Investigation of Thermo-mechanical Degradation of Polypropylene-Low Density Polyethylene Blends Exposed to Simulated Recycling

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the 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.

Statement of Contributions

Chapter 2 and Chapter 5 of this thesis is adopted and modified from a literature review that is a published journal article. I co-authored this manuscript with Dylan Jubinville, Dr. Elnaz Esmizadeh, Prof. Tzoganakis and Prof. Mekonnen. Dylan Jubinville, Dr. Elnaz Esmizadeh and I wrote the majority of the work with Prof. Tzoganakis and Prof. Mekonnen's guidance and supervision. All authors conceived and contributed to this work.

Chapter 3, Chapter 4, and Chapter 5 are reorganized into a manuscript and is submitted for publication co-authored with Dylan Jubinville, Prof. Tzoganakis, and Prof. Mekonnen. I developed the experimental procedures, performed the experiment and wrote the manuscript with the help of Dylan Jubinville. Prof. Mekonnen and Prof Tzoganakis provided guidance, reviewed, and finalized the paper for publication.

Abstract

Polypropylene (PP) and low-density polyethylene (LDPE) are among the most extensively used resins used mainly in the packaging and automotive sectors and are the largest contributor to municipal waste. Plastic waste accumulation in water bodies and landfill is a major environmental concern due to their resistance to microbial attack and slow environmental degradation process. Thus, recycling and reusing of these plastic wastes is a more viable solution than discarding it in the environment. The physiochemical properties and structure change irreversibly during repeated recycling operations. Hence, it is critical to understand the deterioration of properties during multiple processing and reprocessing steps.

In this study, PP blended with 0–10 wt. % of LDPE was subjected to consecutive twin-screw extrusion cycles (0-5 times) to mimic thermo-mechanical recycling. The effect of reprocessing on the rheological, thermal, and mechanical properties of PP/LDPE blends was investigated. An increase in melt flow rate (MFR) and decrease in viscosity was observed for PP and the blends. Differential scanning calorimetry (DSC) results showed that the crystal structure of PP was seriously affected, generating more disorder with reprocessing. Although tensile properties were not substantially affected, all properties had a decreasing trend. While successive thermo-mechanical processing caused chain scission of the PP phase of the blend, the overall property of the studied blend composition maintained mostly acceptable properties. Thus, recycling of PP blends with low-density polyethylene (LDPE) content is a feasible option not only to reduce plastic waste but also to generate value from an otherwise waste product.

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Dedicated to Mom and Dad

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List of Abbreviations

PO	Polyolefins
CAD	Canadian Dollars
Mt	Million tonnes
Bt	Billion tonnes
PP	Polypropylene
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
UHMWPE	Ultra-high-molecular weight polyethylene
MDPE	Medium-density polyethylene
LLDPE	Linear low-density polyethylene
PIB	Polyisobutylene
EPDM	Ethylene propylene diene
iPP	Isotactic polypropylene
sPP	Syndiotactic polypropylene
aPP	Atactic polypropylene
PS	Polystyrene
PVC	Poly vinyl chloride
PET	Polyethylene terephthalate
PUR	Polyurethane
EPS	Expanded Polystyrene
ABS	Acrylonitrile butadiene styrene

PC	Polycarbonate
PMMA	Poly (methyl methacrylate)
PTFE	Polytetrafluoroethylene
MAPP	Maleic anhydride polypropylene
MAPE	Maleic anhydride polyethylene
EPR	Ethylene propylene rubber
NAFTA	North American Free Trade Agreement
USA/US	United States of America/ United States
EU	European Union
CO_2	Carbon dioxide
HSI	Hyperspectral imaging
DMT	dimethyl terephthalate
BHET	bis (hydroxy ethylene) terephthalate
PLA	Polylactic acid
ASTM	American Society for Testing and Materials
MFR	Melt flow rate
FTIR	Fourier transform infrared spectroscopy
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
IR	Infrared
TAI	TA instrument
ATR	Attenuated total reflection
T_m	Melting temperature

$\mathbf{T_c}$	Crystallization temperature
$\mathbf{H_f}$	Melt enthalpy
$\mathbf{H^{\circ}_{f_{PP}}}$	Melt enthalpy of PP at 100% crystallization
$\mathbf{H^{\circ}_{f_{LDPE}}}$	Melt enthalpy of LDPE at 100% crystallization
$\boldsymbol{\eta}$	Shear viscosity
$\boldsymbol{\eta^*}$	Complex viscosity
$\boldsymbol{\eta_o}$	Zero-shear viscosity
$\boldsymbol{\lambda}$	Relaxation time
$\boldsymbol{\omega}$	Angular frequency
$\mathbf{n}$	Power-law exponent
$\mathbf{G^*}$	Complex modulus
$\mathbf{K}$	Consistency index
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_{\mathbf{true}}$	True shear rate
$\dot{\gamma}_{\mathbf{app}}$	Apparent shear rate
$\%\boldsymbol{\chi}_{c_{PP}}$	Percentage crystallinity of polypropylene
$\%\boldsymbol{\chi}_{c_{LDPE}}$	Percentage crystallinity of low-density polyethylene

Chapter 1

Introduction

1.1 Overview

The global production or conversion of polymer resin has grown by 8% in 2018[1] and examining the years of 2017 and 2018 more closely, there was a 9% growth in production from 348-359 Mt[2,3]. Of the 359 Mt of produced plastic, the North American Free Trade Agreement (NAFTA) zone, Asia, and the EU contributed 18, 51, 17 %, respectively. Canada specifically had estimated sales of 10 billion dollars (CAD) in polymer resin and 25 billion dollars (CAD) in plastic manufacturing in 2018 with an average of 4.6 Mt entering the domestic market per annum[4]. **Figure 1** depicts a correlation between rising plastic production against that of an ever-growing global population. This correlation clearly shows that the increasing production levels are dependent on the global population since manufacturers are required to meet the demand[5].

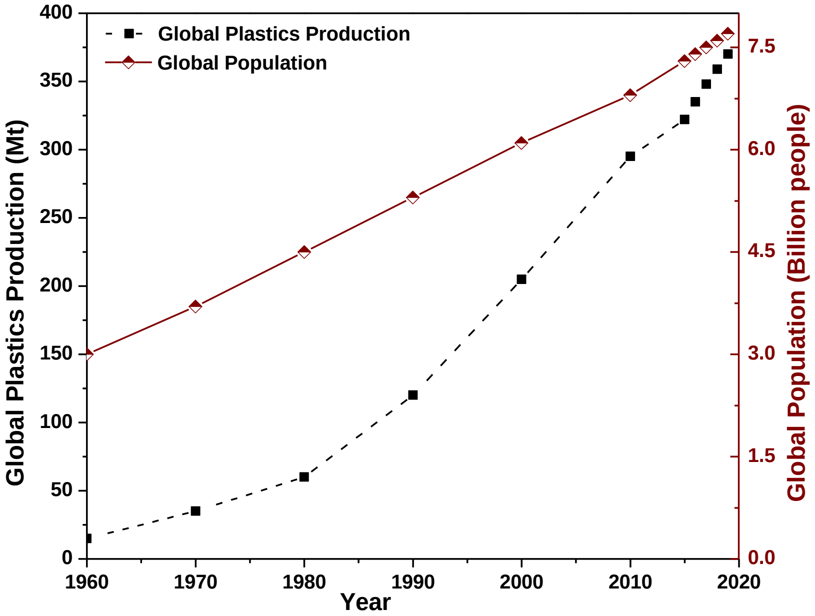


Figure 1: The global plastics production (per million tonnes) against that of the global population (per billion people) from 1960 to 2019[1–3,6–8]

Figure 2 shows another way in which the components are dissected by industry of plastic production. As it is shown, the largest elements are packaging (34%), construction (19%), and transportation (14%) for plastic production as well as the largest potential plastic waste generation[2,7].

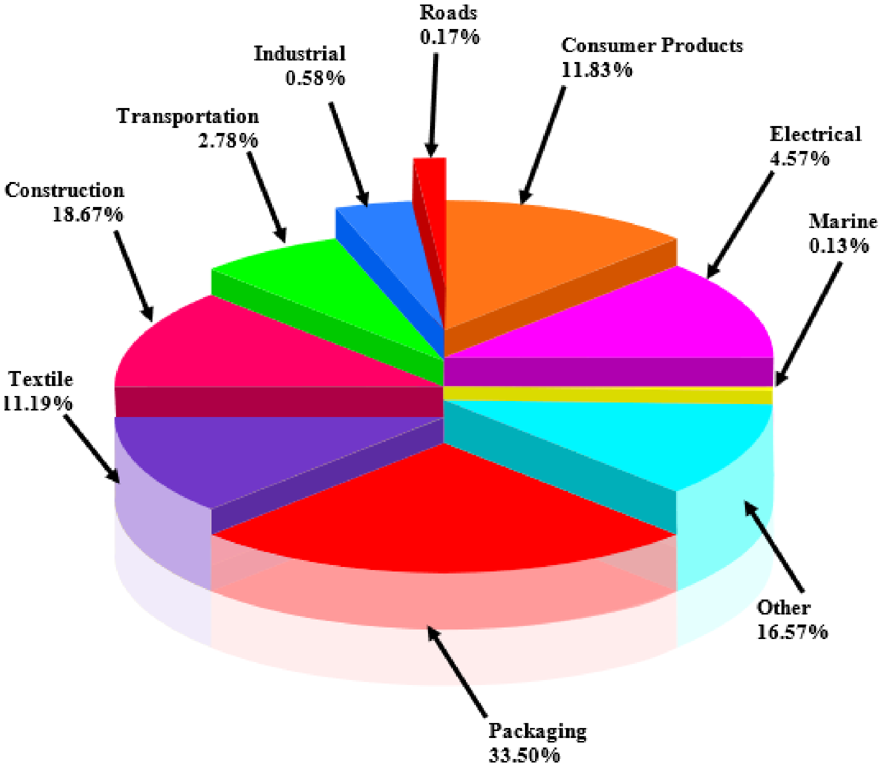


Figure 2: A graphical breakdown, by sector, for the major resin converters in 2018.[1–3,7]

According to the UN Environment Program, about 22-43% of all plastics used globally are sent to landfills which results in plastic accumulation and pollution. During the 2000's, approximately 61 wt. % of plastic, in Europe, was disposed of into landfills. In 2016, Europe had produced around 280 million Mg of plastics and 27 million Mg of plastics was collected as waste, out of which only 31% went to recycling, around 42% incinerated and the rest 27% was sent to landfills[9]. The hard-plastic waste was mainly composed of PP accounting for about 48% of total hard plastic waste. In

Canada, around 9-11% of plastic waste is recycled, 4% is incinerated and the rest is dumped in local landfills[10]. Around 200 tons of plastic waste comprising of 50% polyethylene is generated every year in Qatar[11]. 1.5 million tons of plastic was consumed and only 20% of it was recycled in Australia in 2013. Eriksen et al., has reported that around 5.25 trillion plastic particles is present in the oceans and weighs around 268,940 tons[12]. Neither landfill disposal nor incineration of plastic waste is not the precise solution to this global issue as it releases toxic and greenhouse gases into the atmosphere and/or takes many years (decades) before it can degrade under certain conditions. Plastic accumulation in the sewers can give rise to many diseases as well as the possibility of flood during monsoon season. Plastic waste in water bodies has led to many deaths among fish, turtles, and sea mammals. This is due to entanglement of plastics acting like "ghost nets" and suffocating the marine creatures which ultimately leads to death[13]. Plastic pollution is real and is affecting marine and terrestrial life, soil degradation and causes air pollution.

1.2 Outline of Research

There are multiple research studies on the degradation of polymeric blends such as PP/HDPE, PP/LDPE, etc., but very limited studies are available in the literature comparing plastic waste containing PP with minimal inclusions of LDPE with multiple cycles of dynamic thermo-mechanical re-processing and their degradation behavior.

The objective of the study was to study the degradation behavior of PP/LDPE blends with 0-10 wt. % LDPE. The pathway used to conduct this study was described below:

- Extrusion of neat PP, neat LDPE and PP/LDPE blends using a twin-screw extruder.
- Using a pelletizer to produce pellets for characterization.

- Molding of samples using injection and compression molding equipment to study the mechanical and rheological properties of the samples. Melt flow rate, thermal properties and infrared spectroscopy were also conducted for characterizing the samples.
- Reprocessing of the samples using the extruder for up to five cycles and repeating steps two and three.

A summarized pathway is shown below in **Figure 3**.

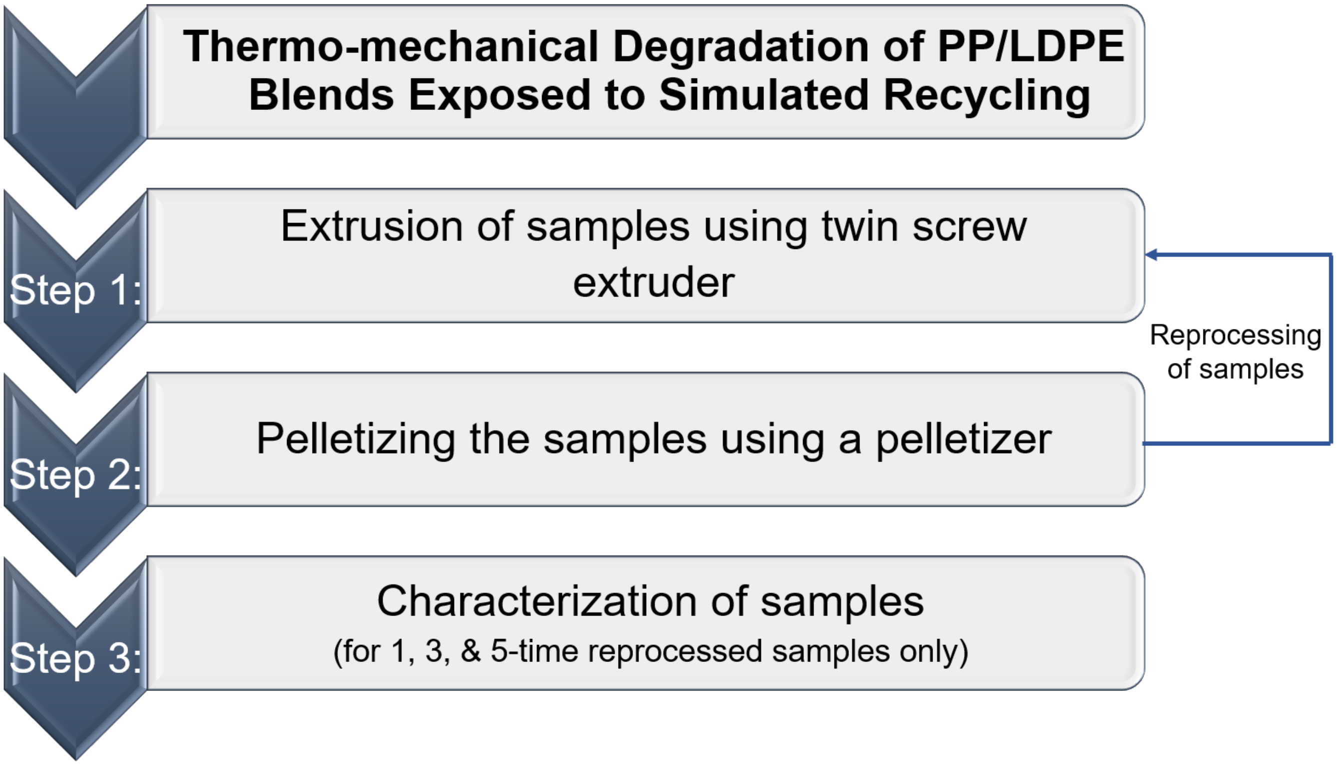


Figure 3: Research pathway to study thermo-mechanical degradation of PP/LDPE blends

1.3 Thesis outline

This thesis is composed of 5 chapters. The scope of these chapters is listed as follows:

- Chapter 1 briefly introduces an overview of plastic production, its relationship with population growth and major sectors of plastic usage. It also outlines the research pathway and thesis outline.
- Chapter 2 provides literature review of polyolefins, types of polyolefins and their properties. It also reviews the effect of polyolefin waste on the environment, sources of plastic waste, circular economy and different methods of recycling techniques.
- Chapter 3 presents the type and grade of polypropylene and low-density polyethylene used to conduct the study. This chapter also presents the different kinds of blends produced and the techniques used to characterize the blends.
- Chapter 4 reports the properties of the polypropylene/low-density polyethylene blends such as melt flow rate, rheological properties, thermal properties, mechanical properties, and infrared spectroscopy.
- Chapter 5 provides the overall summary, conclusions and recommendations for any future work.

Chapter 2

Literature Review

This chapter presents the relevant literature on different types of polyolefins, their properties, production technique, different types of polyolefin blend system, sources of plastic waste and their effect on the environment. Current applications of polyolefins, different types of recycling the plastic waste, and applications for the recycled plastic are also discussed. This review aimed to highlight the need for recycling of polyolefin waste and conversion of the waste into useful articles to minimize the environmental footprint of plastics. A version of this chapter is published as a review paper[5].

2.1 Polyolefins and its types

Polyolefins [PO] are polymers which are produced from compounds having at least one carbon-carbon double bond commonly known as olefins or alkenes. PO molecules are not suitable for higher temperature applications as these molecules have weak van der Waals forces resulting in low melting and crystallization temperatures[14]. The monomers, alkenes, are synthesized by cracking crude oil (i.e. breaking of carbon-carbon bonds in complex organic alkanes) into simpler hydrocarbon molecules. Types of cracking of crude oil include: Thermal, Steam and Fluid Catalytic cracking. Steam cracking is the principle method for producing olefins, lighter alkenes, such as ethylene and propylene; however lighter alkenes can also be produced by a dehydrogenation process of alkane molecules[15]. Large quantities of these polymers can be produced at lower cost by these methods.

The various olefins types are differentiated by the degree of crystallinity. Polyolefins are used for producing wide range of commercial products like pipes, packaging films, household bottles, automobile parts, disposable diapers, food containers etc.[14] The factors responsible for the success of polyolefins are: availability of monomers in large quantity and its low cost, the advances in reactions involving catalyst and ability of the polymers to blend with other polymers.

This class of polymer include high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), ultra-high molecular weight polyethylene (UHMWPE) polypropylene (PP), as well as other α-olefins and combination of these polymers. Majority of commercial products are produced by combining polyethylene and polypropylene and dominate the market in plastic industry but these polymers also contributes majorly to the waste disposed into the ecosystems each year[15]. This is due to its high stability and resistance to degradation; thus, increasing pollution and landfill all over the world. The material not only affects the environment during article production but also its chemical and biological inertness after the product's cycle possess a greater threat[16]. At present, the product recyclability is given a major importance along with the process of manufacture.

2.1.1 Polypropylene

Polypropylene was first commercially produced in the 1950s by G. Natta who produced PP by polymerizing propylene in the presence of an organometallic catalyst, such as titanium and aluminum. Following 1957, the Montecatini company along with Professor Natta produced the first stereoregular polypropylene. Four other processes have been developed since then for the manufacturing of polypropylene which includes slurry, bulk, gas-phase, solution techniques[17]. The slurry process is among the oldest technique to produce PP and generates polypropylene grades with high crystallinity. The gas-phase processes are more economical when compared to that of the liquid phase polymerization method[18]. In 1967, BASF commercialized the first gas-phase route called Novolen, but this process expanded to large scale only after 1983. The two industrially followed process for production for polypropylene is the Borstar process and the Spheripol process. Both these processes utilize loop reactors and gas phase reactors and are known to produce PP with good properties[18].

2.1.2 Polyethylene

Polyethylene (PE) is produced by a free radical polymerization mechanism when a branched structure is desired while linear polyethylene is produced by utilizing a Ziegler-Natta catalyst and other organometallic catalysts[17]. Ziegler-Natta catalysts, invented by Karl Ziegler and Giulio Natta in the 1950s, are catalysts that aid in the controlled polymerization of olefins to produce polymers with high molecular weight and high stereoregularity. Typically, these catalysts consist of transition metals such as titanium, chromium, and zirconium with non-transitional metals[19].

Low-density polyethylene (LDPE) is manufactured by free radical polymerization typically using an initiator of either an organic peroxide or oxygen and the overall process is carried out in either an autoclave or tubular reactor at very high pressures and temperatures[14]. The initiator is injected at different points in the reactor than the feed and thus is at a higher temperature while the heat is removed along the tube by the ethylene/polymer mixture[17]. The conversion of ethylene to polyethylene is higher in tubular reactors than in autoclaves as a result of more efficient heat transfer. The number average molecular weight of LDPE processed is less than 100,000 g/mol and the poly-dispersity index is between 3-20[17].

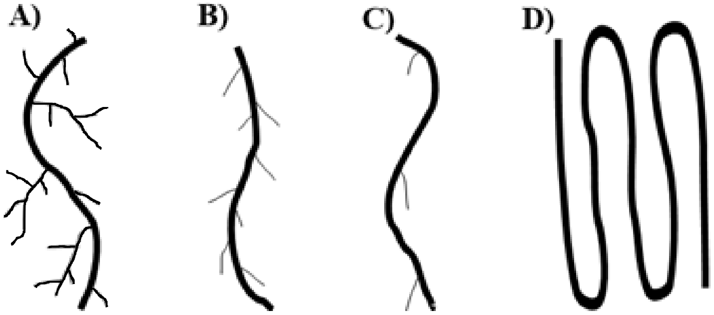


Figure 4: Polymeric backbone (or chain) examples of various Polyethylene types. A) LDPE; B) LLDPE; C) HDPE; and D) UHMWPE

As shown in **Figure 4** , LDPE has both short and long branches that relate to their lower crystallinity reducing the density of the macromolecule. As a result of the lower crystallinity and density, there is an increase in the ductility or toughness and transparency of LDPE allowing it to be used in applications such as food packaging.

