

**Recycling polyethylene terephthalate – based automotive
carpets using chain extenders via reactive extrusion.**

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Polyethylene Terephthalate (PET) is a common polyester used in various applications, ranging from packaging to clothing. The automotive industry utilizes this material to manufacture the velour carpet mats used in cars, rising environmental legislation surrounding this industry has led to the need of developing a recycling process for these velour carpet trims (Murray, 2017). In order to recycle this material, the challenge of polymer degradation must be addressed. To overcome this issue chain extenders will be used to conduct a reactive extrusion recycling method for this material. Pyromellitic dianhydride (PMDA) and 1,3 – Bis(4,5-dihydro-2-oxazolyl) benzene (PBO) will be synergistically used under reactive extrusion conditions, a twin-screw extrusion process was carried out at 60RPM and evaluated at a temperature range of 265-285°C and various chain extender concentrations. The target of this research paper is meeting the 0.7 dL/g I.V. recycling industry target for PET-based materials. Two design of experiments were utilized in this investigation; the first DOE was tested at a constant 265°C, a PMDA concentration of 5wt% and 3.50wt%, and a PBO concentration of 2.00 wt% and 0.75 wt%. The results from this DOE were used to generate a model that estimated a new optimized zone to evaluate, the second DOE evaluated the extrusion temperature, and chain extender formulation. In this second DOE the extrusion temperature was varied at 265 and 285°C and an optimized formulation was evaluated at a PMDA concentration of 3.50 wt% and 1.75wt%, with a PBO concentration of 2.75wt% and 1.00 wt%. Main parameter evaluated was the intrinsic viscosity and the conditions that yielded the highest I.V. value, 1.036 dL/g, was extruded at 285°C with a PMDA concentration of 3.0wt% and PBO at 1.00 wt%. The Mark-Houwink equation was then used to estimate the molecular weight of this material yielding an M_w of 83, 082. While the results obtained in this work met the goal of 0.70 dL/g, the formulation could still be further optimized to 3.0wt% PMDA, 0.05wt% PBO and 285°C to increase the I.V. to 1.20 dL/g.

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Chapter 1

INTRODUCTION

1.1 Motivation

Polyethylene terephthalate (PET) is a very heavily studied polymer when it comes to recycling processes, its various applications from packaging to clothing make it one of the most popularly used polyester in the polymer industry (Li-Na, 2013). While research has proved that recycling polyethylene terephthalate can be recycled by chemical, energy, or mechanical means (Dimonie et al., 2012; Karayannidis & Achilias, 2007; Makkam & Harnnarongchai, 2014; Sinha et al., 2010) it is mostly focused on materials that contain pure PET resins, such as clear water bottles.

Since polyethylene terephthalate is a common material, it is commonly used in applications that require blending it with other materials. One of such applications is the manufacturing of velour carpets used in the automotive industry; polyethylene terephthalate is blended with carbon black to achieve the desired properties. This mixture prevents the material from being recycled using conventional PET-recycling means. Currently the velour-carpet scrap is being sent to landfill, thus, the new regulations will create a need in Canadian manufacturers to develop a method of recycling their product. Sending the material to landfill possesses two problems: the first being the limited amount of space to accommodate for all the waste, while the second problem being the increase in greenhouse gas emissions. In order to meet their environmental goals, the Ontario government has passed a set of acts “Resource Recovery and Circular Economy Act, 2016” and the “Waste Diversion Transition Act, 2016” (Murray, 2017) that will enforce “full producer (ex. Manufacturers) responsibility for making [products] environmentally accountable... [for] reducing waste associated with their products and packaging.(Murray, 2017)” Therefore in order to comply with this program there exists a need in the Ontario manufacturing industry to develop new process lines for the recyclability of their waste products. This thesis, which focuses on recycling velour carpet trims using chain extenders, is focused on overcoming one of these challenges.

1.2 Problem Statement

The recycling method of interest is the extrusion of the velour carpet to re-incorporate the material into the feedstock of the process; thereby promoting a circular economy within this manufacturing process. The main challenge faced when extruding this material is the property loss in the extruder, due to a reduction in molecular weight, which is caused by thermal degradation and shear.

If the issue of polymer degradation of said carpet trims is overcome it would re-introduce four million pounds of carpet trim into Hematite's manufacturing line, aligning the company with Ontario's zero landfill initiative. This current issue causes the leftover trims to experience performance loss when recycled due to the reduction in their molecular weight.

1.3 Research Approach

To measure the success of this project the main objectives will be established:

1. Develop a scalable recycling process flow diagram for this material.
2. Identify additives, ex. Chain extenders, which can be used to overcome polymer degradation.
3. Develop the optimal carpet-chain extender formulation.
4. The research objective is to improve the intrinsic viscosity of the material to be above the recycling industry's requirement (>0.6 dL/g)

1.4 Research problem

Velour carpet trims manufactured for the automotive industry are currently being sent to the landfill due to their non-recyclability. The material cannot be recycled into its process line because its base polymer chains degrade. Thus, a method needs to be established that can prevent polymer degradation in the core structure of this material, polyethylene terephthalate, so that it can be recycled into its process line; thereby complying with the Ontario government's zero landfill initiative.

This paper will test the hypothesis that polyethylene terephthalate (PET) chain extenders can be utilized to overcome polymer degradation of a PET-based material such as velour carpet trims.

1.5 Organization of Document

The thesis is divided into the following chapters:

1. Chapter 1: Identify the motivation for this research based on the requirements set by the Canadian regulations on the automotive industry and the limits of current PET recycling methods.
2. Chapter 2: This chapter illustrates the background of polyethylene terephthalate, its applications, and current waste control practices. The required background information for the relevant chain extenders, intrinsic viscosity and molecular weight will be discussed.
3. Chapter 3: The materials and procedures of velour carpet recycling are demonstrated in this chapter. This process begins with scale-down of the manufacturing sized leftover carpet trims to its pelletization, extrusion and eventual MFR or DSV testing.
4. Chapter 4: This chapter focuses on the analysis of the DOE's used in this project, the first of the DOE's focuses on product formulation screening. Meanwhile, the second DOE focuses on the optimization of said product formulation and extrusion parameters. A final model was generated to estimate the I.V. of the material based on the polymer formulation and processing conditions.
5. Chapter 5: This chapter marks the conclusion of the thesis.

Chapter 2

LITERATURE REVIEW

2.1 PET Introduction

Polyester is a term used for polymers whose base units (monomer) are bonded through an ester linkage, they possess a diverse range of application ranging from automotive to food and textiles. The annual polyethylene terephthalate consumption in 2016 was 76.6 million tons (Bell, 2017); with a predicted growth of 9.70% by 2028 (Fortune Business Insights, 2022). These numbers make polyethylene terephthalate the most consumed polyester in the world, owing to its superior chemical, physical and mechanical properties (Makkam & Harnnarongchai, 2014) impact that this petroleum-based material has is concerning since these polymers are synthetic in nature and are not easily degraded (Sinha et al., 2010). It is because of this that research surrounding polyester recycling methods has seen an increase in recent years.

Research has focused on overcoming polyester's recycling process limitations attributed to hydrolytic and thermal degradation that occur during said process; this degradation affects the recycled material's mechanical properties (Makkam & Harnnarongchai, 2014), thereby reducing the performance capability of the recycled material.

Research has focused on chemical, mechanical and energy recycling methods for Polyethylene Terephthalate; with re-usage of the material needing no further research (Geyer et al., 2016). Energy recycling revolves around recovering the energy stored within the polymer chain through a process called pyrolysis. The energy recovered, approximately 46MJ/kg (Geyer et al., 2016), is then used as an alternative to fossil fuels. Mechanical recycling involves the direct re-processing of the waste material; however, the recycled product contains worst mechanical properties than the virgin product.

To overcome this issue chain extenders are used to overcome chain scission that occurs during conventional recycling process, PMDA is a commonly used chain extender for PET ((Kossentini-

Kallel et al., 2008). Chemical recycling relies on breaking down the PET to its respective monomers, Ethylene Glycol and Terephthalic Acid, so that these monomers can then be reused as base material, resins, to re-synthesize PET ((Geyer et al., 2016) , (Park & Kim, 2014)). The main advantage of chemical over mechanical recycling is on the avoidance of mechanical property loss since chemical recycled PET maintains similar mechanical properties to that of virgin PET(Geyer et al., 2016). There are various methods pertaining the polymer degradation step in chemical recycling; this could be conducted through hydrolysis, glycolysis, aminolysis, etc. (Sinha et al., 2010)

2.2 PET synthesis

As previously stated the monomers used to synthesize PET are Terephthalic Acid (TPA) and Ethylene Glycol (EG), the synthesis of PET involves four main stages which are direct-esterification, pre-polymerization, melt condensation and solid state polycondensation (Li-Na, 2013; Mandal & Dey, 2019). Direct esterification is the process that produces bis(hydroxyethyl)terephthalate (BHET) from EG and TPA, shown in Figure 2-1 as the oligomer intermediate. This process could lead to the PET resins containing the by-product diethylene glycol, which reduces the melting point, lowers the thermal degradation resistance, and lowers UV stability of the material(Mandal & Dey, 2019). Pre-polymerization is conducted at 150-220°C at 100kPa to reach a degree of polymerization (DP) of 30 and viscosity of 5 Pa×s (Mandal & Dey, 2019). Melt condensation is the stage where polymerization occurs to reach DP values of 100. Following Melt condensation solid state polymerization is conducted at 280°C in a helical screw reactor, the DP objective of this process is >150 and the catalyst typically used is antimony trioxide (Mandal & Dey, 2019; Park & Kim, 2014).

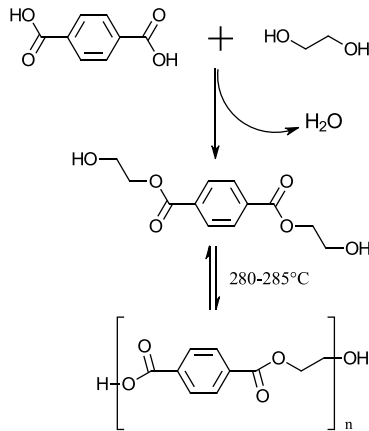


Figure 2-1. Manufacture of PET by direct esterification. Terephthalic Acid and Ethylene Glycol react to generate the intermediate Bis(2-Hydroxyethyl) terephthalate, which then is synthesized to create Terephthalic Terephthalate ($n = 130-150$). (Mandal & Dey, 2019)

2.2.1 Manufacture of PET

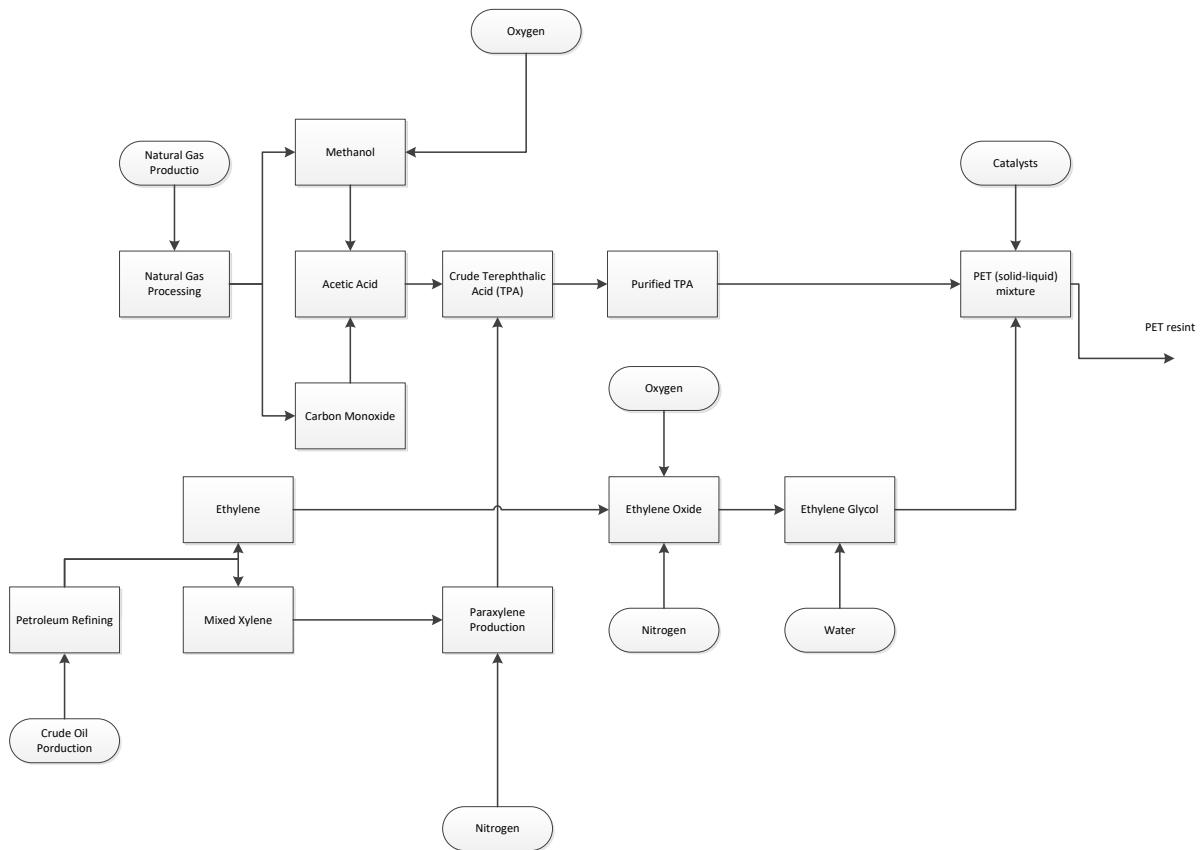


Figure 2-2 PFD for the manufacture of PET resins. (Associates, 2020)

Life cycle assessment is a method used for making evaluation of the environmental impacts that a product has from its raw material extraction to its disposition (Sarda et al., 2022). To conduct an accurate assessment, the manufacturing process of PET production must be mapped and understood. Figure 2-2 summarizes a common manufacturing process for PET resins, this process utilizes natural gas, crude oil, nitrogen, oxygen, and water as the main inputs to produce PET resins, while catalysts increase the efficiency of the PET polymerization reaction. The extraction of natural gas and crude oil is carried out simultaneously during the extraction of crude oil from thousands of meters underground. Methane is the most common natural gas found in these shales; however, other hydrocarbons such as propane, butane can be found in these shales. One factor that influences the type, and efficiency, of natural gas extraction is the porosity of the bed rock that contains said gases. For bedrocks with high porosity a vertical extraction method can be utilized, whereas low porosity bedrocks require a horizontal design. While conventional extraction has two main forms (onshore and offshore), unconventional extraction has various forms; the most common of these extraction methods are summarized in Table 2-1, lastly associated extraction refers to the co-extraction of natural gas and crude oil from the same well. This will play a role in the environmental impact discussed in section 2.2.2.

Table 2-1 Main forms of natural gas extraction and their percent contribution in global production
(Associates, 2020)

| Onshore Conventional | Offshore Conventional | Associated | Barnet Shale | Marcellus Shale | Coalbed Methane |
|---------------------------------|----------------------------------|-------------------|-------------------------|----------------------------|----------------------------|
| 26.90 % | 11.30% | 13.20% | 27.40% | 17.10% | 4.20% |

The extracted crude oil consists of a mixture of various chemicals, these chemicals are separated using a distillation tower. This process utilizes the various boiling points to separate the ethylene,

$T_b = -104^\circ\text{C}$, from the xylene products, $T_b = 139^\circ\text{C}$. In the production process of PET resins, the ethylene is collected in the gas form and xylene in its liquid form.

The extracted natural gas contains a mixture of hydrocarbons, vapor, CO_2 , N_2 , and H_2S ; processing said mixture require the separation of the hydrocarbons via condensation. These condensed hydrocarbons, classified as liquified petroleum as (LPG), are then further processed downstream. The remaining gases need to be further purified to isolate for CO_2 , “gas sweetening” is the method of utilizing reactive solvents to remove said gaseous impurities, amines are commonly used during this removal process.

Following natural gas processing there are two main outputs, methanol, and the by-product carbon monoxide. The methanol undergoes methanol carbonylation process, which involves the methanol-carbon monoxide reaction in the liquid phase under the presence of a catalyst. Said acetic acid is then used alongside the paraxylenes intermediates to produce terephthalic acid. The paraxylene intermediates are produced in parallel through a separate input stream, stemming from crude oil production.

