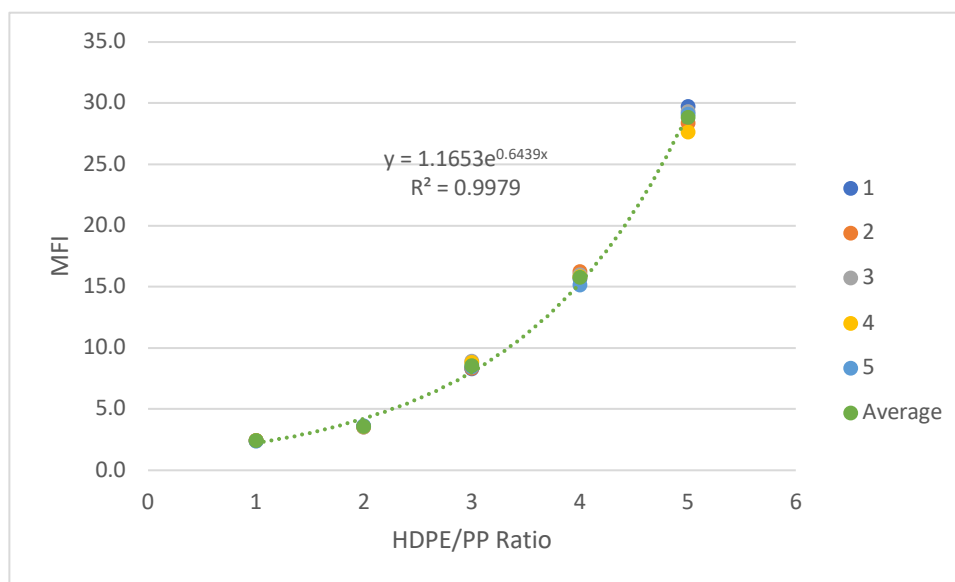


Figure 24. The average MFI values of the recycled blends at each heat history.

Additionally, in this study a wide range of MFI values were obtained to show a statistical significance between each blend at 5 tests per material. A further study into this trend as the gap in MFI closes would only be able to discriminate between groups with sufficiently high data points.

3.4 GPC

GPC results were obtained using Polymer Char's GPC-IR4 (Valencia, Spain) with a Wyatt Dawn Helios II Light Scattering Detector (California, USA). As suggested by ASTM D6474, samples of blends were measured at 8 mg and dissolved in 1,2,4-trichlorobenzene (TCB) at 160 °C. Samples were placed into an autosampler, which filled the vials with 8 mg of solvent and moved the samples into a heating chamber where they were stirred 60 minutes for virgin material, and 120 minutes for recycled material. The increased dissolution time ensures that the recycled polymer had time to properly

dissolve and was not necessary to obtain accurate results for the set of virgin material. As discussed in the introduction, light scattering results regarding the M_w , M_n , and PDI were recorded.

Three replicates were run for the GPC testing, and each data point in Table 17 is the average of those three samples for each blend.

Table 17. The Average of 3 M_w Values of Each Virgin Blend Across Each Heat History.

Heat History	1	2	3	4	5	Average
v100/0	67,000	68,000	75,000	68,000	83,000	72,000
v75/25	158,00	156,000	156,000	155,000	154,000	156,000
v50/50	223,000	228,000	225,000	226,000	225,000	225,000
v25/75	287,000	294,000	295,000	296,000	293,000	293,000
v0/100	367,000	365,000	365,000	370,000	372,000	369,000

Similar to MFI, the \overline{M}_w of each component polymer vary significantly. While the HDPE shows the most variation in \overline{M}_w , there is still a statistically significant gap between 100/0 and 75/25 blends. This lack of variation between the v100/0 blend is an indication that the chain scission in the neat HDPE was competing with the free radicals of polymer chains attaching themselves to various backbone structures, which resulted in chain branching. There is a strong linear fit when the \overline{M}_w is plotted across the blends, which can be observed in Figure 25. With two polymers of vastly different \overline{M}_w , the values of \overline{M}_w scale linearly with the increase of one material in another.