In contrast, high-density polyethylene (HDPE) is a linear polyethylene polymer with very little to no branching formed by a polymerization reaction using a Ziegler-Natta catalyst (e.g. a mixture of titanium tetrachloride and alkyl derivative of aluminum) or supported chromium - Phillips[12, 15, 14]. HDPE cannot be made by free radical mechanisms as the short and controlled branching leads to easy packing of polymer chains resulting in a higher density macromolecule. The low degree of branching and subsequently high ordered chains give higher crystallinity compared to LDPE resulting in increased tensile strength, stiffness, chemical resistance and opacity. The molecular weight of HDPE is controlled during the heterogeneous catalyst polymerization process thus a wide range of HDPE may be obtained with varying molecular weights. HDPE is used in many day-to-day products such as milk bottles, detergent bottles, fuel tanks, piping application for sewage and water circulation, beauty product containers, and many more.

Linear low-density polyethylene (LLDPE), also referred to as ultra-low-density polyethylene (ULDPE), is also produced by using a catalyst such as Ziegler-Natta or supported chromium - Phillips allowing for the copolymerization of ethylene and α-olefins[14]. The co-monomers used for the polymerization are butene, hexene, and octene. These co-monomers typically are responsible for the short branches/sidechains, while; ethylene is responsible for the long linear polymer backbone. As the name suggests, this ethylene-based polymer has a low density with a short-chain branched structure. The molecular weight distribution of LLDPE is typically narrow. It has better mechanical properties as compared to LDPE and also finds application in the form of films in food packaging[20–22].

Ultrahigh molecular weight polyethylene (UHMWPE) like HDPE and LLDPE is produced by using catalysts like Ziegler-Natta but without any co-monomers. As implied by its name, the molecular weight of UHMWPE is usually very high ($>2\text{x}10^6$ g/mol) and because of this feature packing of its atoms is less efficient, resulting in the density of this polymer being very low. UHMWPE finds applications in the medical, electronic (e.g. porous battery separator membranes) and fibre industries because of its exceptional properties, such as high chemical resistance to acids, alkalis, and corrosive gases; low coefficient of friction; excellent wear resistance; and resistance to environmental stress cracking[20–22].

Medium-density Polyethylene (MDPE) and cross-linked Polyethylene are two other grades of PE. MDPE has a linear structure like LLDPE but has a density value that is in between HDPE and LLDPE. MDPE is also produced by the copolymerization of ethylene and α-olefins by using the Ziegler-Natta catalyst. Its main application is in the piping industry primarily used as an overcoating material but also can be found in areas like geomembranes as well[20]. Cross-linked PE is produced by crosslinking molecules through strong chemical bonds (i.e. covalent bonds).

Peroxides and silanes are some of the chemical agents used for crosslinking for the chemical process, while electron radiation is used for physical crosslinking processes. The final product has enhanced toughness, low creep, and also finds an application in piping[20,21].

2.1.3 Other Polyolefins

Polybutene-1 can also be synthesized by using a Ziegler-Natta catalyst when desired for a specific application. It was originally produced to be used as a piping material to transport water. It shows better creep resistance than both PE and PP but ultimately it couldn't make a mark in the market as the pipes underwent huge failure by deforming more quickly when in use[14].

Polyisobutylene (PIB) is a homopolymer of isobutylene and was first synthesized in the 1920s by I.G. Farben by cationic catalytic polymerization. It is used as a binding agent in the making of explosives as well as medical sealants due to its low permeability properties. The lower molecular weight PIB allows for its usages in sealing applications; while, the higher-molecular weight versions are used as toughening agents in plastics[14].

Ethylene propylene diene (EPDM) is a saturated elastomeric thermoplastic material produced by the copolymerization of ethylene/propylene and unsaturated diene with applications typically in the automotive, electrical, coatings and construction industries. Generally, dienes are added with 2 to 5 wt.% and the commonly used ones are dicyclopentadiene (DCPD), 1,4 hexadiene, and ethylidene norbornene (ENB). Ultimately, the overall properties will be dependent on the ethylene to propylene ratio; higher propylene content aids in low-temperature stabilization while high ethylene content provides better strength[23,24]. As well, commercially available grades of EPDM vary on additives (i.e. oil and stabilizers), molecular weight and distribution, type and amount of third monomer unit (i.e. ENB), and the resulting microstructure. Compared to regular diene rubbers, EPDMs main benefits are its high resistance to ozone and temperature, good heat aging resistance, good chemical resistance, excellent abrasion, and tear resistance as well as low specific gravity[23]. Typically, EPDM is produced by vanadium-based catalysts initiated by alkyl-aluminum compounds; however, in the past couple of decades, soluble metallocene catalysts have been investigated. The benefits of using metallocene catalysts (e.g. Ziegler catalysts) include the avoidance of using toxic vanadium, their ability to affect the random distribution of monomers, and control over the materials molecular weight distribution[24].

2.2 Properties of Polyolefins

PO resins involve weak Van Der Waals forces which result in their low melting and crystallization temperatures, thus making it inappropriate for applications that may require higher temperatures and pressures without further modification[14]. The monomers, olefins, are synthesized by the cracking of crude oil (i.e. the breaking of carbon-carbon double or pi-bonds in complex organic alkanes) into simpler hydrocarbon molecules.

The properties of PP depend on the crystallinity, molecular weight, and distribution as well as the type of co-monomer used. The increase in crystallinity improves properties like stiffness, flexural strength, and yield stress, but also decreases the material’s toughness like impact strength[25]. PP is more versatile when compared to other polyolefins due to its superior properties (i.e. chemically resistant to many chemicals and superior abrasion resistance). The aforementioned properties of polypropylene can be controlled in many ways during its polymerization and its crystallinity is determined by the internal structure which gives different properties as well (e.g. mechanical and thermal properties). The tacticity of PP generates three sub-classes for it: isotactic (all substitution groups aligned on the same side of the molecule), syndiotactic (alternating substitution groups along molecule), and atactic (random arrangement of substitution groups along molecule).

Isotactic polypropylene (iPP) is most widely used when compared to its other stereoisomer configurations (e.g. syndiotactic polypropylene (sPP) and atactic polypropylene (aPP)) because of its exceptional mechanical and thermal properties. Atactic PP finds application in adhesives and some low-cost applications. The melting point of iPP is 165 °C due to the stereoregularity while a non-stereospecific PP has a melting temperature window of 160-170 °C. Polypropylene finds application in many areas including, but not limited to, the automotive and textile industries. In the automotive industry, PP finds use in bumpers, gas cans, and internal components (e.g. dashboards)[20]. When PP is spun into fibers containing a high molecular weight, it is successfully used as ropes, upholstery, and carpets in the textile industry. In the food industry, it is used in the form of disposable food containers that are made by a thermoforming process.

Similar to PP, polyethylene is a thermoplastic polymer with high chemical resistance, toughness, remarkable insulating properties, low coefficient of friction, etc.[16]. There are many forms of polyethylene that differ in the nature of branching[20].

The various polyolefin types, differentiated by the degree of crystallinity and associated physical properties, are used for producing a wide range of commercial products like pipes, packaging films, household bottles, automobile parts, disposable diapers, food containers, etc.[14]. The main factors responsible for the success of polyolefin production are the availability of monomer units, the cost of the raw materials (i.e. petroleum prices), recent advancements in polymerization reactor technology, and chemistry. As shown in **Figure 5**, polypropylene in 2018 held the largest PO market share of 19.3% (69 Mt) which is an increase of 24% from 2010 (56 Mt) in applications of food packaging, snack wrappers, hinged caps, microwaveable containers, thermoplastic pipes, interior automotive components, banknotes, etc.[2,26]. On the other hand, HDPE and LDPE held a global market share of 12.2% (44 Mt) and 17.5% (63 Mt), respectively, in 2018[2]. Since 2010, HDPE production increased by 23% in the products of toys, milk bottles, shampoo bottles, thermoplastic pipes, houseware appliances, etc.[2,26]. LDPE has also increased in the amount converted since 2010 by 25% in the finished consumer goods of reusable bags, food trays, and containers, agricultural films, food packaging, cling wrap, etc.[2,26]. Lastly, all other polymers (e.g. PVC, PET, PUR, PS as well as EPS, ABS, PC, PMMA, and PTFE) combined have shown a substantial increase as well year over year. These polymers also contribute greatly to the waste disposed of the ecosystems each year[15]. This is due to its high stability and resistance to degradation; thus, increasing pollution and landfill all over the world. The material not only affects the environment during article production but also its chemical and biological inertness after the product's cycle possesses a greater threat[16]. At present, the product recyclability is given major importance along with the manufacturing process.

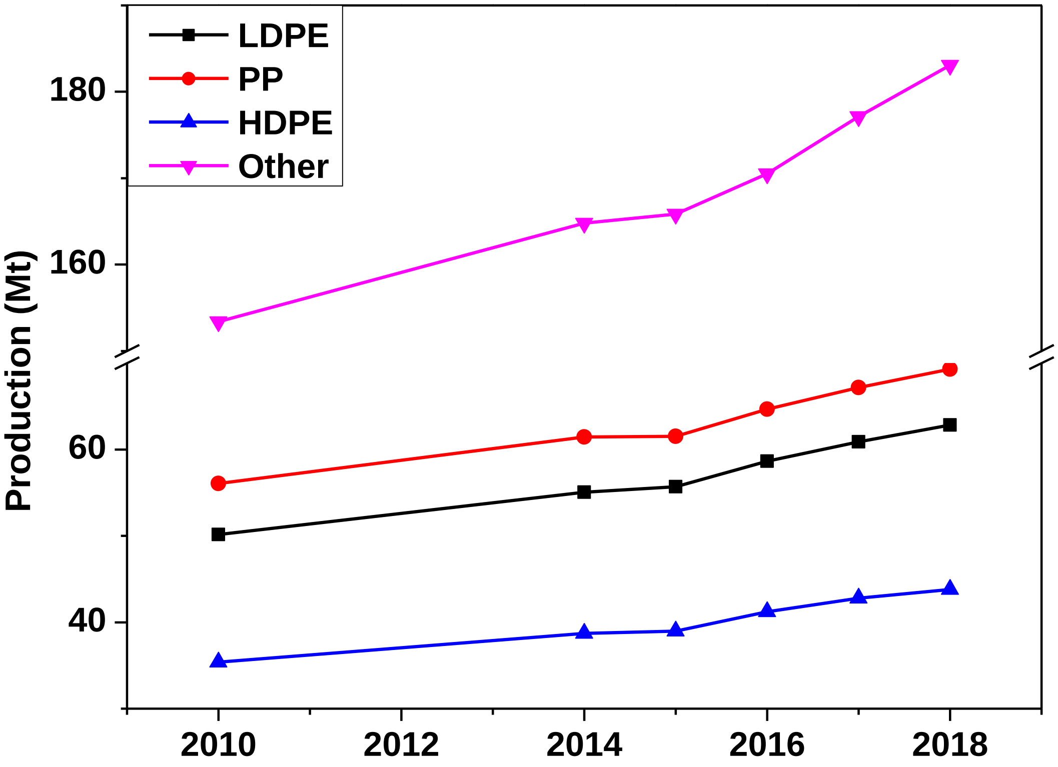


Figure 5: Polyolefin production breakdown over the past four years [2,3,26–30]

2.3 Polypropylene – Low density polyethylene blend system

Polypropylene (PP) and low-density polyethylene (LDPE) are widely used thermoplastic materials by various plastic industries. The processability and impact strength of PP, and environmental stress cracking resistance and heat resistance of LDPE is improved by using blends of PP and LDPE[31]. Liang et al., studied the melt and mechanical characteristics of PP/LDPE blend system with concentrations of LDPE from 0 -100 wt. %. It was concluded that when the melt viscosity of either of the components, i.e., PP or LDPE, is closer to each other in value, the melt flow rate of the blend system was higher than the pure components and reached maximum with 50:50 ratio[31]. Salih et al., compared PP/HDPE and PP/LDPE blends for its mechanical performance[32]. It was reported that as the content of LDPE increased from 0 to 80 wt. % the tensile strength, Young's modulus decreased. Similar observation was observed for impact strength results[32]. The same study showed that the PP/LDPE (80/20) was immiscible from SEM results. To enhance the properties of two immiscible thermoplastic binary system, a third component, a compatibilizer, can be added to make the system more compatible. In case of PP/PE blend system, ethylene-propylene rubber (EPR) is widely used for compatibilization[33]. The propylene and ethylene units in EPR gets inserted within PP and LDPE respectively and improves compatibility. Compatibilizers like maleic anhydride-grafted polypropylene (MAPP) and maleic anhydride-grafted polyethylene (MAPE) are classified as reactive compatibilizers[33]. Tselios et al., in their study blended PP/LDPE with MAPP and poly(ethylene-co-vinyl alcohol) (EVAL) by in situ reaction[34]. The addition of compatibilizers improved the mechanical properties such as elongation at break, tensile strength and impact strength[34]. An increase of 44% in impact strength and 47% in elongation at break was observed when unmodified 75/25 wt.% (PP/LDPE) was compared with 10 wt.% compatibilizers in the same 75/25 wt.% sample. Su et al., in their paper studied the effect of 75/25 wt.% (PP/LDPE) blend with the addition of compatibilizer and antioxidant agent[35]. The compatibilizer was MAPP and antioxidant agent was hindered phenolic. The highest value for tensile strength, %strain at break and modulus was observed for sample with 9 wt% and 0.15% of compatibilizer and antioxidant agent. However, in this thesis, there was no addition of compatibilizer or antioxidant to the PP/LDPE blends. This was to understand the effect of temperature and shear in PP/LDPE blends during multiple extrusion process.

2.4 Degradation mechanism of PP and LDPE

Common degradation schemes of plastics (PP, LDPE, LLDPE, etc.) or their blends can be divided into three types: thermal degradation, mechanical degradation, and thermal oxidative degradation[36]. The properties which typically vary after any kind of degradation are viscosity, melt flow rate (MFR), molecular weight, mechanical properties[37–40]. The degradation mechanism not only affects the properties of the material but also the compatibility of the blends[41]. A simplified schematic of isotactic polypropylene (iPP) and LDPE undergoing a thermo-mechanical degradation mechanism is shown in **Figure 6**. Thermo-oxidative degradation is a type of degradation in which the formation of either peroxyl radical or alkoxy terminate the reaction with the formation of a crosslinked product[41]. As shown in **Figure 6**, the thermo-mechanical degradation of iPP and/or LDPE might lead to the formation of lower molecular weight molecules (e.g. oligomers) due to chain scission or it could lead to the generation of heavier molecules due to cross-linking (mostly in the case of LDPE)[42]. Jin et al., studied the effect of repeated extrusion on LDPE for up to 100 extrusion cycle[43]. It was observed that chain scission and cross-linking occurred simultaneously in case of LDPE. They concluded that up to 40 extrusion cycles LDPE could be reprocessed and no significant change in processability or mechanical properties can be observed, this was due to the simultaneous effect of chain scission and crosslinking mechanism[43].

da Costa et al., studied the effect of degradation of PP during multiple extrusion and temperature during reprocessing[44]. They found that degradation of PP is extensive at higher processing condition while at temperatures below 240 °C and lower extrusion cycles the degradation was not significant. Also, degradation in PP was due to chain scission, i.e., formation of smaller molecules when subjected to multiple extrusion cycles[44].

To protect the polyolefins from degradation, antioxidants are added[45]. Irganox is one such antioxidant added to polyolefins to prevent oxidative degradation. Hindered phenols are added to iPP to stabilize it and is the most preferred antioxidant used for polyolefins. Phenolic antioxidants act as radical scavengers, i.e., it reacts with the radical formed during oxidative degradation and forms unreactive compound[46]. It inhibits oxidation by donating H-atom to the polymer substrate radical. Ambrogi et al., in their study compared natural antioxidants to phenolic antioxidant[47]. From the TGA analysis, it was observed that the phenolic antioxidant was more effective than natural antioxidants. Amongst the natural antioxidant, pomace extract provided long term stability to the polymer[47].

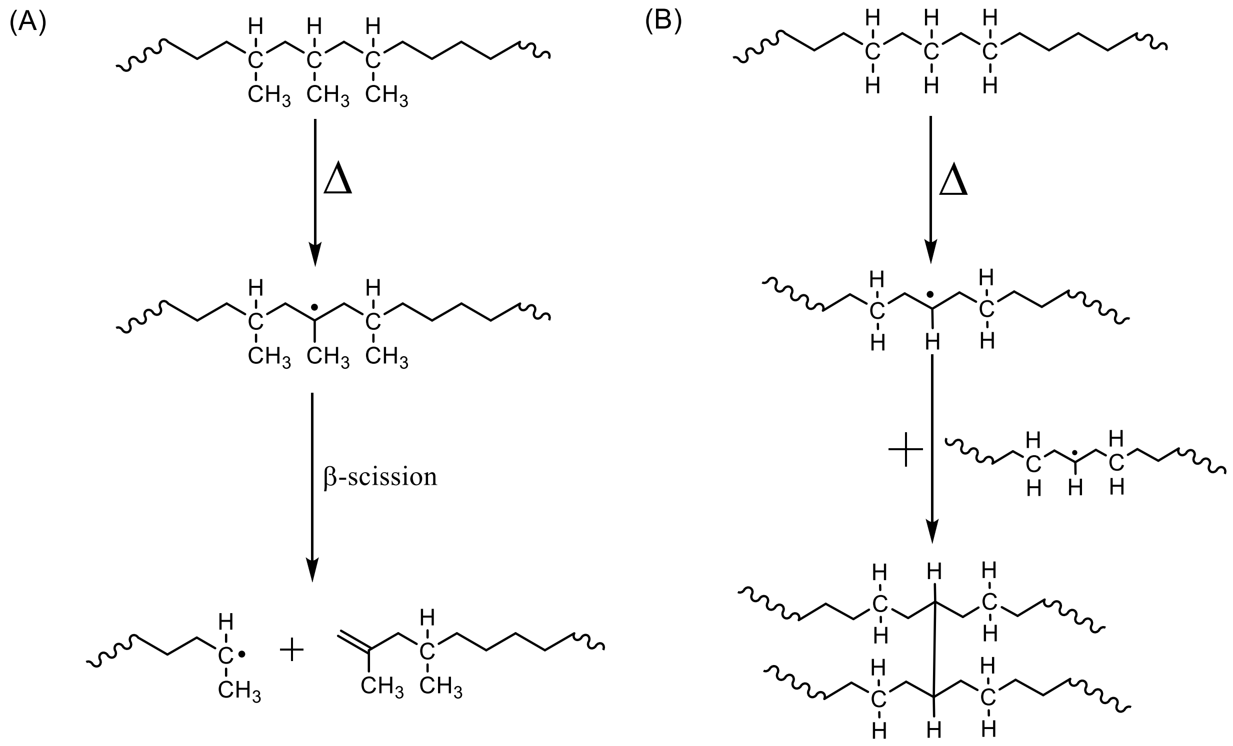


Figure 6: A simplified schematic showing the thermo-mechanical degradation mechanism of (A) iPP; (B) LDPE[41]

2.5 Effect on the environment

2.5.1 Plastic waste

The production and conversion of raw materials into plastic feedstock (i.e. extraction, refining, and transportation) are some of the main contributors to plastic waste accumulation. Pollution due to plastic waste accumulation is an ongoing and everlasting battle as the amount of waste increases each year as plastic conversion rates also increase due to population demands, as shown in **Figure 1** and **Figure 7**. Plastic waste or debris is often characterized by their size into macro (>22 mm), micro- (<5 mm), and nano-debris (>100 nm). Macro-debris encompassed all large size plastic waste from macro- to mega-debris[48], with the most abundant type of product in this category being packaging materials. Micro-debris is usually a product of environmental pollution created by discarded plastic and eventual disintegration[48]. Microplastics are usually a mixture of size, shape, colour, density, etc.[48,49]. Lastly, nano-debris is generated mostly from cosmetics and personal hygiene products as well as the breakdown of post-consumer waste[48].

Each year, 2.01 billion tonnes (Bt) of municipal waste is generated with the higher-earning countries contributing 34% (689 Mt) of that[50]. It has been reported that the global recycling rate is approximately 18% with the EU, NAFTA, and China representing 30, 25, and 9% being the main contributors[51]. Breaking down global plastic waste accumulation in terms of polymer types, LDPE and PP are the two biggest contributors with 57 and 55 Mt being collected each year; while, HDPE is close behind with 42 Mt generated. In Canada alone, 87% of plastic "waste" ends up in a landfill as opposed to being recycled which represents about 9.7 Mt of plastic resin and an estimated loss of 7.8 billion dollars (CAD) capital [4,52]. Another source has reported that the USA has generated an average of 20.8 Mt of plastic resin in landfills between 1990 and 2017[53]. Packaging (mainly polyolefins) material is one of the major contributors towards plastic waste with about 40% (276 Mt) single-use packaging in 2018[50,54]. As shown in **Figure 7**, Europe accounts for 6.5% (17.8 Mt) of the packaging waste collected[2] while another study reports that Australia accounted for 0.33% (0.91 Mt) of the total[55]. It can also be observed in **Figure 7,** that both Canada and the US are both behind the EU in both recycling and incineration or energy recovery rates. It should also be noted that Canada's landfill data, in **Figure 7,** is combined with its incineration data due to their methods of collection.