The secondary major input, crude oil, involves cracking the product and generating ethylene. This ethylene is then processed to create ethylene glycol (EG), which is one of the raw materials required to synthesize PET (Associates, 2020). The ethylene produced from this process is then further processed to the intermediate ethylene oxide. This intermediate is obtained by utilizing oxygen and conducting the vapour-phase reaction under a high temperature and pressure vessels, catalysts can be used to improve the efficiency of this process. The intermediate ethylene oxide can then be used to produce ethylene glycol, this can be commonly achieved by the hydration reaction of the ethylene oxide.

Mixed xylenes are another by-product of the crude oil pathway, this intermediate is also obtained through cracking and is a by-product of petroleum refining. These xylenes will be used as inputs for the generation of terephthalic acid. To achieve this the xylene is first fractioned to obtain the intermediate paraxylene, which is then stripped and oxidized so that when mixed with acetic acid it produces crude terephthalic acid. (Associates, 2020) This reaction will produce crude terephthalic acid, which needs to be purified through hydrogenation, typically conducted over a palladium catalyst at 450°F . This reaction will yield high purity terephthalic acid, which can then be used to synthesize PET.

A common method for producing the PET resins is the esterification of the purified terephthalic acid (PTA) alongside ethylene glycol. However, there are other options for the manufacturing of PET through the dimethyl terephthalate (DMT) intermediate. Said intermediate is key in the chemical recycling of PET since it is one of the oligomers that can be obtained for the re-polymerization of PET. There are two commonly used methods for manufacturing PET pellets. Direct melt phase polymerization can be used to obtain a lower grade polymer, or a second step (solid state polymerization) can be added on top of the melt phase polymerization to produce a higher-grade polymer resin. The first polymerization stage, melt phase polymerization, involves the esterification of the EG and PTA to produce a lower grade polymer resin. In instances where a higher grade is required the resin can be submitted to a secondary polymerization step, where the polymer chains are elongated under the presence of higher temperature and vacuum conditions.

2.2.2 Life Cycle Assessment PET

The tables shown below break down the life cycle assessment of PET from its manufacturing to its waste disposition. The section titled process energy corresponds to the amount of energy required to conduct each process, said material must be transported which is accounted in the transportation energy. Lastly, the emissions section displays the amount, in mass, of emissions generated per step. The bulk of said emissions corresponds to NOX, SOX, COX (Ncube & Borodin, 2012; Sarda et al., 2022).

Table 2-2 PET life cycle analysis summary for its manufacturing and recycling. (Ncube & Borodin, 2012; Sarda et al., 2022)

| Stage | Process Energy MJ/kg | Transportation Energy MJ/kg | Emissions kg/kg |
|--------------------|---------------------------------|--|----------------------------|
| PET manufacture | 83.80 | 0.2 | 2.433 |
| Recycling | 27.07 | 0.2 | 0.170 |
| Landfill | 60.01 | 0.2 | 2.178 |
| Incineration | 32.5 | 0.2 | 2.020 |

The values presented in Table 2-2 correspond to the individual process, meaning, that the process showed in Figure 2-1 is summarized by 83.80 MJ/kg PET of energy requirement. The mechanical recycling process, shown in section 2.4.2, requires an energy of 27.07 MJ/kg PET; while the incineration process, section 2.4.4, requires 6.01 MJ/kg. Lastly the act of sending the material to landfill requires an energy of 32.5 MJ/kg. When combining these sections, the total energy requirement and emissions generated are shown in Table 2-3.

Table 2-3 LCA for each disposal stream (Ncube & Borodin, 2012; Sarda et al., 2022).

| Stream | Process Energy (MJ/kg) | Transport Energy (MJ/kg) | Emission (kg/kg) |
|---------------|-------------------------------|---------------------------------|-------------------------|
| Recycling | 110.87 | 0.4 | 2.603 |
| Landfill | 143.81 | 0.4 | 4.610 |
| Incineration | 116.30 | 0.4 | 4.452 |

2.3 PET Recycling Constraints

The main parameters for PET recycling are contamination and degradation degree, Table 2-4 shows the minimum PET contamination requirements for the recycling industry (Park & Kim, 2014). The contamination requirements are in place since the material is susceptible to fiber breakage and final-product aesthetic problems (Park & Kim, 2014); thus, limiting the contamination in the waste PET leads to a better overall recycled PET material performance property. Common contaminants found in PET waste are PVC, glue, dirt, EVA, and acidic compounds. (Park & Kim, 2014)

Table 2-4 Minimum requirements for PET flake reprocessing. (Park & Kim, 2014)

| Properties | Values |
|----------------------------|--------------------|
| Intrinsic Viscosity | > 0.7 dL/g |
| Melting Temperature | > 240°C |
| Water Content | < 0.02 wt. % |
| Flake Size | 0.40 mm < X < 8 mm |
| Dye Content | < 10 ppm |
| Yellow Index | < 20 |
| Metal Content | < 3ppm |
| Polyvinyl Chloride Content | < 50 ppm |
| Polyolefin Content | < 10ppm |

2.3.1 Acid Contamination

The acid content in PET waste is monitored because acidic compounds function as catalyst for chain scission reactions that target the ester linkage (Park & Kim, 2014). The typical acid contaminants found in PET waste is acetic acid, rosin acid and abietic acid and hydrochloric acid . Acetic acid is produced from the EVA found in the cap liners, abietic acid is produced from the adhesives found in commercial bottles and hydrochloric acid is produced by the PVC flakes found in bottles (Park & Kim, 2014)

2.3.2 Moisture

Hydrolysis is the process in which a water molecule causes chain scission in a polymer chain, thus the moisture content of the waste material needs to be limited. In the PET recycling industry this limit is 0.02%, Table 2-4. During the recycling process there are two degradation stages caused by moisture content in the material; the first stage is attributed to hydrolysis from residual water found in recycled PET and the second stage is caused by thermos oxidative chain scission (Park & Kim, 2014). To lower the moisture content in the sample it is necessary to dry the waste material in an oven.

2.3.3 Labels and adhesives

Approximately 10% of manufactures PET is used in the commercial bottle industry(Park & Kim, 2014), the labels used in this industry are made of ultrathin polyethylene films. These films need to be removed for standard PET recycling process, this is achieved through flotation separation (Park & Kim, 2014). Polyethylene films do not require adhesives; however, other labels that use adhesives require special separation processes. Synthetic glues, typically based on polyvinyl acetate or ethylene vinyl acetate, are broken down with water during the recycling washing process (Park & Kim, 2014).Thermal adhesives, based on EVA, are unaffected by the washing process but are instead removed in the shredding process or label removal process; a common issue found with thermal adhesives is the high risk of there being glue residue attached to the PET (Park &

Kim, 2014). Alkali soluble glue is removed with a 2wt% sodium hydroxide solution, this causes the glue to crumble and separate from the PET (Park & Kim, 2014).

2.3.4 Acetaldehyde

PET degradation reactions produce acetaldehyde as a by-product, the main goal of the reaction is the restore the molecular weight of the material through the recombination of vinyl ester and hydroxyl end-groups; however, this reaction produces vinyl alcohol which in turn produces acetaldehyde through tautomerization(Park & Kim, 2014). There exists a risk of the acetaldehyde contaminating the final recycled PET which poses a safety risk for food industry applications(Park & Kim, 2014). Operating the recycling process under vacuum conditions minimizes the risk of acetaldehyde contamination due to its high volatility(Park & Kim, 2014). Likewise, stabilizers such as 4-aminobenzoic acid could be used to minimize the risk of end-product contamination. (Park & Kim, 2014)

2.3.5 PET degradability

During the PET recycling process, the polymer is susceptible to hydrolytic and thermal polymer degradation; if UV radiation is present in the process, then the PET could also be degraded through photo-oxidation will occur as well (Dimonie et al., 2012). Polymer degradation refers to the breakdown of a long polymer chain into shorter chains; degradation(Dimonie et al., 2012). In thermal-oxidative degradation the resulting products are volatile products such as acetaldehyde (Figure 2-4), cyclic and linear oligomers (Figure 2-4) , and shorter polymer chains containing carboxylic and vinyl ester groups, Figure 2-3. Meanwhile, hydrolytic degradation results in shorter polymer chains with carboxylic acid and hydroxyl ester end-groups(Dimonie et al., 2012), this mechanism is shown in Figure 2-3.

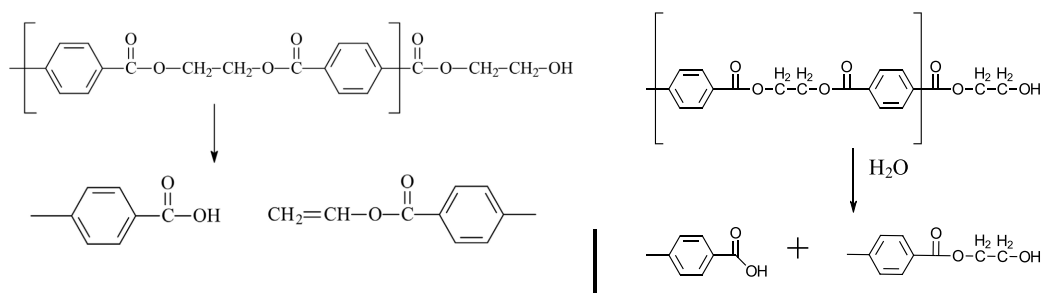


Figure 2-3 Thermal degradation process resulting in carboxyl acid and vinyl-ester end group [left]. PET hydrolysis resulting in carboxylic acid and hydroxyl ester end groups is shown on the right. (Dimonie et al., 2012)

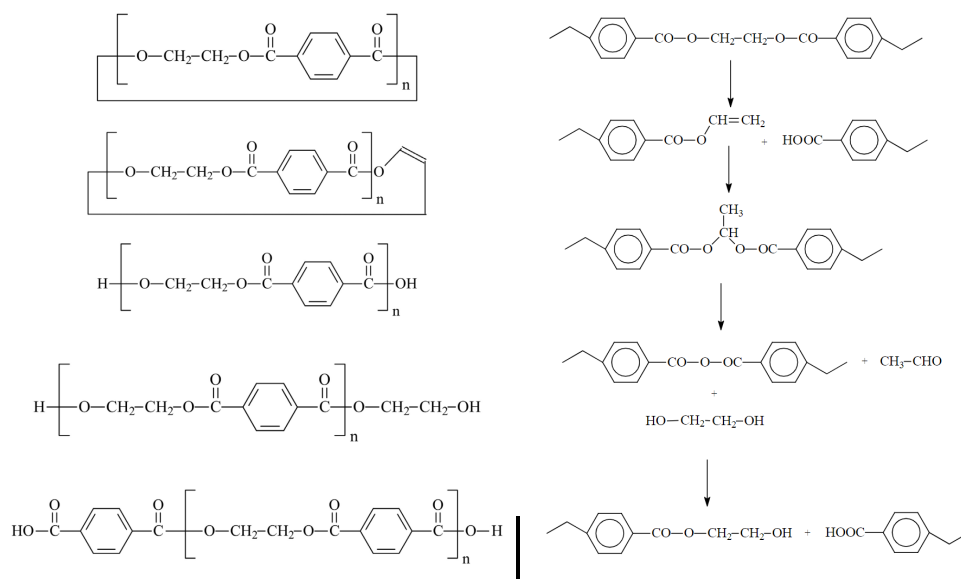


Figure 2-4. Cyclic and linear oligomeric compounds resulted from PET degradation [left]. Acetaldehyde formation is shown on the right. (Dimonie et al., 2012)

Degradation reaction cause a drop in polymer molecular weight, leading to a loss in intrinsic viscosity, melt strength, melt processability and poor mechanical properties (Dimonie et al., 2012), (Geyer et al., 2016). Intrinsic viscosity of virgin PET is approximately 0.72 dL/g (Dimonie et al., 2012); however, degradation can lead to recycled PET to have I.V values of 0.04-0.26dL/g (Dimonie et al., 2012). The formation of shorter macromolecules increases the crystallization capacity of recycled PET making its degradability more pronounced through a process known as chemi-crystallization. (Dimonie et al., 2012; Sinha et al., 2010) This process begins as a chemical process through polymer degradation mechanisms; however, by the end it is a physical process through the crystallization of shorter macromolecule chains (Dimonie et al., 2012). This increased crystallinity leads to an increase in material properties such as the glass transition temperature, melting temperature and density (Dimonie et al., 2012).

2.4 Recycling Process

The standard PET recycling process is shown in Figure 2-5, the process begins with waste PET (PETw) being collected, it is estimated that approximately 30-40% of post-consumer plastic material is collected through garbage containers (Chirayil et al., 2019). Plastic sorting can be conducted automatically through the usage of FTIR techniques, FTIR is used alongside optical color identification cameras to separate the clear PET bottles from other contaminants (Chirayil et al., 2019). A quality check station is performed to ensure all contaminants are sorted out of the recycling stream, following this the waste material is grinded into PET flakes. These flakes are then washed, this is an essential component to remove contaminants such as food leftovers and adhesives. Following the washing station, the flakes are then processed through a sink float separation tank to remove polyolefins from the material (Chirayil et al., 2019). This is achieved through density differences between PET and other contaminants. It should be noted that PVC cannot be separated through sink float separation, due to its similar density to PET. PVC is removed from the system through the incorporation of thermal kilns in the PET flakes, these thermal kilns heat up the PVC, changing its color to black; thereby allowing color sorting of the material (Chirayil et al., 2019). The remaining flakes are then recycled using one of the standard recycling methods (chemical, mechanical, energy) and re-introduced to the market.

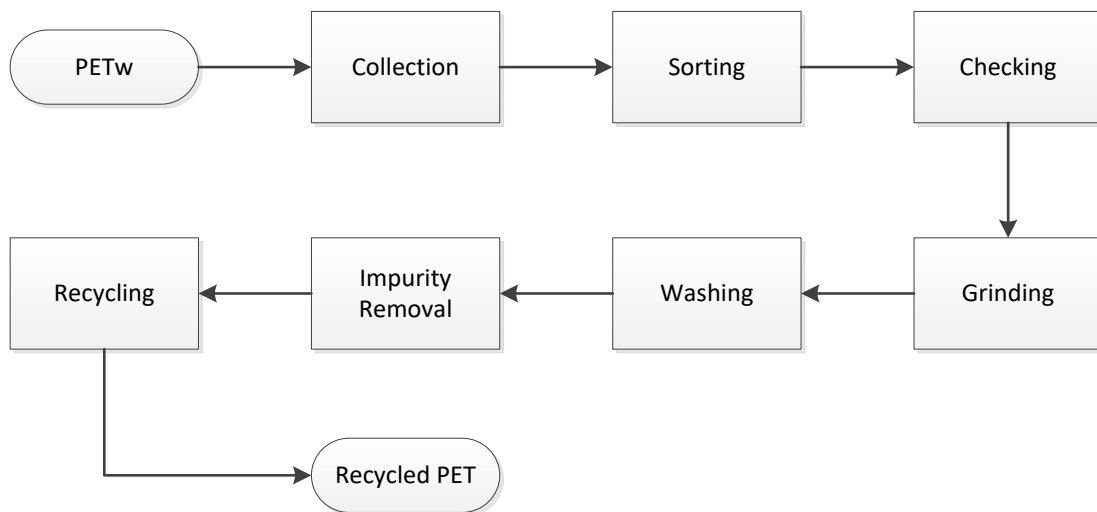


Figure 2-5 PET recycling flow diagram.

The flow diagrams for the specific recycling methods are shown in Figure 5. Primary recycling refers to the reuse of the material without any reprocessing, while efficient this method has a limited number of life cycles for the material. This is because the material will undergo wear and tear with each use, making it unusable after continuous usage. Mechanical recycling is used on thermoplastic polymers such as PET, this is because thermoplastics can be re-melted into recycled products. In a mechanical recycling process, the “Recycling” section in Figure 2-5 refers to the re-extrusion and possible molding of the material back into the final recycled product. Mechanically recycled PET resins are mixed with virgin PET resins to reduce the environmental impact of the material (Chirayil et al., 2019). The main drawback of mechanical recycling is on the fact that the recycled material undergoes downcycling, which is the loss of material properties attributed to polymer degradation that occurs within the recycling process (Chirayil et al., 2019). Chemical recycling is the process in which the PETw is transformed into its base monomers (BHET, TPA, EG) so that these can then be reused to synthesize virgin PET. During chemical recycling process the “recycling” components in Figure 2-5 refers to hydrolysis or glycolysis as common polymer degradation techniques (Sinha et al., 2010), followed by PET synthesis as described in section 1.3 (Chirayil et al., 2019). Chemical recycling does not cause polymer downgrade since it is reintroducing the waste material as feedstock for the generation of virgin PET (Chirayil et al., 2019). Energy recycling is the most efficient approach in reducing the overall volume of waste on the planet since it relies on incinerating the waste to recover the chemical energy stored within the bonds (Chirayil et al., 2019). In the energy recycling process, the material is sent to the incinerator instead of the “recycled” step shown in Figure 2-5. The downside to this alternative is that the fumes generated during the incineration process are toxic to the environment and humans (Chirayil et al., 2019).



