POST CONSUMER RECYCLED (PCR) FILM FINGERPRINTING: RHEOLOGY AND FILM PROCESSABILITY

Kate Holt
University of Michigan Department of Mechanical Engineering
Engineering Honors Program: Capstone Final Report
December 16th, 2022

COLLEGE OF ENGINEERING
MECHANICAL ENGINEERING
UNIVERSITY OF MICHIGAN

Introduction
Problem
The impact that single use plastic has on our environment is drastic. Not only are single-use plastics made from fossil fuels which directly contribute to the accumulation of carbon dioxide in the air and global warming, but also the improper disposal of plastics pollutes our streets and water. The demand for single use plastics has been on the rise [1], however, more environmentally conscious consumers increasingly express interest in purchasing more sustainable products. This consumer behavior has pushed companies, especially consumer product companies, to meet that demand by using more recycled materials in their products and packaging, therefore lowering their carbon footprints [2]. Thin plastic films are very versatile and used in many applications, but only a minimal percentage of those films are recycled properly because they are not accepted in normal recycling bins [3]. Although there exist some options for recycling plastics films, there are still many issues regarding its efficiency and effectiveness. In other words, the current mechanical recycling process allows these thin, film plastics to become contaminated with dirt, grit, and other non-compatible plastics to produce recycled material that may not be a suitable substitute for virgin plastic materials, especially in consumer product packaging.

Background
It is of great importance for Procter and Gamble to reach their goals of incorporating more recycled content into packaging applications. This initiative sets forth two main goals: consumer packaging will be 100% recyclable or reusable and that P&G will reduce virgin petroleum plastic use in packaging by 50%. Integrating more post-consumer recycled (PCR) content into packaging will contribute to a circular economy of plastic, reduce the amount of virgin petroleum plastic used, and validate the claim that plastic packaging is recyclable. However, recycling flexible films is a major challenge. Because thin, flexible films are not accepted in normal recycling bins, in the United States, only about 7% of retail bags and 3% of post-consumer film packaging are properly recycled at Store Drop-Off locations [2]. Moreover, the small percentage of films that are recycled are typically multi-layered, multi-material, and heavily contaminated with materials such as dirt, paper, grit, or other undesirable polymers. In other words, the lack of homogeneity in plastic waste streams is one of the main challenges during the plastics recycling process. Plastic waste streams consist of a mixture of different polymers and contaminants that are generally not compatible with each other, which leads to overall structural weakness from phase separation and weak adhesion between them. Moreover, different types of plastic, such as polyethylene (PE) and polypropylene (PP), have unique melting and processing ranges [4]. There are even differences between the types of polyethylene. Therefore, the manufacturing conditions

for batches of recycled material are inconsistent in their concentrations of materials and contaminants [2]. The mechanical properties required to make thin films are higher than that of rigid plastic applications as they are very thin and need to behave in a certain way for this to be achievable [2]. The contaminants in the recycle stream lead to aesthetic issues that are undesirable, such as discoloration by ink dye [2]. For more PCR materials to be incorporated into thin film processing, there needs to be characterization before the recycling process begins, the process overall must be economical, and there should not be aesthetic compromises [2].

Literature Review
Before jumping into analyzing how or if recycled materials can act as suitable replacements to virgin plastic packaging, it is important to understand current recycling processes available for flexible plastics, different sources of plastic packaging, and how these resins can be analyzed.

Mechanical Recycling. Plastic waste entering the waste treatment process is rarely homogeneous. The plastic waste stream varies widely in its structure, composition, and level of contamination or degradation. It is often a mixture of different plastics, which limits the applications of the recycled product due to its structural weakness [5]. Therefore, plastic waste requires a greater extent of processing compared to other waste materials before it is recycled, and different waste treatment processes must be considered based on its composition. The waste treatment process that is in the scope of this project is the mechanical recycling process. Mechanical recycling of polymers preserves polymer structure and the plastic waste goes through mechanical processes such as shredding, washing, drying, regranulation, and melting. After the plastics are melted, extruded, and pelletized [6]. These pellets can be remelted and formed into a final product with the blown or cast film line or with injection molding, for example. Within mechanical recycling, there are two different configurations of this process: the open loop and closed loop configuration. Open loop configurations often consist of several mechanical processes and are preferred for materials with a higher level of contamination. The waste stream can be a single type of polymer or a mixture. Closed loop configurations, on the other hand, are used for waste material that is only slightly contaminated and the recycled material closely resembles that of the original. This is because the waste material goes through less mechanical processing that changes the structure and properties of the material. Extrusion is the main mechanical process in closed loop systems [6]. The materials under investigation in this study have solely been mechanically recycled.

Polyethylene. As mentioned previously, one of the main issues regarding film recycling is the effectiveness at which the films can be sorted into their specific type before post-processing. Post-processing plastics of the same type is crucial for keeping their proper material properties intact. Polyethylene is the most common type of polymer manufactured today for flexible films, so only research related to polyethylene recycling is discussed. Polyethylene is classified into three main types: high-density polyethylene (HDPE), low density (LDPE), and linear-low density (LLDPE). These types are differentiated by their molecular structure, crystallinity (degree of structural order in a molecule), melting point, density, mechanical properties, and processability. HDPE has the highest density, degree of crystallinity, and melting point out of the three main types of polyethylene. These properties are due to HDPE's linear molecular structure which is characterized by minimal to no branching of its polymer chains. Because of this structure, HDPE is also less permeable than the other types which makes it tougher, but also less

flexible making it more susceptible to cracking. LDPE is characterized by a high amount of long chain branching (LCB). Because of this, it is the least dense, has the lowest crystallinity, and lowest melting temperature relative to the other main types. Due to its less compact molecular structure, LDPE is very flexible, but has lower tensile, impact, and tear strength when compared to LLDPE. LLDPE is characterized by lots of short chain branches. This molecular structure allows the branches to slide against each other upon elongation without getting entangled which make it stronger and more flexible than LDPE. LLDPE's density, melting point, and degree of crystallinity are between that of LDPE and HDPE. However, the appearance is also transparent making it good for both flexible film and rigid applications. Because LDPE and LLDPE polyethylene, especially, appear translucent, it is the most common polymer used to make single use plastic products such as grocery bags, plastic wrap, film, and injection molded parts [6]. More specifically, typically a blend of 80-100% LLDPE and 0-20% LDPE is used in virgin film packaging to take advantage of both of their ideal properties.

Post Consumer Recycled (PCR) Resins. Plastic flexible film waste is differentiated based on its source material into two different categories: post-industrial and post-consumer. Post-industrial waste is recovered from industrial processes and is cleaner and more homogeneous compared to post-consumer waste. Post-consumer waste is recovered from a wider range of sources after it has been used by the consumer and is therefore more susceptible to contamination by other polymers, dust and soil, grease, organic waste, additives, coatings, adhesives, and inks [7]. Post-consumer flexible film waste is further classified into two subcategories: household and non-household (post-commercial). Household waste refers to plastic films that are used to protect the consumer product (primary packaging) or group together primary packages for transportation (secondary/tertiary packaging). Non-household waste refers to waste from any other post-consumer sources, which are primarily films from the agriculture and construction industry [5]. Post-consumer flexible film waste is what this study focuses on.

In order to study how or if PCR resins can be used as a suitable replacement in film packaging, a portfolio of polymer characterization methods for film-grade polyethylene was developed. Various polymer characterization methods that would be helpful in this process were identified, and many analytical techniques for measuring and quantifying thermal, mechanical, chemical and optical properties were researched for potential use in this study. The two main polymer characterization methods that will be used on these PCR resins are rheology and processability into a film.

Rheology. Rheology studies how stress in a polymeric material affects its deformation and/or flow [8]. Rheology tests are usually performed on melted polymers above their glass transition temperature and/or their melting temperature. From these tests, the viscoelastic properties of the polymer sample such as weight average molecular weight, molecular weight distribution, degree of long chain branching, morphology, and creep properties can be characterized. This will provide insight to the materials' thermal transitions, structure, composition, and long-term performance. During experimentation, if the mechanical properties of the post-consumer recycled sample demonstrate significant differences relative to the virgin polyethylene sample, we can further investigate the viscoelastic properties for any abnormal data points, indicative of contamination. There exist many different types of rheometers, but there are three that are the most relevant to this study: the parallel plate rheometer, the on-line rheometer, and the capillary

rheometer. Studying the rheology of materials of interest can also give an important insight into its polyethylene composition and how well it will process on the blown film line.