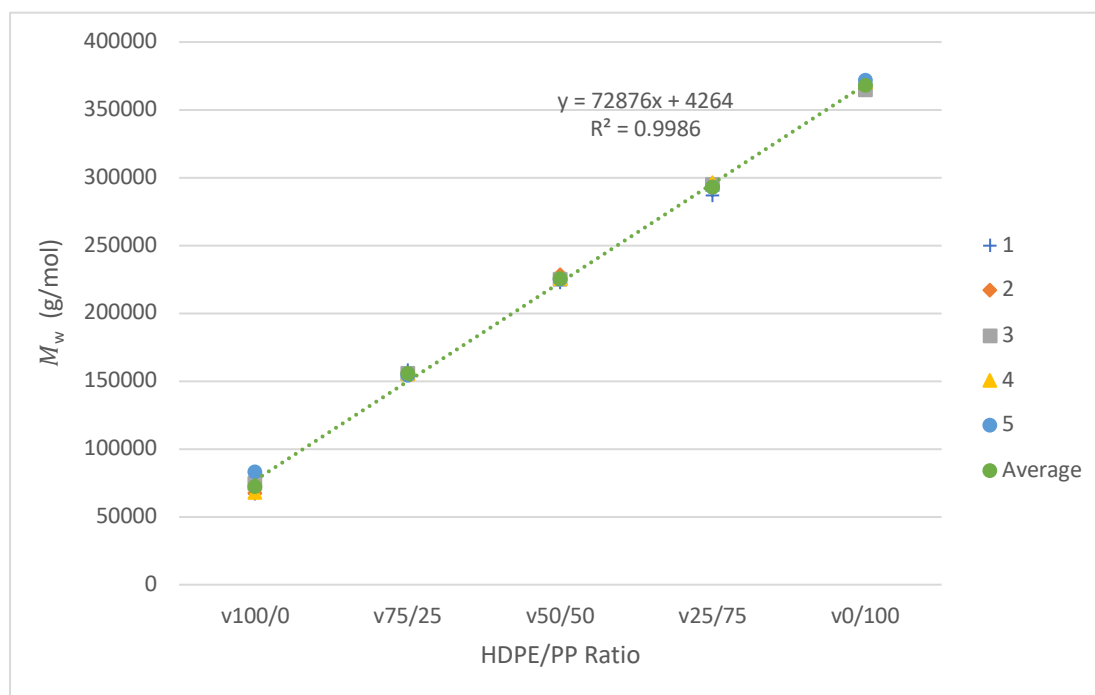


Figure 25. Increase in M_w with the addition of PP to HDPE.

Similar to the virgin counterparts, three replicates were run for the GPC testing, and each data point in Table 18 is the average of those three samples for each blend across each heat history.

Table 18. The Average of 3 M_w Values of Each Recycled Blend Across Each Heat History.

Heat History	1	2	3	4	5	Average
r100/0	114,000	114,000	113,000	115,000	114,000	114,000
r75/25	123,000	123,000	123,000	124,000	124,000	123,000
r50/50	135,000	137,000	140,000	137,000	137,000	137,000
r25/75	148,000	147,000	146,000	148,000	150,000	148,000
r0/100	160,000	163,000	160,000	165,000	160,000	161,000

There is also a convincing linear trend in the recycled material as well, showing distinct regions between blends of ratios. This is shown visually in Figure 26.