Figure 2-6. Process flow diagrams for primary recycling method

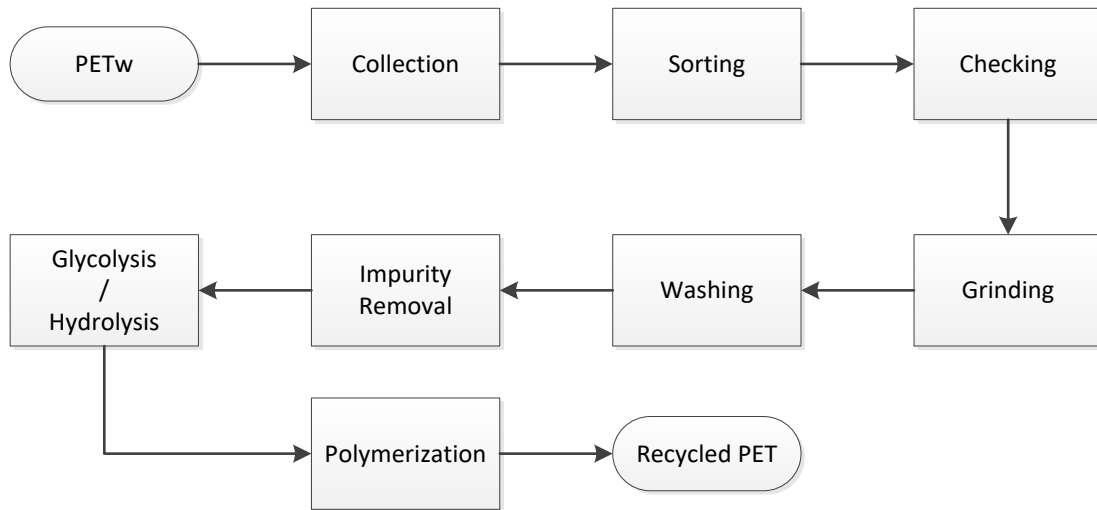


Figure 2-7. Process flow diagram for chemical recycling method. This method focuses on the breakdown of the polymer chain to its base monomer/oligomer to then re-polymerize the material to form PET.

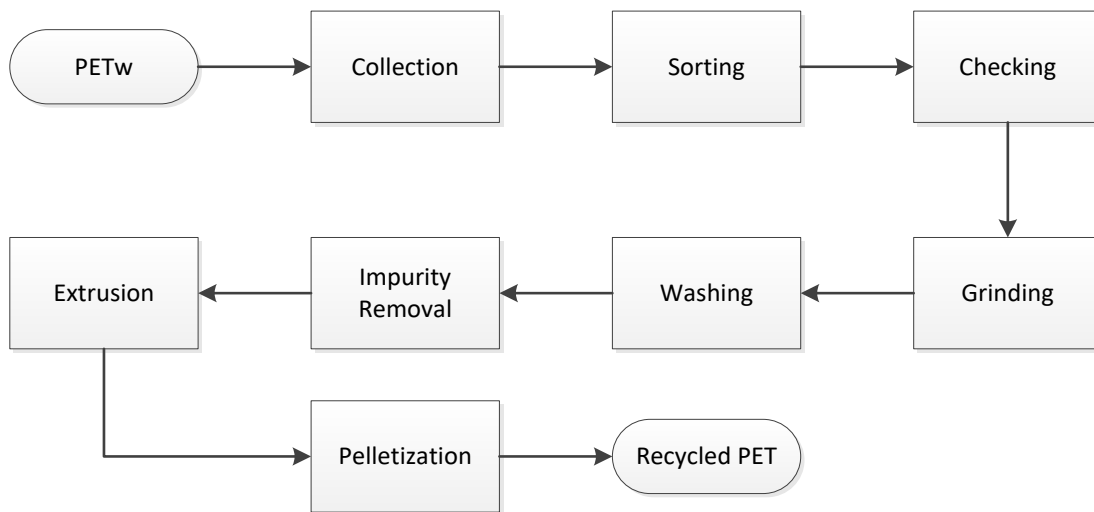


Figure 2-8. Process flow diagram for mechanical recycling. This method focuses on extruding the recycled material into its desired shape.

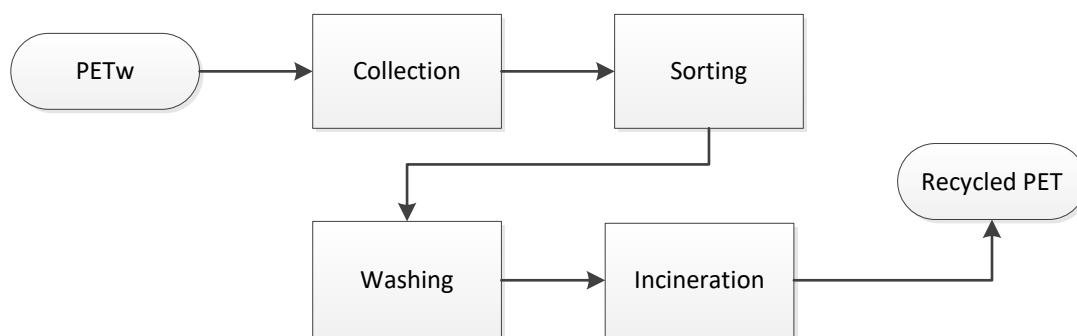


Figure 2-9. Process flow diagram for incineration of PET waste.

2.4.1 Chemical Recycling

There are two common ways of producing PET, polycondensation and polyesterification. In the case of polycondensation the PET is synthesized from its oligomers, dimethyl terephthalate (DMT) and ethylene glycol (EG). While the Poly-esterification reaction is carried out from the base monomer units, terephthalic acid (TPA) and EG.(Karayannidis & Achilias, 2007; Kárpáti et al., 2019) The chemical recycling process is carried out by reversing these reactions, the final product PET is fully depolymerized to its base monomers, or partially depolymerized to its oligomers. These intermediate monomers, or oligomers, are then re-introduced as the feedstock for manufacturing more PET (Chirayil et al., 2019; Karayannidis & Achilias, 2007).

The key step of the chemical recycling process lies in the polymerization process, with the yield, and reaction time being key variables for determining its feasibility (Khoonkari et al., 2015) Typical de-polymerization reactions can take up to 10 hours to achieve acceptable yield percent (Khoonkari et al., 2015; López-Fonseca et al., 2010).

2.4.1.1 Glycolysis

Glycolysis is one of the two biggest chemical recycling processes. The reactants for this process are ethylene glycol and PET; while this reaction can occur without the presence of catalysts, they are favored since they improve the reaction performance. An example of this is reaction time, since without catalysts the normal glycolysis reaction time is not cost effective (Park & Kim, 2014).

The first step of this mechanism involves the cation of the catalyst to react with the carbonyl oxygen and EG's oxygen will react with the carbonyl carbon. This yields the tetrahedral intermediate. To reach a more stable molecule the C=O is restored; however, the polyester chain will be substituted by the EG. The leaving group will contain a O- that will react with the hydrogen ion from the E.G. The presence of the ionic liquid improves the selectivity for BHET, this is because this mechanism yields multiple oligomers alongside BHET (Park & Kim, 2014). Other oligomers are produced since glycolysis is a process that involves partial de-polymerization and other components such as colorants or dyes are not removed (Park & Kim, 2014).

Glycolysis catalysts could be in the form of metals salts (e.g., Sodium carbonate) or ionic liquids (e.g. $[\text{bmim}]^+\text{Cl}^-$) (Khoonkari et al., 2015; Silva et al., 2018). The glycolysis mechanism shown in Figure 2-10 utilizes the ionic liquid $[\text{bmim}]^+\text{Cl}^-$ as the catalyst.

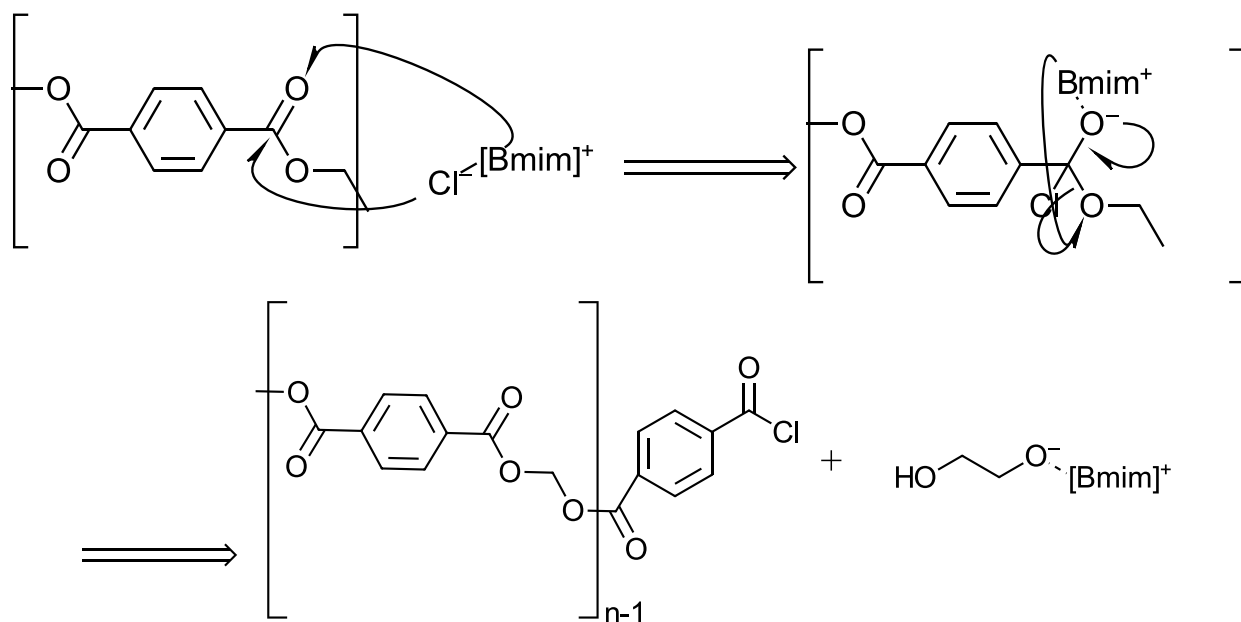


Figure 2-10 Glycolysis of PET using ionic liquid as catalyst. (Geyer et al., 2016)

2.4.1.2 Hydrolysis

In hydrolytic degradation water targets the ester linkage in PET. The first step of this mechanism is the oxygen of the water molecule attacks the carbonyl carbon. This will lead to the C=O bond to break and form an intermediate tetrahedral molecule. To reach stability, the C=O will be re-generated, and the polyester will break the C-O bond holding the TPA and EG together. Water's leftover hydrogen ion then reacts with the negatively charged oxygen in the EG to form neutral EG. This results in the generation of the base units TPA and EG.

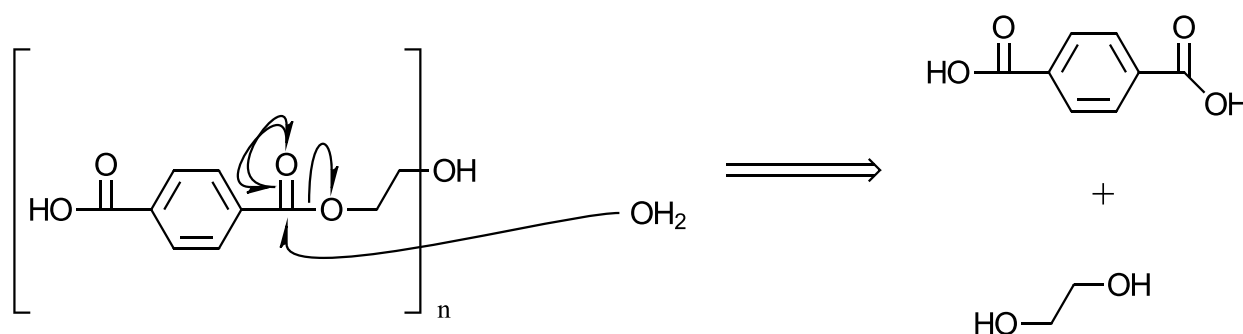


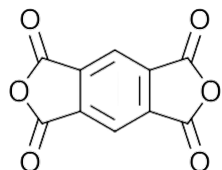
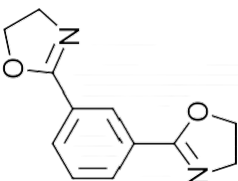
Figure 2-11 Reaction mechanism for depolymerization of PET via hydrolysis.(Geyer et al., 2016)

2.4.2 Mechanical Recycling

As previously stated in section 2.4 mechanical recycling causes downcycling of the material; thereby limited the number of times PET can be recycled. To overcome this constraint chain extenders are used to increase the molecular weight of the material ((Dimonie et al., 2012), (Awaja et al., 2004)), thereby minimizing the effect of degradation on the polymer chain. When a polymer chain degrades it results in monomers being produced; chain extenders function by attaching the end-groups of these monomers (Kossentini-Kallel et al., 2008) shown in section 1.2.5, in doing so the length of the polymer chain is increased. This process is typically conducted in a single or double screw extruder operated at 280-290°C (Awaja et al., 2004; Oromiehie & Mamizadeh, 2004). This in turn increases the molecular weight of the polymer which allows the performance properties of the recycled material to be equal to or greater than that of the virgin material. Commonly used chain extenders for PET recycling are PMDA, and PBO (Awaja et al., 2004; Dimonie et al., 2012; Kossentini-Kallel et al., 2008). Typical chain extender concentrations range

from 0.05-0.3 wt.% (Awaja et al., 2004; Kossentini-Kallel et al., 2008). It is reported that when higher PMDA concentrations are used then the risk of excessive cross linkage forming in the system is higher, leading to gel formation causing chemical, thermal, and rheological instability (Kossentini-Kallel et al., 2008)

Table 2-5 Chain extender summary

| Chain Extender | Molecule |
|---|---|
| Pyromellitic Dianhydride (PMDA) |  |
| 1,3 – Bis(4,5-dihydro-2-oxazolyl) benzene (PBO) |  |

2.4.3 Chain extenders

2.4.3.1 PMDA Mechanism

The PMDA-PET chain extension mechanism the first step consists of the oxygen in PET's hydroxyl group attacking the carbon in the PMDA's anhydride ring. The reaction follows nucleophilic substitution, in which the oxygen in PET hydroxyl group acts as the nucleophile (due to its negative charge); carbon in the anhydride ring has a slight positive charge so it acts as the electrophile. This leads to the C=O bond to break, allowing carbon to bonding to PET's oxygen and the hydrogen breaks free to become ionic hydrogen (Mandal & Dey, 2019); the resulting intermediate molecule is shown in Figure 2-12.

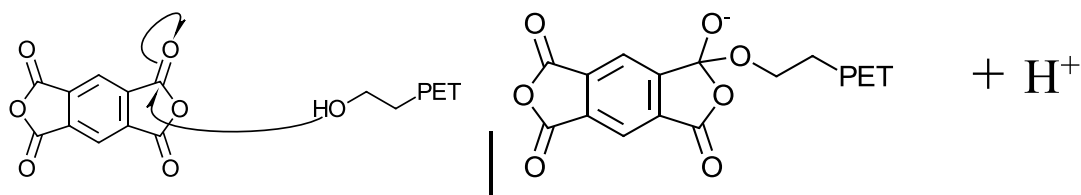


Figure 2-12 First step of PMDA mechanism [left] and the resulting intermediate [right].(Mandal & Dey, 2019)

This intermediate is rapidly re-arranged to a more stable molecule. For this the C=O is restored, and the anhydride C-O bond is broken, this will lead to a negatively charged carboxyl end group at the bottom of the ring, which will stabilize by bonding with the protons. The resulting molecule is shown in Figure 2-13, this image shows the PMDA-PET product for 1 functional group; this is known as “blocking”.