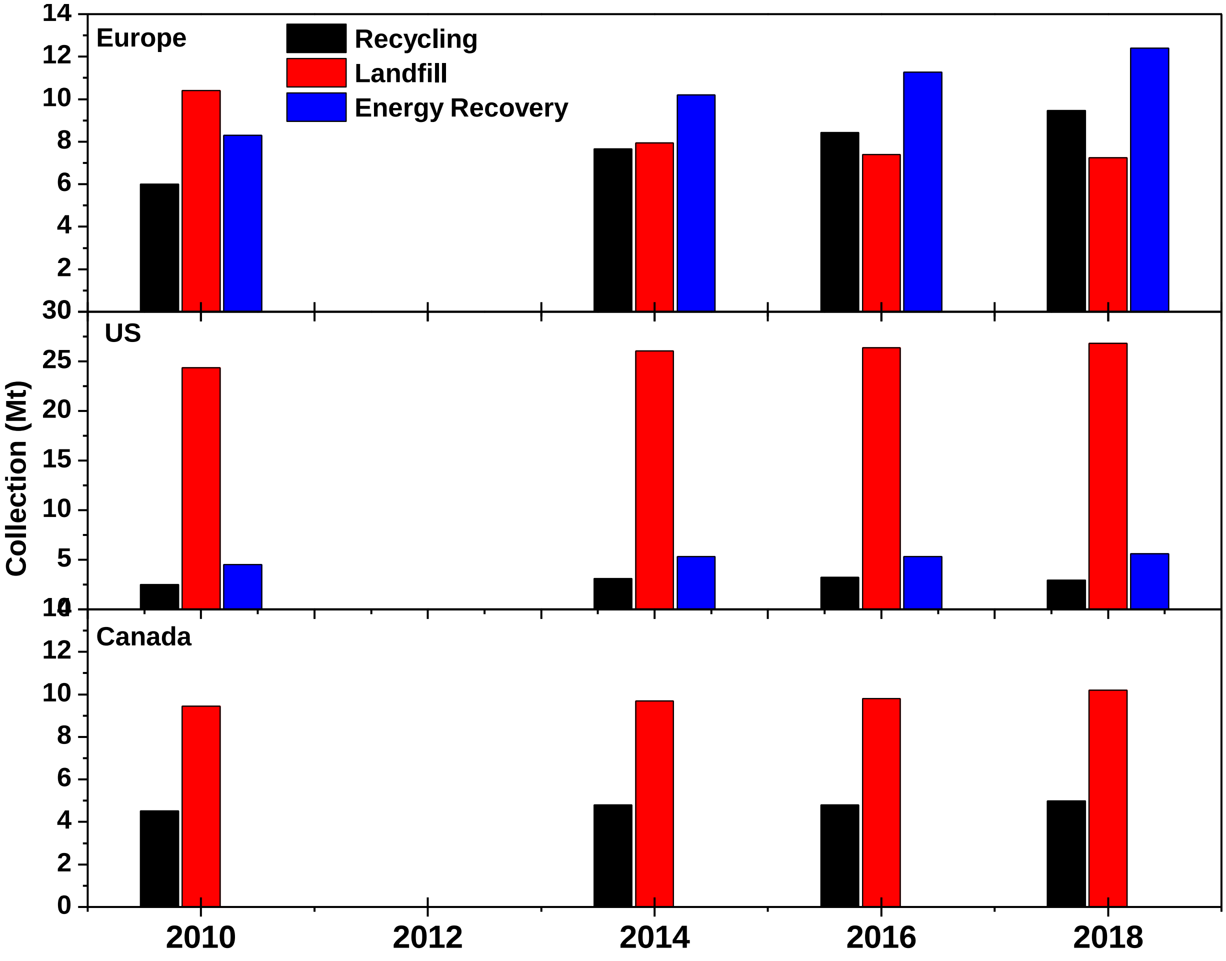


Figure 7: Polyolefin waste collection amount in Europe, by method, over the past decade (adapted from Plastics Europe)[2,3,26–30,56,57]

Most of the polyolefin products on the market have shorter life cycles while in use and is usually thrown away after their usage. The different types of plastic typically have different service life expectations, usages, and environments. Other important considerations with plastic components are that some finished goods are products consisting of only one component (*e.g.* a bottle cap); while others are a part of a system of products (*e.g.* a sealed bottle (cap + bottle) or an assembled vehicle) which are harder to recycle. In terms of service life, some polymers will only have an active service life of one to two years (e.g. filters) and some products may have a service life of 10 or more years (e.g. automotive components).

The depletion of resources and environmental concerns due to plastic waste have pushed researchers and government legislators towards studying the recyclability and reusability of plastic waste. As different polymers break down at many different rates, the collection in a landfill is difficult to correlate with the demand in the same timeline**.** Recycling is the process in which municipal and industrial waste is collected, segregated/separated, cleaned, and reprocessed to yield a new product or become a secondary raw material by offsetting virgin plastic[13]. The current recycling methods implemented globally to reduce plastic waste include thermo-mechanical, -chemical processes, devulcanization, and energy recovery. There is also an alternative to the outlined recycling methods which is the most economical, i.e. reuse.

2.5.2 Circular Economy

Since and even before the industrial revolution the linear cradle-grave economic model greatly depends on easily accessible materials and energy from non-renewable and/or slow to replenishable sources. Due to environmental concern issues as well as price volatility, supply chain interruptions/hindrances and pressure on valuable resources have compelled companies to look for alternative and sustainable materials and energy supplies. According to the Ellen Macarthur Foundation, “A circular economy is one that is restorative and regenerative by design and aims to keep products, components, and materials at their highest utility and value at all times, distinguishing between technical and biological cycles.”[58,59]

The goal of this new economic model is to separate economic development from non-renewable resource consumption, on a global scale. A common theme with a circular economy is sustainability, which arises from the assumption that the modern economic production and consumption cycles systematically have led to a depletion of natural resources while ignoring the socio-economic costs of overuse[60]. Sustainability is generally governed by three principles:

efficiency, consistency, and sufficiency as shown in **Figure 8:** Graphical representation of the nature of sustainability and its components. Adapted from Towards a Sustainable Circular Economy Remarks on Plastic and Wood-waste Sector.

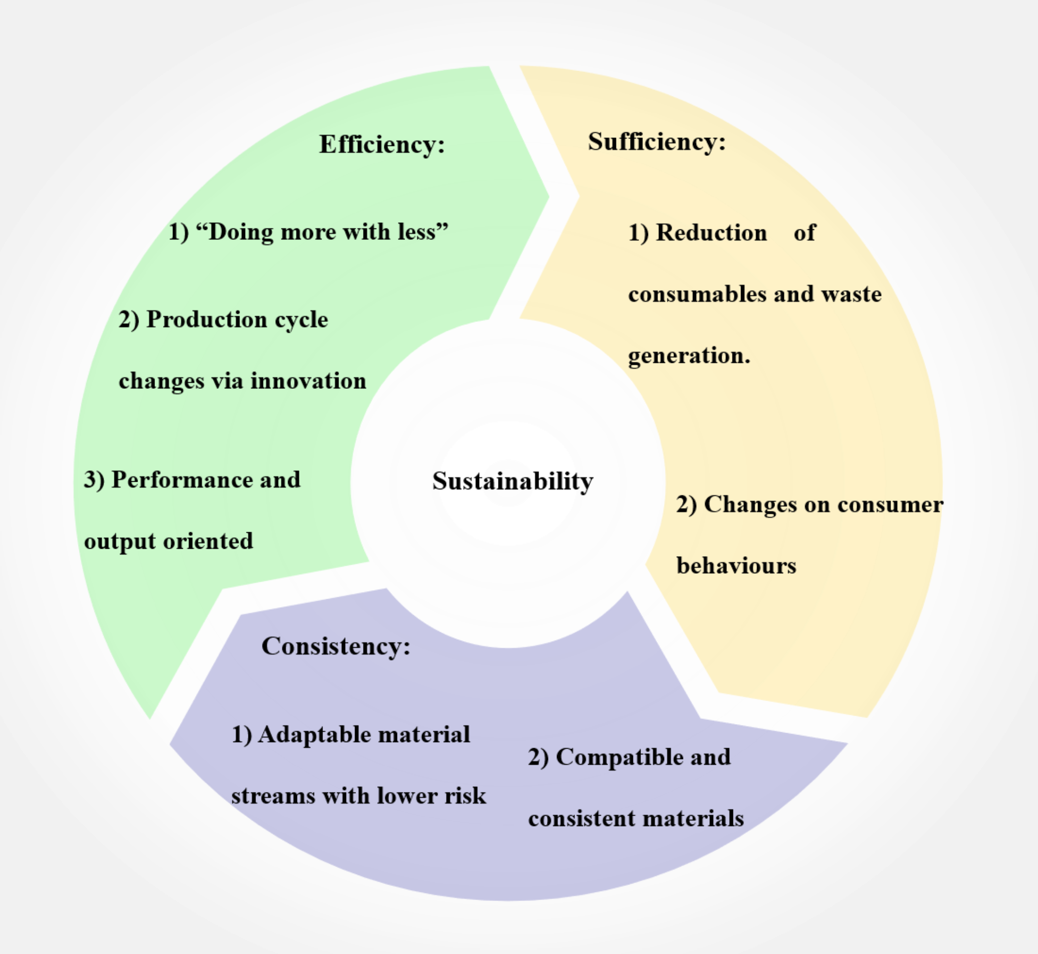


Figure 8: Graphical representation of the nature of sustainability and its components. Adapted from Towards a Sustainable Circular Economy Remarks on Plastic and Wood-waste Sector.[60]

The sufficiency principle relies on lifestyle changes that shift from a very materialistic society with superfluous consumption activity to a more post-materialistic and minimalist attitude[60]. The efficiency principle aims to reduce as much waste as possible while also producing the desired product or service for the end-users. The last principle, consistency, relates to having the material and production as well as their associated energy costs being completely integrated into natural cycles. In other words, the consistency and efficiency principles are dependent on innovations in technology and company incentive direction while, sufficiency is human consumer-mentality which is based on trends and societal views.

With the shift towards a new circular economy, there is room in the market for bio-based and sustainable as well as recycled plastic components to break through and overcome the current petroleum-based market dependence[61,62]. For example, common fillers used in the automotive industry are glass fibre and talc, which are not sustainable or easily recyclable and are typically dense. However, if they were replaced with a more sustainable lightweight bio-based alternative (i.e. plant fibre, wood, or biocarbon based) then the overall environmental impact will be lowered while also helping the fuel economy[63]. Currently, some of the biggest challenges facing sustainable plastics are technological and economic feasibility. Most bio-based or sustainable plastics are difficult to manufacture due to the refining or extraction processes being more expensive and complex when compared to petroleum plastics as well they are not as thermally stable[6465]. Targeted market research projected that by 2020 the production of bioplastics will reach approximately 3.45 Mt representing about 0.96% of the overall global polymer production[64].

Examining one case study of composite systems (e.g. PP with glass fibre and/or talc) that are currently implemented into vehicles are typically difficult and costly to recycle and/or environmentally harmful due to where it may end up. In North America, when automobiles are at the end of their useful lives they are usually given to a dismantler for disposal. The dismantler removes any reusable or recyclable parts as well as any hazardous or valuable materials or components (i.e. catalytic converters)[66]. Vehicle dismantlers have to follow the International Dismantling Information System (ISID), developed by the automotive industry, in order to give directives for the end-of-life of vehicle components[67]. Unfortunately, the sorting after dismantling is increasingly becoming more and more complex as the vehicle components become more complex in design (e.g. polymer blends, multilayered plastics with each layer composed of different plastics types or even metal-based layers, etc.) compared to virgin plastic. The bulk of a vehicle (41%) is typically an unusable mixture of many different types of plastic after dismantling. Although it is important to think of sustainable and alternative materials, the design of the end-of-life component is also an important parameter to consider. In the past few years, considerable research has been devoted to searching for alternatives to the current petroleum and dense filler materials used today for automotive applications. Behazin et al., researched substituting in a sustainable biobased carbon from pyrolysis of miscanthus fiber which is also a carbon-neutral product due to the plants' natural CO_2 absorbance[68–70]. They found that the biobased rigid filler compared well to the conventional formulations, for interior PP-based parts, that are currently implemented while also having a significant reduction in the product’s density resulting in a smaller environmental impact.

2.6 Current Recycling and Reuse Practices

Different techniques of recycling and the reuse technique are presented in the following sections. Mechanical recycling is collecting the waste and then reprocessing it. This technique is widely used worldwide. Chemical recycling technique converts polymers back into monomer units by changing the chemical structure. Energy recovery is a process wherein energy is recovered from the plastic through controlled combustion and conversion into liquid fuel. Lastly, reusing of plastic waste is the most preferable end of life option as plastic produced for a specific application or multicomponent plastics may not possess the required specifications for regular municipal recycling. General keys to successful polymer recycling are:

1) Recycling the material generates business incentives by obeying the laws of economics. Quite often the recycler is faced with an uncertain consistent material supply; changing governmental policies (e.g. curbside pickup frequency and material allowance); and competitive and more reliable products[51,71].
2) Recycled material must be able to be sorted and based on good science and technology[51,71].

Recycling must be compatible with modern infrastructure and population density[71]. For example, the recycling needs of New York City, New York, USA would be much greater than that of Kyoto, Japan.

2.6.1 Thermo-mechanical recycling

Thermo-mechanical recycling, also known as primary recycling, is where the municipal wastes are collected are processed into a product with similar or comparable properties with that of the original one. Thermo-mechanical recycling of polymers is a crucial component of reducing the consumption of non-renewable resources that are needed for the synthesis of the corresponding monomer units. Also, recycling takes less energy than producing new versions of the product[72]. A major limitation in thermo-mechanical recycling is the potential for contamination of waste streams which makes sorting and separation costly and next to impossible without sophisticated equipment. All types of thermoplastics known to mankind can be recycled mechanically and this process is also known as re-extrusion or closed-loop process[13]. Primary recycling method usually involves reducing the size and separating different polymer wastes from a mixture without changing the chemical structure of the recyclates. This method uses lower temperatures and energy compared to chemical, thermal, and enzymatic techniques, allowing the recyclates to retain their structure and most of their molecular weight/ length[72].

The most important step in mechanical recycling is the sorting of various plastics according to the resin type. The process describing this type of recycling begins with segregating the plastics either manually or by automated machines. The steps involved in mechanical recycling are separation and sorting, baling, washing, grinding, and compounding and pelletizing[36]. After the collection of plastic waste, sorting of these wastes is done based on density, chemical composition, size, and color. Wastes which include plastic bottles, fluid containers, metal cans, and Tetra Pak® are first sieved by rotary mechanism and then blown with wind sifter for removing the loose paper. Magnetic separator is used to remove ferrous articles followed by a ballistic separator. These are then placed in the sorting cabin for manual labor checks for some inconsistency and sorts it. Contaminants are removed by magnetic separation or complex spectrophotometric distribution technologies[13]. Separation and identification of plastics can be done in many ways: Fourier Transformed Infrared (FTIR), magnetic density separation, HSI technology, froth floatation method, X-ray fluorescence, laser-induced breakdown spectroscopy and triboelectric separation[73]. The froth floatation method is used for the segregation of plastics from one another[74]. This technique was first discovered by Alter in 1978 citing the difference in the critical surface tension between plastics. The separation of PVC, PET (similar density) by this method was studied by many researchers and it was concluded that around 95-100% of PVC and PET can be separated[75–79]. FTIR technique is another characterization technique used to identify the plastics. FTIR gives the spectra of the sample and compares it to different models present in the database. This is used to identify the type of polymer and segregate it for further processing. Carvalho et al., 2010, presented a paper about the identification of plastics using FTIR. In this paper, PVC, PET, and PS were identified using FTIR and separated by froth floatation method[74]. Warren and Burns (1988) concluded that primary recycling is very easy and can be done without many precautions, but the waste collected must be clean and segregated properly[80,81].

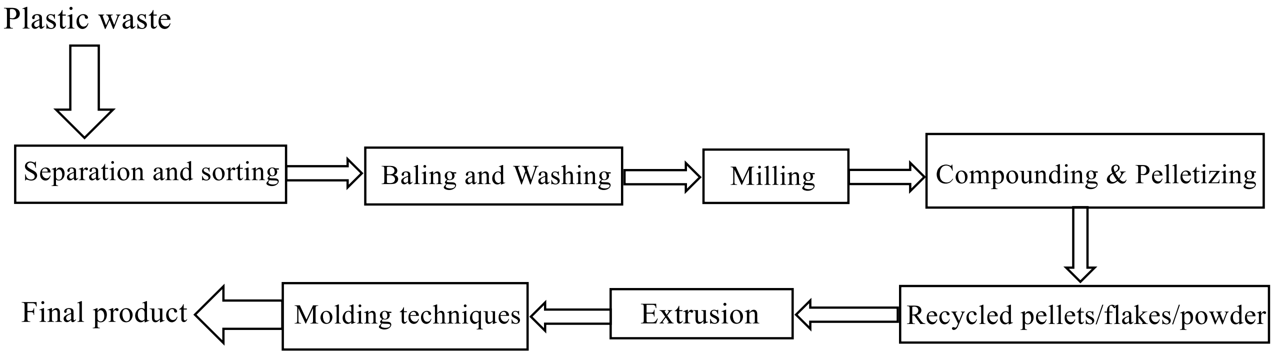


Figure 9: Mechanical recycling process block diagram

The final step in thermo-mechanical recycling, compounding and pelletizing of recyclates, is usually carried out by using either a twin-screw extruder or single screw extruder depending on the amount of mixing required. Once the extruded product is obtained it is passed onto the molding process. The challenges with the recycling of plastics are the low value of the material and additives and fillers present in the plastics[13].

2.6.2 Chemical Recycling

Also known as feedstock recycling and tertiary recycling[82], chemical recycling is a process in which a finished plastic product is reduced into a monomeric form or some new raw material. Chemical recycling of monomer feedstock is increasing in interest as it is ideal for the preservation of finite non-renewable resources as well to decrease non-degradable waste thus protecting the environment. The different types of chemical recycling include gasification, methanolysis, glycolysis, hydrolysis, pyrolysis, hydrogenation, and ammonolysis. The process is selected based on the product that has to be recycled. For example, the degradation of PET to dimethyl terephthalate and ethylene glycol by methanol is called methanolysis[83]. Chemical recycling of PET is a classic example of this technique as it can completely depolymerize into terephthalic acid, dimethyl terephthalate (DMT), bis(hydroxy ethylene) terephthalate (BHET) and ethylene glycol. This process is carried out by treating PET with methanol at 180-280 °C and 20-40 atm. The products of this reaction find applications as plasticizers, textile dyes, antibacterial drugs, epoxy resins, etc.[83]. Gasification is the process by which the carbon-based materials are reacted with air to form simpler molecules. In Europe, the most common types of feedstock recycling methods are Chemical depolymerization, Gasification, Thermal cracking, and Catalytic conversion. LyondellBasell uses its own MoReTec recycling technology, which is a technique of pyrolysis using a catalyst[84]. BASF, one of the leading chemical industry, is also setting up units for chemical recycling of plastics. ChemCycling is the name given by BASF to its chemical recycling process. In this process, the plastic waste is broken down into oil or gaseous products, which can be used as raw materials for any other process by the chemical industries. BASF supports chemical recycling of plastic waste because the amount of landfill and incineration of plastic waste can be reduced, increase in demand for reducing plastic waste and the pyrolysis oil produced can replace fossil feedstock and save natural resources[72]. Advantages of chemical recycling units like pyrolysis and gasification are that the units are very flexible and can be set-up according to the waste that needs to be recycled. The quality of the products from the recycled unit can be controlled and also it generates energy as a by-product[13]. Even though it has several advantages, the main drawback of feedstock recycling is that the segregation before recycling should be perfect. For example, products containing chlorine content, which is directly recycled without any pre-sorting or pre-treatment can produce a product with low quality as it will be corrosive.

In the case of plastic bottles or containers (see **Figure 10**), they can be collected and sent to the reprocessing unit. In the reprocessing unit, the plastic waste is first sorted and shredded. In the sorting unit, the PET bottles are separated from different materials and then ground. The shredded waste is now separated using an air classifier to remove the lighter fraction (e.g. labels). The heavier fraction is washed in a scrubber. This removes the residues contained inside the bottles and any dirt is washed out of the fraction. Then, this output is sent to a sink classifier to remove the base cups (HDPE) and rings (PP) from the PET fraction by using density difference with respect to water. The heavier fraction which sinks into the classifier is then passed through a separator by using magnets to remove any aluminum which might be present in bottle caps with HDPE or PP[83].