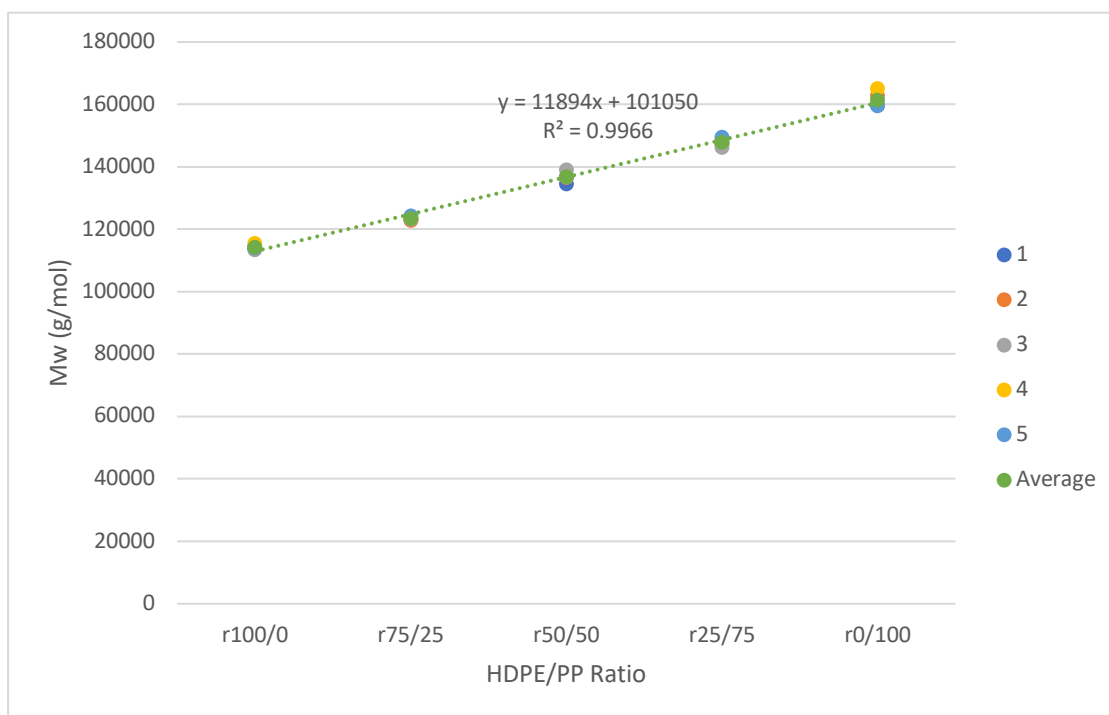


Figure 26. A scatterplot of Recycled Mw values plotted against respective blends.

It's worth noting that the general mixing rule for both the virgin and recycled material holds well, given the linear nature of Figures 25 and 26. These indicate that the weight fraction is a reliable measure of the weight average molecular weight, which should follow from definition of mixing by weight percentage. Observe the mixing rule below.

$$\overline{M}_{wblend} = \omega_A \overline{M}_{wA} + (1 - \omega_A) \overline{M}_{wB}$$

3.6 MFI vs. \overline{M}_w

The correlation between the \overline{M}_w and the MFI is of primary interest in this study. The goal is to observe whether the findings in literature [47] hold over several simulated recycling periods when applied to blends of varying degrees of branching. Figure 27 displays the direct correlation between \overline{M}_w and MFI, while Figure 28 compares the adjusted values suggested by literature according to the equation proposed by Rudin.

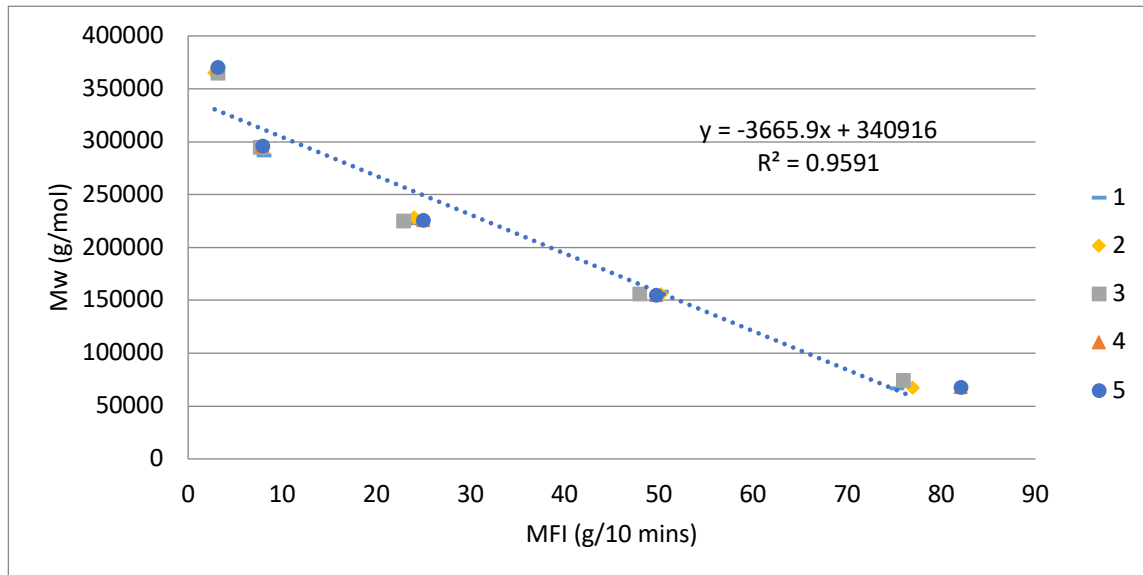


Figure 27. The direct correlation of Virgin Mw vs MFI for each cycle in the heat history.