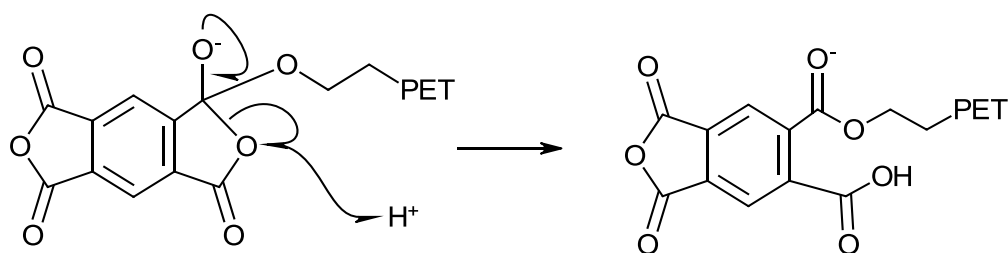


Figure 2-13. Mechanism for intermediate stability [left], PMDA-PET molecule showing blocking [right].(Mandal & Dey, 2019)

PMDA is a tetra functional chain extender, meaning that 1 PMDA molecule can adhere to 4 different polymer chains. The mechanism shown on Figure 2-13 is for one of the functional groups, these steps would be repeated until all four C=O have bonded to a polymer (Mandal & Dey, 2019). Depending on the degree of linkage between PMDA and PET there is different terminology. In the instance when 1 PET is adhered to the PMDA it is called a blocking reaction. A 2:1 PET:PMDA ratio results in a Coupling reaction, and 3:1 PET:PMDA ratio (and above) is known as branching reaction (Mandal & Dey, 2019). There are key points to mention for each type of reaction. Key aspects to note corresponding to each type of reaction are shown bellow.

Blocking reaction: This reaction produces carboxyl groups that hinder the performance of the material by making it more susceptible to hydrolytic degradation.

Coupling reaction: It could result in 2 carboxyl groups as seen in the image at the top; hindering the performance of the material. OR it could result in the generation of a water molecule, which in turn can cause hydrolytic degradation during the processing of the material.

Branching reaction: It could either result in 1 carboxyl group or water (in the case that 3 functional groups react); however, when all 4 functional groups react then only water is generated. This results in 4 PET molecules branching for every water molecule generated.

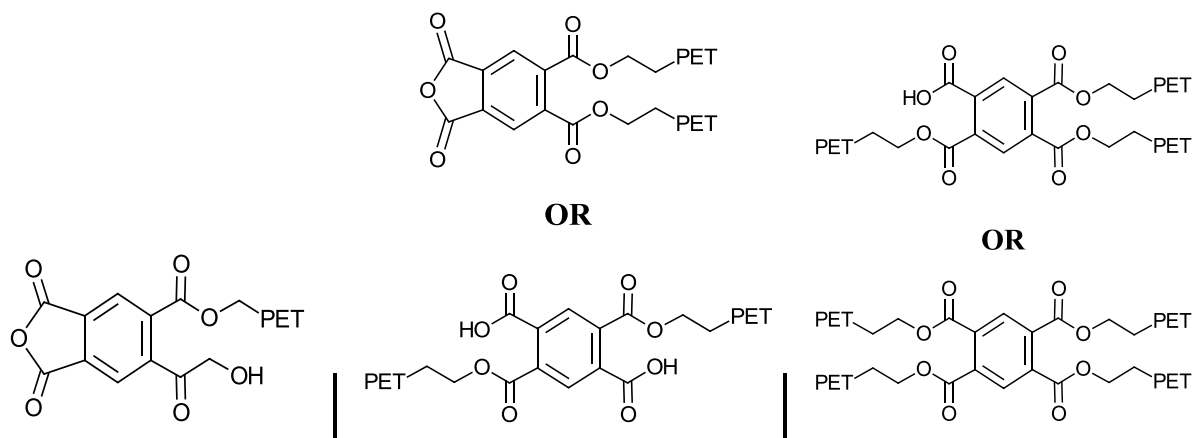


Figure 2-14. PMDA-PET reaction products. Blocking [left] coupling [middle] and branching [right].(Awaja et al., 2004; Mandal & Dey, 2019)

2.4.3.2 PBO Mechanism

PBO targets the carboxyl group of PET rather than the hydroxyl group. The oxazoline ring in PBO reacts with the carboxyl group of the polymer, with the oxygen reacting with the carbon adjacent to the oxygen in the oxazoline ring. This causes the oxazoline C-O bond to break, forcing the carbon to form a double bond with oxygen and in doing so breaking the double bond it already had with nitrogen. This leads to nitrogen becoming negatively charged and thus attracting the hydrogen protons. The opened ring structure is shown in Figure 2-15 [right] (Ramírez-Herrera et al., 2018). This reaction mechanism is identical for both oxazoline rings resulting in a maximum 2:1 PET:PBO ratio.

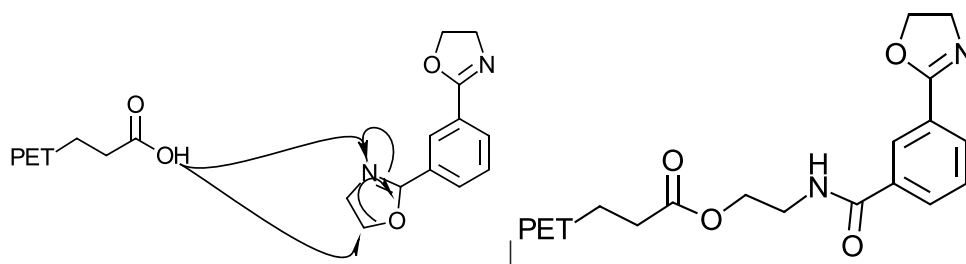


Figure 2-15 PBO-PET mechanism [left] and resulting product [right]. (Dimonie et al., 2012; Ramírez-Herrera et al., 2018)

2.4.4 Energy recycling

Due to the nature of polymers, long hydrocarbon chains, there is intrinsic energy that is stored in each material. Energy recycling is the method focusing on recovering the energy stored within the bonds of said polymer chain. There are two main methods for energy recycling: Pyrolysis and Carbonization.

Pyrolysis is conducted via an incinerator, via which heat is applied (200-900°C) for up to 1 hour with the main products being aromatic and aliphatic hydrocarbons (Geyer et al., 2016).

Meanwhile, carbonization is carried out at a higher temperature (350-1550°C) and focuses on generating activated carbon as the main product (Geyer et al., 2016). These recycling methods can then be used to aid in the generation of electricity of a city or apply the energy in a different stage of the PET manufacturing process. (Sinha et al., 2010)

Energy recycling is a method that is being phased out due to the high number of dangerous by-products generated (ex. Various dioxins) during said incineration and/or carbonization process. (Sinha et al., 2010)

2.5 I.V Theory

Viscosity is the measure of a fluid's resistance to flow due to the friction that occurs between the moving surfaces. The two most common types of viscosities are dynamic and kinematic; dynamic viscosity refers to the fluid's internal resistance to flow, while kinematic viscosity refers to the ratio between the dynamic viscosity and density. The equation to obtain the dynamic viscosity is

Newton’s law of viscosity and the kinematic viscosity formula is just the ratio of dynamic viscosity to density, both formulas are shown in Table 2-6.

Table 2-6 Main fluid viscosity formulas

| Equation | Formula |
|-----------|----------------------------|
| Dynamic | $\tau = \mu \frac{du}{dy}$ |
| Kinematic | $v = \frac{\mu}{\rho}$ |

In polymer engineering viscosity is an important parameter that affects the polymers processability and provides a “sneak peak” into the polymer’s properties prior to testing. Viscosity has an influence in polymer processing since it is not the same to injection mold or extrude a material with a high viscosity compared to one with a low viscosity. A higher viscosity polymer will require more pressure to conduct all these processes (injection molding, extruding, and transporting), which means a higher processing cost. Similarly, since viscosity is proportional to molecular weight one can guess the material properties of two distinct types of polymers without the need to conduct all the tests. For example, a polymer that has a higher viscosity will have higher tensile strength, impact resistance and modulus than a polymer with a lower viscosity, we know this without doing the tests.

2.6 Intrinsic Viscosity Testing Methods

2.6.1 Dilute Solution Viscometry Test

A commonly used equipment for evaluating the viscosity of a polymer is the Ubbelohde viscometer, Figure 2-16, the analysis of this equipment centers around point 6 on Figure 2-16, this is because fluid flow will occur through that section.



Figure 2-16 Schematic of a standard Ubbelohde viscometer. (SI Analytics TM Ubbelohde Viscometers for Manual, n.d.)

Poiseuille's law is used to analyze the fluid flow on section 6 of the Ubbelohde viscometer; from equation [1] it is assumed that the change in volume is constant, and the initial time is zero. The resulting equation [2] is re-arranged to isolate the viscosity term η , resulting in equation [4]. Since section 6 of the Ubbelohde is a fixed pipe the change in pressure (ΔP) can be described as ρgh ; of which g and h would be constant. This results in equation [5], from which we collect the constant under an umbrella constant κ and the viscosity formula for the fluid flow through the Ubbelohde viscometer is obtained.

$$\frac{dV}{dt} = \frac{\pi R^4}{8\eta} \left| \frac{\Delta P}{\Delta x} \right| \quad [1]$$

$$\frac{\Delta V}{t} = \frac{\pi R^4}{8\eta} \left| \frac{\Delta P}{\Delta x} \right| \quad [2]$$

$$\eta \frac{\Delta V}{t} = \frac{\pi R^4}{8} \left| \frac{\Delta P}{\Delta x} \right| \quad [3]$$

$$\eta = \frac{t\pi R^4}{8\Delta V} \left| \frac{\Delta P}{\Delta x} \right| \quad [4]$$

$$\eta = \frac{t\pi R^4}{8\Delta V} \left| \frac{\rho gh}{\Delta x} \right| \quad [5]$$

$$\eta = \kappa \times t \times \rho \quad [6]$$

Where $\kappa = \frac{\pi R^4 gh}{8\Delta V \times \Delta x}$.

2.6.1.1 Relative Viscosity

The viscosity term from equation [6] is then used to calculate a viscosity intermediate term necessary for the inherent viscosity calculation according to ASTM D4603 standard.

The first intermediate viscosity term that can be obtained is the relative viscosity, relative viscosity corresponds to the ratio between the solution and solvent viscosity; seen in equation [7].

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}} \quad [7]$$

Substituting equation [6] onto equation [7] results in equation [8]. For notation $\eta_o \equiv solvent$ and $\eta \equiv solution$

$$\eta_{rel} = \frac{\eta}{\eta_o} = \frac{\rho \times t \times \kappa}{\rho_o \times t_o \times \kappa} \quad [8]$$

Since κ is constant it can be eliminated; likewise, the density can be eliminated because the solution is assumed to be dilute, meaning that the solution density will be similar to the pure solvent. This results in the relative viscosity formula [9], in which the time ratio of the solution and pure solvent yield the relative viscosity.

$$\eta_{rel} = \frac{t}{t_o} \quad [9]$$

Where t is Ubbelohde test time for solution and t_o is the Ubbelohde test time for the pure solvent.

2.6.1.2 Reduced Viscosity

Reduced viscosity term refers to the ratio between the viscosity increment and the mass concentration, as seen in equation [10].

$$\eta_{red} = \frac{\eta_i}{c} \quad [10]$$

This viscosity increment is known as the specific viscosity, which explains the degree that the solvent's viscosity has increased. Since the pure solvent's maximum viscosity is η_o and the relative

viscosity is higher than it, it can be concluded that the polymer increased the viscosity of the solvent, the degree to which it has increased it is known as the viscosity increment or specific viscosity.

$$\eta_i = \eta_{sp} = \frac{\eta}{\eta_o} - \frac{\eta_o}{\eta_o} = \eta_{rel} - 1 \quad [11]$$

Substituting this value back into equation [10] yields the reduced viscosity.

$$\eta_{red} = \frac{\eta_{rel}-1}{c} \quad [12]$$

2.6.1.3 Inherent Viscosity

Inherent viscosity is the ratio of the natural logarithm of the relative viscosity to the mass concentration of the polymer. This parameter is important because it is plotted in a viscosity vs. concentration curve along with the reduced viscosity. These curves are then extrapolated and the y-value at the point of intersect corresponds to the intrinsic viscosity (I.V). This test method is in accordance with ASTM D2857.

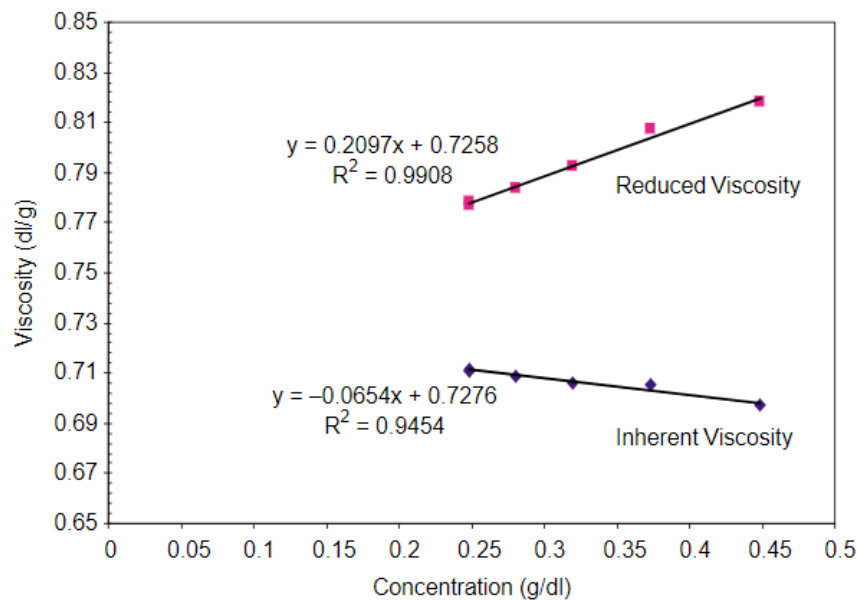


Figure 2-17. Sample graph of relation between reduced and inherent viscosity, the intersect corresponds to the inherent viscosity. (Farah et al., 2015)

2.6.1.4 Intrinsic Viscosity

Intrinsic viscosity is defined as the reduced specific viscosity in the limit of “infinite dilution”, in other words, it is the evaluation on the effect that a single polymer chain strand has on the viscosity of the solvent. This is an important parameter since it is evaluating the individual polymer strands, so it eliminates the sources of error such as entanglement and branching. The longer the individual polymer chain is, the higher the I.V will be and the higher the MW of the polymer. Having said this, a higher I.V. value will reduce the flowrate of the material.

Important parameters to consider during I.V evaluation is the test temperature, the polymer concentration and the type of solvent used in the experiment. These three will have an influence on the final I.V obtained,

Two equations commonly used in papers are the Billmeyer equation, which stems from the ASTM D4603 and the Schulz-Blaschke equation. The Billmeyer equation has the advantage of not needing to construct the graph on Figure 2-17, the relative viscosity is required (which is only dependent on the time). Meanwhile, the Schulz-Blaschke equation is independent on temperature; however, one test run is required to obtain the constant K_{SB} , once this constant is obtained the formula can be used.

Table 2-7. Equation used to obtain the intrinsic viscosity of a material (ASTM D4603 - Inherent Viscosity of PET by Glass Capillary, 2003)

| Equation | Formula |
|--------------------------|--|
| Billmeyer equation | $[\eta] = \frac{0.25(\eta_{rel} - 1 + 3 \ln(\eta_{rel}))}{c}$ |
| Schulz-Blaschke equation | $\frac{\eta_{rel} - 1}{c} = [\eta] + K_{SB}[\eta] \times (\eta_{rel} - 1)$ |

2.6.2 MFI Testing & Theory

The MFI test is an experiment that measures the flow of the material through a fixed size orifice, since viscosity is related to the flow of a material the MFR test can be used to obtain the I.V value. This test consists of placing a small amount of solid material inside the MFR barrel, once within the chamber a specified amount of time is allowed to elapse (known as the melt time), after the time is completed, a small weight is applied at the top of the barrel to force the molten material to come out through a small orifice at the bottom, see Figure 2-18. The flowrate of this material in units g/10min is measured and then correlated to its respective I.V using the machine's own calibration curve, see Figure 2-19.