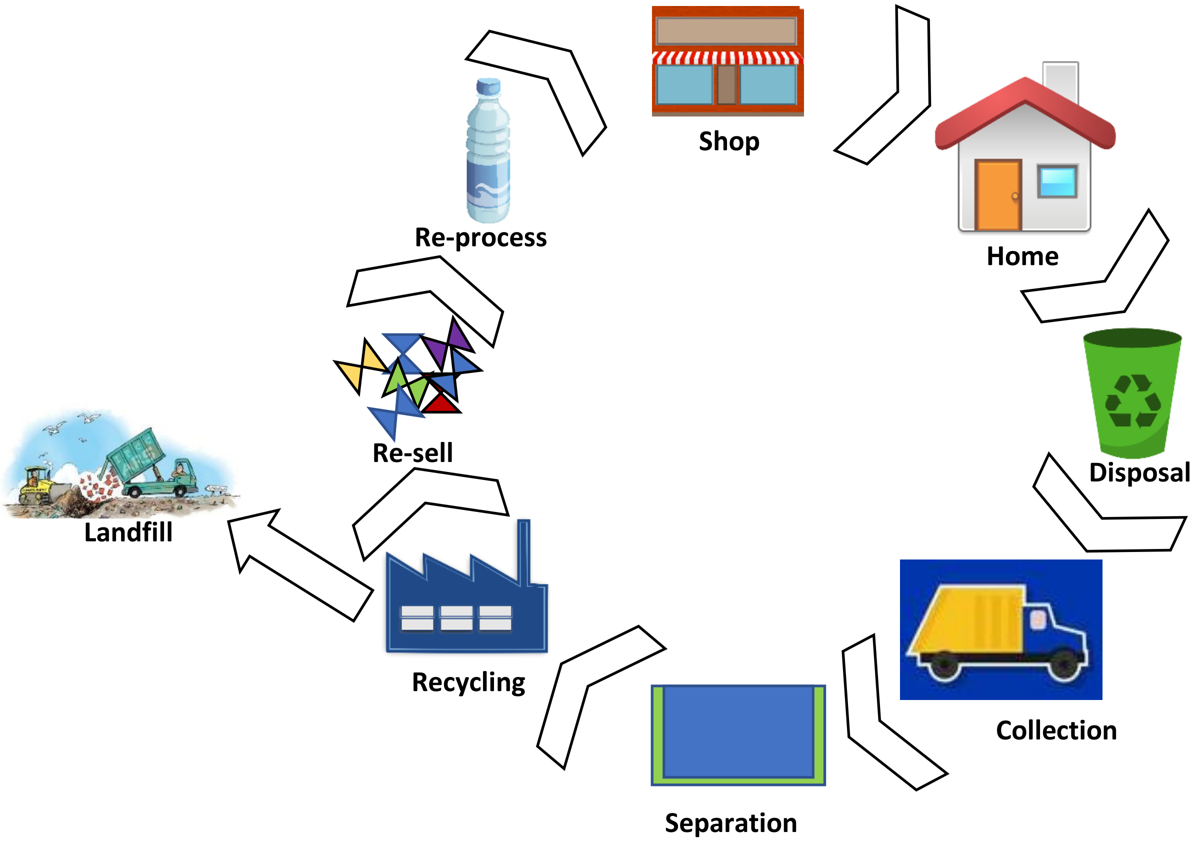


Figure 10: Recycling process flow of commodity waste plastics (e.g. PET bottles)

Pyrolysis of HDPE is another example of chemical recycling. This process yields light olefins and automotive fuel hydrocarbons[85–87]. Microwave-assisted pyrolysis using activated carbon yielded better hydrocarbon products than conventional coke bed[85].

Another form of chemical recycling of mixed polymer wastes is to use solvent extraction techniques for the purposes of turning the waste plastic into valuable resources of high purity (e.g. monomer units) to create new products. Generally, solvent extraction allows for the removal of impurities (e.g. additives), dissolution of homo- and heterogeneous polymers, and finally reprecipitation[51]. The polymer waste is dissolved into an ideal solvent and the selected polymer units are crystallized. Ideally, a good solvent that can either dissolve the target polymer or all other constituents will be a good candidate for selective dissolution. Overall, the dissolution process is predominately affected by the type of solvent as well as the polymer type, size, molecular weight, and dissolution temperature, time, and concentration[51].

2.6.3 Energy Recovery

Energy recovery is a process wherein the plastics are burnt and the energy, which is released in the form of heat is utilized and used for different applications. Another term given for this process is incineration. This technique was being widely followed since the beginning of plastics era but due to the toxic gases released during incineration, which in turn causes global warming this process has become less favourable. Incineration reduces the amount of waste dumped into landfill and also produce energy from the wastes[73]. Also, plants within the city limits, energy production, continuous feed resulting in high yield are additional advantages of incineration technology. Calorific values of known plastics are given in **Table 1**. The limitations of energy recovery include expensive operation, high maintenance cost, inviable results for materials with high moisture and chlorinated compounds, and high ash content[88]. On burning, plastics releases toxic and noxious dioxins that cannot be released directly into the atmosphere[36]. Thus, environmental regulations must be followed, pollution prevention measures have to be incorporated and the process has to be carefully monitored.

Table 1: Calorific values of plastics[73,89,90]

Polymer type	Calorific value (MJ kg^{-1})
Polyethylene terephthalate (PET)	24.13
Polyethylene (PE)	43.3-46.5
Polypropylene (PP)	46.5
Polystyrene (PS)	41.9
Polyvinyl chloride (PVC)	18.0
Polycarbonate (PC) – Bisphenol A	31.53
Polylactic acid (PLA)	15.73

In a typical energy recovery process, the collected plastic waste is first pretreated and then sent into an incinerator where the waste is burnt. Ash collected from this step is disposed into landfills. The gas emitted during combustion is cooled for removal of air pollutants and the heat recovered (via steam generation) is used for electricity production. Toxic gases released are treated (SOx, NOx) and sent to emission stack from where they are released into the atmosphere. The residues from the plant are disposed to disposal sites[91].

Chapter 3

Materials and Methods

This chapter presents with the type of materials used and the characterization techniques employed to study the blends.

3.1 Materials

PP (grade: Pro-fax 6301) and LDPE (grade: LM 0724 A) samples were supplied by INGENIA Polymers. PP had a density (ρ) and melt flow rate (MFR) of 0.90 g/cm^3 and 15.9 ± 0.02 g/10min (at 230 ˚C, 2.16 kg), respectively in accordance with ASTM D792 and ASTM D1238. The density and MFI values of LDPE were 0.9 g/cm^3 and 7.8 ± 0.3 g/10min (at 230 ˚C, 2.16 kg), respectively following ASTM D792 and ASTM D1238. Neat PP, neat LDPE, and the blended samples were prepared using a co-rotating twin-screw extruder as shown in **Table 2**. The samples were reprocessed for up to 5 cycles using a twin-screw extruder. 0 (no processing), 1, 3, and 5 times reprocessed samples were then injection molded and characterized for studying the effect of thermo-mechanical re-processing on the physical and mechanical properties of the blends.

Table 2: Sample code and composition

Sample Code	PP (%wt.)	LDPE (%wt.)
100/0	100	0
97.5/2.5	97.5	2.5
95/5	95	5
92.2/7.5	92.5	7.5
90/10	90	10
0/100	0	100

3.2 Melt Mixing/ Compounding

The PP and LDPE blends were prepared by using a Leistritz co-rotating twin-screw extruder with 10 heating zones and a mass flow rate of 1 kg/hr. The screws had a diameter, an L/D ratio, and a screw speed of 34 mm, 30:1, and 200 rpm, respectively. The temperature profile was set between 120 ℃ at the feeder and 200 ℃ at the die and across the 10 heating zones in order to provide sufficient melting without the risk of degradation. The extrudate temperature was approximately 200 ℃ as confirmed with an IR temperature gun measurement. The extruded strands were fed directly into a pelletizer to generate consistent pellets for further extrusion and injection molding.

3.3 Injection Molding

A HAAKE Mini-Jet Pro by Thermo Scientific was used to injection mold the samples. The injection temperature was set to 200 ℃ with a pressure of 650 bar to produce Type V tensile specimen (ASTM 638-14). A set of 5 specimens were produced for each sample (e.g. 0, 1, 3, and 5 times reprocessed) to test the changes in the mechanical properties.

3.4 Characterization Techniques

3.4.1 Parallel Plate Rheometry

The ASTM D4440-15 standard was followed to study the rheology of the specimens using parallel plate rheometer. Briefly, **s**ample specimens with a thickness and diameter of 2 and 25 mm, respectively, were prepared using compression molding in an appropriate mold. A parallel plate rheometer (TAI AR2000) was then employed to study the rheology of the PP/LDPE blends. A frequency sweep of 0.1-100 rad/sec at 180, 200, and 220 ℃ was performed on all samples. A constant strain of 0.05% (within the linear viscoelastic region) at a gap of 1.2 mm was set to test all the samples.

3.4.2 Capillary Flow Measurement

A Galaxy V Kayeness capillary rheometer was used to measure the viscosity of the blends at three different temperatures (180, 200, and 220 °C) in accordance with ASTM D3835-16. The capillary die used had a length to diameter (L/D) ratio of 40:1 and diameter of 0.02 inch. The shear rate was varied from 100 to 1000 sec^{-1}. These shear rates were kept constant for all the samples across all three temperatures.

3.4.3 Melt Flow Rate (MFR)

Melt flow rate of all the blends was measured according to ASTM D1238 at a temperature of 230 °C with a load of 2.16 kg using a Kayeness instrument. Both neat PP and LDPE were also measured at 230 °C to maintain similarity.

3.4.4 Differential Scanning Calorimeter (DSC)

The thermal analysis of the blends was conducted using a differential scanning calorimeter (DSC Q2000) with an autosampler manufactured by TA instruments (USA). The DSC experiments were conducted under a nitrogen flow at a rate of 50 mL/min. The sample preparation consisted of gathering thin slices from the middle of the injection molded material and placing ~7-8 mg in an aluminum T_{zero} pan. The sample was then heated at 2 °C/min up to 210 °C, held there for 5 min before cooling down at 2 °C/min to -20 °C, and heated again at 2 °C/min up to 210 °C. For this study, the melting temperature (T_m), crystallization temperature (T_c), and melt enthalpy (H_f) were taken during the second heating cycle to remove the thermal history of the processing. For comparison, all blends were tested using the same method. The percentage crystallinity of PP and LDPE phases within the blend was determined using **Equation 1** and **Equation 2.**

$$\textbf{EQUATION 1: } \%\boldsymbol{\chi_{c_{PP}}} = \left(\frac{\boldsymbol{H_{f_{PP}}}}{\boldsymbol{H^0_{f_{PP}}}}\right) \cdot \mathbf{100}\%$$

$$\textbf{EQUATION 2: } \%\chi_{c_{LDPE}} = \left(\frac{H_{f_{LDPE}}}{H^0_{f_{LDPE}}}\right) \cdot 100\%$$

The melt enthalpy (H_f) for the separate and distinct PP and LDPE peaks (see **Figure 15(A-D)** and **Figure 16(A-F)**) were used along with the heat of enthalpy for their theoretical 100% crystallized versions, $H^0_{f_{\mathrm{LDPE}}} = 289\, J/g$ and $H^0_{f_{PP}} = 207.1\, J/g$[92–94].

3.4.5 Polarized optical microscopy

The crystal structure of PP, LDPE, and their blends was investigated using an Olympus BX53M polarizing optical microscope (Melville, NY, USA) equipped with a 20× objective under polarized light. All samples were prepared as 0.5 mm thick films using a compression molder at 180 °C.

3.4.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the neat polymers and blends was used to observe how successive rounds of thermo-mechanical degradation would affect the overall thermal stability of the polymers. A TGA Q500 from TA instruments (USA) was used in this investigation. Each test consisted of a sample weighing ~15-16 mg and a temperature ramp of 5 °C/min was applied from 20–600 °C in a nitrogen environment with a flow rate of 40 mL/min.

3.4.7 Tensile Properties

The tensile test was conducted on a Universal Testing Machine (Mandel - Shimadzu (AGS-X)) at a constant crosshead speed of 10 mm/min for the individual polymers and the PP/LDPE blend systems according to ASTM D638-14 Type V.

3.4.8 Fourier Transform Infra-Red Spectroscopy (FTIR)

Samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet 6700 model, Thermo Scientific unit. Spectra was collected, in transmission mode, between 600-4000 cm^{-1} with a resolution of 4 cm^{-1} at 64 scans.

Chapter 4

Results and Discussion

4.1 Parallel Plate Rheology

The curves in **Figure 11(A-F)** shows the viscosity profile of the neat polymers and blends that have undergone 0, 1, 3, and 5 reprocessing cycles using a parallel plate rheometer at 200 °C. As expected, a shear thinning behavior of the neat and blend polymer systems were evident from the curves. Additionally, the viscosity of the samples decreased as the reprocessing cycle increased from 1 to 5, except for the LDPE sample (0/100, **Figure 11F**). The shift in viscosity from a higher modulus to a lower modulus was likely attributed to the decrease in molecular weight as a result of the shear and temperature exposure during recycling. Such a decrease in the molecular weight of the polymer resulted in a decrease in chain entanglements that led to an increase in the polymer chain's mobility while lowering the viscosity[40]. The transition to a Newtonian fluid, from shear thinning behaviour, occurred smoothly at lower shear rates for LDPE (0/100) at all three temperatures (**Figure 11F, Figure A1F** and **Figure A2F**). Pure PP (100/0) and PP/LDPE blends exhibited Newtonian like behaviour at lower shear rates and transitioned to shear thinning like behavior upon reaching higher shear rates. The successive addition of LDPE in the blend did not cause any effect in the transition behavior for the PP/LDPE blend samples. Also, there was no major change in the transition from a Newtonian behaviour to a shear thinning behaviour as the number of reprocessing cycles increased and as temperature rose from 180 to 220 °C (see **Figure 11, Figure A1** and **Figure A2)**. The neat LDPE exhibited higher viscosity as compared to PP in agreement with another study[95]. The complex viscosity of LDPE sample (0/100) did not show significant change after five cycles of extrusion. This was due to chain scission and cross-linking occurring simultaneously in the LDPE sample. From literature, it is clear that at lower temperatures of processing conditions cross-linking prevails in LDPE[41,43,96]. The shear viscosity of the blends was fitted to the Carreau viscosity model (**Equation 3**) and plots are shown in **Figure 11**.

$$\textbf{EQUATION 3: } \boldsymbol{\eta(\omega) = \eta_0 * [1 + (\lambda\omega)^2]^{\frac{(n-1)}{2}}}$$

where η is the shear viscosity (Pa.s); η_o is the zero-shear viscosity (Pa.s); λ is the relaxation time; ω is the angular frequency (rad/sec); and n is the power-law exponent for Carreau model.

The experimental findings and Carreau model fit are shown in **Figure 11** are represented by markers and solid lines, respectively. It was observed that the model fits well the experimental data with some deviations at frequencies above 100 rad/sec. The Carreau model parameter values at 200 °C, are reported in **Table A5**. The zero-shear viscosity increased as the amount of LDPE increased, while n is almost constant for all the one-time processed samples. For neat LDPE, the zero-shear viscosity was higher for the fifth (5th) cycle than the unprocessed, or 0 times reprocessed, indicating an increase in molecular weight as well as branching or entanglement[97].

The viscosities of the compounds decreased as the temperature increased from 180-220 °C (**Figure 11**, **Figure A1**, and **Figure A2**). This was due to the free volume increase that resulted in an increase in chain mobility[31,98]. The Carreau model parameters for 180 °C and 220 °C are also reported in **Table A5** (**Appendix A**).

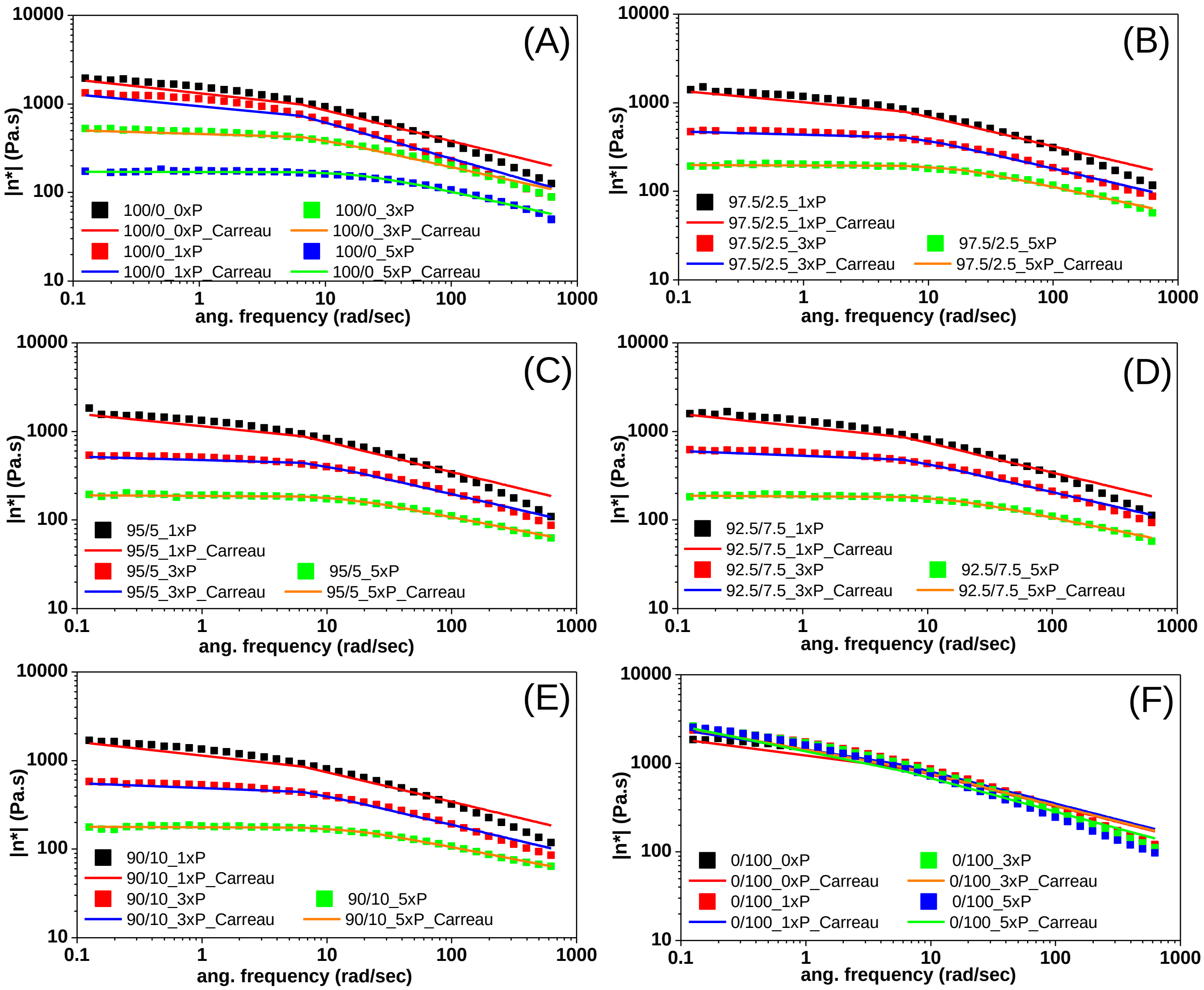


Figure 11: Complex viscosity vs. angular frequency at 200 °C. (A) 100/0 – 0, 1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1,3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

The complex modulus (G*) for neat PP and the blends decreases after every reprocessing (**Figure 12**). 1, 3, and 5 times reprocessed LDPE samples showed no significant change in trend compared to the unprocessed neat LDPE sample. Moreover, the PP/LDPE blends exhibited a similar viscosity and complex modulus trend as the pure PP after repeated extrusion cycles. The addition of LDPE in successive increments did not cause any observable change in the rheological characteristics of the blend. This was perhaps because the LDPE fraction in the blend was substantially lower (maximum 10 wt. %) than the PP fraction to cause a significant change in the viscosity profile. Spicker et al., in their study showed that complex modulus decreased after successive reprocessing steps for neat and regrind PP samples[40] that is in agreement with this study.

