Recycling of HDPE

by

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ABSTRACT

High-Density polyethylene (HDPE) is the most used polymer on earth. Since it is used in such large quantities, it has become the most extensively produced polymer on the planet. Unfortunately, the rate of reusing or recycling HDPE is far behind the rate of production leading to plastic pollution. Most of this waste plastic ends up in landfills or incineration to recover energy. Plastic production consumes a lot of energy and is associated with CO2 emissions. This method of disposing plastic only adds to the environmental pollution rather than improving it. Primary reasons for low recycling rate appear to be more political and financial. In the US, the rate of recycling was less than 10% whereas Japan showed a recycling rate of more than 80%. The other aspect of low recycling is financial. In order to make recycling a financially viable process, efforts have to be made to streamline the process of waste collection, segregation and technically feasible process. This study focusses on the technical aspect of the issue. Even though efforts have been made to recycle HDPE, none of the processes have been recycle HDPE with financial viability, recovering full value of plastic, minimum CO2 emissions and minimum change in properties of the polymer. This study focusses on effective recycling of HDPE with minimum change in its properties. Dissolution has been used to dissolve the polymer selectively and then reprecipitating the polymer using a non-solvent to obtain the polymer grains. This is followed by mixing additives to the polymer grains to minimize degradation of the polymer during the extrusion process. The polymer is then extruded in an extruder beyond its melting temperature. This process is repeated for 5 cycles. After each cycle, the polymer is tested for its properties using the Tensile Testing, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), and Dynamic Mechanical

Analysis (DMA). It was observed that the rheological properties of the polymer were maintained after the 5th recycle whereas the mechanical properties deteriorated after the 2nd recycle. Also, increase in carbonyl index was observed after 5th recycle.

DEDICATION

To my parents

Renu Saini

Rakesh Saini

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CHAPTER 1

INTRODUCTION

The consumption of plastics has increased exponentially in the past 50 years. The reason being low cost and its applications in various fields such as food packaging - crates, trays, milk bottles, caps; transport – cars, buses, airplanes, bikes, rockets, satellites; housewares - ice trays, spoons, forks, fabrics, wash bottles, garbage containers, trash bags; sports and entertainment - toys, ropes, fishing nets, rackets; electronics – mobile phones, laptops, electric switches, insulation and miscellaneous - manufacturing containers, dispensing bottles, tubing, plastic bags, pharmaceutical and squeeze bottles, films food packaging (frozen foods), laminations, pipes, garment packaging, stretch film, etc. With such a wide variety of applications and convenience offered by plastics, it is impossible to imagine our lives in the modern world. On one hand, it has led to revolutionary advancements in the field of science and technology and on the other hand, it has created a problem of disposal resulting in plastic pollution.

According to a study conducted by Geyer et al. in 2015, the global production of plastics had increased to 380 million tons (Mt) from 2 Mt in 1950, annually. If we follow the current trend, we will produce more than 25000 (Mt) of plastic by 2050.[1] According to the Environmental Protection Agency (EPA)[2] of USA, approximately 35.7 Mt of plastic was generated in 2018. However, recycled plastic accounted for only 3.09 Mt which was less than 10 percent. The other 90 percent was either incinerated, landfilled or even worse ended up in oceans or littered. Since plastic takes a long time to decompose, this plastic waste will remain on earth for hundreds of years. These plastic products majorly constitute of high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET). Polyurethane (PU), polystyrene (PS), polyamide, polyacrylate, and polyesters. These groups constitute 92% of the total plastics produced in the world. Out of the total plastics production in the world, PE alone accounts for 36%.