Blown Film Line and Production. The blown film extrusion process is one of the most common ways to make polyolefin film. With this method, the resin pellets are melted by subjecting them to heat and pressure inside the barrel of a turning extruder and finally forcing the polymer melt through a narrow circular slit in a die. The result is a thin film in the form of a "bubble" that is then cooled and rolled up on a core. The extruder consists of a "hopper" that aids in dropping the resin pellets into the extruder feed throat in a periodic and uniform manner. This style of feeder is called the loss-in-weight feeder that measures the weight of materials fed into the extruder from a special weight hopper and determines the rate at which material is consumed. Proper mixing in the extruder is necessary to avoid film defects and is achieved by a long enough screw design that allows for this. Additionally, a screenpack located at the end of the screw just before the die helps to slightly increase the back pressure in the screw which in turn leads to enhanced film quality. The polymer melt is then extruded through a circular die in the form of a thin-walled tube. This tube is expanded into a long "bubble" of desired diameter and correspondingly decreases thickness while still in the molten stage which expands further from the volume of air inside the bubble. As the bubble moves away from the die, it is cooled by ambient air both internally and externally while it is supported by guide rollers to prevent it from swaying from side to side. At the top of the system the driven nip rollers confine the air inside the bubble as it collapses it into a double layered film and pulls the film web upward. Finally the film is wound onto a core using a driven center winder [9]. There are a few processing parameters that have been identified in order to qualify and quantify the processability of the PCR resins and how they compare to the virgin resins: bubble stability, melt pressure, and even extruder feeding rates.

Hypothesis
During this study, it is necessary to understand the compositions of the PCR and determine how these other polymers, dirt, and grit contaminants are affecting film processability and end state mechanical properties. In order to deal with the challenge that contaminated recycled films pose, a portfolio of polymer characterization and testing methods have been developed in order to create a resin fingerprint and heat map for (PCR) film grade polyethylene. Essentially, a wide variety of analytical lab tests that have been run on the current PCRs P&G has in house will help to determine what lab tests will result in the most efficient and cost effective for determining resin composition, organized in the format of a decision tree or flowchart . Next, characterizing those PCRs based on its thermal, mechanical, optical, and chemical properties will help to both determine if they can potentially be used in P&G packaging and also help identify contamination in these films which could lead to potential upstream recycling opportunities. A heat map will be created from this data and allow for a quick evaluation of whether or not a new PCR could be used in a variety of P&G packaging applications.

This study focuses on the thermal, processability, and mechanical characteristics of the PCRs. Within rheology, results from different rheometers, such as the parallel plate, online, and capillary rheometer will be used to determine how similar the PCR samples are to the controls in terms of their LCB composition. Within film production and analysis, certain processing parameters, bubble stability, melt pressure, and even extruder feeding rates, will be analyzed to see how unexpected behavior in these categories will impact the film production process. The

PCR with the most similar composition to virgin materials and most desireable film processability parameters will determine the PCR that will perform the best in P&G film packaging. The best rheology test methods for analyzing processability were determined and will be integrated into the decision tree, and threshold values that set the cut off for a "good" vs. "bad" PCR was also determined in order to be integrated into the heat map.

Methods and Approach
In this study, melt flow characteristics of PCR material was studied using three different rheometers and compared to that of virgin resins in order to determine if the composition and melt flow behavior of the PCRs was similar enough to that of the controls and could therefore be a suitable replacement for virgin materials. Within composition, it was most important that the PCR materials were made up of a similar linear-low density polyethylene composition to the virgin materials. Additionally, the processability of the PCRs of interest were studied by comparing their certain processing parameters (bubble stability, melt pressure, and extruder feeding rates) to that of the control materials. The PCRs with the most desirable processing parameters were identified to be more suitable to use in P&G packaging applications than materials that did not have ideal processing parameters.

Materials Overview
In this study, there are eight PCRs of interest, PCR 1-8, coming from both post-household and post-commercial sources. Additionally there are two controls that we will compare our PCR behavior to: a 100% LLDPE resin and a resin composed of 80% LLDPE and 20% LDPE.

In regard to the film production process, there are two film gauges of interest, 50 micron and 10 micron films. The 10 um films are representative of thin film packaging and films used by P&G joint venture partners. 50um films are representative of flow wraps and sealant films used in many P&G applications. Additionally, each film gauge has its respective control: the 50 micron control is the 80/20 blend and the 10 micron control is the 100% LLDPE. Each PCR is blown into these size films: three 10 micron and three 50 micron with varying PCR content (100% PCR, 50 wt.% PCR and 50 wt.% virgin control, and 25 wt.% PCR and 75 wt.% virgin control). For example, a 50 micron 50/50 film is 50 wt.% PCR and 50 wt.% 80/20 blend. So, in total, 48 films were made.

Rheology
Using different rheometers, the parallel plate, online, and capillary rheometer, the LLDPE composition of the PCR materials was predicted. Additionally, depending on how close the PCR LLDPE composition was to the control, a prediction was made as to how well the PCR sample would process on the blown film line.

Parallel Plate Rheometer. The parallel plate rheometer as seen in Figure 1 quantifies the deformation and flow of viscoelastic materials by inducing shear deformation and measuring the resultant stress response.
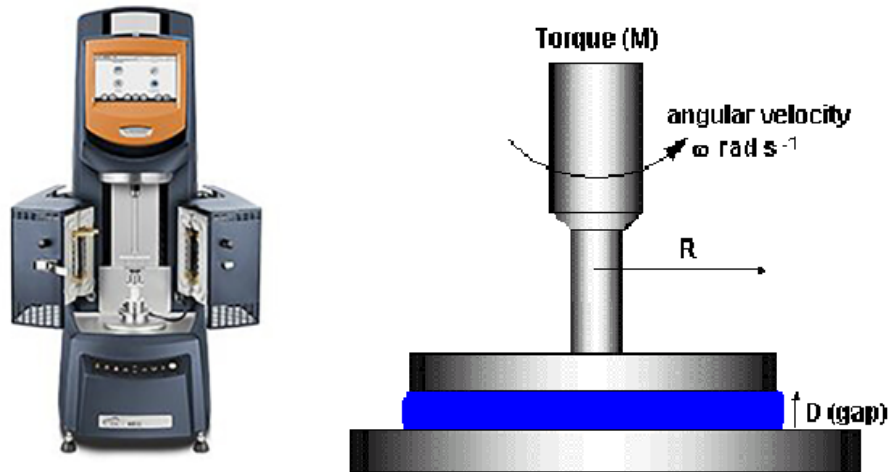
Figure 1. The left image [10] shows what a parallel plate rheometer looks like. The image on the right [11] shows the actual parallel plates of the rheometer. The material is melted between two plates at a specified gap and temperature. Then the plates oscillate back and forth as increasing frequency to output curves showing how the complex viscosity, loss modulus, and storage modulus change.

The output of an oscillatory parallel plate rheometer study is a set of curves that shows how the complex viscosity, storage modulus (G'), and loss modulus (G'') of the material change as a function of angular frequency as seen in Figure 2.
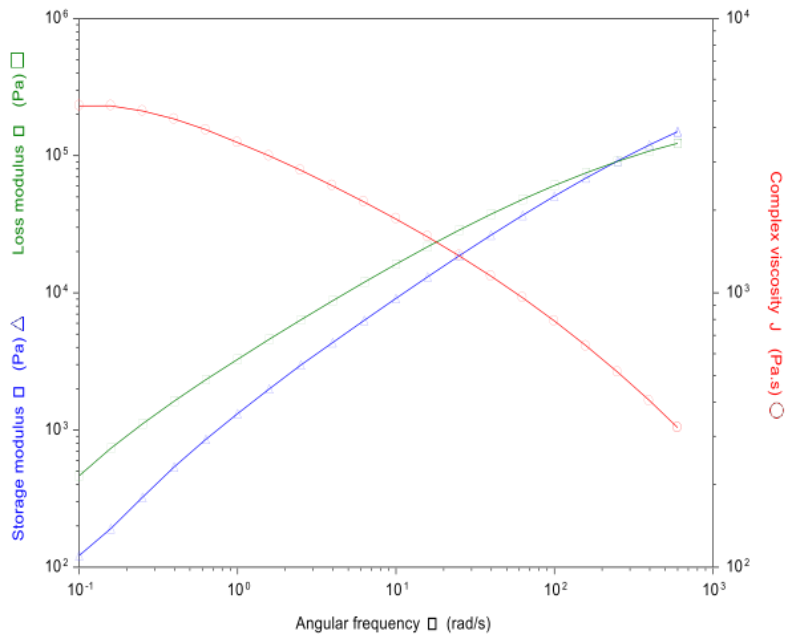

Figure 2. This set of curves is the output of a typical oscillatory parallel plate rheometer run. The graph shows angular frequency in radians/second on the x-axis and loss modulus in Pascals (green), storage modulus in Pascals (blue), and complex viscosity in Pascal*seconds (red) on the double y-axis.