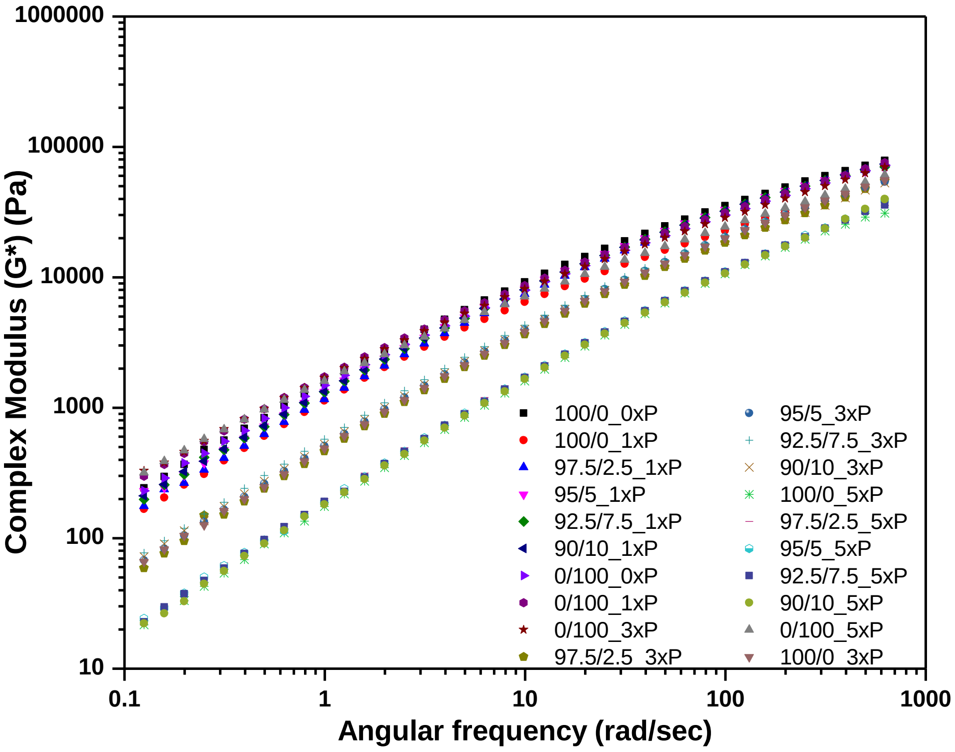


Figure 12: Complex modulus vs angular frequency at 200 °C.

4.2 Capillary Rheometry

Capillary rheometry is one of the common techniques to study rheological properties of PP, PE, and their blends because of its resemblance with typical polymer processing operations, such as extrusion and injection molding due to its ease of use among other factors[98]. One of the factors that determines the flow characteristic of PP is the heterogeneity/blend effect. **Figure 13** (**A-F**) presents the viscosity versus shear rate for neat PP, neat LDPE, and the PP/LDPE blends at 200 °C. The Rabinowitsch correction was applied to the data points in order to calculate the true shear rate. Bagley correction was neglected because the capillary used had a large L/D ratio.

Similar to parallel plate rheometry, the blends exhibited a reduction in their shear viscosity values as the number of reprocessing cycles increases from 1 to 5. This also confirmed the decrease in molecular weight and increase in mobility due to chain scission resulting from the exposure to temperature and shear during reprocessing. Also, an increase in the temperature in the rheometer from 180-220 ℃ resulted in a decrease in viscosity for all the investigated samples (**Figure 13, Figure A3** and **Figure A4**). This observation is in agreement with a previous study for LDPE/PP blend by Liang and Ness (1998)[31]. Alle et al., also studied and reported the PP/LDPE blend flow in a capillary rheometer at 190 ℃[99]. Results of this study indicated that as the amount of LDPE in the blend increased as compared to the PP, the viscosity of the blend reduced similar to the observation noted in this study[99]. LDPE showed a slight increase in shear viscosity at the 1st and 3rd reprocessing cycle but decreased at the 5th extrusion cycle (**Figure 13F**). The slight increase in the shear viscosity at the 1st and 3rd cycle reprocessing of LDPE can be attributed to crosslinking[96]. On the other hand, the reduction in viscosity with the 5th time reprocessing was not significant enough to correlate it with degradation. From **Figure 13**, it was noted that all samples showed shear thinning behavior for shear rates of 100-1000 s^{-1}. Mitsoulis et al., studied the flow behaviour of PP melt in a capillary rheometer at different temperatures. PP displayed shear thinning behaviour above 1 s^{-1} shear rate and viscosity reduction with the increase in temperature[100]. A power-law model (**Equation 4**) was employed here at 180, 200, and 220 ℃ to describe the shear thinning behavior of the material.

$$\textbf{EQUATION 4: } \boldsymbol{\eta(\dot{\gamma}) = K * (\dot{\gamma})^{n-1}}$$

where η is the shear viscosity; K is the consistency index with unit Pa.s^n; and n is the power-law exponent.

The power-law model fits well over the range of experimental data and the parameters K and n that was determined is described in **Table A6**.

The consistency index (K) is the primary relationship between the viscosity of the polymer and temperature. From **Table A6**, it was noted that the consistency index (K) decreased for each sample with the increase in number of extrusion cycle. Here, as the temperature increased from 180-220 ℃, the consistency index showed a downward trend meaning it is becoming a shear thinning fluid. It can be noted that the exponent (n) of the power-law model was similar for each blend, and for each reprocessing cycle (**Table A6**). In order to compare the K value of different fluids, the values of n should be comparable. An n value close to 1 indicates the fluid tends to go from a shear thinning to shear thickening; and n>1 imply that the fluid acts as a shear thickening fluid[101]. Since the value of n here was between 0 and 1, it can be concluded that the observed blends have shear thinning behavior.

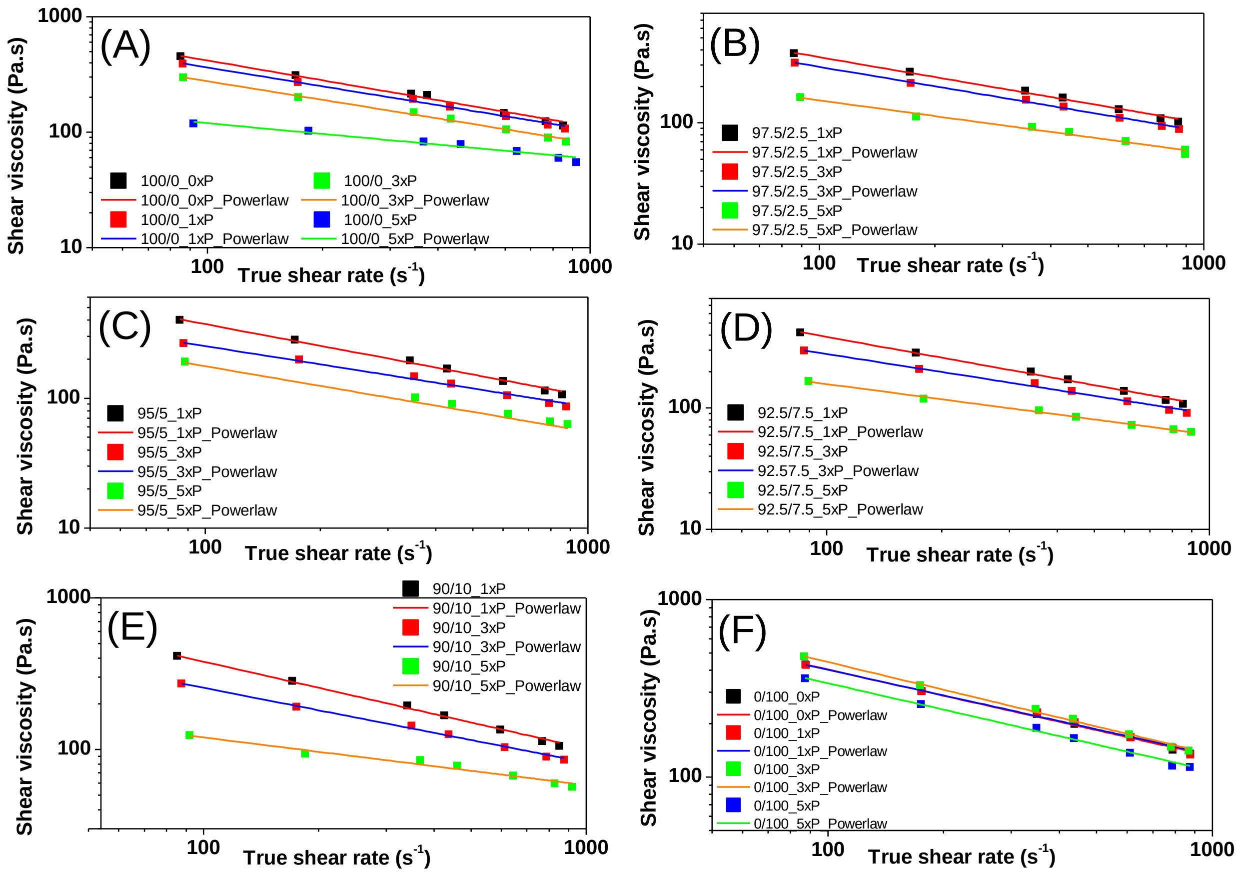


Figure 13: Capillary flow of all samples at 200 °C with power-law model fit (A) 100/0 – 0,1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1, 3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

4.3 Melt flow rate (MFR)

The MFR of the blends drastically increased with an increase in the number of reprocessing from 1 to 5 times. The MFR increased from 16 ± 0.0 g/10 min (0 times reprocessed) to 113 ± 13 g/10 min (5 times reprocessed) for neat PP. Esmizadeh et al., also reported a similar observation for PP[102]. Similarly, the formulated blends (see **Table 2**) have shown an increase in MFR as the processing cycle increased from 1 to 5 as shown in **Figure 14**. The MFR of neat LDPE decreased slightly after one processing cycle, this might be due to the crosslinking of LDPE as reported in the literature[103]. For 1 to 5 times reprocessed, the MFR of LDPE shows no significant change meaning that thermo-mechanical degradation is not a limiting factor for multiple extrusion processes. A study conducted by Soumia-Amina Kadbi et al. exhibited that recycled LDPE that was exposed to thermal or light degradation during manufacturing and/or mechanical sorting resulted in an increase in crosslinking. They confirmed this by examining FTIR and finding the amount of degradation from the carbonyl (1720 cm^{-1}) and methylene (~723 cm^{-1}) groups[103].

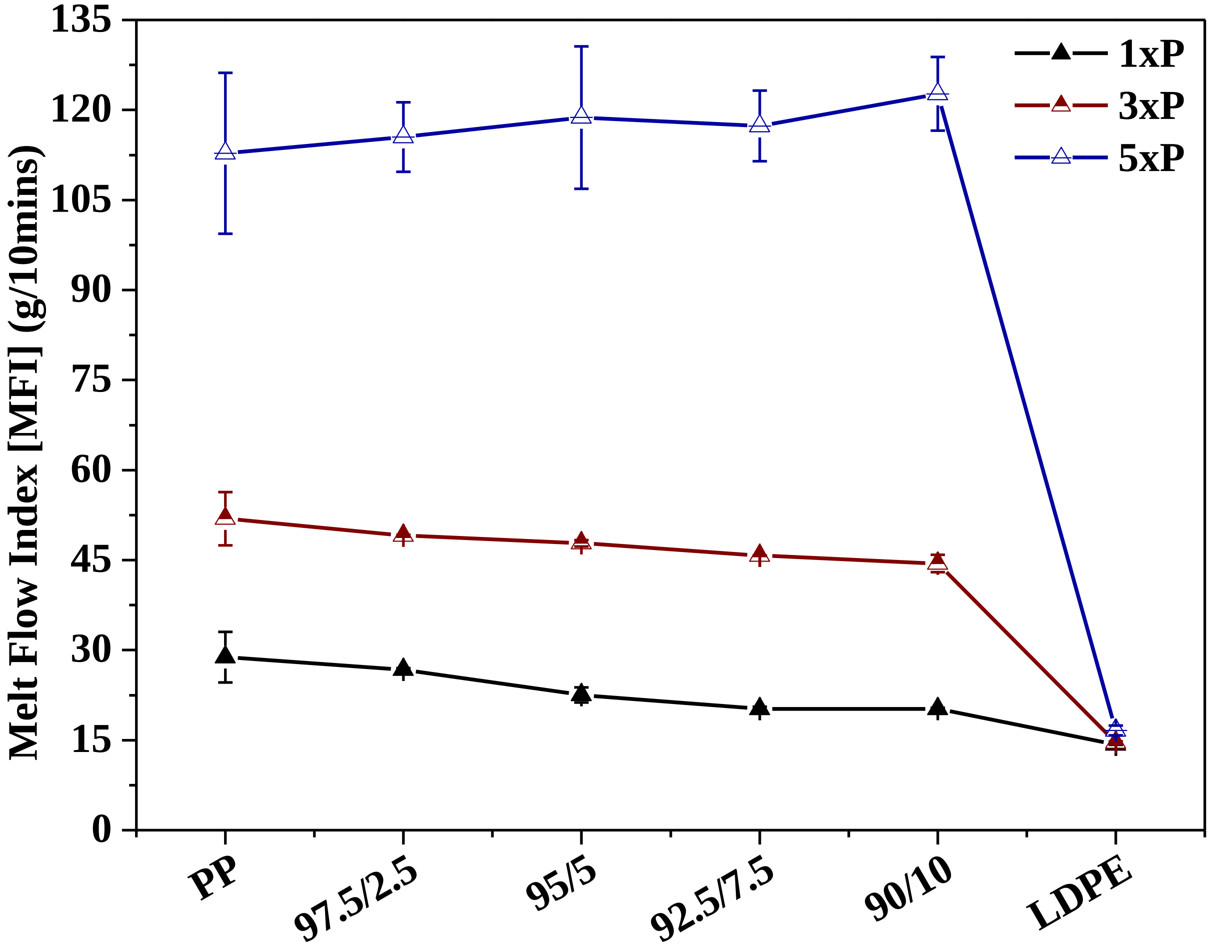


Figure 14: MFR vs. blend composition after 1, 3, and 5 times reprocessed.

PP on the other hand was the opposite case, with increase processing the MFR of the PP virgin and within a blend increased significantly due to thermal mechanical and oxidative degradation resulting in chain scissions which can be seen in the FTIR **Figure 23A** and **Table A7**.

4.4 Thermal properties - DSC

Figure 15 (A-D) shows the second heating and first cooling thermographs for the virgin and multi-processed PP and LDPE. LDPE's melting peak shape remained unchanged in all the investigated reprocessing cycles (0–5 times) as shown in **Figure 15C**. In contrast, PP started to display a shoulder region after the first-time reprocessing (**Figure 15A**). The lower temperature in **Figure 15A** was related to the melting of incomplete (β-form) crystalline structures at lower temperatures and the higher temperature peak was associated with the melting of the more perfect (α-form) crystalline structure[104]. Also, it was found that the melting region of PP began to broaden with increasing reprocessing cycles, which indicated thermal and shear induced degradation that caused chain scission as well as the generation of oligomers forming new imperfect crystalline structures. Upon examination of **Figure 15D**, there was a shift to higher temperatures with each reprocessing cycle indicating that the crystallization rate is increasing resulting in the crystallization period being quicker[105]. This was likely due to the thermo-mechanically induced degradation causing recycled LDPE to crosslink and form smaller crystals as shown in the MFR data (see **Figure 14**) and the crystallization tables (see **Table A1-Table A4**).

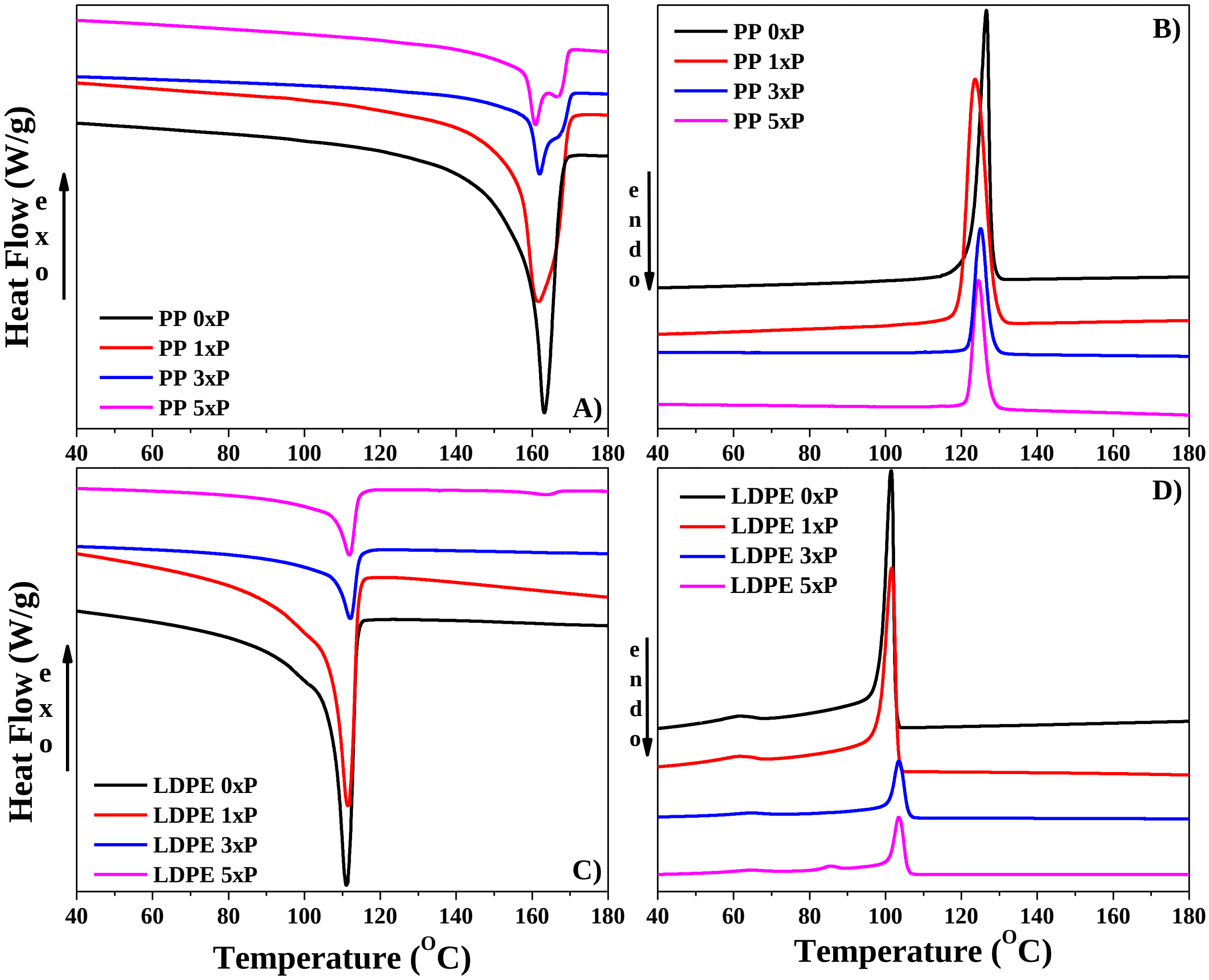


Figure 15: Thermograms of virgin and recycled PP and LDPE. (A) 2nd heating cycle for PP at 0, 1, 3, and 5 time reprocessed; (B) 1st cooling cycle for PP at 0, 1, 3, and 5 time reprocessed; (C) 2nd heating cycle for LDPE at 0, 1, 3, and 5 time reprocessed; (D) 1st cooling cycle for LDPE at 0, 1, 3, and 5 time reprocessed.

Figure 16 (**A-F)** displays the DSC thermograms of the blends of PP and LDPE with 0, 1, 3, and 5 times reprocessed. As noted from **Figure 16A** and **Figure 16D**, the increase in the LDPE content in the blend led to the incursion of a second lower heating peak development and the same for its the blends crystallization peaks. **Figure 16B** and **Figure 16C** followed similar trends to those previously outlined (see **Figure 15A** and **Figure 15B**) in that PP began to exhibit a second heating peak. Additionally, the increase in the LDPE content in the blend generated another melting peak. Lastly, the T_c of the PP and LDPE were spaced apart while in a blend causing it to exhibit two distinct T_c peaks for the blend ratios with ≤ 5% LDPE content. This illustrated an incompatible interaction between the PP and LDPE phases after blending[95]. The LDPE T_c in the blends was shifted to a higher temperature than its neat form due to the mutual nucleating effect of PP and LDPE.

A study conducted by Mofokeng et al. reported the influence of blending ratios of LDPE/PP on their mechanical, thermal, morphological, and rheological properties. They observed that a decrease in the PP peak intensity and a broadening of the melting region was attributed to a decrease in crystallinity brought on by the extrusion and blending process. Moreover, they noted that the melting peaks did not shift in temperature indicating that the lamellae crystal thickness of PP and LDPE blends resemble those in the virgin polymers[95].

As shown in **Figure 15(A-D)** and **Figure 16(A-F)**, PP has a crystallization temperature of around 119 ± 0.2 °C; while, LDPE has a 2 crystallization temperatures of 102 ± 0.0 °C and 62 ± 0.1 °C which represents primary crystallization of thicker lamellae and secondary crystallization of thinner lamellae, respectively. This means that PP will cool and crystallize first providing stiffness followed by the LDPE providing ductility. Mofokeng et al. have also observed this result and stated that the addition of LDPE seems to delay the crystallization of PP, which was illustrated by a slight shift in the crystallization temperature while within a blend[95].

As presented in **Table 3** and in the **Appendix A** (see **Table A1 - Table A4**), the crystallinity of virgin PP is higher than that on LDPE, with a crystallinity of 67 and 50%, respectively. It was observed that the addition of LDPE with a PP main phase has ultimately decreased the PP phase's crystallinity while the LDPE phase's crystallinity increased. It has been noted that the inclusion of any LDPE content within a PP matrix hinders the chain folding hence slightly lowering the crystallization temperature[95]. Overall, the blending of the two polymers together has a greater effect on the crystallization of LDPE compared to the PP phase.