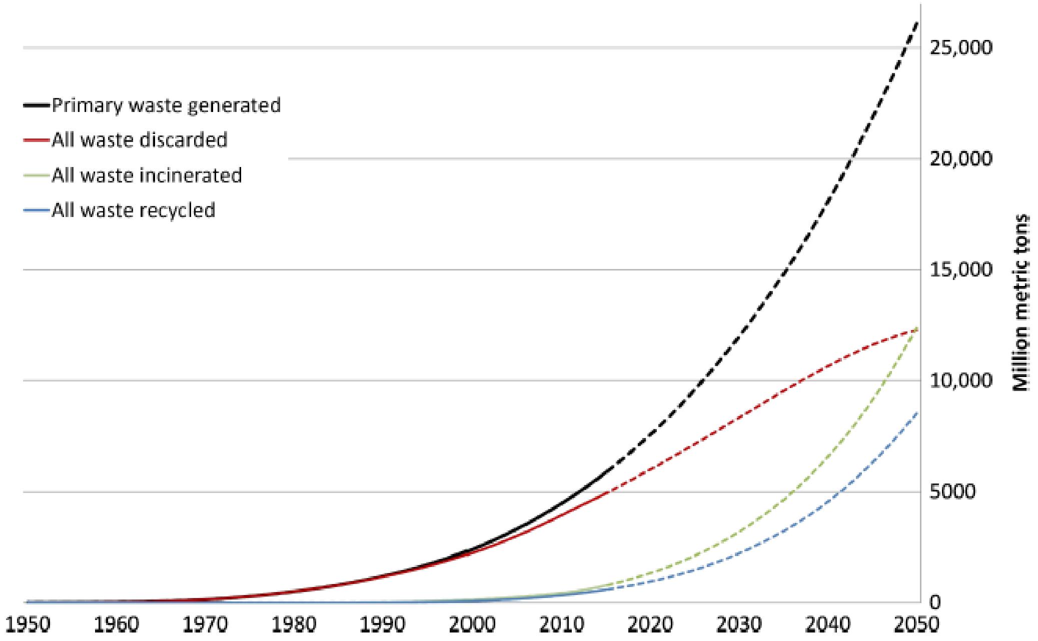


Fig 1. Prediction of plastic waste generation until 2050[1]

Recycling

With such excessive use of plastic products and poor waste management, it is only natural that most of the plastic ends up as a waste. However, efforts are being made in the right direction to improve the waste management and protect the environment. One such effort can be seen in the Kamikatsu village of Japan. The citizens of the village are so well educated about plastic waste management that they practically produce zero waste. The recycling rate in this village is around 80 percent.[3] Such practices could help to increase the recycling rates all over the world.

The recycling techniques can be classified into four major categories: Primary, Secondary, Tertiary and Quaternary[4]. In Primary recycling, the plastic products which are flawed during an industrial process are shredded and remolded back into useful products. Since this flawed product is in the industrial environment, it is not contaminated. Hence, this kind of recycling is simple and easy. Secondary recycling refers to the recycling of used plastic products. Hence, they are contaminated. Before recycling the waste plastic, it has to go through multiple steps of preparation. Primary and secondary recycling both fall under the category of mechanical recycling. Mechanical recycling can include some or all of the following steps depending on the source of waste:

Collection: For recycling the post-consumer plastic waste, it needs to be collected from the local municipality

Sorting: This can be done based on type of plastic, color, size and density

Washing: Water, caustic soda, surfactants can be used to wash the waste plastic depending on the contamination or source of waste

Crushing: The waste plastic is cut into small sizes of plastic

Extrusion and pelletization: The waste plastic can then be extruded into thin filaments and pelletized to be sold as a final product. [5]

Tertiary or chemical recycling involves breaking down the polymer into small molecules or monomers. Depending on the chemical composition of the polymer, techniques such as hydrolysis, aminolysis, glycolysis, methanolysis or acid cleavage can be used to depolymerize the polymer into monomers.[5-9] Pyrolysis, hydrogenation or hydrocracking is also used to convert plastics into high calorific value fuels. The techniques mentioned above could prove to be useful only when the separation of contaminants is not feasible and economical.[10] Also this way of recycling does not preserve the value added to the polymer during the polymerization stages.

One of the methods involved in chemical recycling is dissolution/precipitation technique. In this technique, the polymer is dissolved in suitable solvent and precipitated using a non-solvent. This simple technique results in recovery of a very high purity polymer.

The other category is classified as quaternary recycling. In this method, the energy stored in the polymer is utilized by using them as a secondary fuel to burn (incineration of plastic). This incineration of plastic takes place along with other solid waste collected. This causes a release of harmful greenhouse gases which can also include acids, aldehydes, aromatic compounds, dioxins, etc. [11] This type of recycling is usually on the bottom of the list to recycle the polymer because it not only wastes away the money, resources and value added to the polymer but also increases the risk of global warming.