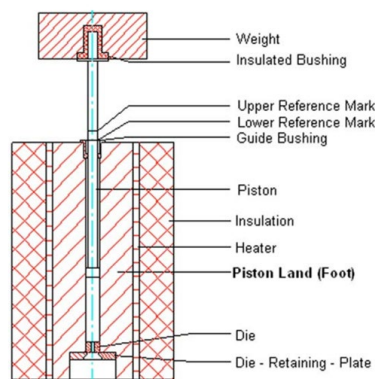


Figure 2-18 Schematic of MFI chamber.

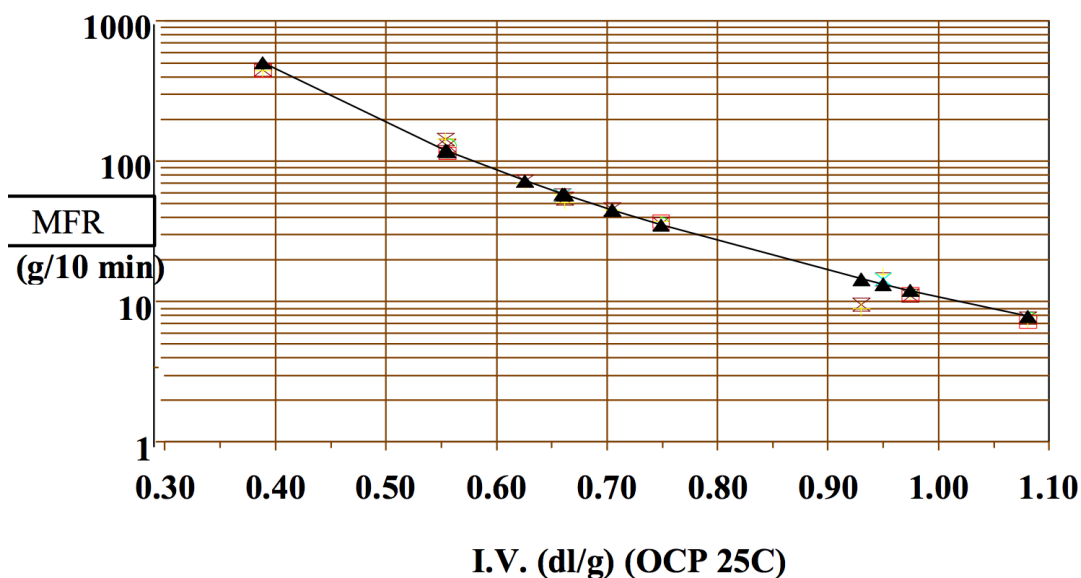


Figure 2-19 Calibrated I.V. - MFR curve for testing PET using the machine used in this experiment (Dynisco, n.d.)

2.6.3 Mark Houwink Equation

Intrinsic viscosity is directly proportional to molecular weight, a polymer with a higher molecular weight will have longer polymer chains; these chains will promote entanglement which in turn increase the material’s intrinsic viscosity. Since these properties are proportional to one another they can be related using empirical formulas, the Mark Houwink equation correlates the intrinsic viscosity of a material to its molecular weight. The equation shown below represents the Mark Houwink equation for polymers dispersed in a solvent.

$$[\eta] = K \times Mw^a \quad [13]$$

Where The K & “a” are constants that depend on the solvent and temperature. For PET dissolved in a 60/40 phenol-tetrachloroethane solvent at 30°C the constant values are: K = 4.68E-4, and a = 0.68. (Jabarin, 1987; Sanches et al., 2005)

Chapter 3

MATERIAL AND METHODS

3.1 Material

The base material used in this thesis was obtained from the Hematite manufacturing facility, it is a 1200GSM grade velour carpet. These carpets are the leftover trims from their manufacturing process. These carpet trims use polyethylene terephthalate (PET) as the base material, the structure of the PET is a core & sheet formation. In which the interwoven inner core is protected by an outer sheet, the difference in these two forms lies in the strength of the structure with the core being a much stronger structure with a higher melting point (260°C) than the sheet (110°C). In addition to the base material liquid nitrogen (-196°C) was used to pre-treat the PET as a preparation step prior to milling.

Pyromellitic dianhydride (PMDA), $C_{10}H_2O_6$, obtained from Sigma-Aldrich with an assay of 97%, is one of the chain extenders used in the reactive extrusion process. Pyromellitic dianhydride is an organic compound that has four active sites, each corresponding to a C=O, capable of binding with up to four different molecules. The second chain extender used in this project is 1,3-bis(4,5-dihydro-2-oxazolyl) benzene (PBO), $C_{12}H_{12}N_2O_2$. This compound has two active sites, corresponding to a C-N, which are capable of binding with up to two molecules. The chain extender process was carried out inside a twin screw extruder through a reactive extrusion reaction at temperatures ranging from 260-285°C. Prior to the extrusion process the carpet material was placed inside an oven to remove free water from the molecule and limit the amount of moisture absorption by the PET, this % moisture content was recorded prior to extrusion using an OHAUS MB45 moisture analyzer.

3.2 Grinding Process

Since the material that was received in the laboratory was manufacturing sized material (leftover carpet trims) the first step is to reduce the size of said carpet trims to lab-scale samples. To do this the velour carpet was first cut into smaller square pieces using scissors, Figure 3-1, these were then submerged in liquid nitrogen for 6 minutes to make the carpet brittle enough so that it could be

easily milled, Figure 3-2 shows the milled material post grinding. The milled sample was then stored in an oven overnight to reduce the moisture content in the velour carpet and limit the amount of moisture absorption since PET is hygroscopic.



Figure 3-1 Raw material from Hematite's manufacturing plant [left] and sample cut down by scissors [right]



Figure 3-2 Milled form of the velour carpet

The product being processed is a velour carpet, due to the soft outer layer the milled product results in a cotton-like material with multiple fibre strands. Processing these fine fiber strands pose an extrusion risk since they cannot be easily homogeneously blended with the chain extenders, resulting in heterogeneous chain extension; portions of the extrudate strand with high degree of chain extension and other sections with little degree of chain extension.

This heterogeneous mixing is a risk because the success of this project lies in the rate of chain extension being greater than the rate of polymer degradation caused by thermal, shear and water being present inside the extruder. The sections with low chain extenders will have a higher risk of polymer degradation overcoming chain extension, while the regions with high amount of chain extender will have a risk of gel formation due to excessive cross linkage.

3.3 Extrusion Process

3.3.1 Pelletization

Prior to feeding the material to the extruder the ‘carpet fluff’ was pelletized to reduce the risk outlined in section 3.3.2. The pelletization process was carried out by forming small pellets from the carpet trims, these pellets improved the homogeneous blending of the carpet with the chain extenders. Figure 3-3 shows the comparison of a pelletized sample blended with chain extenders vs an un-pelletized (“cake”) sample; it can easily be seen that the pelletized form allows for better blending of the raw materials since it increases the surface area of the carpet fluff as compared to its alternate cake form. This increase in surface area allows for better mixing and chain extension distribution among the entire milled carpet trims.



Figure 3-3 Milled sample "cake" [left] vs pelletized form [right]

3.3.2 Reactive extrusion mixing

The reactive extrusion process was carried out inside a twin screw extruder (Thermo-Haake minilab) at a temperature range of 260-285°C. A prior study was conducted to determine the optimal screw speed of this extruder with these chain extenders, and it was determined to be 60RPM (Butt et al., 2017; Sun et al., n.d.). The extrusion process was conducted following the drying process in step 3.2, the samples were removed, and their moisture content was analyzed. Analyzing the moisture content prior to extrusion is key to limit the risk of hydrolysis occurring inside the extruder. The carpet was then blended with the chain extender and fed to the extruder at the specified conditions.

During the extrusion process the torque was maintained at around 32nM, this value had to be constantly monitored to ensure there was no pressure buildup inside the extruder. This build up of pressure could be caused by gel formation caused due to excessive cross linkage when reactive PET with the chain extenders. The gel formation would result in clogging of the die and halt the extrusion process, Figure 3-4 shows an example of gel formation and die clogging. Once all the extrudate was collected the sample was stored inside a vacuum oven.

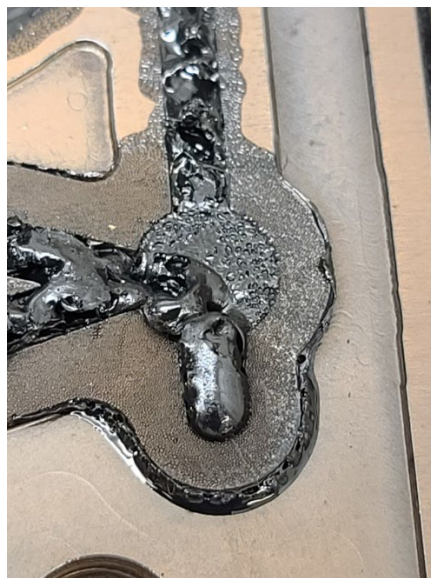


Figure 3-4 Gel formation blocking the extruder die

3.3.3 Drying conditions

All drying conditions prior and post extrusion were carried out inside a vacuum oven at 70°C for a time of 12hrs.

3.4 MFI Testing & Prep

Melt Flow Index (MFI), used interchangeably with Melt Flow Rate (MFR), is one of the tests used to determine the effectiveness of the chain extension process. The machine used was a Dynisco LMI 4000 melt indexer which has a calibrated I.V. curve for PET evaluation (Dynisco, n.d.), Figure 2-19 shows this curve.

After the extrudate was dried the material was grinded using a Reutsch ZM200 grinder into fine pieces, Figure 3-3 shows an example of these fine pellets. These fine pellets, $m = 6g$, were then fed to the MFI machine and their flowrate was determined as per ASTM D1238. This ASTM involves utilizing a weight of 2.16 kg and allowing for a residence time of 7 minutes. The time it took for the material to fall was recorded along with its mass.



Figure 3-5 Fine pellet sample obtained after high RPM grinding of the extrudate, prior to MFR testing.

3.5 DSV Testing & Prep

The solute used in dilute solution viscometry (DSV) was 60/40 phenol-1,1,2,2-tetrachloroethane (w/w/) at a concentration of 99.5% and a 0.5wt% velour carpet concentration. The testing was carried out by first preheating a hot plate to 110°C. 50mL of the 60/40 phenol TCE solvent was measured in a volumetric flask, a previously weighed PET trim (0.50g) was placed inside said flask with the solvent. This flask was then set on the hot plate and allowed to stir for 15minutes. The solution was continuously checked for dissolved PET, after the carpet had fully dissolved the sample weighed it was then transferred to a Buchner flask for a vacuum filtration process. The (pre-dried and pre-weighed) filter paper (Whatman, 42 ashless) was used to collect any undissolved material, this filter paper was then stored overnight inside an oven and weighed to measure the residuals. Following this step, the necessary volume of 60/40 phenol-TCE solution was added to the filtered solution until the combined volume reached 100mL. This 100mL solution was then pre-heated to 30°C, after this pre-heating process 15mL was removed and placed in DSV vials. The DSV program was run to evaluate the I.V. of the solution.

Chapter 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter presents the results and the relationship between temperature, chain extenders and the intrinsic viscosity of the velour carpet trims. The intrinsic viscosity was obtained using melt flow index (MFI) and dilute solution viscometry (DSV). This chapter will also report on the experiments covering statistical analysis of the processing conditions (polymer formulation and temperature) during extrusion. In addition to the beforementioned the chapter will explain the method used to evaluate the I.V. of the material for an impure PET sample. To finalize a predictive model will be shown that estimates the I.V. and molecular weight of the velour carpet based on chain extenders and extrusion temperature. The research objective was to develop a manufacturing process that could be scaled up to the Hematite manufacturing plant for the recycling of their velour carpet material.

The research flow diagram is shown in Figure 4-1. The screw speed was studied by a previous research group that studied this material's reactive extrusion reaction. In their study it was found that 60RPM was the optimal screw speed for limiting polymer degradation occurred caused by shear and thermal degradation (Butt et al., 2017; Sun et al., n.d.).

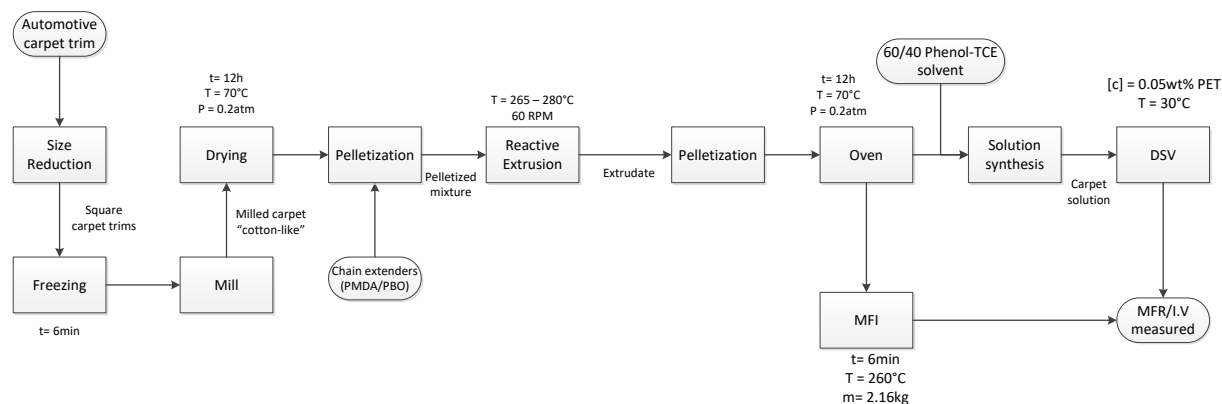


Figure 4-1 Research flow diagram used for the completion of the project

The research was carried out following a 2² design of experiment with each chain extender, PMDA & PBO, corresponding to one factor and a high/low concentration was chosen per factor. The first design of experiment was used to screen the process using the MFR measurements, Table 4-3 summarized the DOE used in this initial stage of the development of the product formulation. In the screening process the parameters used were obtained from past research that was conducted on this material. The extrusion parameters used in this screening design were maintained at a constant 265°C & 60RPM.

Table 4-1 Summary of the screening parameters for the first DOE

| Factor (Chain Extender) | High (wt.%) | Low (wt.%) |
|----------------------------|----------------|---------------|
| PMDA | 5.00 | 3.50 |
| PBO | 2.00 | 0.75 |

Constant Temperature = 265°C

Following the evaluation of the MFR results an optimized new formulation was obtained, and the new design of experiment was conducted around the new levels; for this second DOE temperature was introduced as a third factor to consider making it a 3² DOE; in doing so the impact that the processing conditions can have on the chain extender will be quantified and accounted for in the final model.

Table 4-2 Summary of the second DOE focusing on optimizing both process and product formulation.

| DOE | Factor | High level | Low level |
|-----|-----------------------|------------|-----------|
| #2 | PMDA | 3.50 wt.% | 1.75 wt.% |
| #2 | PBO | 2.75 wt.% | 1.00 wt.% |
| #2 | Extrusion Temperature | 265°C | 285°C |

The parameters for the new chain extender levels were obtained using the model from DOE #1 (Table 4-1), the analysis and calculation for these new parameters are shown in section 4.3.1.

4.2 Process Constraints

The process shown in Figure 4-1 starts with the carpet trims that have been previously cut, these were then submerged in liquid nitrogen and milled in the lab's mill. The milled product was dried

overnight and fed to the extruder along with the chain extender. The extrudate was dried and tested for MFI or DSV.

In this process there were three major findings for overcoming the processing hurdles of these velour carpets, said processing constraints are outlined below.

1. Heterogeneous chain extender – carpet mixing
2. MFI testing deviation
3. 60/40 solvent synthesis

The first processing constraint is the adequate mixing of the chain extender with the carpet trim to ensure a homogeneous feed to the extruder. This constraint is caused by several factors, the first being the difference in form factors between the milled carpet and the chain extenders. Both PMDA and PBO have a powder form factor, thereby maximizing the surface area for reactions; however, the milled carpet is present as fiber strands. Mixing the two materials in a beaker, without any liquid media, is not possible since the chain extenders travel across the void space of the milled carpet with little carpet-chain extender mixing.

The second challenge is the high-test result variability for the MFI tests. The ASTM D1238 and equipment I.V curve specify testing parameters for testing the MFI of pure PET. However, these testing parameters were found to not be accurate for the velour carpets that had PET mixed with other additives. Due to this the optimal MFI testing conditions had to be established for this material.