Table 3: Crystallization table for PP, LDPE, and their blends for 1-time reprocessed samples

1xP (PP/LDPE)	**Degree of Crystallinity (%) - PP**	**Degree of Crystallinity (%) - LDPE**
PP	67.2 ± 2.6	/
97.5/2.5	66.7 ± 0.1	1.1 ± 0.2
95/5	54.3 ± 0.7	1.2 ± 0.1
92.5/7.5	53.2 ± 0.7	2.1 ± 0.0
90/10	49.1 ± 2.8	3.4 ± 1.7
LDPE	/	49.7 ± 0.9

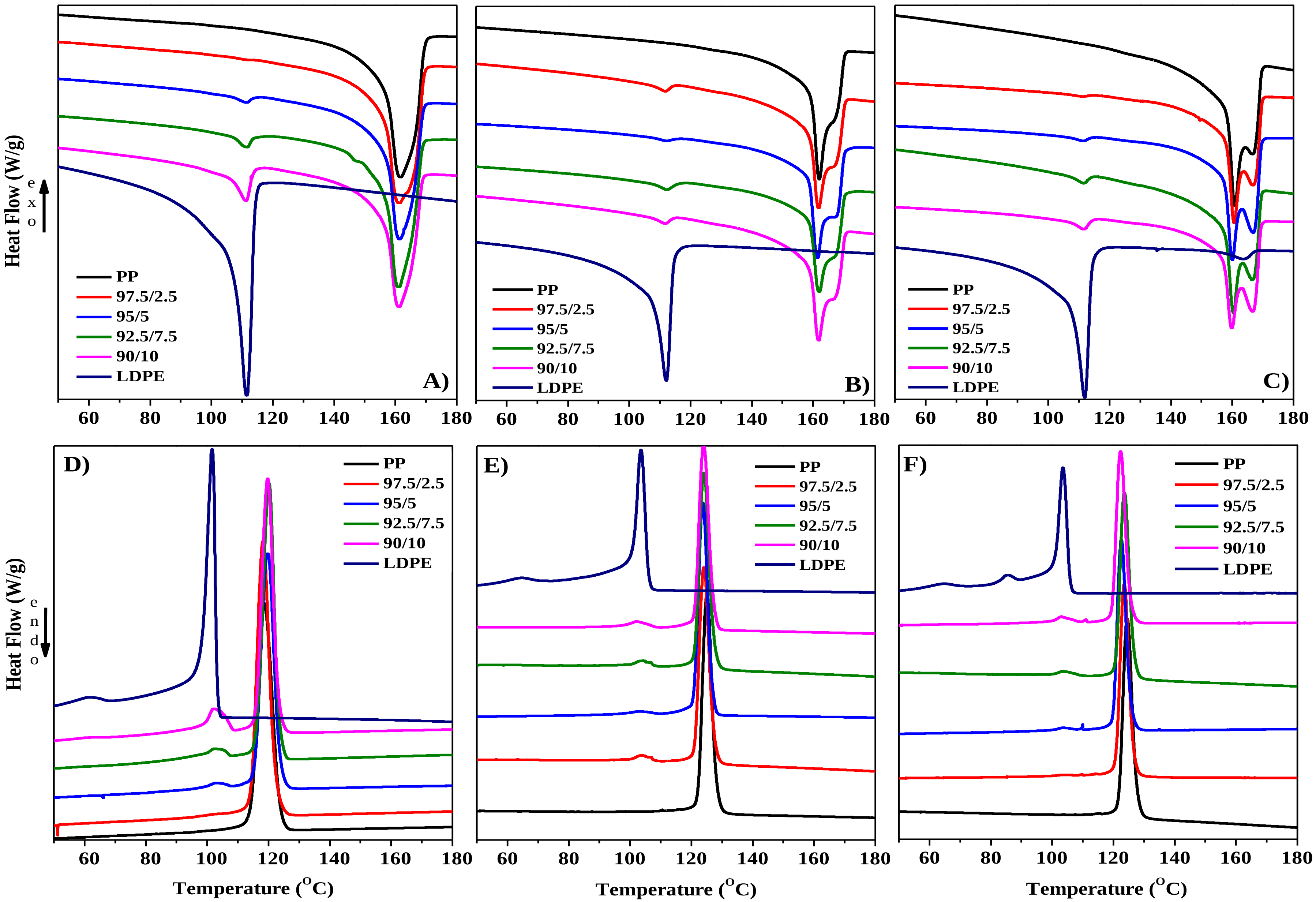
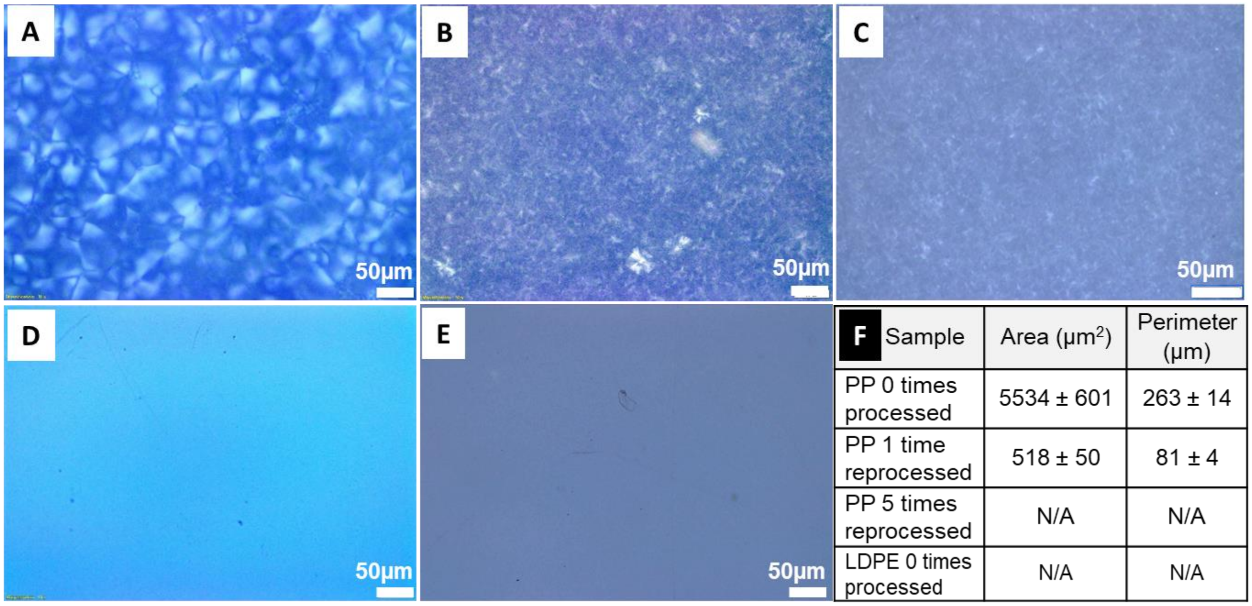


Figure 16: Thermograms of virgin and recycled PP/ LDPE blends. (A) and (D) 1 times reprocessing for the blends; (B) and (E) 3 times reprocessing for the blends; (C) and (F) 5 times reprocessing for the blends.

4.5 Polarized optical microscopy

Optical microscopy reveals that as PP is repeated reprocess the crystals become smaller and fewer in number where by 5 times reprocessed no distinguishable crystal could be observed, as shown in **Figure 17** (**A-F**). This correlates well with the crystallinity percentage obtained by DSC in **Table A1**. The loss of crystal size and quantities also explains the decrease in velocity and lowered mechanical properties such as tensile strength and elongation, as shown in **Figure 13(A-F)** and **Figure 22(A-C)**. A study conducted by C. Aumnate et al. found similar results to what is present in this thesis.[39] Comparison of Figure 8D and 8E demonstrated that the LDPE specimen did not reveal any crystals under polarized optical microscopy and no changes were observed with successive processing. This is because LDPE chain fold structures contains ethylene units and the segment length of these units limit the crystal lamella thickness resulting in crystals considerably smaller (< 50 nm) compared to PP[106], which may not be detectable by an optical microscopy.



Sample	Area (µm^2)	Perimeter (µm)
PP 0 times processed	5534 ± 601	263 ± 14
PP 1 time reprocessed	518 ± 50	81 ± 4
PP 5 times reprocessed	N/A	N/A
LDPE 0 times processed	N/A	N/A

Figure 17: Optical micrograph of (A) PP with no processing; (B) PP with 1-time reprocessing; (C) PP 5 times reprocessing; (D) LDPE no processing; (E) LDPE 5 times processed; (F) PP and LDPE crystal structure size

Figure 18 show the transparency of PP, LDPE, and one of the blends from the onset of simulated recycling to the final round. It can be seen in the image that the addition of LDPE into a PP matrix began to produce cloudiness in the film due to LDPE being more translucent than transparent. It was interesting to note as well that there appears to be no visible signs of chemical degradation (i.e. no change in colour) even after 5 times reprocessed. This signifies that although the molecular chains are reducing due to shear and thermal stresses, the polymer has not begun to generate smaller degradation by-products (e.g. peroxy-radicals) that can create of colors to the samples. This observation correlates well with the FTIR spectra and DSC thermograms.

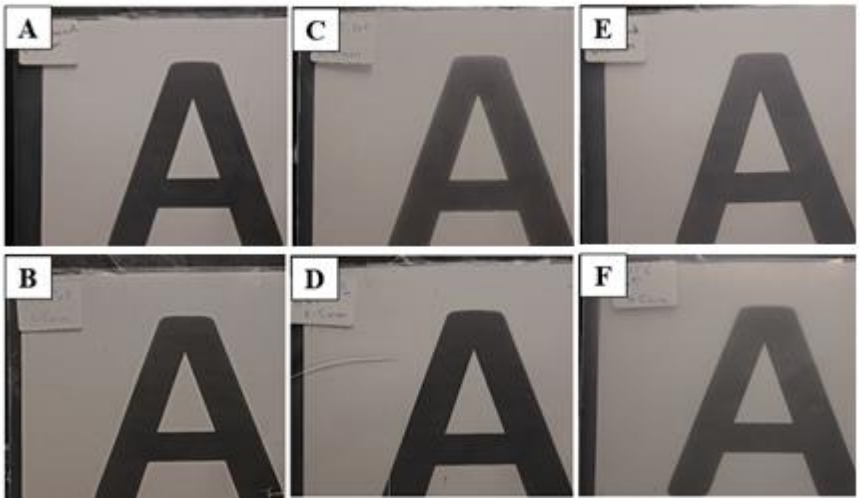


Figure 18: Film transparency test. A) PP at 0 times processed; B) PP at 5 times reprocessed; C) 95/5 at 1 time reprocessed; D) 95/5 at 5 time reprocessed; E) LDPE at 0 time reprocessed; and F) LDPE at 5 time reprocessed.

4.6 Thermal Stability - TGA

One of the desirable characteristics of these semi-crystalline thermoplastic, PP and LDPE, is their thermal stability. **Figure 19 (A-D)** shows typical TGA while **Figure 20 (A-D)** shows typical derivative thermogravimetry (DTG) of the neat polymers, and the blends at the studied reprocessing cycles. In **Figure 19 (A-D),** it can be seen that LDPE starts to degrade at 399 ± 5 °C while the onset to degradation (e.g. 1% sample loss) for PP is 370 ± 1 °C making LDPE the more thermally stable of the two neat polymers; all blends follow a multi-step degradation process. This high thermal degradation temperature indicated wide industrial application for both polymers. Mourad reported high onset degradation temp (around 380 °C) of PP/LDPE blend even under an air atmosphere [107]. Throughout the studied blends and all reprocesses, PP was the limiting factor that decreased the blends overall thermal stability. The lower stability of PP was due to the tertiary carbons in the backbone being susceptible to attack allowing for easier decomposition and breakdown of the main chain. As shown in **Figure 19 (A-D)** the binary blends of PP/LDPE fall nicely in between the two individual neat polymers with the stability increasing with increase in the LDPE content. This implied that the addition of LDPE act as a thermal stabilizing agent of the PP matrix. A similar trend was confirmed in a few studies conducted by other researchers[11,107–110].

As the blends were reprocessed repeatedly the thermal stabilities of all the blends began to move closer to that of neat PP. This was again due to the PP in the blend degrading first producing shorter chains and lower crystallinity, which allowed chain mobility with less energy (e.g. heat).

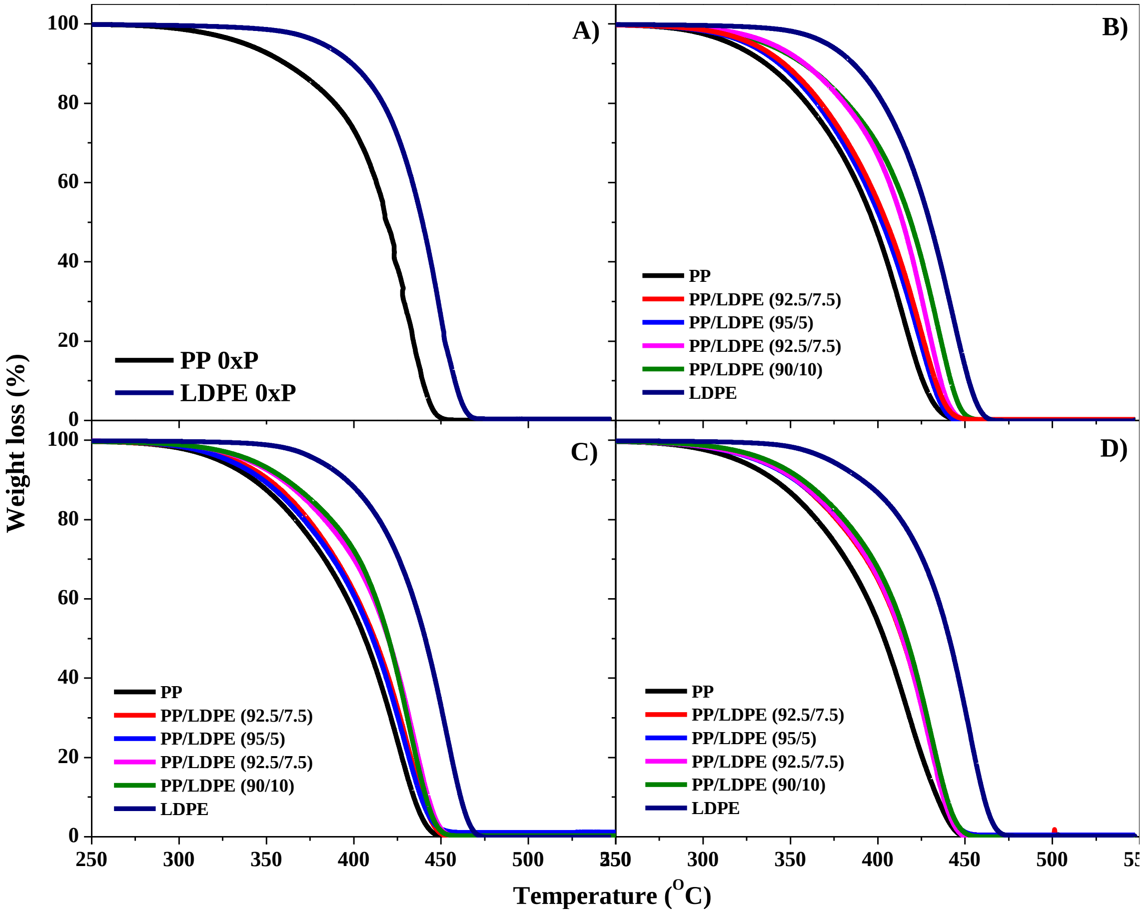


Figure 19: TGA degradation curves for the neat polymers and their blends. (A) 0 times reprocess for the blends; (B) 1 times reprocessed for the blends; (C) 3 times reprocessed for the blends; (D) 5 times reprocessed for the blends.

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Figure 20 displays the weight derivative curves of neat PP and LDPE as well as their blends. PP shows a broader peak indicating a heterogenous combination of polymer chain molecular weights; while, LDPE has a more narrow and sharper peak indicating a more homogenous molecular chain distribution. As the blends are continuously reprocessed their weight derivative curves became broader as secondary shoulders began to appear indicating the generation of smaller molecules (e.g. oligomers) and other volatiles as a result of thermo-mechanical degradation. Much like other properties, neat LDPE's thermal stability remained relatively unaffected with successive extrusions.

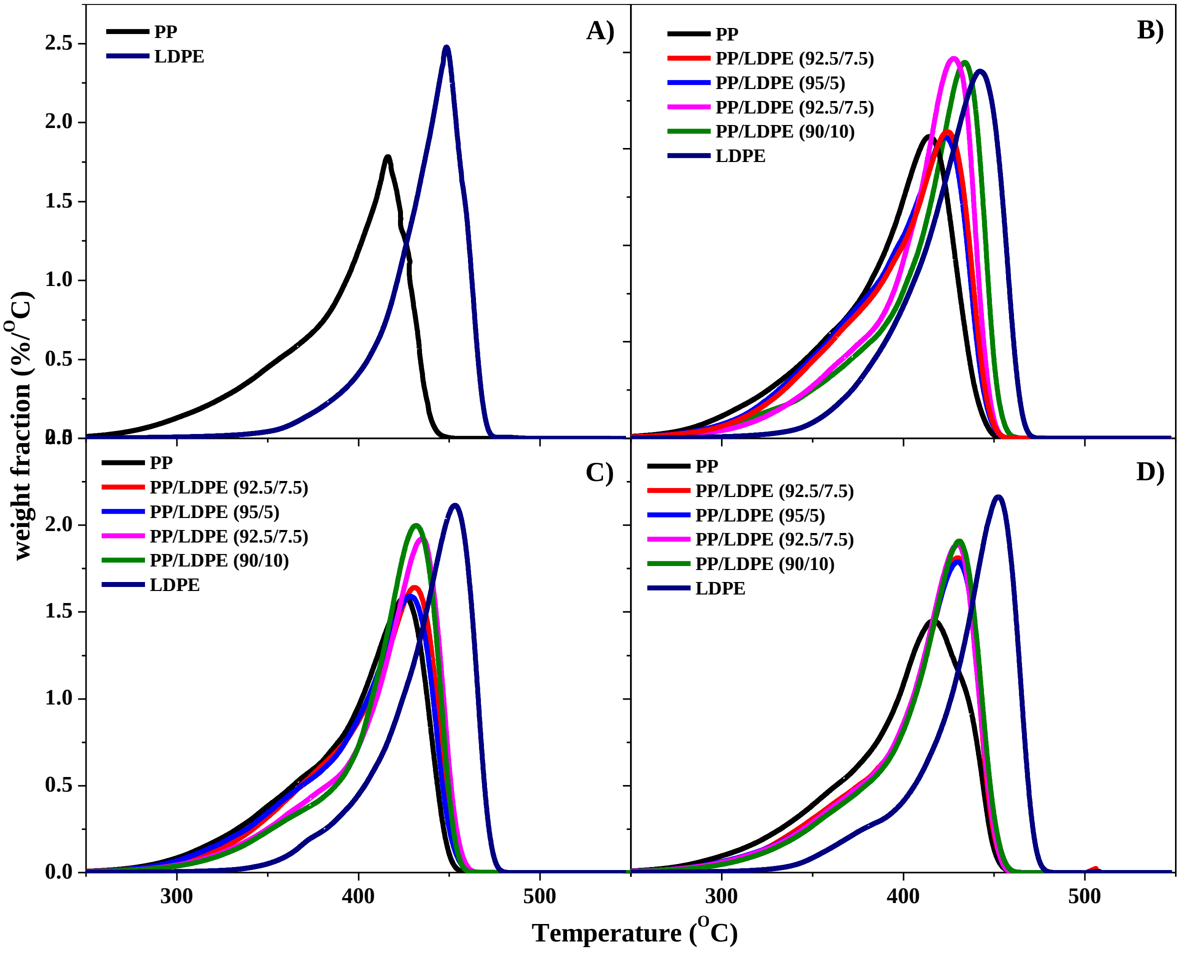

Figure 20: TGA weight derivative curves for the neat polymers and their blends. A) 0 times reprocess for the blends; B) 1 times reprocessed for the blends; C) 3 times reprocessed for the blends; D) 5 times reprocessed for the blends.

4.7 Tensile Properties

As shown in **Figure 21**, even after one-time processing with an extruder the tensile properties of PP and LDPE were affected. In the case of PP, it experienced a 19% and 16% decrease in tensile strength and modulus, respectively, as a result of thermo-mechanical processing mediated chain scission. However, in the case of LDPE there was a statistically significant ($p<0.05$), but very slight increase in its tensile strength (3%) and modulus (7%). The increase can also be attributed to thermo-mechanical degradation and chain scission; however, Kadbi et al. has observed that upon LDPE being broken down it begin to crosslink increasing its viscosity as shown in the MFR and Rheology sections above[103]. The percentage elongation at break data followed the same trends (**Figure 22C**).