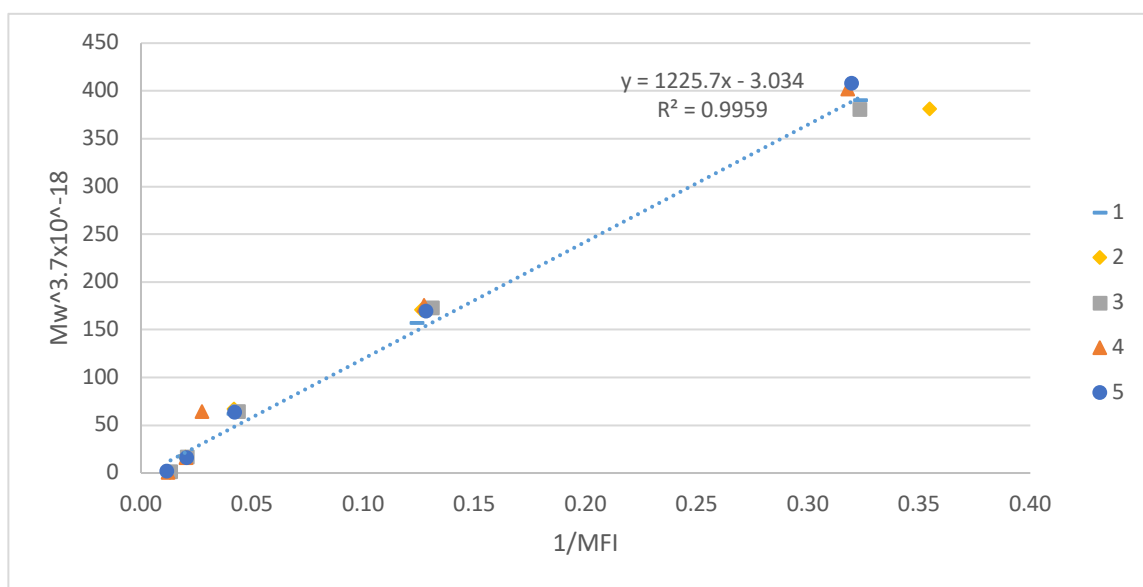


Figure 28. The adjusted correlation between Virgin Mw and MFI for each cycle in the heat history.

As previously stated, this work expands on literature by investigating how blends of polymers behave in comparison to their neat counterparts. In Rudin's study, a more

linear correlation between \overline{M}_w and MFI can be achieved by adjusting the \overline{M}_w to the degree of $(\overline{M}_w^\alpha) \times 10^{18}$ (where α is between 3.4-3.7) when compared to the direct counterpart, which is demonstrated here in Figures 28 and 29. This study found that an α of 3.7 gave the most favorable results for the virgin material. It is an important indication that this trend does not change with blending materials, as the results can potentially be generalized and used to diagnose a wider array of virgin polymers.

Conversely, the post-consumer material was plotted according to the suggestion by Rudin. The results and a discussion are as below; refer Figures 29 and 30.