The third constraint is a similar case to the second one. The relevant ASTM standard, ASTM D4603, is not fully applicable for the material used in this experiment since it is a PET-based material that is mixed with other additives. Therefore, the adequate testing process for I.V. of PET-based velour carpets had to be researched.

4.2.1 Heterogeneous reaction in extruder

As stated in section 4.2 the lack of homogeneous mixing between the chain extenders and the milled carpet posed a constraint to process since it impacted the quality of the extrudate. The first constraint from this stems from the fact that the milled carpet generates fiber strands, these fiber strands represent “noise” in the reaction since they do not contain PET. Therefore, mixing the chain extenders with the milled carpet containing multiple of these fine strands will be fruitless. The second constraint lies in the lack of homogeneous mixing in the extruder, since the chain extension process is carried out via reactive extrusion the ratio of carpet: chain extender being fed to the extruder must be representative of the concentrations. The extruder used in this experiment relies on manually feeding the material to the hopper, therefore each “batch” fed to the extruder should have the right ratio. If this ratio is not obtained there will be heterogeneous properties along the extrudate strand due to having sections with varying chain extender concentrations.



Figure 4-2 Comparison of the same extrudate strand with heterogeneous mixing. The strand on the left demonstrates the sharkskin defect and the strand on the right is perfect.

The image shown on Figure 4-2 show that within the same extrusion processes there is a variation in the processability of the material. Shark skin occurs due to the improper flow properties of the polymer out of the die of the extruder; however, having sections of the strand that present this issue supports the fact that

the “flow properties” of the material vary within the strand. These heterogeneous flow properties are caused by the heterogeneous feeding of material due to improper chain extender-carpet mixing. The image shown in Figure 4-2 corresponds to a low/low formulation at 265°C; however, this issue was persistent with all formulations that were fed with improper mixing. Also, the only material that had a consistent flow property is the extrudate of the pure carpet trim without chain extenders; this further supports the theory of the impact that heterogeneous mixing of the raw material has on the extrudate strand.

This process constraint was reduced with the pelletizing of the mileld carpet, as shown in Figure 3-3. The pelletization of this material allowed for the reduction of the fiber surface area and the agglomeration of the carpet’s core (made of PET); this reduced the void space of the carpet mills and promoted better mixing. This improved the homogeneity of the reactive extrusion process, allowing for more uniform extrudate strands.



Figure 4-3 Comparison of extruder feed stock when un-pelletized [left] and pelletized [right]

4.2.2 Melt Flow Index

The curve shown in Figure 2-19 is applicable for the following processing conditions (Dynisco, n.d.):

- $T = 285^{\circ}\text{C}$
- $\tau = 360$ seconds
- $m_{\text{weight}} = 2160\text{g}$

The above-mentioned testing conditions are for pure PET resins, and they served as a starting point for determining the optimal testing conditions of the PET-based velour carpet. The initial results shown in Table 4-3 show a high standard deviation due to the inadequate testing conditions. These results were obtained at 285°C , at that temperature the material's flowrate was high and there was significant error when measuring the time. Hence the low time recordings for these values found in Table 4-3. Since the material was exhibiting a high flowrate, the testing temperature was reduced to 250 and 260 °C. Of which the optimal temperature was found to be 260°C shows the MFR results obtained with the optimized temperature.

Table 4-3 Comparison of the MFR test result for the low/low formulation

| Temperature | Sample Size | Average test Time (s) | Average MFI standard deviation |
|--------------------|--------------------|------------------------------|---------------------------------------|
| 285 | 8 | 01.79 ± 00.93 | ± 96.62 |
| 250 | 8 | 05.67 ± 02.04 | ± 66.83 |
| 265 | 6 | 42.79 ± 20.15 | ± 02.59 |

Table 4-3 shows that the temperature in the MFR machine is inversely proportional to the test time, this is due to the thermal degradation of the polymer chain that occurs at higher temperatures. The polymer chain length will be reduced due to thermal degradation, this reduction in chain length

will reduce the degree of intermolecular bonding; thereby, reducing the polymer's ability to resist flow. This explains why a lower testing temperature was chosen for this material, the lower temperature would allow a longer testing time and thereby improving the accuracy of the time measurement; this led to a lower deviation of MFI measurement and more consistent readings. This is since the impact that one second has in the final MFR measurement is greater with time measurements of 1-3 seconds as opposed to 20-60 seconds. Having said this, one would expect the lowest temperature test at 250°C to result in the longest test time; however, this was not the case. At 250°C the MFR temperature is oscillating the melting point of the core structure in the PET carpet; therefore, the material that would melt and flow out of the die would be mostly the outer sheet and some of the other lower melting point additives. This would be seen by the actual un-melted material that would be left in the barrel of the MFR machine, Figure 4-4 shows an example of this. Therefore, the best MFR testing temperature was found to be 260°C for this material.



Figure 4-4 Die blockage due to testing temperature being too low at low/low formulation ($T_{MFR} = 250^{\circ}\text{C}$)

The average standard deviation shown in Table 4-3 was calculated by considering the standard deviation of each batch. A sample calculation is shown in Equation 4-1, there were three different batches that were evaluated at an MFR temperature of 285°C; the standard deviation of each of these batches was obtained and averaged to calculate the standard deviation of the entire DOE level.

Equation 4-1

$$\begin{aligned} S.D._{avg} &= \sqrt{\frac{\sum s_i}{k}} \\ &= \sqrt{\frac{129^2 + 33^2 + 102^2}{3}} \\ S.D._{avg} &= 96.62 \end{aligned}$$

4.2.3 Dilute Solution Viscometry

Due to material procurement limitations of the 60/40 solution, it was decided that the solvent would be synthesized in the laboratory using TCE and phenol crystals that were in stock. The mixing was conducted under the ASTM D4603 conditions (110°C and 10 minutes), and the material was allowed to rest overnight. The main challenge with this process is the crystallization of the solvent after it was cooled to room temperature, Figure 4-5. This recrystallization suggests that the phenol was not fully dissolving in the TCE solvent, this recrystallization occurs due to the TCE's inability to hold the phenol molecules in the lattice crystal after losing its mobility. This phenomenon was experienced at random, with some mixtures experiencing recrystallization and other solutions behaving perfectly. The random recrystallization suggests that this 60/40 mixture is at the upper limit of how phenol can dissolve in the TCE lattice structure; since this method of synthesis was inefficient the focus was on the MFI test results until the phenol/TCE solvent could be procured from a supplier.

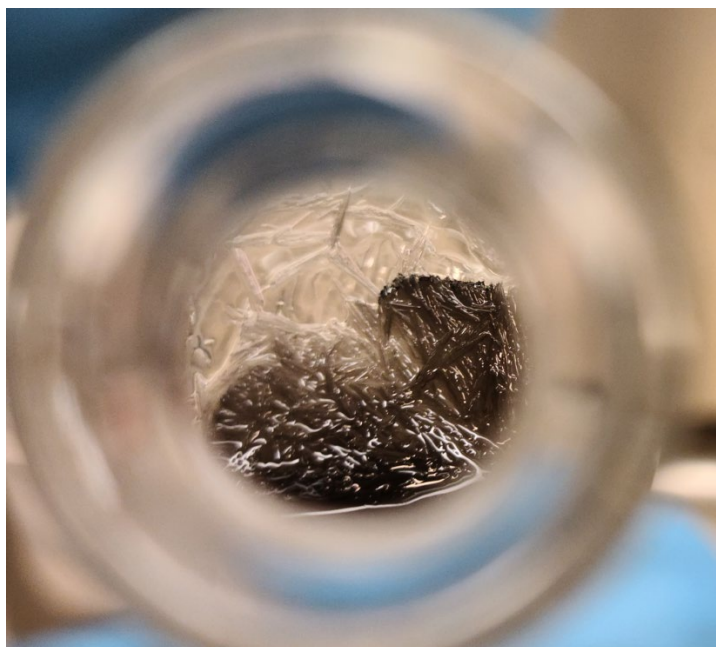


Figure 4-5 Recrystallization of 60/40 phenol/TCE solvent. This image was taken after the pure carpet trim was introduced to the solvent.

When the 60/40 solvent was procured it was utilized in the laboratory and recrystallization was not experienced in any of the tested samples. The only constraint lay in the carpet's ability to dissolve in the solution; it was found that certain formulations of velour carpet trim would not dissolve in the solvent due to gel formation. This gel formation forms in the extruder due to excessive cross linkage in the polymer chain making it insoluble in the 60/40 solvent. Figure 4-6 shows an example of the velour carpet that had experienced gel formation, the swelling of the material in the solvent is a clear indication of gel formation. This swelling occurs to the fact that polymer gels can absorb a small amount of solvent.



Figure 4-6 Carpet trim inside the 60/40 solvent [left] and carpet trim swelling due to gel formation [right]

The 60/40 solvent is capable of dissolving PET; however, it is not a suitable solvent for the entirety of the velour carpet. This is because said carpet contains multiple additives and not all are capable of dissolving in the 60/40 solvent, due to this the filtration step mentioned in section 3.5 was incorporated. This filtration step was an addition step to the ASTM standard for I.V. evaluation of PET using DSV, following said step the material was removed and weighed prior to analysis. Table 4-4 shows the amount of material lost per DOE formulation.

Table 4-4 Summary table of mass retained in the filtration process of the solution synthesis for DOE#2.

| Level (PMDA/PBO) | Temperature | Mass Loss (g) | Average mass loss (g) |
|---------------------------------|-------------|----------------------|-----------------------|
| Pure Carpet | 265 | 0.003 | |
| Low/Low | 265 | 0.188 | 0.131 ± 0.126 |
| Low/High | 265 | 0.280 | |
| High/Low | 265 | 0.052 | |
| High/High | 265 | <i>Gel formation</i> | |
| Pure Carpet | 285 | 0.008 | |
| Low/Low | 285 | 0.018 | 0.136 ± 0.097 |
| Low/High | 285 | 0.020 | |
| High/Low | 285 | 0.034 | |
| High/High | 285 | 0.237 | |
| <i>Combined average:</i> | | | 0.132 ± 0.110 |

The average mass loss for the entire process is 0.132 ± 0.018 with temperature having a negligible effect on the amount of material retained during the filtration process. This is to be expected since the mass that is retained does not participate in the reactive extrusion between PET-chain extenders, they are inert components in this recycling process.

4.3 Statistical Analysis

4.3.1 DOE #1

As stated in section 4.1 the first stage of the design of experiment was a screening stage that utilized the MFR measurements as the main evaluation source following the parameters specified in Table 4-1, the summary of the experiment's main results are shown in Table 4-5.

Table 4-5 Summary of the MFR results obtained from the first DOE.

| Level (PMDA/PBO) | Average MFR (g/10min) |
|------------------|-----------------------|
| Pure Carpet | 373 ± 056 |
| Low / Low | 300 ± 052 |
| Low / High | 121 ± 120 |
| High / Low | 530 ± 110 |
| High / High | 409 ± 192 |

Table 4-6 ANOVA summary for the MFR test results conducted in DOE#1

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|--------------------|----|--------|--------|---------|---------|
| Model | 3 | 408648 | 136216 | 05.42 | 00.008 |
| Linear | 2 | 377054 | 188527 | 07.51 | 00.005 |
| PMDA | 1 | 286754 | 286754 | 11.42 | 0.004 |
| PBO | 1 | 96520 | 96520 | 03.48 | 0.067 |
| 2- Way Interaction | 1 | 3558 | 3558 | 00.14 | 0.711 |
| PMDA*PBO | 1 | 3558 | 3558 | 00.14 | 0.711 |
| Error | 17 | 426929 | 25113 | | |
| Total | 20 | 835577 | | | |

The MFR results shown in Table 4-5 and the correlation between MFR-I.V. shown in Figure 2-19 will not yield I.V. that meet the target 0.65 dL/g. However, the ANOVA analysis for these test results, Table 4-5, demonstrates that the chain extenders (particularly PMDA) have an impact on the flow properties of the carpet trims. The graph shown in Figure 4-9 demonstrates the impact chain extenders have on the I.V. The contour plot demonstrates that at extrusion temperature of 265°C the PBO concentration has a limited impact on the I.V. of the material, thereby justifying the findings shown in this ANOVA table. Due to this it was decided to develop a model to estimate a new formulation of chain extenders capable of meeting the research goal. This is since the current melt flow index results were not expected to yield an I.V. capable of meeting said research goal.

The model obtained from this design is shown in Equation 4-2 **Error! Reference source not found.**, where the parameter X_1 is the PMDA concentration (%) and X_2 is the PBO concentration (%). Despite the different MFR testing temperature, Figure 2-19 was used as an estimate for the initial guess for setting an MFR target of 10 g/10min (corresponding to an I.V = 1.0 dL/g).

Equation 4-2

$$MFR = -103 + 149X_1 - 136X_2 - 3.7X_1X_2$$

The graph shown on Figure 4-7 shows that each chain extender level on the both the Y and X axis with each MFR value being represented by each data point. It is seen that the value with the highest MFR measurement is found in the high/low PMDA/PBO formulation, while the lowest MFR measurement is obtained at the low/high PMDA/PBO formulation. As previously mentioned in section 2.6.1.4 the molecular weight of the polymer is inversely proportional to its flowrate; therefore, the zone of interest is surrounding the low/high PMDA/PBO formulation.

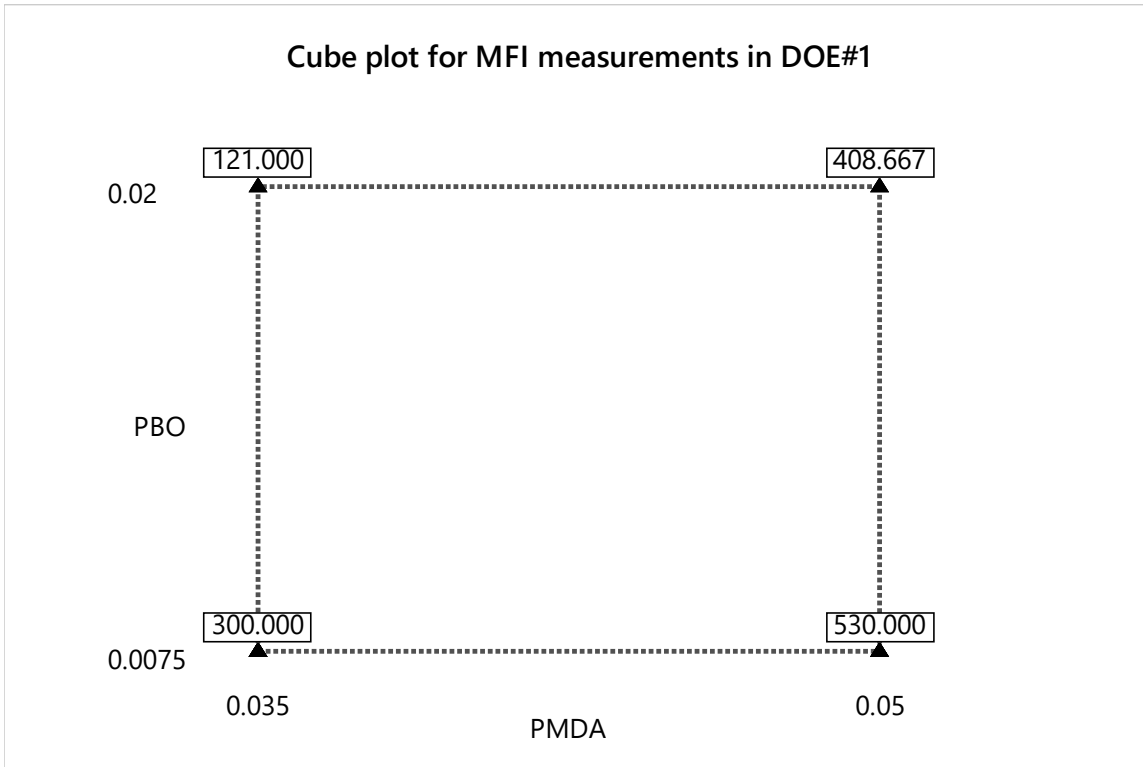


Figure 4-7 Cube plot for the MFI measurements performed in DOE#1. The values shown in each point correspond to the flowrate (g/10min) for each factor and level.