Looking at how the storage modulus as a function of frequency of the PCRs is a good indication of the melt strength of a material: the faster G' increases with frequency, the higher the melt strength [12]. The Cox-Mertz Transformation transforms the data into a curve showing how the

actual viscosity changes as a function of actual shear rate. Using the Carreuu Yasuda model fit on these curves outputs zero-shear rate viscosity at the Newtonian plateau and shear thinning index in the downward sloping region of the curve. The zero shear-rate viscosity is indicative of both the material's weight average molecular weight (MW) and degree of long chain branching (LCB), with a higher zero-shear rate viscosity meaning a higher MW and more LCB. The shear thinning index is an indicator of the material's molecular weight distribution, with a material's viscosity decreasing faster (steeper downward slope) indicating a wider molecular weight distribution as seen in Figure 3.
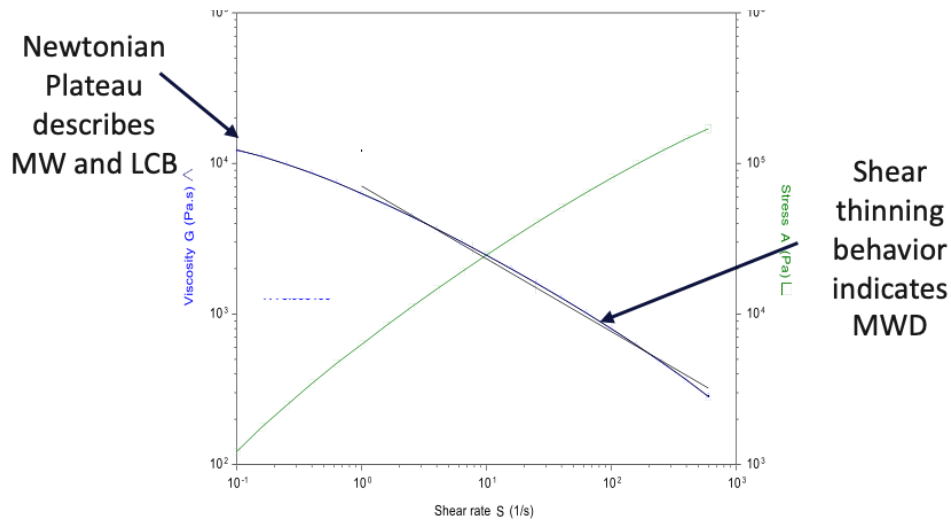

Figure 3. This figure shows the Cox Mertz transformation and the Carreau Yasuda model fit to the data. The graph itself plots shear rate in 1/seconds on the x-axis and viscosity in Pascal*seconds (blue) and stress in Pascals (green) on the y-axis. The Newtonian plateau pointed out on the graph describes the zero-shear rate viscosity, MW, and LCB while the shear thinning behavior in the power law region of the curve describes MWD.

The specific parallel plate rheometer and oscillatory settings that were developed in order to give repeatable results in this study are proprietary and not reported.

As mentioned previously, looking at how the storage modulus as a function of frequency of the PCRs is a good indication of the melt strength of a material: the faster G' increases with frequency, the higher the melt strength. Curves to show how different materials' storage modulus change with frequency can be seen in Figure 4.
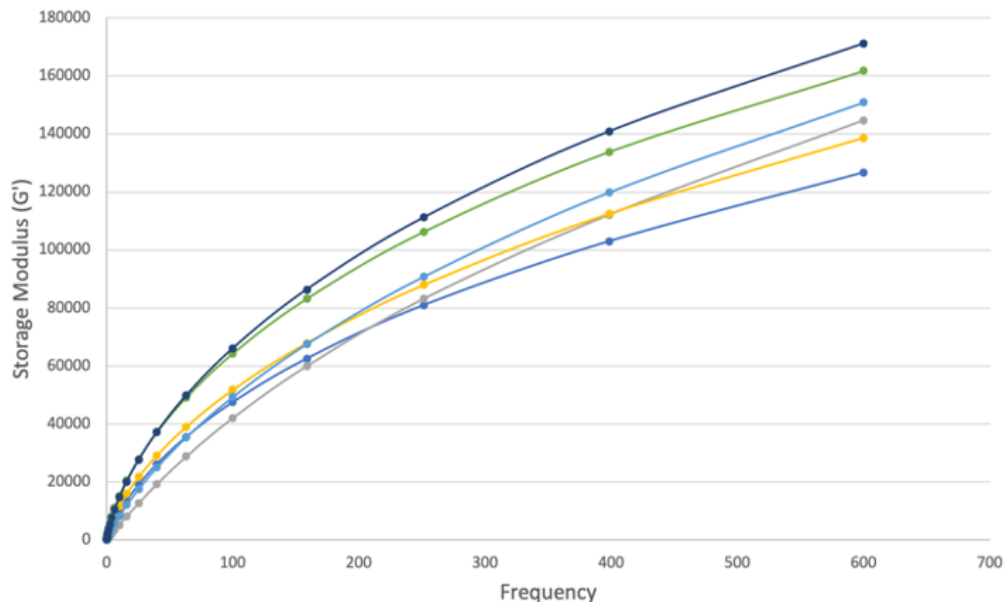
Figure 4. In this figure, the angular frequency in radians/second is plotted on the y-axis and the storage modulus (G') is plotted on the y-axis. Each different color curve represents a different material. The material in dark blue represents the material with the highest melt strength because it has the fastest G' increase over the same frequency range of all the materials.

As outlined in the background, a higher melt strength is associated with long-chain branching in LDPE while lower melt strength is associated with both LLDPE and HDPE. Because we are looking for PCR resins with a similar LLDPE composition to the controls (at least 80% LLDPE), the slower G' increases with frequency, the higher the percentage of LLDPE. Frequency sweeps were performed for each material in order to compare how fast their relative storage moduli were increasing relative to each other. Comparing these curves will give us a qualitative ranking of PCR from highest to lowest melt pressure.

Online Rheometer. The on-line rheometer is another instrument that measures the viscosity of materials but at higher shear rates that are more similar to the shear rates materials experience during extrusion and processing. It does this by melting and mixing material in an extruder and single screw and pumping material through capillaries of different lengths at different speeds as seen in Figure 5.
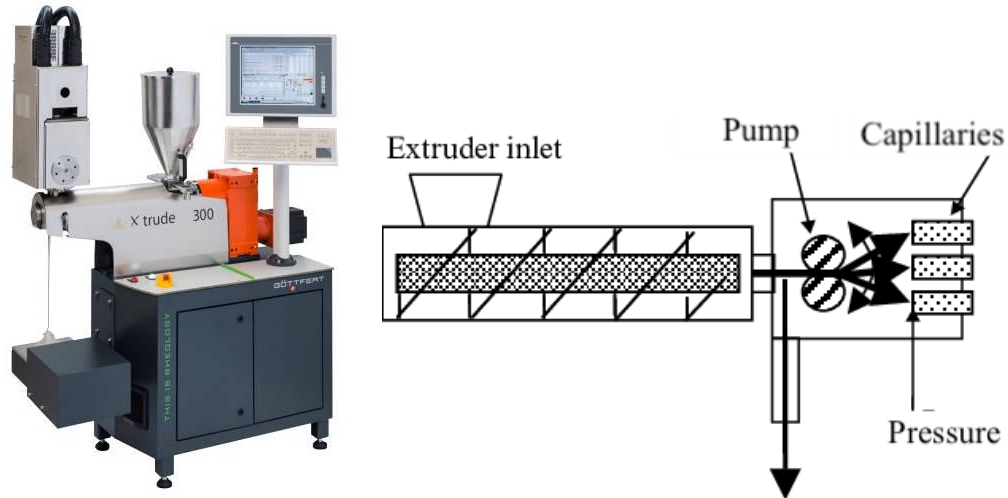
Figure 5. The figure on the left [13] shows what a pilot scale on-line rheometer looks like and the image on the left [14] is a schematic representation of how material flows through an on-line rheometer. The entrance pressure as indicated on the diagram is measured as it flows through the three capillaries of different lengths.