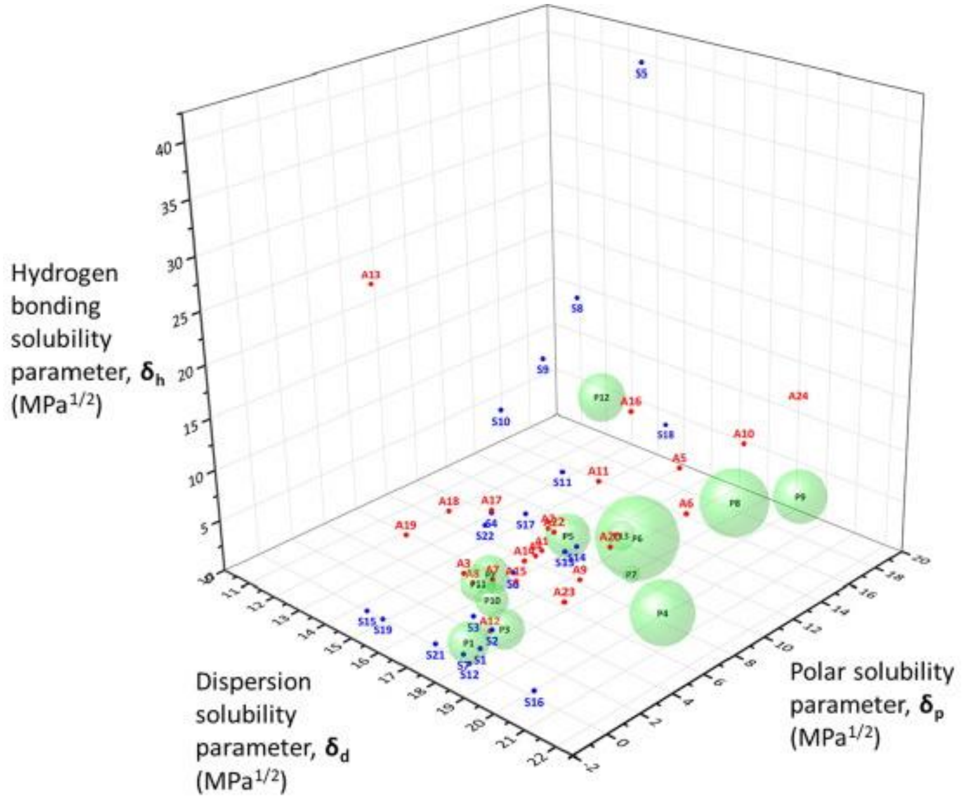
Considering all the parameters, dissolution/reprecipitation technique was thought to be the best approach for recycling of polymer which is the topic of research in this study. This technique has been combined with the use of additives during the extrusion process to minimize the degradation of HDPE.

Selection of solvent

The selection of solvent plays a very important role in the feasibility of this process. The solvent should be such that it should minimize the steps involved in separation of HDPE from other polymers. If possible, the selected solvent should dissolve only the desired polymer. However, there are other factors that need to be considered during its selection. This includes volatility, temperature of dissolution i.e. energy required to dissolve the polymer, compatibility with non-solvent, heat capacity, difference between the boiling points of the solvent and non-solvent, health hazards. An ideal solvent would be non-volatile, very high saturation point of solubility, dissolves the polymer at room temperature, low heat capacity, large gap between boiling points of solvent and non-solvent for easier and high purity separation using distillation and no health hazards.

There have been many theories that have tried to explain the solubility of a polymer in a solvent. One such theory is the Flory-Huggins (FS) theory. It considers the traditional solution theory of lattices to explain the solubility of polymers. This theory holds good for polymer solutions with moderate concentrations but has its limitations when it comes to dilute solutions and high concentration polymer solutions. [12] Hence this theory has been modified over time by several researchers for accurate prediction of solubility. Some of the commonly known theories are Hildebrand and Scott (HS), Burrell, and Hansen. The HS theory considers the difference in solubility parameters of solvent and polymer to determine solubility. This is based on the cohesive energy density of the solvent. However, factors such as hydrogen bonding have not been considered. To overcome this problem, Burrell modified the theory to incorporate the hydrogen bonding factor. However, other factors such as crosslink density, molecular weight and, temperature which play an important role in determining the solubility of a polymer, were not considered this theory. Hansen has further modified this theory in order to help with some of the inconsistencies provided by earlier theories. Hansen considers factors such as non-polar/dispersion, polar and hydrogen bonding to minimize the limitations of earlier theories.[13]