Thus, the PMDA low concentration of DOE #1 was set as the new upper limit for DOE#2 while the lower limit of PMDA was chosen to be at the halfway point of 3.5wt% (upper limit) and 0wt%. This halfway point was chosen as a conservative estimate of PMDA concentration, too low of a concentration and the rate of thermal degradation would overcome the rate of chain extension; thereby reducing the molecular weight of the material. Too high of a concentration and gel formation would occur; therefore, this halfway point of 1.75wt% PMDA was chosen as the lower limit to provide an estimate of the proper direction for a possible third DOE.

With the PMDA concentrations chosen at (1.75wt%, 3.50wt%) the model shown in Equation 4-2 was re-arranged and the corresponding concentrations of PBO were obtained at (1.00wt%, 2.75wt%). A sample calculation for one of these levels is shown below.

Equation 4-3

$$10 = -103 + 149(3.5\%) - 136X_2 - 3.7(3.5\%)X_2$$

$$X_2 = 2.75\%$$

These new factors were used in DOE#2, summarized in Table 4-2, in which the levels proposed in DOE#2 are lower than the levels in DOE#1.

Table 4-7. ANOVA summary for DOE#1

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|--------------------|----|--------|--------|---------|---------|
| Model | 5 | 250504 | 50101 | 3.08 | 0.101 |
| Blocks | 2 | 2984 | 1492 | 0.09 | 0.914 |
| Linear | 2 | 247483 | 123741 | 7.61 | 0.023 |
| PMDA | 1 | 139752 | 139752 | 8.60 | 0.026 |
| PBO | 1 | 107731 | 107731 | 6.63 | 0.042 |
| 2- Way Interaction | 1 | 37 | 37 | 0.00 | 0.964 |
| PMDA*PBO | 1 | 37 | 37 | 0.00 | 0.964 |
| Error | 6 | 97499 | 16250 | | |
| Total | 11 | 348002 | | | |

Table 4-7 summarizes the ANOVA analysis for the model shown in Equation 4-2; the p-value for the individual effect that each chain extenders have on the material's flow properties is <0.05 validating their impact on the material's property. Meanwhile, the interaction between PMDA*PBO is shown to be statistically insignificant; this disagrees with the theory behind their synergistic effect discussed in section 2.4.3. This is explained by the analysis conducted above surrounding Figure 4-9. While the individual chain extender parameters are statistically significant, the overall model is found to contain a p-value >0.05. This is caused by the large standard deviation that was obtained during the initial phase of MFI testing. Having said this, utilizing the correlation shown in **Figure 2-19** it is found that the current formulation yields a maximum I.V. of 0.53 dL/g.

This is not sufficient to satisfy the research goal of 0.70 dL/g; hence, the model was used to provide an estimate for the new optimized estimate of chain extender formulations.

4.3.2 DOE #2

As previously mentioned, the second phase focused on optimizing both the processing conditions and product formulation. The new levels of PMDA and PBO were calculated using Equation 4-2 and an additional temperature level was introduced at 285°C. This second temperature was chosen based on other experiments that performed reactive extrusion at these elevated temperatures (Awaja et al., 2004; Bimestre & Saron, 2012; Kossentini-Kallel et al., 2008). Table 4-2 summarizes the design of experiment; the pure sample, not part of this 2³ design DOE, represents the processing of the carpet trim without chain extender. This provides a reference value to quantify the impact the chain extenders had on the material's property.

In this second stage DSV was the main testing method, Table 4-8 summarizes the test results for this 2³ DOE.

Table 4-8 Summary of the DSV test results for the second DOE

| Temperature | Factor (PMDA/PBO) | I.V. (dL/g) | Sample Size |
|-------------|-------------------|----------------------|-------------|
| 265°C | Pure Carpet | 0.457 ± 0.003 | 7 |
| | Low/Low | 0.748 ± 0.007 | 7 |
| | Low/High | 0.709 ± 0.022 | 9 |
| | High/Low | 0.432 ± 0.016 | 6 |
| | High/High | <i>Gel formation</i> | |
| 285°C | Pure Carpet | 0.200 ± 0.035 | 3 |
| | Low/Low | 0.598 ± 0.002 | 3 |
| | Low/High | 0.740 ± 0.094 | 3 |
| | High/Low | 1.036 ± 0.032 | 6 |

| | | |
|-----------|-------------------|---|
| High/High | 0.292 ± 0.035 | 8 |
|-----------|-------------------|---|

The note worthy thing is the gel formation that occurs at the high/high (PMDA/PBO) formulation at 265°C. This gel formation prevents the analysis of intrinsic viscosity due to its insolubility property. It is for this reason that this factor was not accounted for in the data analysis.

The formulations which exceed the research objective ($\eta = 0.650 \text{ dL/g}$) are:

- 265°C low PMDA, low PBO with an $\eta = 0.748 \text{ dL/g}$
- 265°C low PMDA, high PBO with an $\eta = 0.709 \text{ dL/g}$
- 285°C low PMDA, high PBO with an $\eta = 0.740 \text{ dL/g}$
- 285°C high PMDA, low PBO with an $\eta = 1.036 \text{ dL/g}$

In order to determine the optimal formulation and processing temperature within the values obtained in this experiment an ANOVA analysis was conducted, section 4.3.4 shows the ANOVA analysis for DOE#2. Figure 4-8 shows a graphical summary of the results obtained in this DOE.

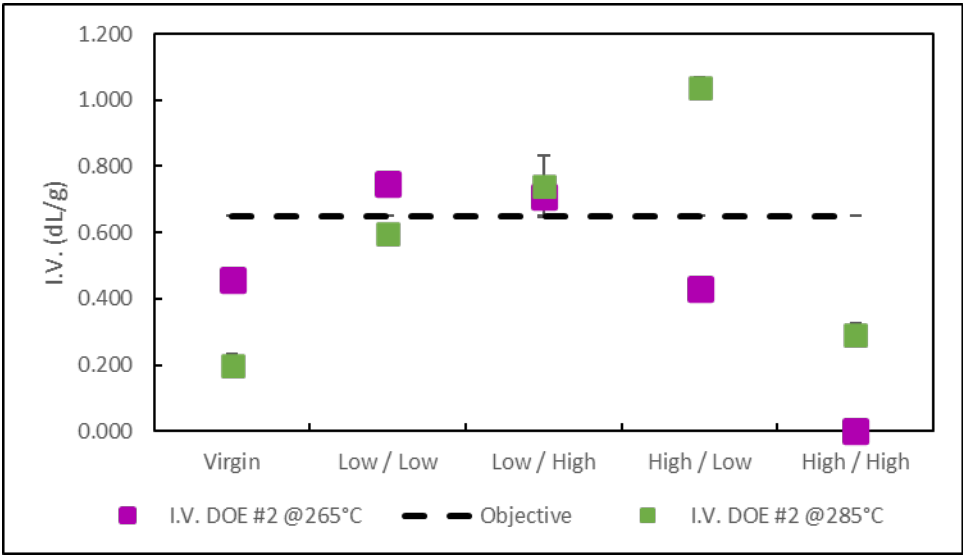


Figure 4-8 Plot summary of the I.V. values obtained (y-axis) with respect to each of the DOE formulations, with the addition of the pure carpet trim.

Figure 4-8 shows that without chain extenders a higher extrusion temperature decreases the viscosity of the material, which is to be expected due to the increase in thermal degradation. The low/low and low high (PMDA/PBO) formulations demonstrate an increase in viscosity of the carpet trims, showing the effects of the chain extenders on the length of the polymer chain. However, these two formulations oscillate the minimum I.V. (dL/g) value specified by the recycling industry. The highest viscosity achieved in this DOE was at the 285°C high/low (PMDA/PBO) formulation.

4.3.3 Temperature Study

Temperature will affect the chain extender-carpet trim reaction since it will determine how much energy is provided to the system for the reaction to occur, but it also affects the polymer chain since it can lead to thermal degradation. Figure 4-9 and Figure 4-10 show the contour plots of the carpet's I.V. as a function of their chain extender formulations, Figure 4-9 shows the viscosity values at a constant extrusion temperature of 265°C; while Figure 4-10 shows the viscosity values at a constant extrusion temperature of 285°C.

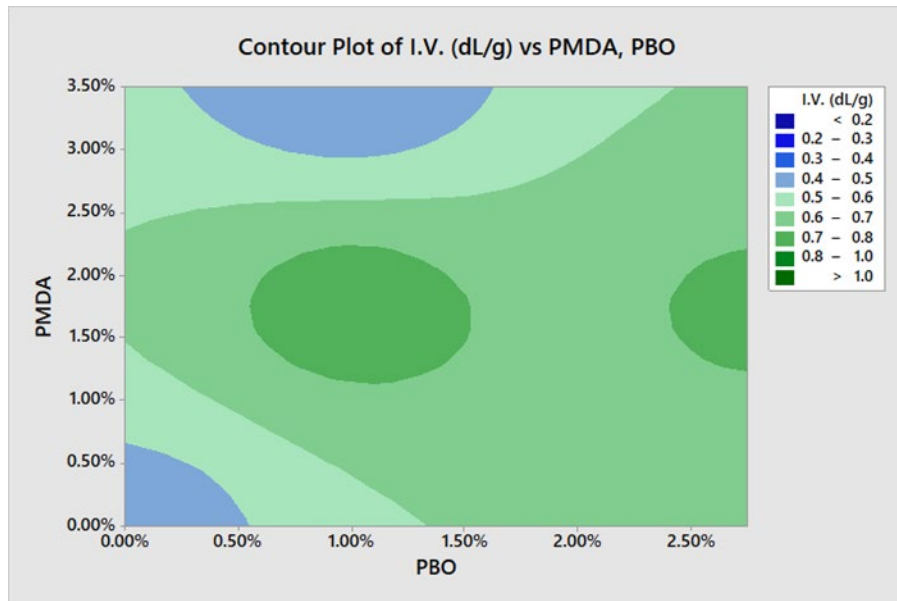


Figure 4-9 Contour plot of the relation between I.V. (dL/g) and the chain extenders PMDA/PBO at an extrusion temperature of 265°C.

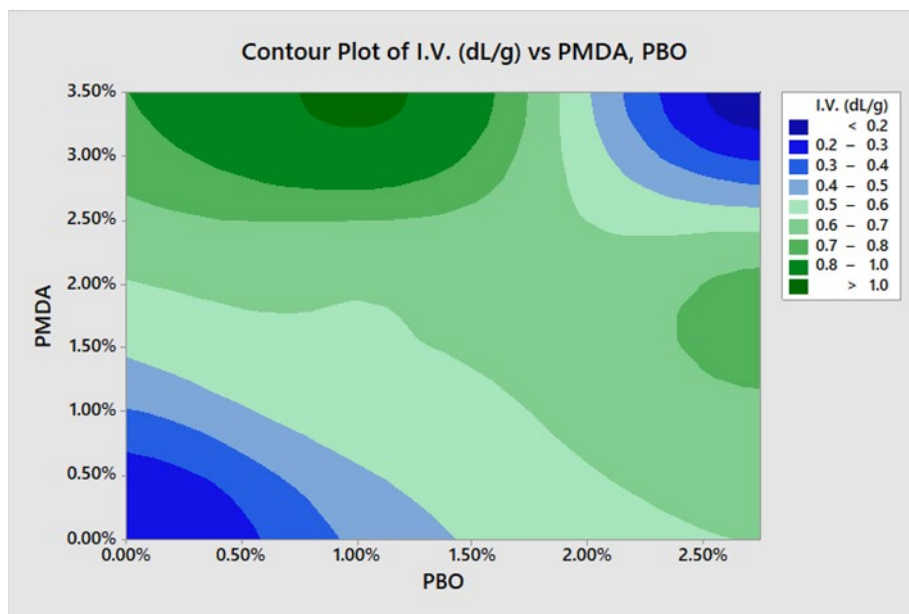


Figure 4-10 Contour plot of the relation between I.V. (dL/g) and the chain extenders PMDA/PBO at an extrusion temperature of 285°C

Comparing both contour plots at the two different processing temperatures shows that extruding at 285°C yields better I.V. values than at 265°C. The highest value that can be obtained in this PMDA/PBO formulation zone at 265°C is 0.7-0.8 dL/g; while the highest values obtained at 285°C is >1.0 dL/g. The melting point of PMDA is 285°C so this processing temperature will cause PMDA to melt with the carpet during the reactive extrusion process. Once inside the extruder the melted PMDA will have better dispersion thereby increasing its extent of reaction with the PET core. This is seen by analyzing the Y-axis of both figures, in Figure 4-9 regardless of the PBO concentration there is no clear difference between the low PMDA and high PMDA concentrations. Meanwhile there is a very distinct difference between the low and high concentration levels of PMDA shown in Figure 4-10 which is caused by the increase in temperature that improved the PMDA-PET reaction.

4.3.4 ANOVA

Table 4-9 shows the summary of the ANOVA analysis for DOE#2, the p-values of each factor being much lower than 5%, this analysis is done at a 95% confidence interval, prove that their impact on the I.V. of the velour carpet is statistically significant.

Table 4-9 Summary of the ANOVA results for DOE#2

| Source | DF | Adj SS | Adj MS | F-value | P-value |
|-------------------|----|---------|---------|---------|---------|
| Model | 6 | 3.18612 | 0.53102 | 606.48 | 0.000 |
| Linear | 3 | 1.87179 | 0.62393 | 712.59 | 0.000 |
| Temp | 1 | 0.51870 | 0.51870 | 592.40 | 0.000 |
| PMDA | 1 | 1.04953 | 1.04953 | 1198.67 | 0.000 |
| PBO | 1 | 1.53879 | 1.53879 | 1757.46 | 0.000 |
| 2-Way Interaction | 3 | 1.96671 | 0.65557 | 748.73 | 0.000 |
| Temp*PMDA | 1 | 0.70193 | 0.70193 | 801.68 | 0.000 |
| Temp*PBO | 1 | 0.03527 | 0.03527 | 40.29 | 0.000 |
| PMDA*PBO | 1 | 1.08571 | 1.08571 | 1239.99 | 0.000 |
| Error | 35 | 0.03065 | 0.00088 | | |
| Total | 41 | 3.21676 | | | |

Table 4-9 was obtained from using the values shown in Table 4-4 following the parameters specified in Table 4-2. This table shows interaction terms between the temperature and the chain extender as well as an interaction term between the chain extenders themselves. This interaction is shown on Figure 4-11, as it can be seen the lines for each factor are intersecting signifying that each of these factors have a correlated impact on the intrinsic viscosity. So taking the topic discussed in section 4.3.3, temperature will have an impact on the PMDA's ability to react with PET and also affect the I.V. of the velour carpet since it would influence the degree of thermal

degradation. The analysis was halted at a 2-Way Interaction since the I.V. for the 265°C, high PMDA, high PBO level could not be obtained; thereby, preventing 3-way interaction analysis.

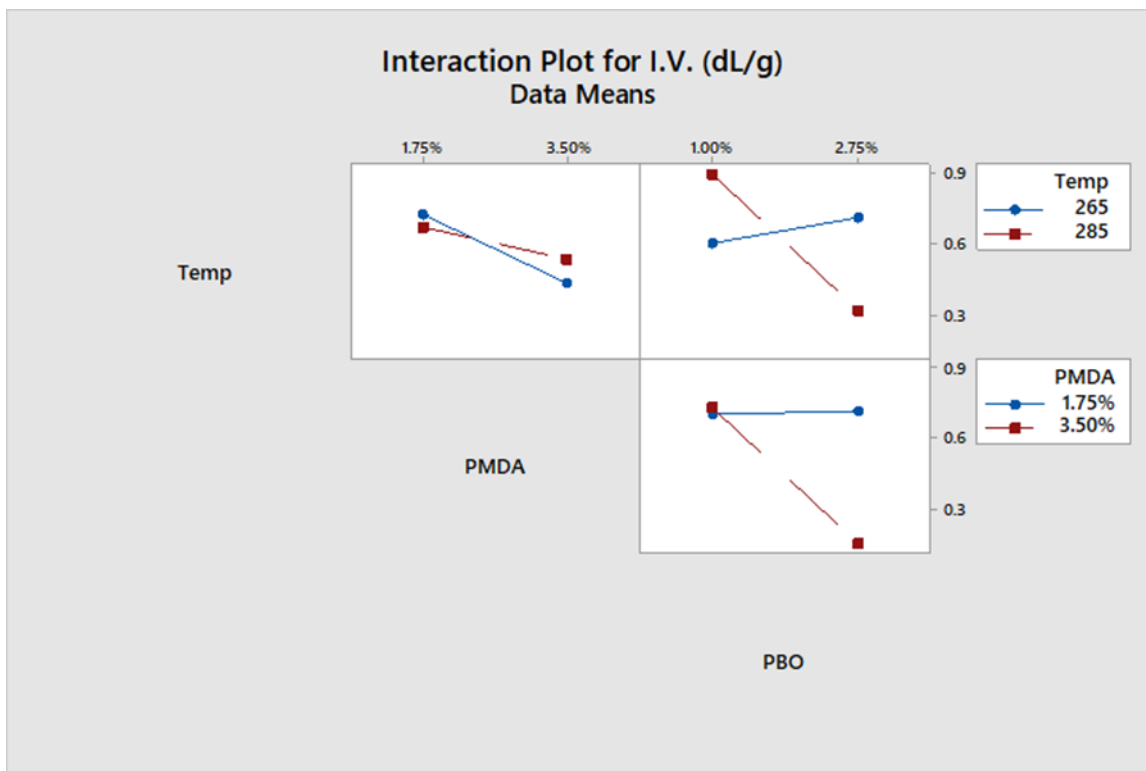


Figure 4-11 Interaction plot between each of the factors studied in this DOE.