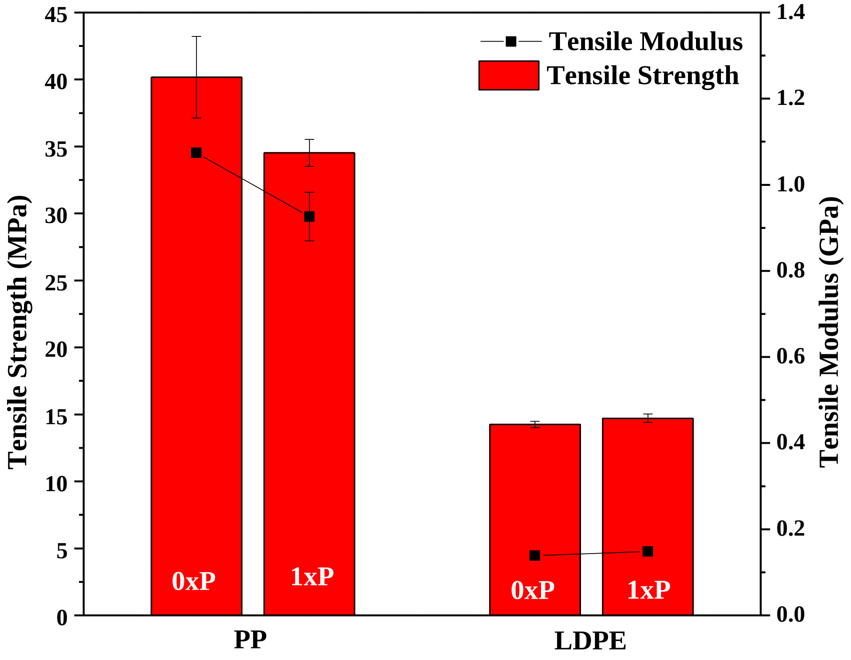

Figure 21: Tensile strength and modulus of the 0 and 1-time reprocessed neat polymers (i.e. PP and LDPE).

Figure 22 (A-C) illustrates the effect of adding LDPE into a PP matrix at low concentrations as well as how multiple reprocesses of the same blend in relation to its tensile properties (Young's modulus, tensile strength, and elongation at break). It is typical to observe a decrease in tensile modulus when adding a soft material (e.g. LDPE) into a stiff material (e.g. PP). The reduction in the blends overall crystallinity will also lower the blends Young's modulus. This occurs as a result of the increase in the number and size of amorphous regions giving more ductility to the material. **Figure 22 (A-C)** showed that the one-time reprocessed samples with a slight addition (< 5%) of LDPE in the PP matrix had little effect on the tensile strength. However, when 7.5 and 10 %wt. of LDPE was added there was a modest increase in properties, which may be attributed to the LDPE content acting as a functional filler within the PP matrix rather than an impurity due to agglomeration. The same trend was observed for the elongation at break. A study conducted by Mofokeng et al. noted that when LDPE concentrations were < 10 wt. % there was little to no changes due to PP's stiff nature. Nevertheless, as the LDPE content increased between 10 and 30 wt.% [95], a good adhesion between the two phases was noted, signifying partial miscibility based on the smooth morphology observed under SEM (freeze fracture surface imaging)[95].

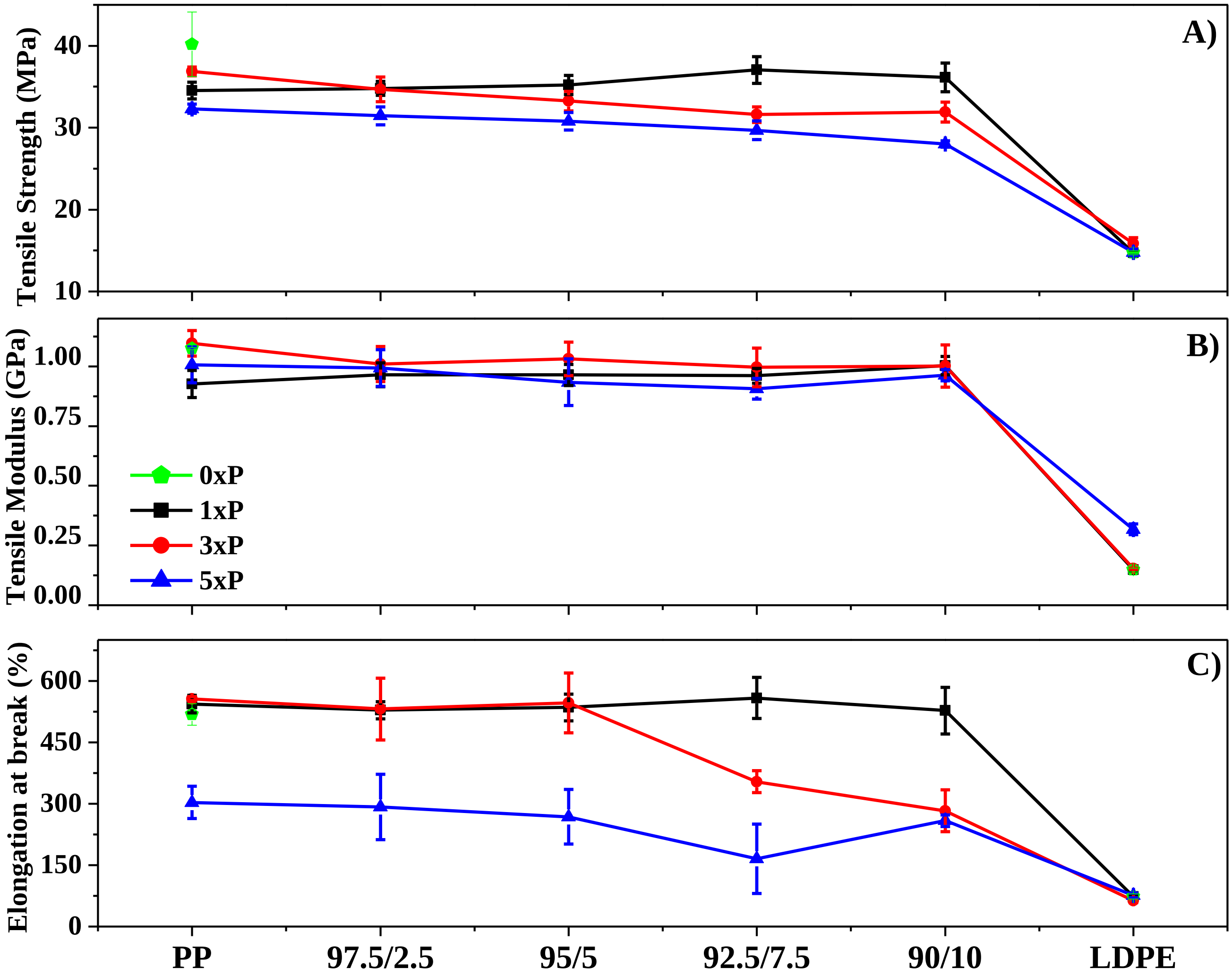

Figure 22: Tensile strength (A); tensile modulus (B); and (%) elongation at break (C) of the formulated blends of PP and LDPE

As the number of processing cycles of the blends increased, the tensile properties displayed progressive reduction, with the greatest reduction being the 5 times reprocessed as expected. This was due to chain scission as a result of the thermo-mechanical degradation. The exception to this was the Young's modulus (**Figure 22B**). Multiple reprocesses led to a slight increase in modulus which was a result of more chain entanglements between shorter oligomer chains as there was a decrease in the blends overall crystallinity as shown in the **Appendix A** (see **Table A1** - **Table A4**).

4.8 Fourier Transform Infrared Spectroscopy

The FT-IR spectra of all samples are shown in **Figure 23** (**A-C**) and **Figure A5** – **Figure A7**. Neat PP and neat LDPE sample spectra coincide well with the literature data[111,112]. The broad and intense band around 3000 cm^{-1} was due to CH stretching (**Figure 23A**). The intensity of the peak of PP between 3000 - 2750 cm^{-1} decreased gradually as the processing cycle increased from zero to five cycles. In **Figure 23A**, around 2700-3000 cm^{-1} for pure PP unprocessed sample, the peak tends to be flat. This might be due to film thickness and total absorption of peak. The peak observed between 1386 – 1353 cm^{-1} and 1477 – 1432 cm^{-1} was due to methyl group vibrations. This is in agreement with the literature[113]. Even though these peaks showed some decrease in intensities with increase in processing cycles, it is worth mentioning that only a slight effect can be detected. The IR peaks at 840, 1000 and 1200 cm^{-1} were attributed to C-CH$_3$ stretching[113,114]. In this study, these peaks were seen at 842, 970 and 1170 cm^{-1} and these did not show significant change up to 5 times of reprocessing. **Figure 23C** shows the IR spectra for 90/10 (PP/LDPE) sample for 1, 3- and 5-time reprocessing cycle. The spectra showed both PP and LDPE characteristic, even though the differences between the characteristics are not sizable. The peak at 720 cm^{-1} which can be seen only in LDPE IR spectra (**Figure 23B**) was also seen in all the PP/LDPE blends (**Figure 23C** and **Figure A5** - **Figure A7**). This peak's intensity increased progressively as the amount of LDPE increased from 2.5 to 10 wt. %. LDPE IR spectra (**Figure 23B**) showed three intense peaks at ~

2900, 1470, 1370 and 720 cm^{-1} which corresponds CH_2 asymmetric stretching, bending deformation, CH_3 symmetric deformation and rocking deformation, respectively. Gulmine et al. and Rajandas et al., also reported similar observation for LDPE[112,115]. A progressive increase in the intensity of a small transmission band at ~ 1370 cm^{-1} was noted with the increase in the re-processing cycle from zero to five-time reprocessing of LDPE. This band represented methyl group and its increase was indicative of the extrusion re-processing mediated branching of the LDPE[116] with more abundant methyl group that eventually led to the crosslinking[117]. This was the only change in IR spectra of LDPE after five cycles of extrusion.

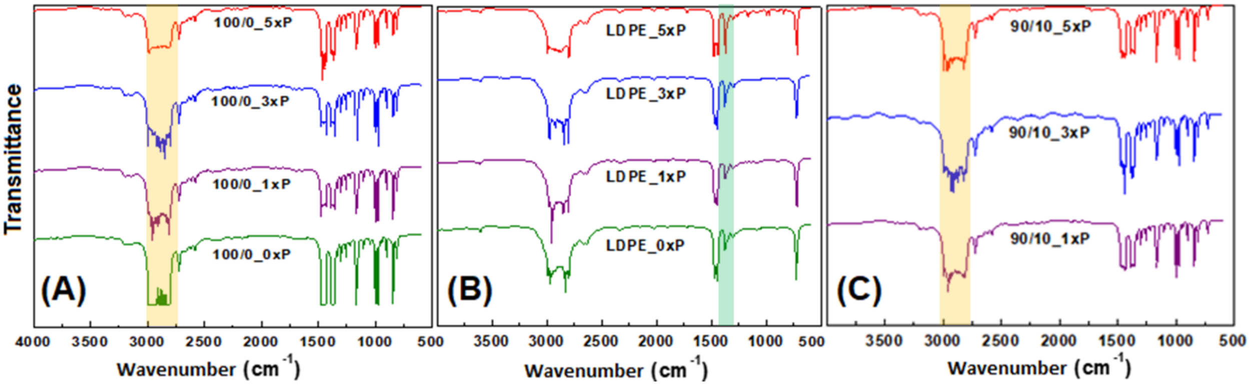

Figure 23: FTIR spectra of (A) 100/00 (PP), (B) 0/100 (LDPE) & (C) 90/10 (PP/LDPE) as a function of processing cycles.

Chapter 5

Conclusions and Recommendations

Polyolefins are the most versatile class of polymers with appealing physical and chemical properties. As a result, they are by far the most commonly used plastics in a range of single-use commodity and engineering applications and consequently the most abundant plastics present in the waste. High-class segregation of waste is the most important step that has to be ensured by industries for successful recycling and revitalization of plastics. Contaminants like food bits, blood, or dirt present in the plastic, especially after consumer use is detrimental to successful recycling. The recycling of contaminated waste inevitably deteriorates the properties of the recycled product, in addition to higher processing costs. Another main challenge facing recycling is the cost and difficulty of sorting and separation of complex plastic components (e.g. polymer blends, multilayered plastics with each layer composed of different polymer types or even metal-based layers, etc.) compared to their virgin plastic counterparts.

This study investigated the effect of thermo-mechanical recycling on the properties of PP that contained small concentrations of LDPE blend additives (0 – 10 wt.%). To simulate recycling, controlled thermo-mechanical reprocessing of the samples was employed and the impact of the reprocessing on the properties of the samples was investigated. The decrease in viscosity and increase in melt flow rate of all the samples indicated degradation due to chain scission except for the case of pure LDPE where the opposite was observed due to crosslinking. The viscosity of the PP/LDPE blends (virgin and recycled material) were in between neat PP and neat LDPE components. TGA analysis also supported that pure PP and PP/LDPE blends undergo thermo-mechanical degradation due to chain scission and formation of smaller molecules. Tensile testing of the blends after reprocessing for up to five cycles showed decrease in properties and this can again be attributed to thermo-mechanical degradation occurring during the extrusion cycles. All the blends behave more like neat PP after multiple extrusion as determined from rheology, DSC, and TGA analysis. It can be concluded that addition of LDPE (up to 10 %wt.) does not affect the blend system substantially. Recycling of polyolefins, like PP and PE, is being studied extensively so as to reduce plastic waste ending up in the water bodies and landfill. This study showed that low concentrations of LDPE in PP does not affect the system and the characteristics of PP dominates. It can also be concluded that property deterioration in all the samples is not that significant even after five extrusion cycles. Thus, recycling of PP/LDPE systems with low concentrations of LDPE can be conducted using the typical thermo-mechanical processes, such as extrusion and injection molding. Furthermore, it can be noted that blend systems that resemble the studied composition do not require advanced sorting or separation process to be reprocessed and recycled for a range of commodity and industrial applications. Overall, direct reprocessing of PP/LDPE blend does not only reduce the cost of production but also eases environmental concerns regarding plastic waste.

Future work to further progress this research work and fully understand the effect of the reprocessing includes investigation of the change in the molecular weight, environmental stress crack analysis, color analysis, and impact strength. Also, increasing the reprocessing cycle number beyond 5 cycles (e.g. for up to 10 cycles) and analyzing the change in properties and increasing the amount of LDPE in the blend system provides useful information and broader understanding of the reprocessibility and change in structure – property of PP/LDPE blend systems. Recycling of plastics is not the end step but redesigning the process to input the recycled powder/flake/pellets or article to produce a product completes the circular economy. Furthermore, re-designing and simplifying the existing polyolefin-based products with a deliberate intention of recyclability such as reducing or avoiding multi-layering, combining non-plastics with plastics is an integral part for the success of plastic recycling.

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Appendix A

Table A1: Crystallinity percentage for virgin and recycled PP and LDPE.

Material	**Degree of Crystallinity (%)**
PP – 0xP	67.7 ± 2.6
PP – 1xP	67.2 ± 2.6
PP – 3xP	58.7 ± 3.01
PP – 5xP	57.7 ± 1.5
Material	**Degree of Crystallinity (%)**
LDPE – 0xP	58.8 ± 1.7
LDPE – 1xP	49.7 ± 0.9
LDPE – 3xP	42.3 ± 2.4
LDPE – 5xP	38.2 ± 3.4

Table A2**:** Crystallinity percentage for 1 times reprocessed PP/LDPE blends.

1xP (PP/LDPE)	**Degree of Crystallinity (%) - PP**	**Degree of Crystallinity (%) - LDPE**
PP	67.2 ± 2.6	/
97.5/2.5	66.7 ± 0.07	1.1 ± 0.2
95/5	54.3 ± 0.7	1.2 ± 0.1
92.5/7.5	53.2 ± 0.7	2.1 ± 0.01
90/10	49.1 ± 2.8	3.4 ± 1.7
LDPE	/	49.7 ± 0.9

Table A**3:** Crystallinity percentage for 3 times reprocessed PP/LDPE blends.

3xP (PP/LDPE)	**Degree of Crystallinity (%) - PP**	**Degree of Crystallinity (%) - LDPE**
PP	58.7 ± 3.01	/
97.5/2.5	46.9 ± 1.3	0.6 ± 0.2
95/5	44.1 ± 0.1	0.6 ± 0.04
92.5/7.5	44.4 ± 0.3	1.2 ± 0.1
90/10	41.2 ± 0.6	2.02 ± 0.03
LDPE	/	42.3 ± 2.4

Table A**4:** Crystallinity percentage for 5 times reprocessed PP/LDPE blends.

5xP (PP/LDPE)	**Degree of Crystallinity (%) – PP**	**Degree of Crystallinity (%) – LDPE**
PP	57.7 ± 1.5	/
97.5/2.5	47.3 ± 2.5	0.3 ± 0.01
95/5	45.9 ± 0.9	0.8 ± 0.04
92.5/7.5	45.9 ± 0.1	1.4 ± 0.2
90/10	41.2 ± 1.01	2.2 ± 0.02
LDPE	/	38.2 ± 3.4

Table A5: Fitting parameter, Carreau model, for all samples

Blends (PP/LDPE)	**Cycle**	**Zero Shear viscosity (η_o)**			**Power-law index (n)**			**Relaxation time (λ)**		
		180 °C	**200 °C**	**220 °C**	**180 °C**	**200 °C**	**220 °C**	**180 °C**	**200 °C**	**220 °C**
100/0	0	2919	1825	1379	0.589	0.650	0.650	2.568	0.882	1.279
0/100		2748	1803	1205	0.611	0.643	0.657	1.235	1.175	1.173
100/0	1	1837	1243	776	0.637	0.592	0.685	0.685	0.565	0.428
97.5/2.5		2133	1327	763	0.643	0.668	0.662	0.887	0.704	0.374
95/5		2426	1537	1085	0.621	0.660	0.603	0.906	0.797	0.438
92.5/7.5		2330	1541	969	0.641	0.664	0.677	1.057	0.867	0.587
90/10		2547	1567	1046	0.642	0.664	0.676	1.181	0.921	0.671
0/100		3363	2279	1498	0.610	0.638	0.646	1.787	1.741	1.2
100/0	3	828	499	294	0.664	0.688	0.719	0.316	0.207	0.143
97.5/2.5		811	469	321	0.654	0.668	0.662	0.283	0.179	0.106
95/5		829	516	351	0.649	0.673	0.753	0.319	0.192	0.341
92.5/7.5		1042	593	378	0.654	0.676	0.670	0.431	0.258	0.148
90/10		878	546	339	0.660	0.667	0.692	0.366	0.247	0.148
0/100		3556	2457	1527	0.603	0.641	0.634	2.295	2.588	1.324
100/0	5	290	182	115	0.670	0.724	0.706	0.084	0.087	0.044
97.5/2.5		307	197	122	0.684	0.693	0.735	0.103	0.063	0.046
95/5		307	189	114	0.666	0.723	0.737	0.090	0.077	0.43
92.5/7.5		329	187	125	0.688	0.712	0.798	0.121	0.071	0.086
90/10		298	178	110	0.686	0.726	0.764	0.109	0.680	0.050
0/100		3902	2536	1543	0.592	0.620	0.640	3.536	3.165	2.184

Table A6: Fitting parameter, Power-law model, for all samples

Blends (PP/LDPE)	**Cycle**	**Consistency Index (K)**			**Power-law index (n)**		
		180 °C	**200 °C**	**220 °C**	**180 °C**	**200 °C**	**220 °C**
100/0	0	9508	5805	3985	0.386	0.429	0.458
0/100		5148	3830	2892	0.493	0.511	0.528
100/0	1	6986	4411	3393	0.417	0.458	0.475
97.5/2.5		7708	4289	2242	0.405	0.455	0.509
95/5		8744	4789	3504	0.387	0.445	0.477
92.5/7.5		5277	5277	3834	0.432	0.432	0.439
90/10		7687	5347	4229	0.407	0.426	0.444
0/100		4861	3667	2426	0.510	0.520	0.549
100/0	3	4686	3231	755	0.426	0.466	0.633
97.5/2.5		5279	3395	1564	0.421	0.465	0.541
95/5		4457	2175	2045	0.449	0.532	0.503
92.5/7.5		2696	2696	1948	0.507	0.507	0.528
90/10		1337	2465	1626	0.573	0.507	0.541
0/100		6090	4853	3329	0.478	0.481	0.507
100/0	5	1977	491	518	0.532	0.693	0.652
97.5/2.5		2110	1116	887	0.526	0.569	0.557
95/5		1965	1795	1152	0.533	0.496	0.525
92.5/7.5		1078	1078	914	0.583	0.583	0.559
90/10		1600	510	1058	0.556	0.686	0.530
0/100		3743	3310	1719	0.526	0.505	0.580

Table A7: FTIR peak change for PP and LDPE

Polymer	**Wavenumber (cm^{-1})**	**Type of vibration**	**Reason**
Polypropylene (PP)	1386 – 1353 cm^{-1}	CH_3 bend	Chain scission
	1477 – 1432 cm^{-1}	CH_2 bend	
Low-density polyethylene (LDPE)	1370 cm^{-1}	CH_3 bend	Cross-linking

Note: In case of PP, the intensities of peaks after 5 cycles of extrusion decreased slightly, which indicated chain scission. While, in the case of LDPE the intensity increased after 5 cycles of extrusion, which indicated cross-linking[118,116].