By comparing the pressures in three capillaries and using equations to solve for apparent wall shear stress and shear rate and applying correction factors, you can get the actual viscosity as a function of actual shear rate. These specific calculations and how the data was manipulated were developed with the help of the P&G sponsor and are proprietary information. The online rheometer can also be used to qualitatively determine the melt strength of the materials. The entrance pressure measurement output by the on-line rheometer is an indirect measurement of the extensional viscosity of a material. Curves to show how different materials' entrance pressures change with shear rate can be seen in Figure 6.
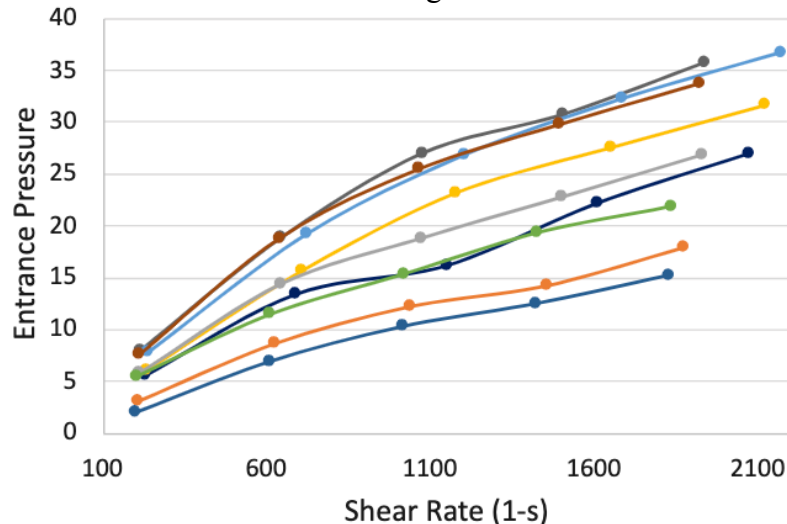

Figure 6. This figure plots the shear rate in 1/seconds on the x-axis and the entrance pressure in Pascals on the y-axis. Each color represents a different material. The three curves at the top of the graph in dark gray, light blue, and brown have the highest entrance pressure for a given shear rate and therefore have the highest melt strength.

9

By plotting the entrance pressure data on the y-axis and the actual shear rate on the x-axis, it can be seen that materials with higher entrance pressures for a given shear rate will have greater melt strength. As outlined in the background, a higher melt strength is associated with long-chain branching in LDPE while lower melt strength is associated with both LLDPE and HDPE. Because we are looking for PCR resins with a similar LLDPE composition to the controls (at least 80% LLDPE), the lower entrance pressures for a given shear rate, the higher the percentage of LLDPE. Each material's entrance pressure as a function of actual shear rate was determined in order to compare how large their relative entrance pressures were relative to each other and qualitatively rank the PCR from highest to lowest melt pressure.

Capillary Rheometer. The capillary rheometer measures the shear viscosity and elasticity of viscous materials at high shear rates and is very similar to the online rheometer in that way. However these test methods differ because the capillary rheometer has a melting reservoir that holds the melted polymer while a piston pushes material through one capillary die instead of three. The force at which the piston forces material through the die is controlled in order to maintain a specified strain rate as seen in Figure 7.
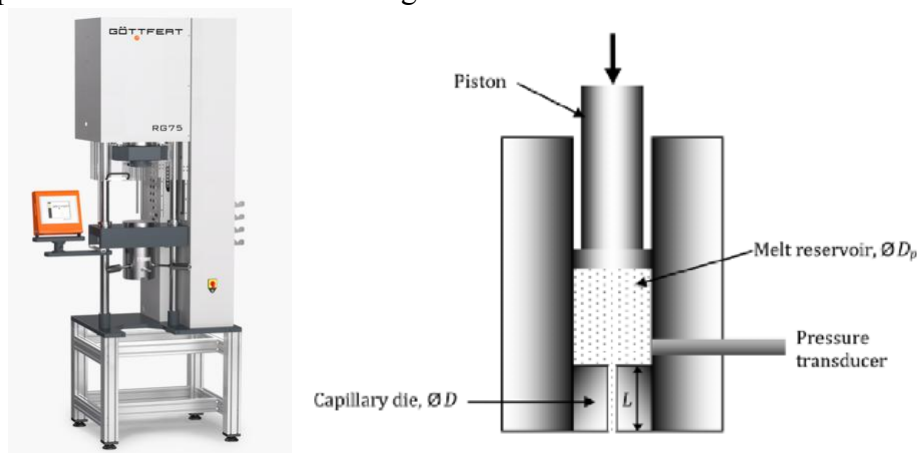

Figure 7. The image on the left [15] shows what an actual capillary rheometer looks like and the image on the right [16] is a schematic of how material flows through a capillary rheometer. The entrance pressure as well as the apparent wall shear stress are both recorded in the machine's outputs.

However, it also compares the pressures in different size capillaries and uses equations to solve for apparent wall shear stress and shear rate and finally the actual viscosity as a function of actual shear rate after applying correction factors. The data can be further manipulated to get the extensional viscosity as a function of shear viscosity. Again, these specific calculations and how the data was manipulated were developed with the help of the P&G sponsor and are proprietary information. The ratio of the extensional viscosity and shear viscosity is known as the Trouton ratio and is used to nondimensionalize the extensional viscosity. A modified version of this parameter was developed in order to normalize the viscosity to account for differences in molecular weight. This method was verified by testing virgin control blends of varying weight percent of LLDPE and LDPE as seen in Figure 8. As you can see, as the weight percent of LDPE increases, the modified Trouton ratio also increases.
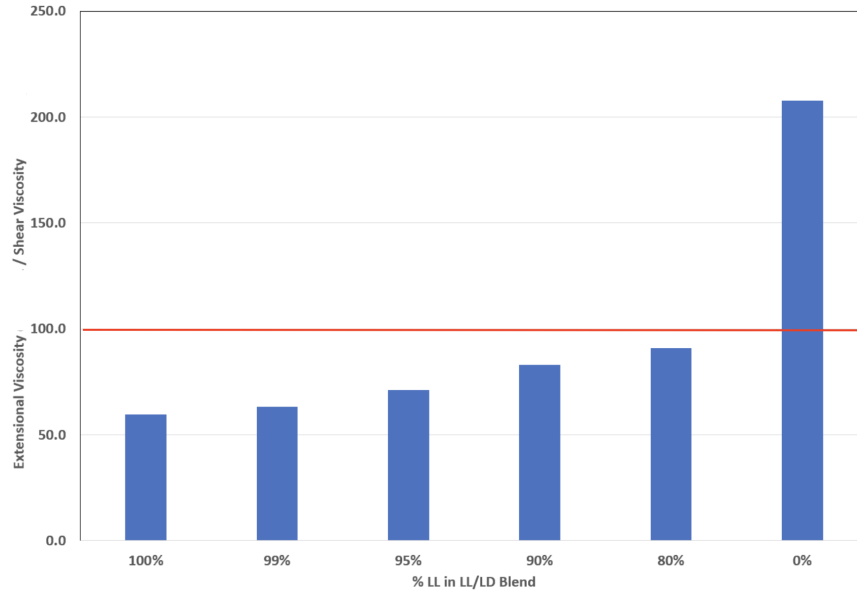
Figure 8. This figure plots the percent LLDPE in a known LLDPE/LDPE blend on the x-axis and the ratio of extensional viscosity to shear viscosity (the modified Trouton ratio) on the y-axis. The red line at 100 on the y-axis indicates the "cutoff" point. Below the line, the materials are composed of greater than 80% LLDPE while above the line, the materials are composed of less than 80% LLDPE.