The 3D graph shown in the figure 2 uses spheres to represent the solubility of polymer in a particular solvent. If the solvent sphere is within the polymer sphere, it means that the polymer is soluble in the solvent.[13] This makes the selection of solvent for a polymer easier. However, as discussed earlier, there are other parameters that need to be considered while selecting the solvent. In case of HDPE, solvents such as Toluene, xylene, Benzene, carbon tetrachloride and acetone seemed suitable. Considering all the parameters such as solubility, chemical hazards, volatility, cost, heat capacity; Toluene was concluded to be the best solvent for HDPE and hexane as the non-solvent in this case.



Solvents	
S1	Benzene
S2	Toluene
S3	Xylene
S4	Ethyl acetate
S5	Water
S6	Chloroform
S7	Carbon tetrachloride
S8	Methanol
S9	Ethanol
S10	2-propanol
S11	n-propanol
S12	Acetone
S13	Decalin
S14	Cyclohexanone
S15	DCM
S16	Isooctane
S17	Carbondisulfide
S18	THF
S19	Acetonitrile
S20	Hexane
S21	CYHA
S22*	CO_2

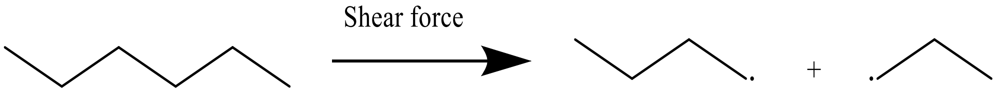
Polymers	
P1	HDPE
P2	LDPE
P3	PP
P4	PS
P5	PMMA
P6	PET
P7	PVC
P8	Polyvinylacetate
P9	Polyacrylonitrile
P10	Polybutadiene
P11	Polyisobutylene
P12	PA
P13	PC

Additives		
A1	DEHP	Phthalate Plasticizers
A2	MEHP	
A3	DiNP	
A3	DOA	Adipate Plasticizers
A5	TBBPA	Halogenated Flame retardants
A6	Pentachlorophenol	
A7	Perm Rubin F6B Hoechst	Azo derived Pigments
A8	Perm Gelb GRL02 Hoechst	
A9	Perm Lackrot LC Hoechst	
A10	Red Iron Oxide	Metal Oxide Pigment
A11	Bisphenol A	Hindered Phenolic type Primary Antioxidants
A12	BHT (ionol)	
A13	Irganox 1135	
A14	Irganox 1076	
A15	2,3,5-trihydroxybutyrophenone	
A16	Butylated hydroxyanisole	
A17	4-Hydroxymethyl-2,6-di-tert-butylphenol	
A18	α-tocopherol	
A19	Topanol CA	
A20	Irganox 1010	
A21	Ascorbic acid	Hydroxylated Acid Antioxidant
A22	Santonox	Thioether type Secondary Antioxidants
A23	Irgafos 168	Phosphite type Secondary Antioxidants
A24	Hydroxyphenylbenzotriazoles	Hindered amine UV Stabilizer

Figure 2. Solubility diagram for polymers and additives based on Hansen solubility parameters

Mechanism of degradation

Degradation of a polymer can alter the mechanical, rheological, and structural properties of the polymer. Hence it is important to understand the mechanism of degradation. The degradation of a polymer during processing usually depends on several factors. Some of the important factors that need to be considered are shearing forces, temperature, oxygen content, impurities, and catalysts. Depending on the conditions, degradation can follow different mechanisms. During processing of the polymer, the polymer melt is subjected to high shearing forces. The shear forces between the polymer, screw and barrel of the screw results in chain scission of the polymer. The scission of the polymer chain generates free alkyl radicals ($R^{\cdot}$). Such degradation can be referred to as thermo-mechanical degradation. This can be understood from the following reaction.