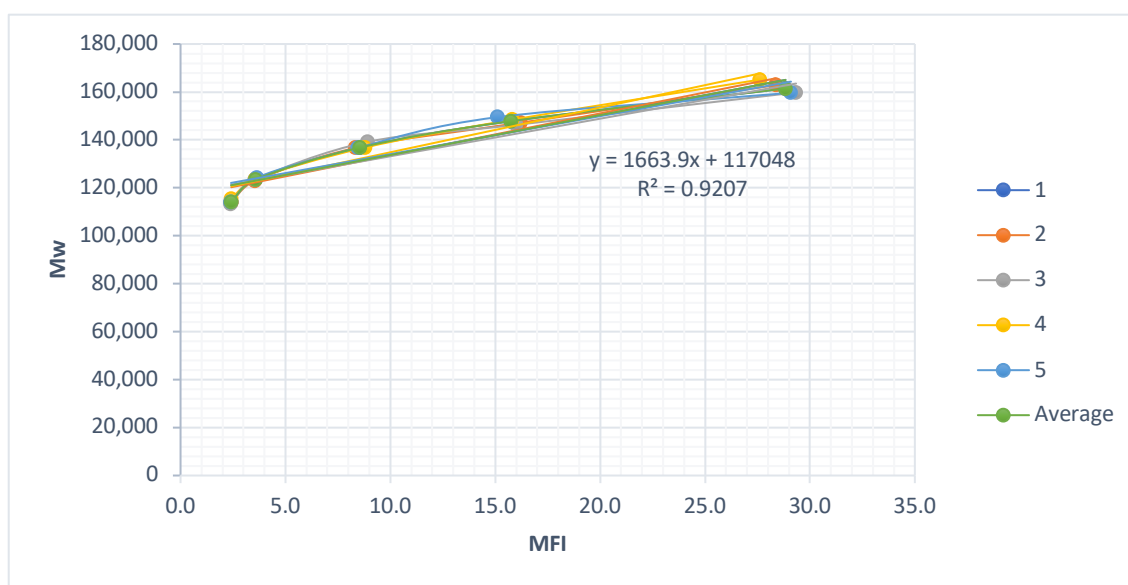


Figure 29. The direct correlation of Recycled Mw vs MFI for each cycle in the heat history.

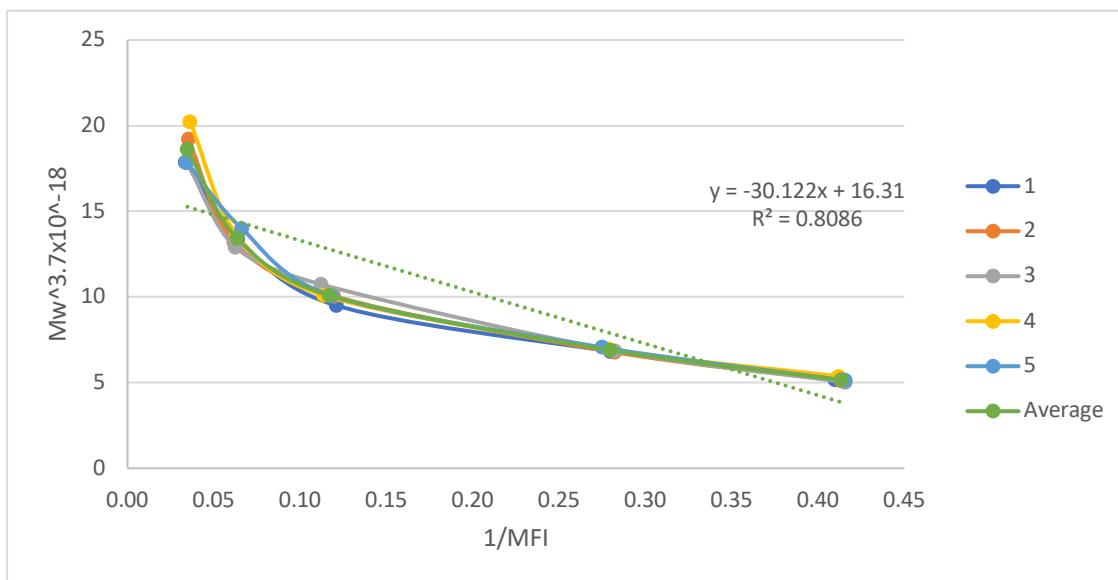


Figure 30. The adjusted correlation between Recycled M_w and MFI for each cycle in the heat history.

In this case of the post-consumer plastic, adjusting the values according to literature with an α of 3.7 gave the strongest correlation coefficient, but was still not as accurate a description as plotting the raw data against each other. This shows that the limitations by the authors were correct, and as varying degrees of polymers are mixed with unknown or unpredictable additives, there is no guaranteed relationship to model the \overline{M}_w vs MFI. In this case, it is more likely to predict the \overline{M}_w by plotting the MFI directly for some reasonably known or consistent post-consumer material.

Figure 30 most accurately follows a natural log decrease in the relationship, which is modeled with a trendline in Figure 31 below.