The development of this parameter is important for decoupling the effects LCB has on molecular weight when comparing behavior and curve shapes of unknown PCR materials to that of virgin materials. Because this study was done on control blends as well as PCRs of unknown composition, a linear calibration curve can be constructed to quantify the percent LLDPE composition in the PCRs.

Blown Film Analysis
As mentioned previously, the goal for the blown film analysis was to determine which PCR would process the best on the blown film line. A team at P&G made the various films as outlined in the materials overview using their pilot scale blown film line to analyze how the bubble stability, changing melt pressure, and variable PCR feedstock affected the processability of each PCR as seen in Figure 9. Ultimately, the few PCR materials that processed the best are meant to be determined.

Figure 9. This figure shows what an actual pilot blown film looks like [17]. On the right of the image, pellets get fed into the extruder at a constant throughput, melted and mixed at the extruder turns, causing pressure to push melted material up through a circular die. Air gets blown into the material to create a "bubble". At the top, the bubble flattens to create a double layered film as it's rolled up on the core.

Bubble Stability. Bubble stability refers to whether a uniform polymer flow up the machine is possible without the "bubble" moving from side to side. Figure 10 shows what ideal bubble stability behavior looks like versus less than ideal behaviors, such as tearing and dancing.
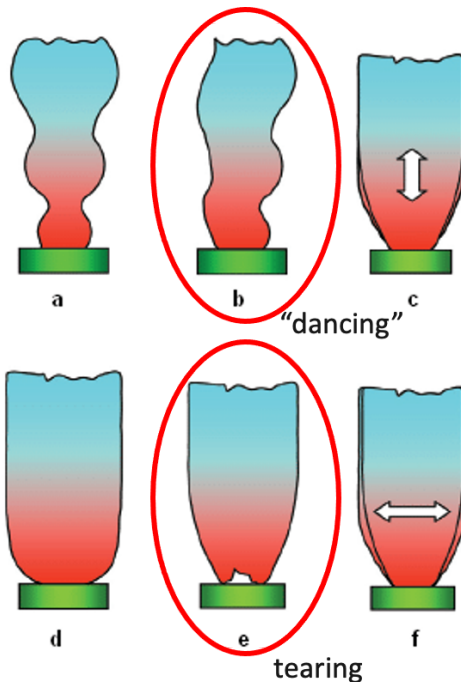

Figure 10. The image on the left shows the ideal behavior of a bubble, a uniform polymer flowing up the machine without it moving from side to side. The left image [18] shows less than ideal bubble behavior. The dancing and tearing were the most common undesirable behaviors that were noticed.

12

Dancing can cause uneven film width and thickness as well as wrinkles, all of which can affect the film mechanical properties. In order to fix this behavior, we had to adjust die temperatures as well as the air ring blower power. Tearing is a result of gels or contamination that don't melt at the same temperature LLDPE and LDPE melt at which cause holes in the bubble when pushed through the die. Tearing can cause both uneven film width and thickness because the bubble is losing air through the holes in the film.

The bubble stability for each PCR was determined by visual inspection of the films while being blown. The number of times tearing and/or dancing were observed during the time in which the film was being produced was recorded.

Melt Pressure. The melt pressure of each of the PCRs were monitored while being produced on the film line. A build up of unmelted polymer contaminants in the extruder screen pack/filter caused the pressure to increase too much over time. The pressure during production was observed to make sure it didn't exceed machine limits so production wouldn't shut down. Also, how much the melt pressure increased over time while polymer melts were flowing through the machine was determined by plotting melt pressure (recorded as one of the blown film line machine outputs every 30 seconds) against the amount of time each film was being run as seen in Figure 11.
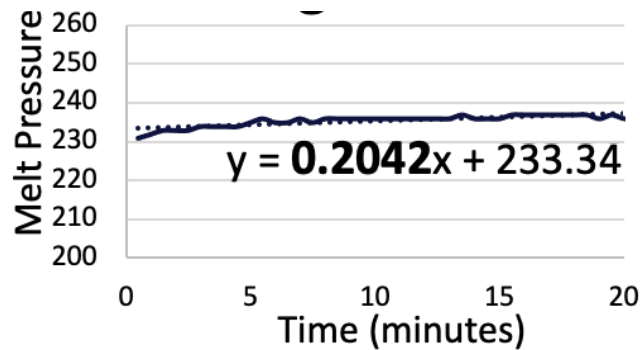

Figure 11. This figure plots the time in minutes on the x-axis and the back melt pressure in the extruder in torr on the y-axis. A linear fit was applied to this curve in order to determine the slope. The slope is indicative of how much the melt pressure increased over time which in turn informs how much contamination there is in the film. A slope of 0.2 is relatively low.

The slopes of the melt pressure versus time curves were compared for each material to see how much the pressure was increasing over time for each material. A steeper slope means that the pressure is increasing more quickly and there may be more undesirable polymer or dirt contamination in that PCR resin that is not compatible with LLDPE or LDPE. To ensure more confidence in these results, the screen pack from the extruder was changed out between each material to make sure there was no contamination build up from a specific PCR that was affecting a different PCR's increase in melt pressure.

Pelt Size Variability. In terms of pellet size and variability, it was important to have uniform sizing from individual pellet to pellet to ensure even feed rates. It was clear that some PCR materials had more size variation than others as seen in Figure 12, however it was unclear whether or not this had any effect on the film production process.
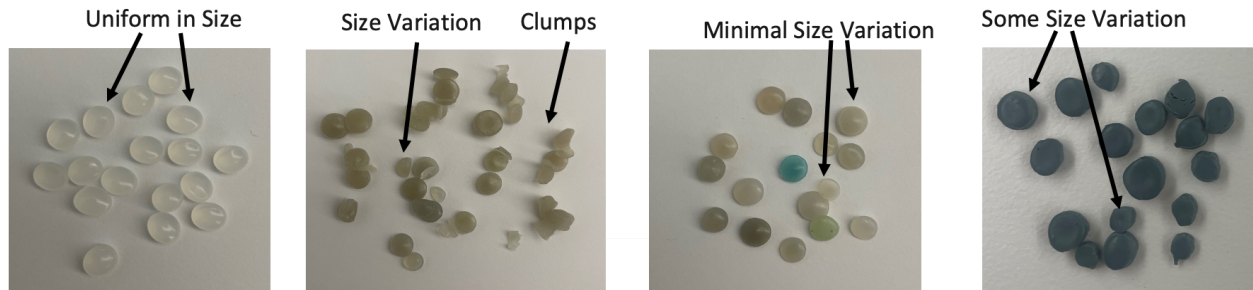
Figure 12. These images show how different pellets from different sources can either be uniform in size (left) or display large size variation and clumping (middle and right). This non-uniform behavior impacts how much the extruder speeds up or slows down in order to maintain uniform melt flow to the die.

After noticing that the extruder screw speed was speeding up and slowing down while the machine was set at a constant throughout for some of the material and not others, it became clear that variable pellet sizes had some impact on the production process. After more research, it was determined that the variable pellet size could be causing extruder RPM to be changing over time. The variable pellet sizes were causing uneven feed rates into the extruder and slippage in the screw. Both of these ultimately cause non-uniform polymer melt flow into the die which causes uneven film thickness [19]. In order to quantitatively determine the pellet size variability, how much the extruder speed changed over the time in which the PCR was being made on the blown film line was plotted as seen in Figure 13.
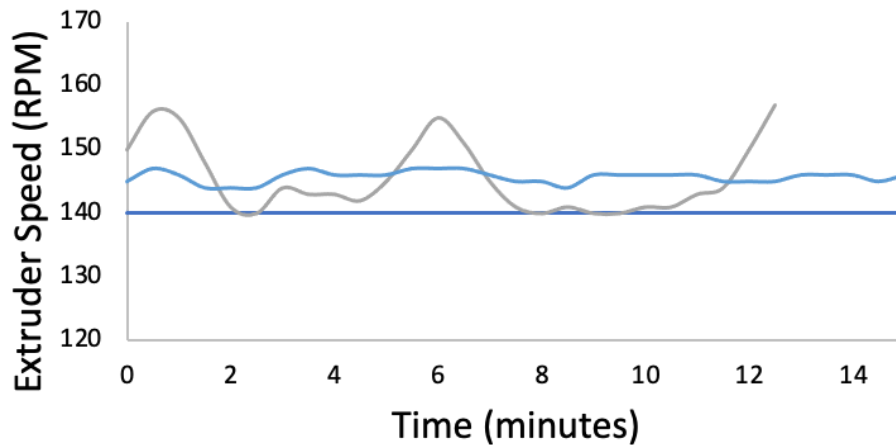
Figure 13. This figure plots time in minutes on the x-axis and the extruder speed in RPM on the y-axis. The dark blue curve shows no variation over time while the light blue and gray curves show how the extruder speeds up or slows down in order to maintain uniform melt flow to the die.