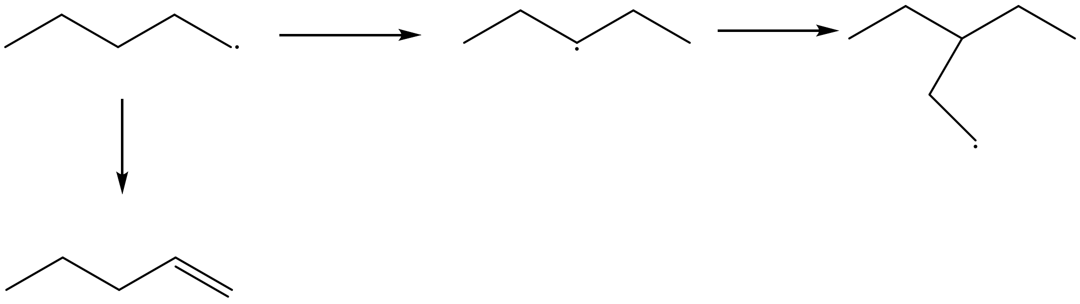


... Eq. 1

After the formation of free alkyl radicals, it can lead to several side reactions. These side reactions can either follow one of the 2 routes or both the routes simultaneously.

In route 1, the free radicals on a polymer chain attack other polymer chain. This can cause long branching of the polymer chains, short branching of polymer chains, vinyl group formation or even cross linking in extreme cases. Thus, changing the length of the polymer alters the molecular weight of the polymer. In route 2, the free alkyl radicals react with oxygen present in the environment to form peroxy radicals ($ROO^{\cdot}$). These peroxy radicals can react with polymeric chains to form more free alkyl radicals and hydroperoxides. Furthermore, these hydroperoxides can decompose into alkoxy radicals ($RO^{\cdot}$) and hydroxy radicals ($^{\cdot}OH$). The alkoxy radicals then react with the polymer chains to give more alkyl free radicals and alcohol (R-OH) whereas the hydroxy radicals react with the polymer chains to give more free alkyl radicals and water.[14, 15] These side reactions can thus lead to a variety of compounds which include hydroperoxides, aldehydes, ketones, esters or carboxylic acids. According to most scientists, HDPE degradation usually follows this mechanism when the processing temperature is below 230 C – 250 C. [14]

Route 1:



Route 2

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \qquad \text{...Eq. 2}$$

$$RO\dot{O} + RH \longrightarrow ROOH + R^{\bullet} \qquad \text{...Eq. 3}$$

$$ROOH \longrightarrow R\dot{O} + \dot{O}H \qquad \text{...Eq. 4}$$

$$2\,ROOH \longrightarrow R\dot{O} + ROO^{\bullet} + H_2O \qquad \text{...Eq. 5}$$

$$R\dot{O} + RH \longrightarrow ROH + R^{\bullet} \qquad \text{...Eq. 6}$$

$$\dot{O}H + RH \longrightarrow H_2O + R^{\bullet}$$

…Eq. 7

$$RO\dot{O} + R^{\bullet} \longrightarrow ROOR$$

…Eq. 8

$$R\dot{O} + R \longrightarrow ROR$$

…Eq. 9

As mentioned earlier, shearing forces developed during processing are responsible for generation of these free radicals which leads to degradation. The degradation is also affected by speed of the screw. According to Gonzalez et al, higher the screw speed higher is the degradation.[16, 17]. Conversely, the degradation can be minimized with lower extrusion rates. Moreover, the degradation can be further reduced by lowering the oxygen content or extruding in vacuum. Herken et al showed that the degradation can be kept at minimum if the vacuum pressure is low enough.[18]

In addition to proper design and operating conditions, the use of antioxidants or additives is the most common way of controlling degradation. These antioxidants can be classified as primary and secondary antioxidants. Primary antioxidants are of two types: chain breaking donors (CBDs) and chain breaking acceptors (CBAs). CBDs are antioxidants which donate hydrogens to free alkyl radicals and themselves form stable radicals. CBAs scavenge the free radicals by attaching themselves or a part of themselves to the free radicals. However, the primary antioxidants cannot scavenge free radicals like OH and RO. In order to stabilize these radicals, hydroperoxide decomposers are used. These are known as the secondary antioxidants. Phenolic groups, aromatic amines, hydroxylamines, C-radical scavengers, phosphites and phosphonites, organosulphur compounds are some of commonly used additives for stabilization.[14] In this research, Pentaerythritol Tetrakis(3-

(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), also know as Irganox 1010 and tris(2,4-di-tert.-butylphenyl) phosphite, also known as Irgafos 168, has been used. Irganox 1010 is a primary antioxidant which belongs to a sterically hindered phenol group whereas Irgafos 168 is a secondary antioxidant.