The model obtained from the ANOVA analysis is shown in Equation 4-4, in which X_1 represents the temperature ($^{\circ}\text{C}$), X_2 represents the PMDA concentration (wt.%) and X_3 represents the PBO concentration (wt.%). Table 4-10 summarizes the accuracy of the model, in which the adjusted R^2 value being 98.88% and the S value being so low demonstrate that the model fits very closely with the data. Meanwhile the residual of the model is shown in Figure 4-12, the values shown in these plots it can be concluded that the model shows no bias in the data.

Table 4-10 Model summary showing the corresponding fit of this model to the data.

| S | R^2 | R^2_{adj} | R^2_{pred} |
|--------|--------|--------------------|---------------------|
| 0.0295 | 99.05% | 98.88% | 98.22% |

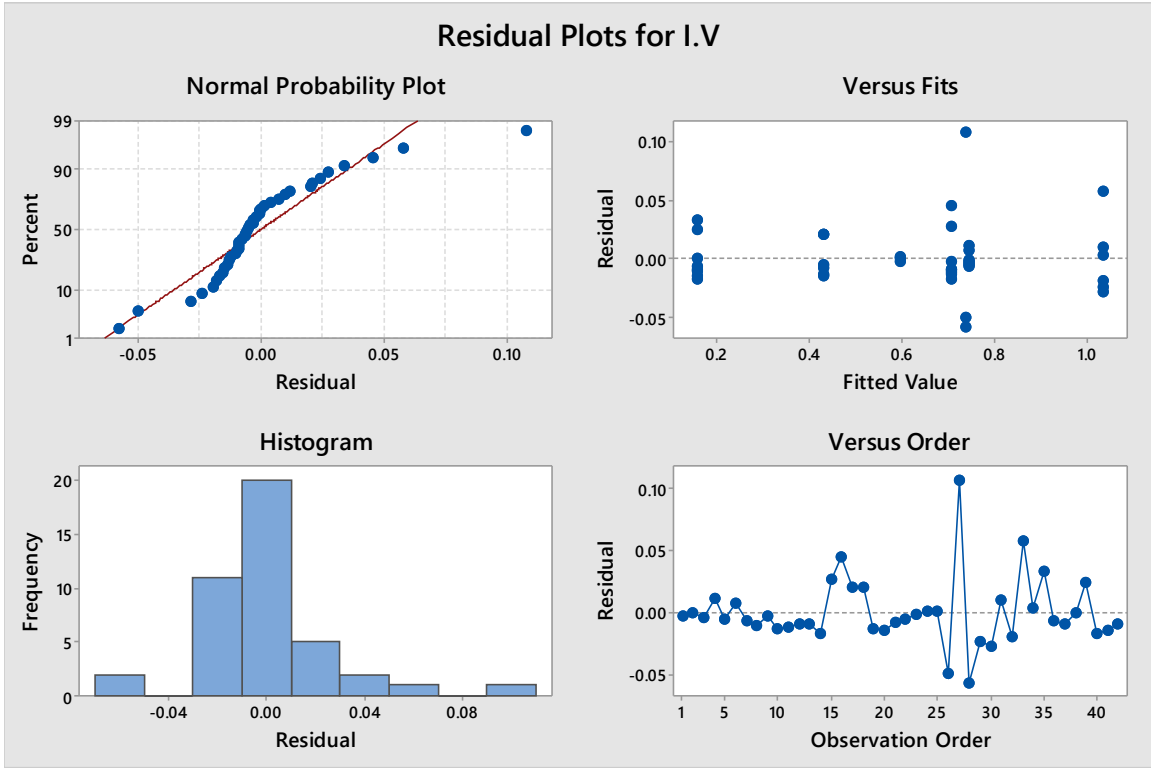


Figure 4-12 Summary of the residual plots for the model shown in Equation 4-4

Equation 4-4

$$\eta\left(\frac{dL}{g}\right) = 13.835 - 0.05031X_1 - 555.5X_2 - 80.3X_3 + 2.1537X_1X_2 - 0.5149X_1X_3 - 3330.7X_2X_3$$

Using Equation 4-4 a new intrinsic viscosity of the material was estimated to be $1.23 \frac{dL}{g}$ under the following parameters: $T = 285^\circ\text{C}$, $[\text{PMDA}] = 3.0 \text{ wt.}\%$, $[\text{PBO}] = 0.05 \text{ wt.}\%$. These findings align with past research (Awaja et al., 2004; Dimonie et al., 2012; Kossentini-Kallel et al., 2008), however, recycling PET-based material such as velour carpet requires a higher concentration of chain extenders. In this experiment it was found that a PMDA concentration of 3.00wt% was required, as opposed to the 0.005wt% used in some experiments, the reason being that velour carpets contain fillers and additives that can hinder the extent of reaction between the PET

molecule and the chain extender. Thus, a higher concentration is required in order to achieve the same degree of chain extension.

4.3.5 Molecular Weight

With the values obtained from DOE#2 the molecular weight of the PET, which composes the core of the carpet trim, can be obtained using the Mark-Houwink equation shown in section 2.6.3. Using the constant (K, and a) values reported by (Jabarin, 1987; Sanches et al., 2005) for PET dissolved in 60/40 phenol/1,1,2,2, tetrachloroethane solution the molecular weight can be calculated and the relationship between the molecular weight and intrinsic viscosity of the velour carpet can be estimated.

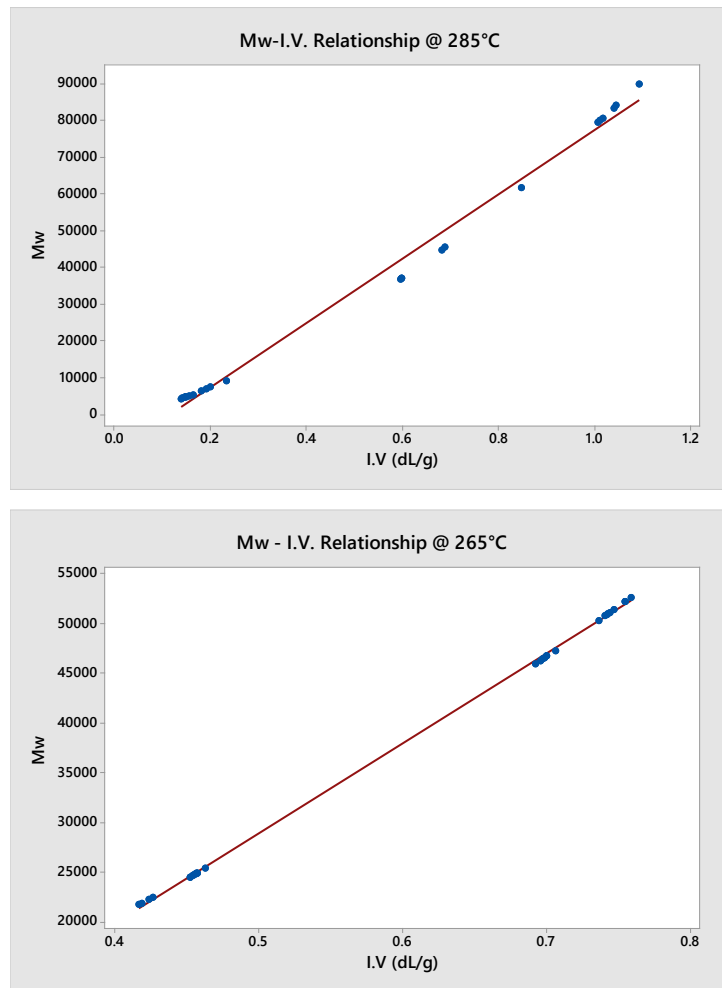
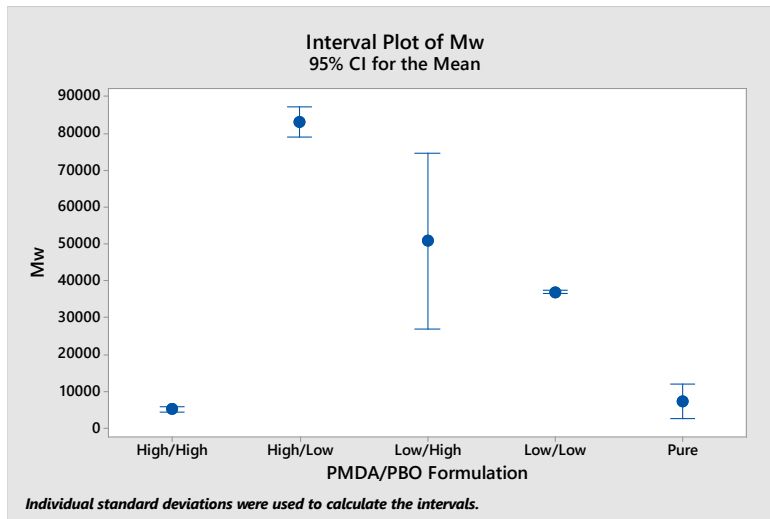


Figure 4-13 Relationship between I.V. (dL/g) and MW of the velour carpet trim

Figure 4-13 displays the relationship between the I.V. (dL/g) and molecular weight of the carpet trims. The graph displays the relationship for extrusion at 265 and 285°C, shown in purple and green, respectively. While the extrusion temperature does not affect the relationship between the Mw and the I.V. of the carpet trim, it does play a role in allowing the material to reach higher I.V. values. As seen in Figure 4-13 the extrusion temperature of 285°C reached higher Mw values, reaching a MW as high as 83,000. The effect that temperature has on the reaction between the chain extenders and PET is what drives the difference in the molecular weights achieved. While a higher molecular weight is desired, a value that is too high would lead to excessive cross linking and gel formation, which poses processing constraints as discussed in section 4.2.3.



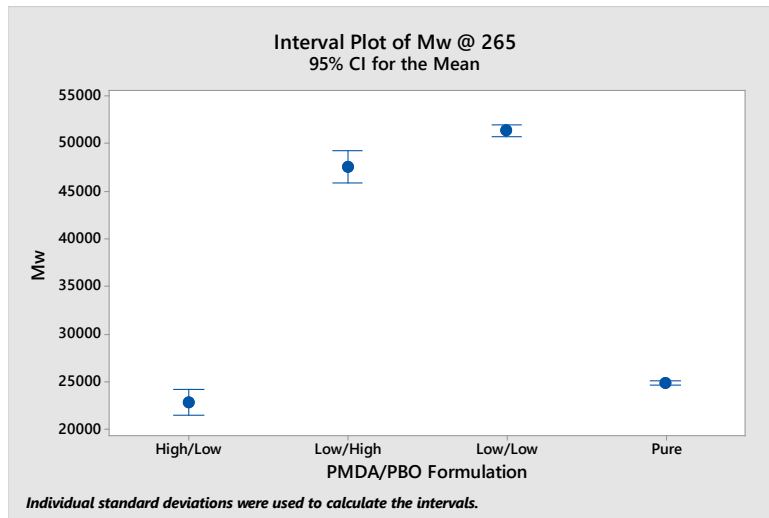


Figure 4-14 Interval plot for the Mw distribution according to the DOE#2 Formulation @285°C [top] and 265°C [bottom].

The plots shown in Figure 4-14 display the performance each chain extender formulation had on the molecular weight of the carpet trim. As expected, and due to the proportionality relationship between molecular weight and I.V., the formulation that contains the highest molecular weight is the “High/Low” (PMDA/PBO) formulation when extruded at 285°C.

Table 4-11 Summary of the DSV test results for the second DOE

| Temperature | Factor (PMDA/PBO) | Mw | Sample Size |
|-------------|-------------------|----------------------|-------------|
| 265°C | Pure Carpet | 24,935 ± 215 | 7 |
| | Low/Low | 51,389 ± 703 | 7 |
| | Low/High | 47,582 ± 2,152 | 9 |
| | High/Low | 22,935 ± 1,283 | 6 |
| | High/High | <i>Gel formation</i> | |
| | Pure Carpet | 7,449 ± 1,876 | 3 |
| | Low/Low | 37,019 ± 167 | 3 |

| | | | |
|-------|-----------|----------------|---|
| 285°C | Low/High | 50,820 ± 9,586 | 3 |
| | High/Low | 83,082 ± 3,827 | 6 |
| | High/High | 5,254 ± 943 | 8 |

Table 4-11 summarizes the calculated molecular weights according to each level proposed in DOE#2. The effect of polymer, thermal, degradation is quantified by the molecular weight difference between 265 and 285°C. The molecular weight of the PET chain at 285°C is on average 70% lower than the molecular weight of the same material processed at 265°C. The highest molecular weight that was obtained was at the 285°C extrusion temperature and “High/Low” (PMDA/PBO) formulation, with an average molecular weight of 83,082. Since the molecular weight is directly proportional to the intrinsic viscosity of the material, the behaviour displayed in Table 4-11 is the same as the one shown in Table 4-8.

Chapter 5

CONCLUSIONS

The recycling of velour carpets posed processing and testing limitations; from a processing perspective there is an upper limit to the chain extender concentration due to gel formation. Meanwhile evaluating the material using standard MFR or DSV methods posed a challenge because the known pure PET testing conditions do not apply to this velour carpet material, which is PET-based. New testing parameters were determined for MFR to improve the testing accuracy, the temperature for this method was lowered to 260°C in order to improve flow of the material out of the die and reduce the impact of human error when measuring the flow time. Likewise, the DSV sample preparation steps were created using the ASTM standard as the foundation; however, a filtration step was added to remove the additives and fillers in the carpet trim that would not be able to dissolve in the 60/40 phenol-1,1,2,2-tetrachloroethane solvent.

The processing conditions were determined in DOE#2, in which temperature was introduced as a variable alternating between 265°C and 285°C. This addition of temperature was made with the intent of improving PMDA mixing in the extruder thereby improving the ability of PMDA to react with PET. The comparison between Figure 4-9 and Figure 4-10 shows that temperature influences PMDA's ability to react with PET and thereby increase the length of the polymer chain. From DOE#2 it was found that the parameters 3.5wt% PMDA, 1.0 wt.% PBO and 285°C yield an acceptable I.V. of 1.036 ± 0.032 dL/g, resulting in an estimated M_w of 83,036. The ANOVA analysis for this experiment proves that the parameters evaluated in this research are statistically influential to the I.V. of the material, as shown in Table 4-1. The graphs shown in Figure 4-11 prove the interaction between temperature and the chain extenders, which was then used to improve the accuracy of the regression model. Said model was then used to predict a new optimized carpet I.V. value of 1.23 dL/g, which is achieved under the following processing parameters: 3.0 wt.% PMDA, 0.05wt% PBO and 285°C.

Chapter 6

RECOMMENDATION FOR FUTURE RESEARCH

The intent behind this research project is to design a recycling path for the velour carpet trims being sent to land fill. This project was able to establish an optimal processing temperature, chain extender formulation, and adequate testing conditions that produce reliable results. Having said this there are aspects to this project that could be improved; these are listed below:

- Perform DOE analysis on optimal size reduction of carpet trim being fed to the extruder.
- Conduct a DOE to account for unaccounted variables in this project, such as residence time.
- Scale up of extrusion operation to a manufacturing scale equipment and determine new processing and product-formulation conditions.
- Evaluate different extruder and screw designs, for example comparing a twin-screw vs single screw design; or experimenting with different screw heads.
- Evaluate the extrudate's physical properties at various chain extender concentrations to correlate the material's performance to its formulation and processing conditions.

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