The variability was quantified by looking at the PCRs' relative standard deviations from the extruder speed mean. A higher standard deviation from the mean extruder speed indicated that the extruder had to speed up and slow down more often and the pellets were more variable.

Results

After performing various rheology tests on various PCR materials and comparing them to the control samples, the PCR that had an ideal LLDPE composition was determined. The best test method to determine the percent LLDPE composition in the PCRs was also determined. The film

production processing parameters determined from the film production process were found for each PCR. Evaluating PCRs based on rheology and their processing parameters allowed for a ranking of the PCRs from most suitable to least to be determined.

Rheology

Based on tests and results using the parallel plate, on-line, and capillary rheometers, both a qualitative and quantitative determination of the PCRs' LLDPE:LDPE composition was determined.

Parallel Plate Rheometer. As mentioned previously, looking at how the storage modulus as a function of frequency of the PCRs is a good indication of the melt strength of a material: the faster G' increases with frequency, the higher the melt strength. A higher melt strength is associated with long-chain branching in LDPE while lower melt strength is associated with both LLDPE and HDPE. Because we are looking for PCR resins with a similar LLDPE composition to the controls (at least 80% LLDPE), the slower G' increases with frequency, the higher the percentage of LLDPE. Because the frequency sweeps performed for each material in order to compare how fast their relative storage moduli were compared increasing relative to each other, only a quantitative ranking was determined to rank the PCRs from highest to lowest melt strength and increasing LLDPE as seen in Table 1.

Table 1. This table ranks the PCR based on their melt strength relative to each other based on the parallel plate rheology data with a lower score indicating a lower melt strength and highest LLDPE %. The materials from highest LLDPE composition to lowest are the 100% LLDPE control, PCR 2, PCR 1, PCR 3, PCR 4, and finally PCR 5.

	Material					
	100% LLDPE	PCR 1	PCR 2	PCR 3	PCR 4	PCR 5
Qualitative Melt Strength Ranking	1	3	2	4	5	6

Based on this table, the PCR with the highest LLDPE percent composition is PCR 2, however this method is only qualitative and doesn't give an actual number for this percent composition.

Online Rheometer. The online rheometer can also be used to qualitatively determine the melt strength of the materials. The entrance pressure measurement output by the on-line rheometer is an indirect measurement of the extensional viscosity of a material. By plotting the entrance pressure data on the y-axis and the actual shear rate on the x-axis, it can be seen that materials with higher entrance pressures for a given shear rate will have greater melt strength. As outlined in the background, a higher melt strength is associated with long-chain branching in LDPE while lower melt strength is associated with both LLDPE and HDPE. Because we are looking for PCR resins with a similar LLDPE composition to the controls (at least 80% LLDPE), the lower entrance pressures for a given shear rate, the higher the percentage of LLDPE. Because each material's entrance pressure as a function of actual shear rate for each material was compared to

each other, only a quantitative ranking was determined to rank the PCRs from highest to lowest melt strength and increasing LLDPE as seen in Table 2.

Table 2. This table ranks the PCR based on their melt strength relative to each other based on the on-line rheology data with a lower score indicating a lower melt strength and highest LLDPE %. The materials from highest LLDPE composition to lowest are PCR 3, PCR 1, the 100% LLDPE control, PCR 2, the 80/20 control blend, PCR 5, PCR 4, and finally PCR 7.

	Material								
	100% LLDPE	**80/20 Blend**	**PCR 1**	**PCR 2**	**PCR 3**	**PCR 4**	**PCR 5**	**PCR 6**	**PCR 7**
Qualitative Melt Strength Ranking	4	6	2	5	1	8	7	9	3

Based on this table, the PCR with the highest LLDPE percent composition is PCR 3, however this method is only qualitative and doesn't give an actual number for this percent composition. Additionally, the qualitative ranking from the on-lin rheometer does not match up with the qualitative ranking done from the parallel plate rheometer.

Capillary Rheometer. The ratio of the extensional viscosity and shear viscosity determined by experiments done on the capillary rheometer is known as the Trouton ratio and is used to nondimensionalize the extensional viscosity. A modified version of this parameter was developed in order to normalize the viscosity to account for differences in molecular weight. This method was verified by testing virgin control blends of varying weight percent of LLDPE and LDPE. As the weight percent of LDPE increases, the modified Trouton ratio parameter also increases. By determining the ratio of our control materials and PCRs, we can classify each based on their modified Trouton ratio: LLDPE heavy material has a ratio less than 100 while a LDPE heavy material has a ratio greater than 200. Any ratio between 100 and 200 is balanced. Each modified Trouton ratio was determined for each material as shown in Table 3.

Table 3. This table shows each of the PCRs' modified Trouton Ratio. Any ratio below 100 was classified as LLDPE heavy, any ratio above 200 was classified as LDPE heavy, and any ratio between 100 and 200 was classified as balanced.

	Material							
	PCR 1	**PCR 2**	**PCR 3**	**PCR 4**	**PCR 5**	**PCR 6**	**PCR 7**	**PCR 8**
Modified Trouton Ratio	21.3	60.1	12.5	93.3	108.0	97.3	48.1	59.5
LLDPE Classification	LL Heavy	LL Heavy	LL Heavy	LL Heavy / balanced	balanced	LL Heavy / balanced	LL Heavy	LL Heavy

Because this study was done on control blends as well as PCRs of unknown composition, a linear calibration curve can be constructed to quantify the percent LLDPE composition in the PCRs as seen in Figure 14.
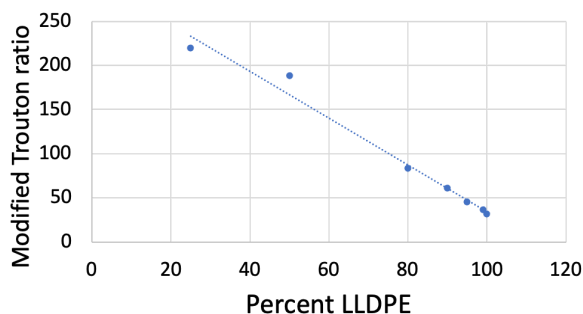

Figure 14. This figure shows the calibration curve created from the ratios of the known LLDPE/LDPE blends. The slope of this linear fit is -2.65 and its y-intercept is 299.35. Based on this information, the approximate percent LLDPE composition of the unknown PCR materials can be determined.

Using the calibration curve's slope and y-intercept, the approximate percent LLDPE composition of the PCRs can quantitatively be determined as seen in Table 4.

Table 4. This table shows the approximate percent LLDPE composition of the PCRs based on the calibration curve created from the control blends data. The PCRs with the highest to lowest LLDPE composition from the capillary rheology method are PCR 1, PCR 3, PCR 7, PCR 2, PCR 8, PCR 4, PCR 6, and PCR 5.

Material								
	PCR 1	PCR 2	PCR 3	PCR 4	PCR 5	PCR 6	PCR 7	PCR 8
Approximate % LLDPE	99	90	99	78	72	76	94	80

Blown Film Analysis
Bubble Stability. The bubble stability for each PCR was determined by visual inspection of the films while being blown. The number of times tearing and/or dancing were observed during the time in which the film was being produced was recorded. It was difficult to count the number of times this undesirable behavior occurred because the film production process would have to be diligently watched the entire time each film was being produced. Because of this, instead of recording an exact number of holes that formed, there was a range assigned to each material instead. Thes ranges were 0 to 1, 2 to 5, and greater than 5 noted instances of undesirable behavior. A table comparing the number of undesirable behaviors observed for each PCR compared to each other and the controls is shown in Table 5.