CHAPTER 2

MATERIALS AND METHODS

Dissolution process

Waste High Density Polyethylene (HDPE) pellets were provided by Plastics General in Chandler, Arizona. Hexane and Toluene of ACS grade were purchased from VWR Chemicals. Additives Irganox 1010 was purchased from Sigma Aldrich and Irgafos 168 was purchased from Combi-blocks. Stainless Steel 316 filter cloth was purchased from McMaster Carr. To dissolve the polymer, a 1000 ml round bottom flask was used. HDPE pellets were then added to the flask along with Toluene. The mixture was then heated using a hot oil bath. To ensure complete and homogeneous solution, the mixture had to be continuously stirred and kept at 110 C. Since the boiling point of Toluene is 110 C, the heating had to be done using a reflux condense to avoid any loss of solvent. The mixture had to be continuously stirred for complete dissolution of all the HDPE pellets in the flask. The concentration of the solution had to kept at 2% for easy flow of solution. Solution of higher concentration led to loss of polymer during transfer of the solution from one vessel to another. In order to remove any foreign material or impurities from the solution, it was filtered through a SS 316 filter cloth. In order to get rid of the smallest impurities, the pore size of the filter was kept at 0.0034 inches. During the filtration process, a small amount of HDPE precipitates on the filter due to cooling from atmosphere. Hexane was added to this solution to completely precipitate the polymer. The ratio of hexane to toluene is 1:1. In order to collect the precipitated HDPE, the mixture was then passed through a buchner funnel with a vacuum and a filter paper of size Q5. Filtration had to be carried out multiple times until a clear mixture of solvent/not solvent was obtained to prevent any loss of HDPE.

The experimental set up is shown in figure 3. The HDPE precipitate was then left for drying in the fumehood overnight. In order to remove the Toluene completely from the HDPE pellets, they were vacuum dried in oven at 85 C for 12 hours. The size of the dried pellets of HDPE were uneven and hence could lead to improper mixing of additives. Uneven size of pellets could also lead to overheating or underheating of pellets due to hotspots inside the extruder. To avoid this problem, the HDPE pellets were crushed to a fine powder using a coffee grinder. Figure 4 shows the images HDPE before and after crushing. The powdered HDPE has a considerable amount of static charge on it. This could lead to loss of product. To overcome this problem, an antistatic gun was used.

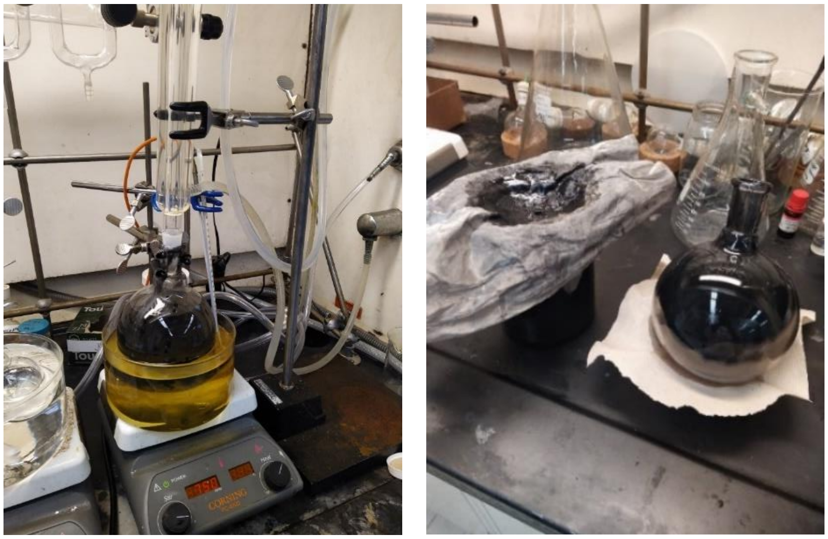


Figure 3a. Experimental set up for dissolution, filtration and reprecipitation of HDPE