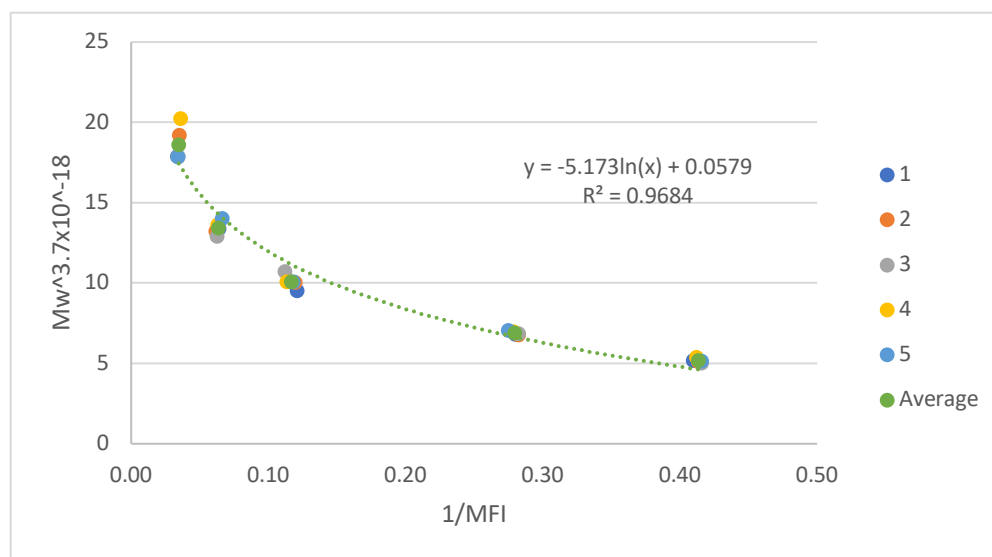


Figure 31. Natural Log Fit of Post-Consumer Plastics

This is an indication that reliably predicating the \overline{M}_w of a material blend is possible through some in-house modeling of reasonably consistent post-consumer products.

4.0 CONCLUSIONS

Thermal characterization showed that both virgin and recycled polymer blends were sufficiently separate in melting temperatures, re-crystallization temperatures, enthalpy, and heat of fusion from one another, i.e., that 25% increments of one material in another was enough to discern thermal characteristics from one another. Only the post-consumer plastics showed evidence of contamination, and both were largely unaffected by 5 processing histories via twin-screw extrusion. ANOVA testing on the blend's MFI and \overline{M}_w values show that each blend was statistically significant from one another, meaning that these results are useful for polymers of widely varying viscosities and \overline{M}_w .

This study expands the results found in literature that a correlation between MFI and \overline{M}_w can be deduced using the Mark-Houwink relation for linear virgin blends of HDPE and PP by exploring this relationship on blends of HDPE and PP. This study also expands and shows that a direct relationship between the MFI and \overline{M}_w can be achieved more accurately for post-consumer waste of HDPE and PP blends; moreover, that the most reliable method for predicting \overline{M}_w via MFI testing should come from empirically deriving the material systems in a lab first.

Mixing rules were also explored in this study and agree with results from literature. Melt enthalpy values and \overline{M}_w values for the blends of polymers were accurately shown to follow a linear mixing rule considering the weight fraction of the component polymers. This is an acceptable consideration in favor of a volume fraction because the densities of HDPE and PP are essentially the same. MFI values were found to follow a quadratic relationship for virgin blends, and a natural log correlation for post-consumer

plastics. The correlation of $\frac{1}{MFI} = G\overline{M}_w^x$ shows that a linear relationship is achievable for virgin plastics, but that an empirically derived relationship can be achieved to more accurately predict \overline{M}_w from MFI testing.

It is established in literature [47] that linear chains of neat polymer hold a consistent correlation between the \overline{M}_w and MFI, and this paper expands this by analyzing blended polymers of varying degrees of branching with several iterations of processing histories. Results of this expansion seem to uphold the findings for linear virgin polymers, allowing the conclusion that this relation can be more generalized to blends of virgin polymers of similar chemical structure. However, these results do not hold for the post-consumer plastics used in this study. A direct relationship of the \overline{M}_w and MFI can be observed to predict linearity more accurately between the characteristics, and that a natural log function most accurately predicts a relationship of materials studied here.

This can still be a useful tool for industries who use relatively consistent raw materials from the post-consumer handling market. Examples include bottling companies (Coke, Pepsi, Nestle, etc.) who reclaim their PET bottles for recycling, and even carpet textiles who receive Nylon, PP, or the more common PET from the same supplier. These suppliers for the textile industry have a standard cleaning and processing procedure and will tend to collect recycled polymers from the same locations. Quality control checks are already a common practice at these facilities, so with a couple of known raw material supplies' MWD (within some standard variance) and the continuous testing of MFI, some information about the physical properties of the product being produced can be inferred. If the direct correlation is insufficient, the use of these quality control measures can lead to a refined correlation that is not necessarily linear and more useful for industry.

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