Table 5. This table shows how many undesirable behaviors (dancing/tearing) occurred during the film production process for each material. The materials with the most desirable behavior were PCR 2, PCR 3, and PCR 5. The materials with the least desirable behavior were PCR 4, and PCR 6.

	Material									
	Virgin LLDPE	**80/20 Blend**	**PCR 1**	**PCR 2**	**PCR 3**	**PCR 4**	**PCR 5**	**PCR 6**	**PCR 7**	**PCR 8**
Number of Undesirable Behaviors Observed	0 - 1	0 - 1	2 - 5	0 - 1	0 - 1	> 5	0 - 1	> 5	2 - 5	2 - 5

Melt Pressure. A measurement of the increase in melt pressure for a material indicated how much polymer or grit contamination is in that material. How much the melt pressure increased over time while polymer melts were flowing through the machine was determined by plotting melt pressure (recorded as one of the blown film line machine outputs every 30 seconds) against the amount of time each film was being run as seen in Figure 15.
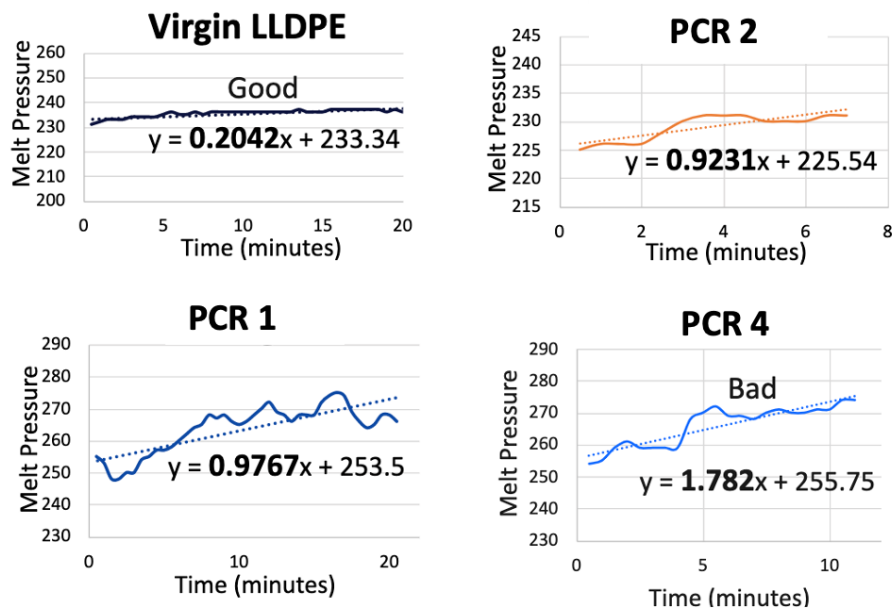

Figure 15. This figure plots the time in minutes on the x-axis and the back melt pressure in the extruder in torr on the y-axis. A linear fit was applied to these four curves in order to determine the slope. The slope is indicative of how much the melt pressure increased over time which in turn informs how much contamination there is in the film. A slope of 0.2 is relatively low in the virgin 100% LLDPE material while a slope of 1.7 for PCR 4 is very high.

A steeper slope means that the pressure is increasing more quickly and there may be more undesirable polymer or dirt contamination in that PCR resin that is not compatible with LLDPE or LDPE and is not melting in the extruder. Included in Table 6 is the slope of each material in order to compare the materials against each other and to the controls.

Table 6. This table shows the slopes of the melt pressure vs. time curves for all of the PCRs of interest as well as the control materials. PCR 8's slope increased the least, which means it has the least amount of contamination, while PCR 4's slope increased the most, which means that it has the most contamination.

	Material									
	Virgin LLDPE	**80/20 Blend**	**PCR 1**	**PCR 2**	**PCR 3**	**PCR 4**	**PCR 5**	**PCR 6**	**PCR 7**	**PCR 8**
Slope	0.20	0.24	0.98	0.92	1.5	1.8	0.51	1.1	1.5	0.45

Pelt Size Variability. The variable pellet sizes were causing uneven feed rates into the extruder and slippage in the screw. Both of these ultimately cause non-uniform polymer melt flow into the die which causes uneven film thickness. In order to quantitatively determine the pellet size variability, how much the extruder speed changed over the time in which the PCR was being made on the blown film line was plotted. The variability was quantified by looking at the PCRs' relative standard deviations from the mean extruder speed. A higher standard deviation from the mean extruder speed indicated that the extruder had to speed up and slow down more often and it was more variable. The material's relative standard deviations from the extruder speed mean are shown and compared in Table 7.

Table 7. This table shows each material's standard deviation from their respective mean extruder speeds. PCR 8 had the lowest standard deviation, meaning that it had the most uniform pellets and most uniform polymer melt flow into the die. PCR 1 had the highest standard deviation, meaning that it had the least uniform pellets and least uniform polymer melt flow into the die.

	Material									
	Virgin LLDPE	**80/20 Blend**	**PCR 1**	**PCR 2**	**PCR 3**	**PCR 4**	**PCR 5**	**PCR 6**	**PCR 7**	**PCR 8**
Extruder Speed Standard Deviation	0.0	1.2	5.5	2.1	1.4	1.8	1.7	1.8	1.6	1.2

Discussion

The best rheology test methods for analyzing certain characteristics of polyethylene were determined and are shown in the pros and cons list in Table 8. This list outlines the rheology instruments used in this study and what each instruments' results are most beneficial for.

Table 8. This list outlines the rheology instruments that were used in this study and what each instruments' results are most beneficial for. For example, if you are interested in determining viscosity at low shear rates, I would recommend using the parallel plate rheometer because, with my current methods for the on-line rheometer, you only get viscosity curves at high shear rates. Additionally, the best method for quantitatively determining the LLDPE percent composition in the materials, is the capillary rheometer.

Parallel Plate Rheometer		On-line Rheometer		Capillary Rheometer	
Pros	Cons	Pros	Cons	Pros	Cons
Less material needed	More variability results	Extensional viscosity / melt strength	More material	Short data collection period (~5 minutes)	More material
Short data collection period (~5 minutes)	No viscosity data at high shear rates	Viscosity at high shear rates	Longer data collection period (~30 minutes +)	Quantitative LL/LD composition	No zero-rate viscosity (with current method)
Viscosity at low shear rates	Quantitative LL/LD composition	Shear thinning behavior at high shear rates	Quantitative LL/LD composition		Long data / post processing analysis
Onset of shear thinning					

Throughout this study, it was also important to determine threshold values for each material property of interest that set the cut off point or range of values that determined a "good" vs. "bad" PCR. This information will be integrated into the heat map discussed in the conclusion section. This is a compilation of values based on studies done in the winter and summer, but the data analysis conducted in the fall only confirmed these threshold values and helped feel more confident in these values. A complete list of the properties of interest in my study, the method in which the values for each property, and what a "good" and "bad" range of values is for each property was determined but cannot be shown, as it is proprietary information. These threshold values will be used to construct the PCR heat map.

Conclusion
Based on all of the results from my various test methods a heat map was constructed depicting how much the PCRs' property values varied from the control material and how the property values compared to the threshold values described above. A 0, -1, or -2 was assigned accordingly depending on if a PCR's property value was within, barely within, or outside the threshold values described earlier. Both of the control materials were given a 0 in each category because they all fell in the range of the threshold values described. Within viscosity, a PCR got a 0 if it fell in the middle range of its threshold value, a -1 if it was barely within that range, and a -2 if it was outside of that range. Within LLDPE/LDPE composition, a PCR that was in the desired threshold range got a 0, any that was just outside of the range got a -1, and any that was far out of the range got a -2. This same analysis was done for each of the properties of interest shown in the

first row of Table 9. Again, specific threshold values and ranges for the properties of interest are not presented because it is proprietary information.