Figure 3b. Experimental set up for dissolution, filtration and reprecipitation of HDPE

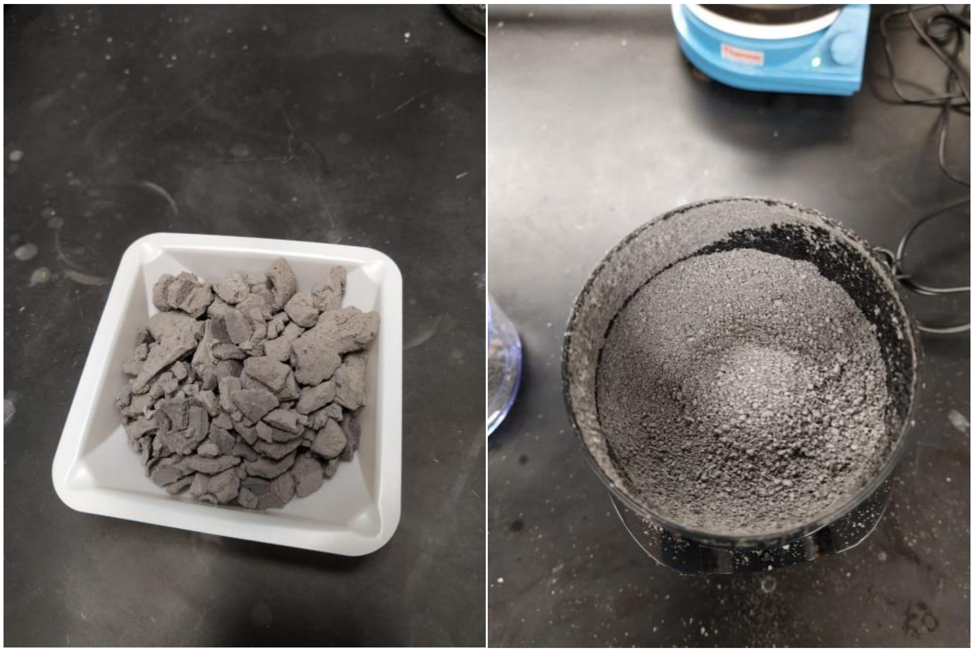


Figure 4. Reprecipitated HDPE before and after crushing

CHAPTER 3

EXPERIMENTAL METHODS

Extrusion

The extrusion process was carried out in a filabot extruder EX2. In the extrusion process, the powdered HDPE was slowly added to the hopper of the extruder. At the same time, the additives Irganox 1010 and Irgafos 168, with a concentration of 450 and 750 ppm respectively, were slowly added to the hopper of the extruder.[19] The extrusion was carried out at an optimum temperature of 230 -235 C with speed of the extruder varying between 25-30 rpm. This resulted into long thin filaments of HDPE. The extrusion set up is shown in figure 5. These filaments were then fed to a crusher to obtain small filament pieces (for easier addition of filaments into the round bottom flask for the next cycle of dissolution). The small filament pieces also have a considerable static charge on them which necessitates the use of antistatic gun. Once this step is complete, the characterization of the polymer is done. This completes one cycle of recycling. Following the same procedure, the polymer was recycled 5 times.

Figure 5. Extrusion set up

Characterization

FTIR

IFS 66v/S vacuum FT-IR by Bruker optics was used to run Fourier transform infra-red (FTIR) spectroscopy at 4 cm^{-1} resolution and 32 scans. The IR spectra was collected with KBr beam splitter, DLTAGS detector and using the ATR sample module in a vacuum environment of 5 mbar. To prepare the specimen for FTIR, the pellets were compressed into a thin and smooth sheet using a melt press. The carbonyl index was determined using SAUB method. This method uses the area under a specific region to provide greater coverage of C=O band and increased precision. To determine the carbonyl index, the area in the region of 1650-1850 cm-1 was considered which represents the formation of non-volatile carbonyl oxidation products. The vinyl index was determined by measuring the intensity for vinyl CH group at 908 cm^{-1}. This gives the number of C=C bonds per 1000 C atoms.