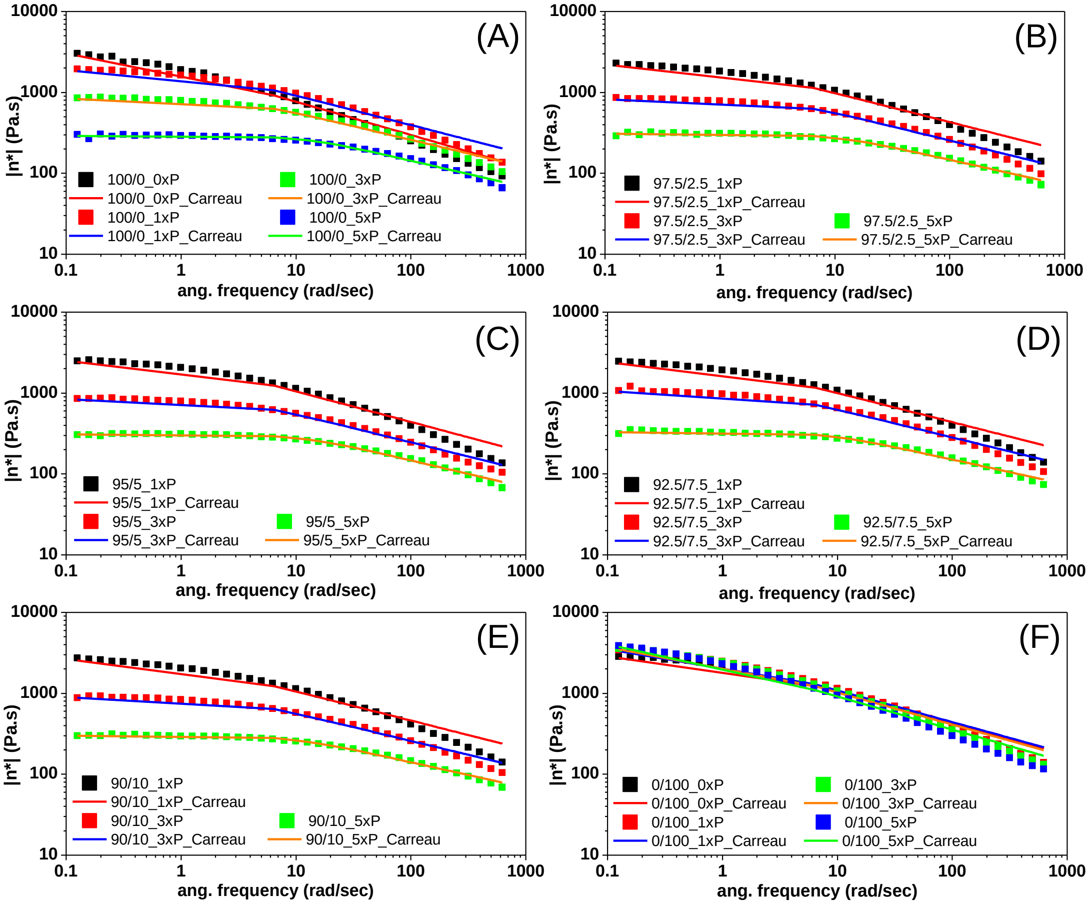

Figure A1: Complex viscosity vs angular frequency at 180 °C (A) 100/0 – 0,1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1,3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

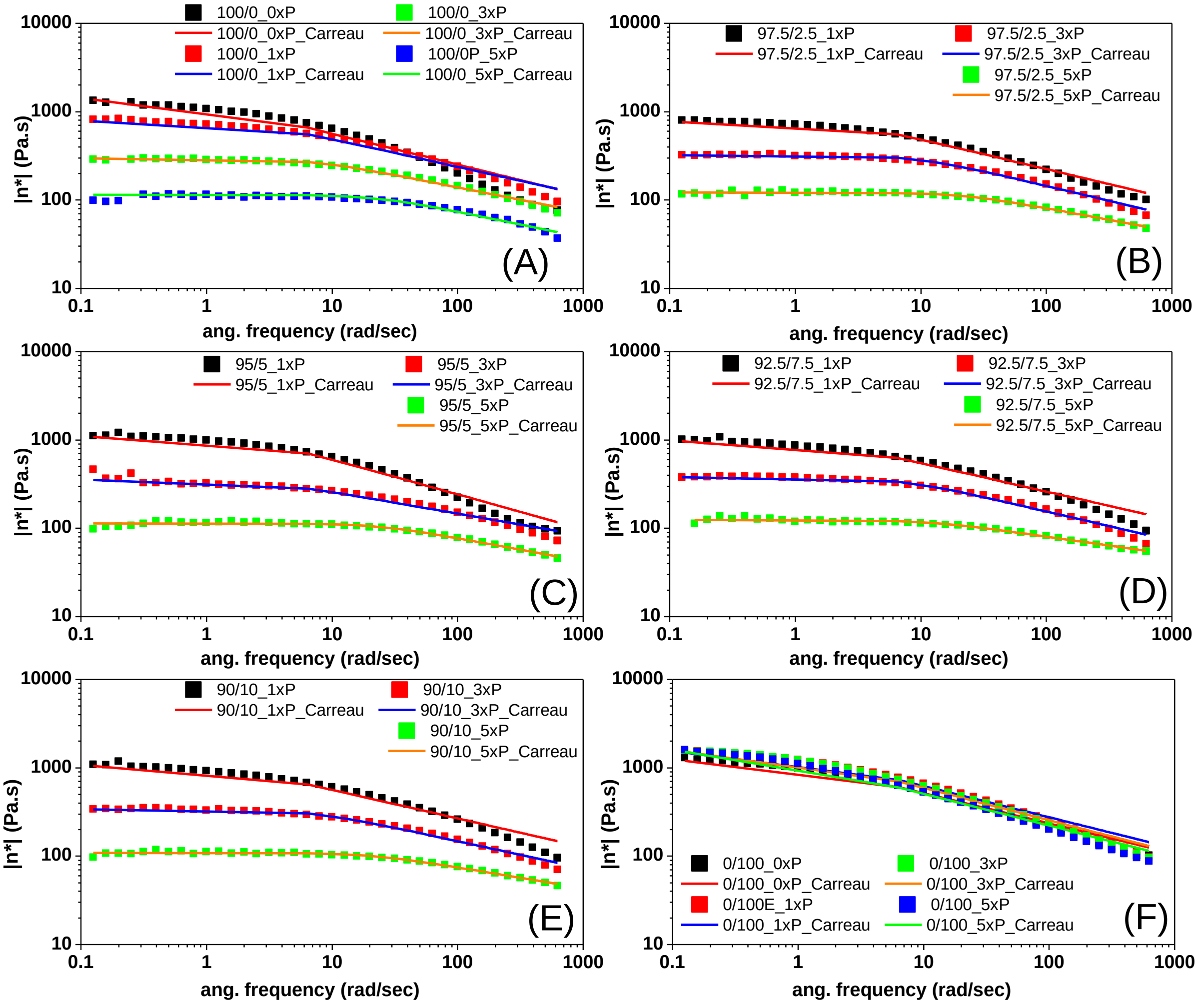

Figure A2: Complex viscosity vs angular frequency at 220 °C (A) 100/0 – 0,1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1,3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

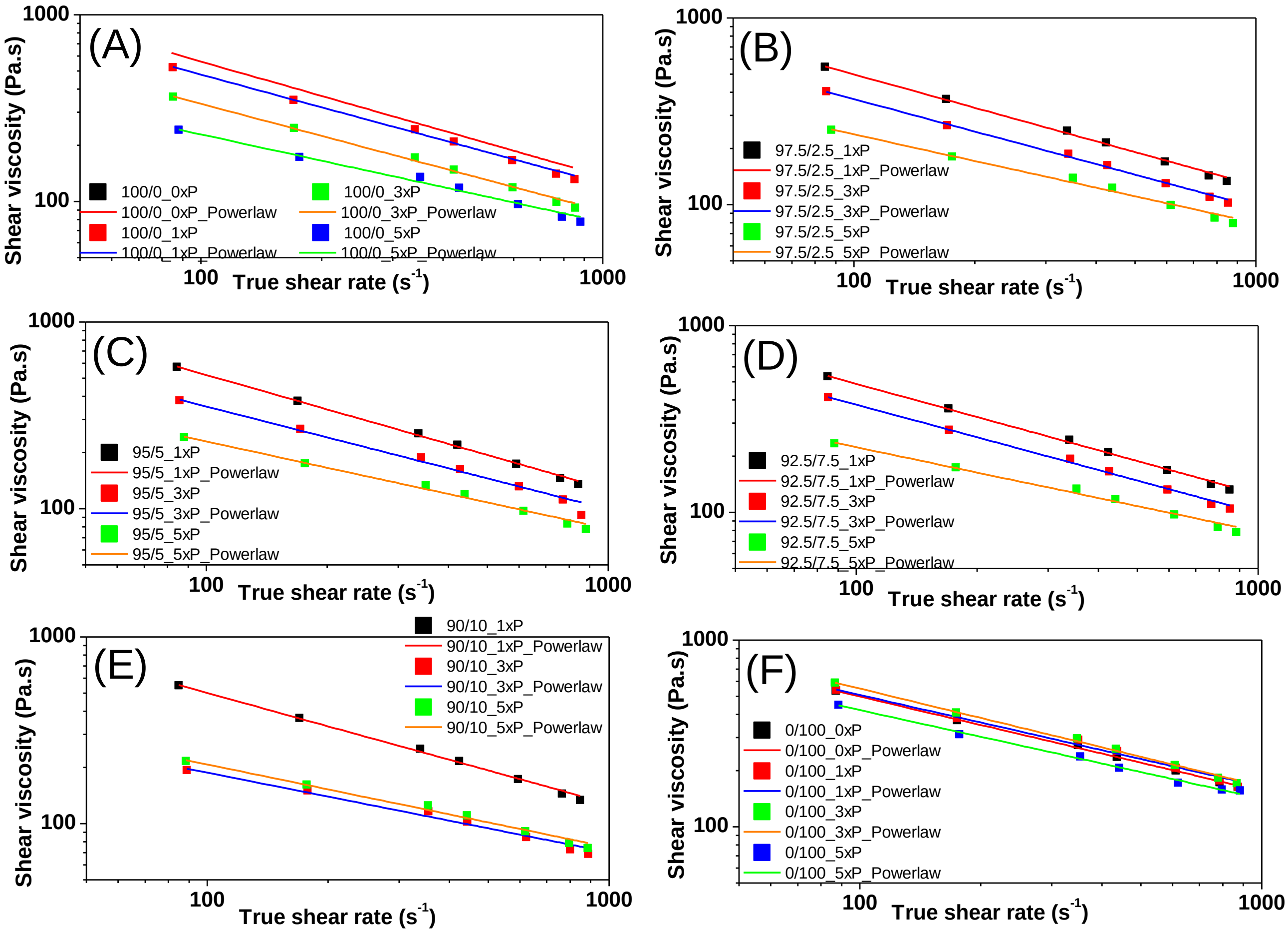

Figure A3: Capillary flow of all samples at 180°C with power-law model fit (A) 100/0 – 0,1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1,3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

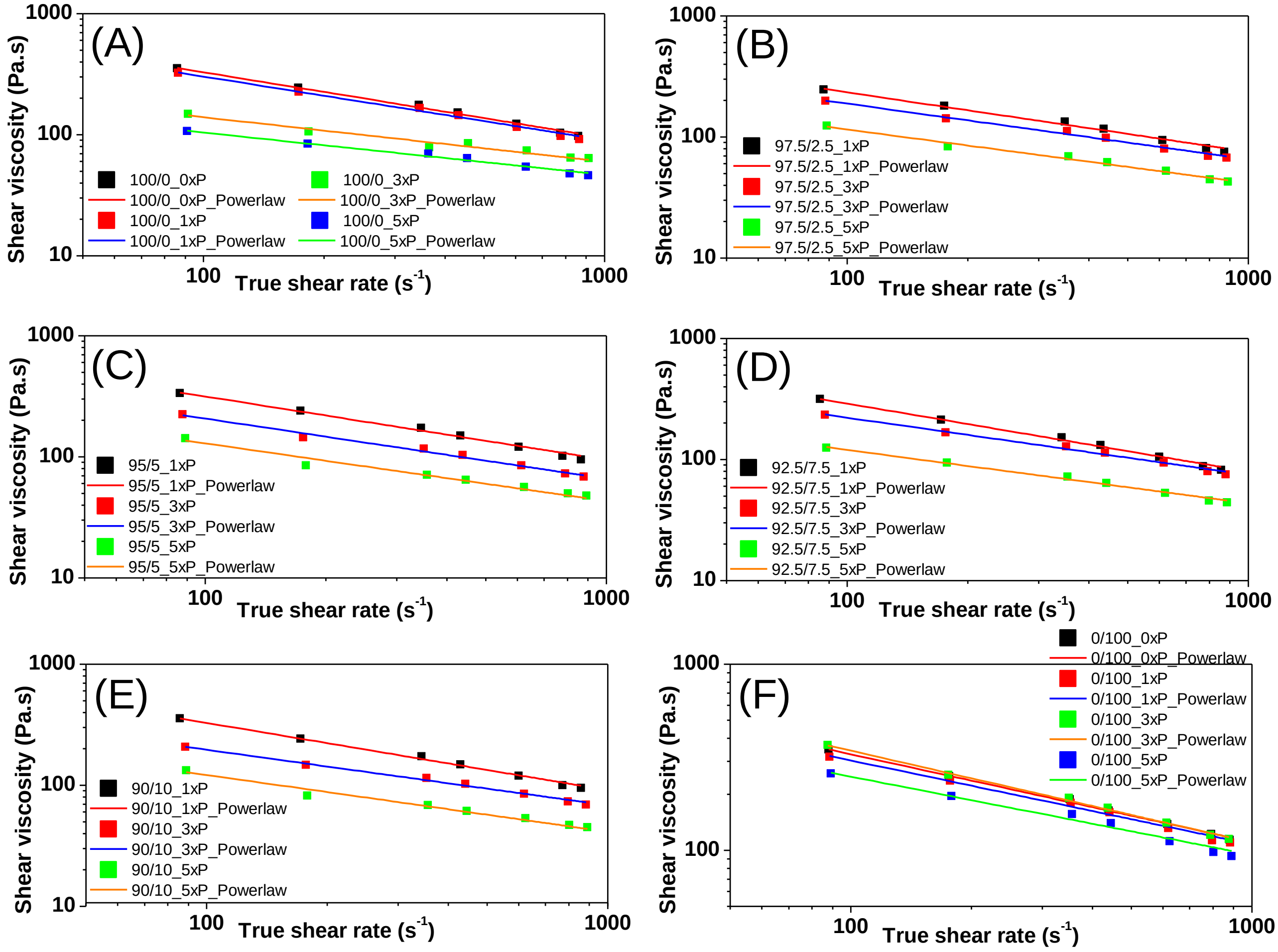

Figure A4: Capillary flow of all samples at 220°C with power-law model fit (A) 100/0 – 0,1, 3, and 5 times reprocessed; (B) 97.5/2.5 – 1,3, and 5 times reprocessed; (C) 95/5 – 1,3, and 5 times reprocessed; (D) 92.5/7.5 – 1,3, and 5 times reprocessed, (E) 90/10 – 1,3, and 5 times reprocessed; and (F) 0/100 – 0,1,3, and 5 times reprocessed.

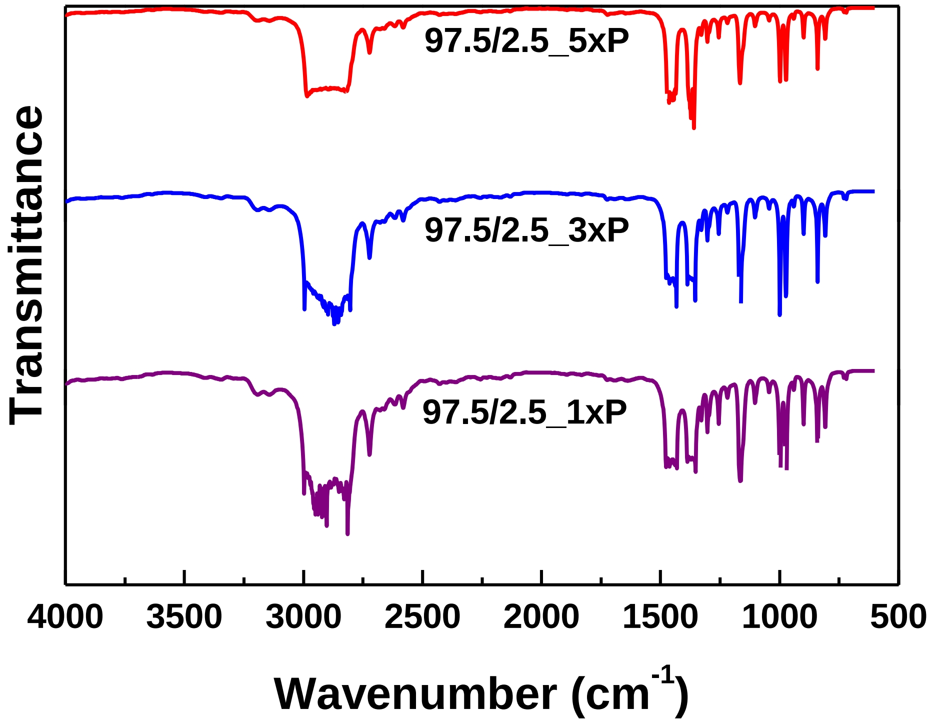

Figure A5: FTIR spectra of 97.5/2.5 (PP/LDPE) as a function of processing cycles

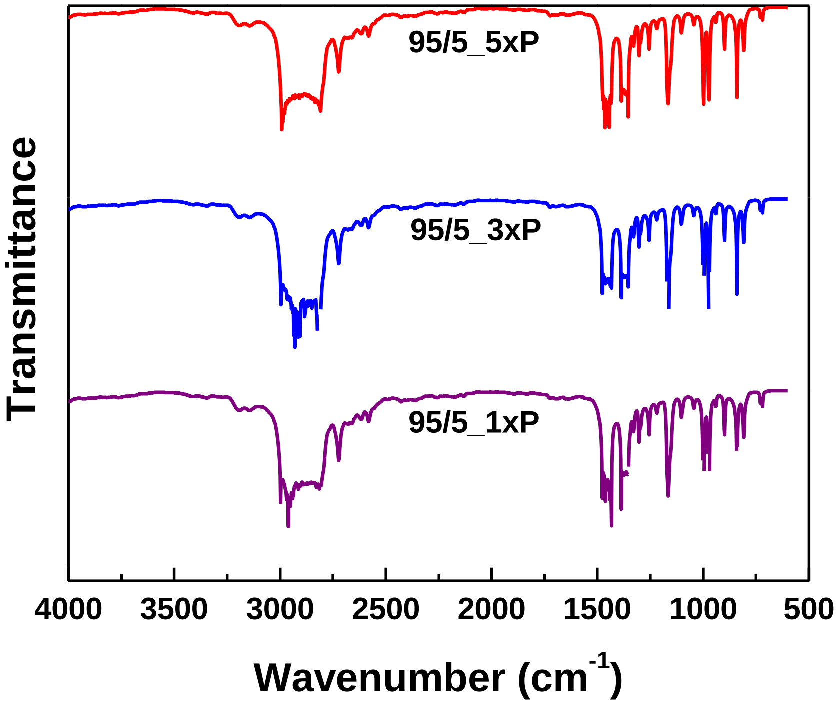

Figure A**6:** FTIR spectra of 95/5 (PP/LDPE) as a function of processing cycles

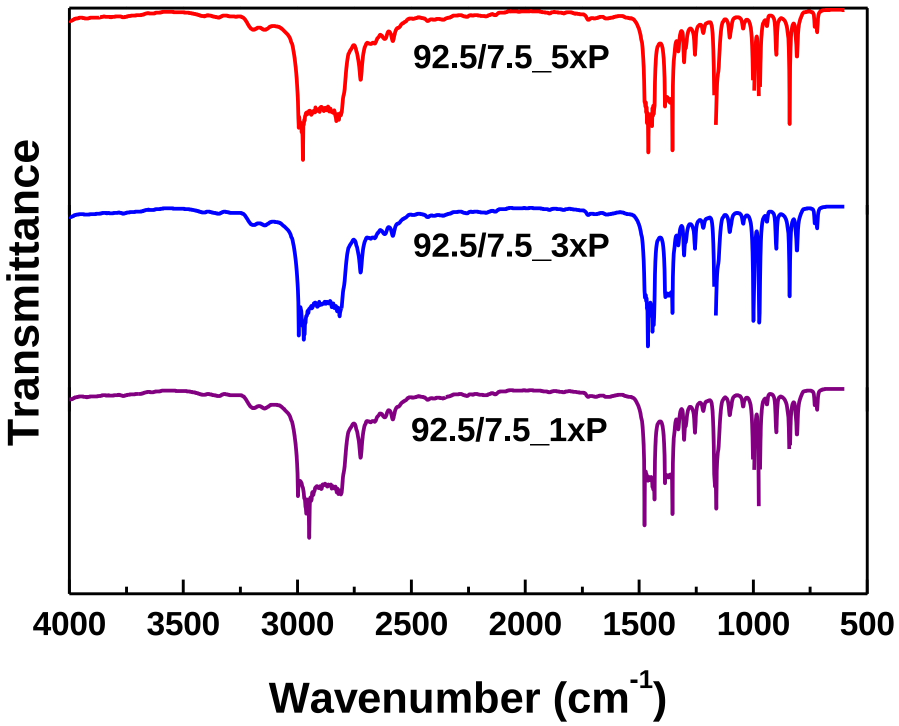

Figure A7: FTIR spectra of 92.5/7.5 (PP/LDPE) as a function of processing cycles