Table 9. This table shows how each of the PCRs' resin behavior and film processability parameters compared to the 100% LLDPE and 80/20 blend controls. The control film was used as a baseline and a 0, -1, or -2 was assigned accordingly depending on how much each of the PCRs' property values (for viscosity shear thinning, LL/LD composition, bubble stability, increase in melt pressure, and pellet size variability) varied from the control material and how the property values compared to the threshold values described above. Using this scoring matrix, the PCRs that performed the best were PCR 2, PCR 5, and PCR 8, while the PCRs that performed the worst were PCR 4, PCR 6, and PCR 1.

	Viscosity	Shear Thinning	LL/LD Composition	Bubble Stability	Increase in Melt Pressure	Pellet Size Variability
100% LLDPE	0	0	0	0	0	0
80/20 Blend	0	0	0	0	0	0
PCR 1	-2	-1	0	-1	-2	-2
PCR 2	0	0	0	0	0	-1
PCR 3	-2	-2	0	0	0	-1
PCR 4	-1	-1	-1	-2	-2	0
PCR 5	0	0	-2	0	-1	0
PCR 6	-1	0	-1	-2	-1	0
PCR 7	-2	-2	0	-1	0	0
PCR 8	-	-	0	-1	0	0

After completing this table of values and identifying the PCRs most suitable for use in packaging, it was important to weigh each factor that goes into the mapping to get a more accurate score for each of the PCRs. After discussing each property of interest with sponsors and building intuition by working with these instruments more, each of the properties were weighed in order to more accurately score the PCR. Based on this weighting scheme, a final score of the PCRs was determined and is shown in Figure 10.

Table 10. Based on each of the material's property values described in Table 9, a weighted score was created to more accurately score the PCRs. This was done by taking 100 minus the percent deviation the material property value was from threshold values. This value was then multiplied by the weight to get the final score. Using this scoring matrix, the PCRs that performed the best were PCR 2, PCR 3, and PCR 5, while the PCRs that performed the worst were PCR 4, PCR 6. PCR 1, PCR 7, and PCR 8 were average.

PCR	Score
PCR 1	87
PCR 2	97
PCR 3	99
PCR 4	80
PCR 5	98
PCR 6	80
PCR 7	91
PCR 8	91

As you can see from the table, the PCRs that performed the best and are most likely to be used in P&G packaging applications are PCR 2, PCR 3, and PCR 5. However, rheology and processability parameters are not the only PCR characteristics that should be studied in order to determine whether or not a PCR is a suitable replacement for its virgin counterpart. Studies regarding contaminant identification and film mechanical and optical properties, in addition to others, are necessary in order to complete the full resin fingerprint of the PCR resins of interest.

The methods, results, discussion, and conclusions from these studies were passed along to a team at P&G who will continue to work on this project and characterize more PCRs using the methods outlined. Additionally, in order to find PCRs that are appropriate for different film applications within P&G's vast range of products, the weighting scheme of each property of interest can be adjusted. For example, if the LLDPE/LDPE composition does not have to be greater than 80% for baby care packaging, it could be weighted lower and a new score for the PCRs could be determined.

The desired business outcome from this project is first to have a time and cost-efficient way to select a PCR that meets specified requirements. Additionally, accessible data on PCRs will allow for greater incorporation of PCR into packaging and replacing its virgin material, which contributes directly to P&G recycling goals. This set of tests will both identify shortcomings of PCR resins to make upstream and downstream recommendations to our resin suppliers and also educate the community on the key polymer properties to consider for optimal packaging performance. This study of film PCRs will work in conjunction with the PCR resin digital portal that already exists for rigid PCRs. A preliminary database page consisting of method development and techniques to evaluate PCRs based on their compositions is expected to be ready in late December 2022 with a launch date of June 2023.

References

[1] January 09, 2020 C. L. (2022, May 16). *Single-use plastics 101*. NRDC. Retrieved December 15, 2022, from https://www.nrdc.org/stories/single-use-plastics-101

[2] SPC - Design for Recycled Content Guide. (n.d.). Retrieved February 1, 2022, from https://recycledcontent.org/

[3] Horodytska, O., Valdés, F. J., & Fullana, A. (2018). Plastic flexible films waste management – A state of art review. Waste Management, 77, 413–425. https://doi.org/10.1016/j.wasman.2018.04.023

[4] Marsh, R., Griffiths, A. J., Williams, K. P., & Evans, S. L. (2006). Degradation of Recycled Polyethylene Film Materials Due to Contamination Encountered in the Products' Life Cycle. Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science, 220(5), 593–602. https://doi.org/10.1243/09544062JMES234

[5] Merrington, A. (2017). Recycling of Plastics. In Applied Plastics Engineering Handbook (pp. 167–189). Elsevier. http://dx.doi.org/10.1016/B978-0-323-39040-8.00009-2

[6] Kutz, M. (2017). Applied plastics engineering handbook (pp. 27-53). Willam Andrew. http://dx.doi.org/10.1016/B978-0-323-39040-8.00002-X

[7] Horodytska, O., Valdés, F. J., & Fullana, A. (2018). Plastic flexible films waste management – A state of art review. Waste Management, 413–425. https://doi.org/10.1016/j.wasman.2018.04.023

[8] Polymer Diagnostics Inc. (n.d.). Rheology. Rheology – Viscoelastic Testing of Plastics | Polymer Diagnostics, Inc. Retrieved February 2, 2022, from https://www.polymerdiagnostics.com/techniques/rheology

[9] *A guide to polyolefin film extrusion* . (n.d.). Retrieved December 16, 2022, from https://www.lyondellbasell.com/globalassets/documents/polymers-technical-literature/A_Guide_to_Polyolefin_Film_Extrusion.pdf

[10] *Discovery HR 30 - Ta Instruments*. TA Instruments -. (2022, September 27). Retrieved December 15, 2022, from https://www.tainstruments.com/hr-30/

[11] *Using cement paste rheology to predict concrete mix design problems ...* (n.d.). Retrieved December 16, 2022, from https://www.researchgate.net/publication/242561645_USING_CEMENT_PASTE_RHEOLOGY_TO_PREDICT_CONCRETE_MIX_DESIGN_PROBLEMS_TECHNICAL_REPORT

[12] Wang, L., Jing, X., Cheng, H., Hu, X., Yang, L., & Huang, Y. (2012). Rheology and crystallization of long-chain branched poly(L-Lactide)s with controlled branch length. *Industrial & Engineering Chemistry Research*, *51*(33), 10731–10741. https://doi.org/10.1021/ie300524j

[13] *On-line melt index rheometers*. LMS Thailand. (n.d.). Retrieved December 15, 2022, from https://www.lmsinstruments.co.th/product/processability-on-line-systems/on-line-melt-index-rheometers.html

[14] *The on line rheometer set-up. | download scientific diagram - researchgate*. (n.d.). Retrieved December 16, 2022, from https://researchgate.net/figure/The-On-Line-Rheometer-set-up_fig1_242645976

[15] GmbH, G.Ö.T.T.F.E.R.T.W.-P. (n.d.). *Capillary rheometer*. GÖTTFERT. Retrieved December 15, 2022, from https://www.goettfert.com/products/capillary-rheometer

[16] *Sketch of the capillary rheometer. | download scientific diagram*. (n.d.). Retrieved December 16, 2022, from https://www.researchgate.net/figure/Sketch-of-the-capillary-rheometer_fig3_257802375

[17] *Laboratory extruder and testing equipment – Nekousaz PSA (Nekousaz polymer Sanat Aria Co..)*. Nekousaz PSA Nekousaz polymer sanat Aria Co. (n.d.). Retrieved December 15, 2022, from https://www.nekousaz.com/product/laboratory-extruder-and-testing-equipment/

[18] *1 film blowing bubble instabilities. (a) draw resonance (b) helical ...* (n.d.). Retrieved December 16, 2022, from https://www.researchgate.net/figure/Film-blowing-bubble-instabilities-a-Draw-resonance-b-Helical-instability-c-Frost_fig3_299885458

[19] Frankland, J. (2018, October 23). *Extrusion: Pellet geometry can impact output*. Plastics Technology. Retrieved December 15, 2022, from https://www.ptonline.com/articles/extrusion-pellet-geometry-can-impact-output