Tensile Test

Instron E3000 was used to perform the tensile test on HDPE specimens by ASTM D-1708 method. The specimens were tested with a rate of 0.05 mm/s at room temperature to determine the mechanical properties of the polymer such as Young's modulus, tensile strength at yield point and elongation at break. To prepare the specimens for tensile test, a melt press was used. Two aluminum sheets of size 6 x 6 inches and thickness 1/8 inch was used. The HDPE pellets were heated up to 170 C for 5 min and compressed at a pressure 1 MPa. The compressed HDPE was allowed to cool naturally for 10 min. Specimens were then cut using a die of the specified size.

Differential Scanning Calorimetry

A Q2000 DSC from TA instruments was used to obtain thermograms of waste and recycled HDPE. The material was first heated from room temperature to 200 C. The sample was heated at a rate of 10 C/min. Nitrogen atmosphere was used for blanketing during the heating and cooling of the sample. Weight of empty pan and lid varied around 51 mg whereas the amount of sample varied around 5 mg. The thermograms were analyzed using Universal Analysis software.

Rheology

A discovery hybrid rheometer (DHR) of TA instruments was used to determine the rheological properties of the waste and recycled samples of HDPE in an open atmosphere. A peltier plate parallel plate geometry was used with a diameter of 25 mm. Flow sweep was carried out at 190 C with a shear rate from 0.01 1/s to 50 1/s in an open atmosphere. The cell gap was kept as 200 um This was further used to calculate melt flow rate (MFR) of the polymer using the following formula[20]:

$$\tau = 9.13 * 10^4 \text{ L}$$

$$\gamma = 1.83 \text{ MFI}/\rho$$

where τ is shear stress in dyne/cm2

L is the load in Kg

γ is shear rate in 1/s

MFI is g/(10 min)

ρ is the density of the polymer in g/cc = 0.93

The values of the constants have been calculated using the geometrical parameters of a melt flow apparatus.

The DHR was further used to run dynamic mechanical analysis to determine the viscoelastic properties of the waste and recycled HDPE specimens in an open atmosphere. A peltier plate parallel plate geometry was used with a diameter of 25 mm. Frequency sweep was carried out at 190 C with an angular frequency from 0.01 rad/s to 100 rad/s. The cell gap was kept as 1 mm and strain at 0.1 % to obtain a dynamic rheological response in the viscoelastic region. Amplitude sweep was carried out to determine the viscoelastic region of the polymer at 190 C.

CHAPTER 4

RESULTS AND DISCUSSION

Dissolution time

To prepare a solution of a HDPE in Toluene, it was necessary to determine the appropriate concentration of solution so that the filtration process is simpler. If the concentration of solution is high, the solution would just stick to the walls of the container or would just precipitate on the filter. This would not allow filtration of unwanted particles from the solution. Poulakis et al studied the effect of recycling on HDPE using dissolution and reprecipitation. The concentration of the solution was 10 wt% for their experiment. Hence, this study was started with a preparation of 10 wt% concentration solution. However, this solution was too viscous to flow from the beaker to the filter. Hence, 5 wt% concentration solution was prepared. Although this solution was able to flow, it could not pass through the filter and would just precipitate. Ultimately, a 2 wt% concentration was prepared which was able to flow and pass through the filter.

During the dissolution of HDPE pellets in Toluene, it was observed that HDPE pellets would swell up and led to increase in volume of solution. This increase was observed to be around 15-20%. Hence, selection of appropriate vessel size is critical to avoid overflow of solution.

The time required for dissolution of HDPE pellets was observed to gradually increase with each cycle of recycling. During the first cycle, complete dissolution of waste HDPE pellets was achieved in 60 minutes whereas the dissolution time increased to 180 minutes after first cycle. After the second cycle, the time needed to dissolve HDPE completely was more than 15 hours. The third cycle needed more than 22 hours whereas fourth cycle needed more than 30 hours for complete dissolution of the polymer. This gradual increase in dissolution time could be attributed to long chain branching (LCB) or crosslinking of the polymer. Due to crosslinking or LCB, the solvent molecules find it difficult to penetrate the densely entangled polymer. Thus, preventing the polymer chains to dissolve in the solvent.[21, 22]

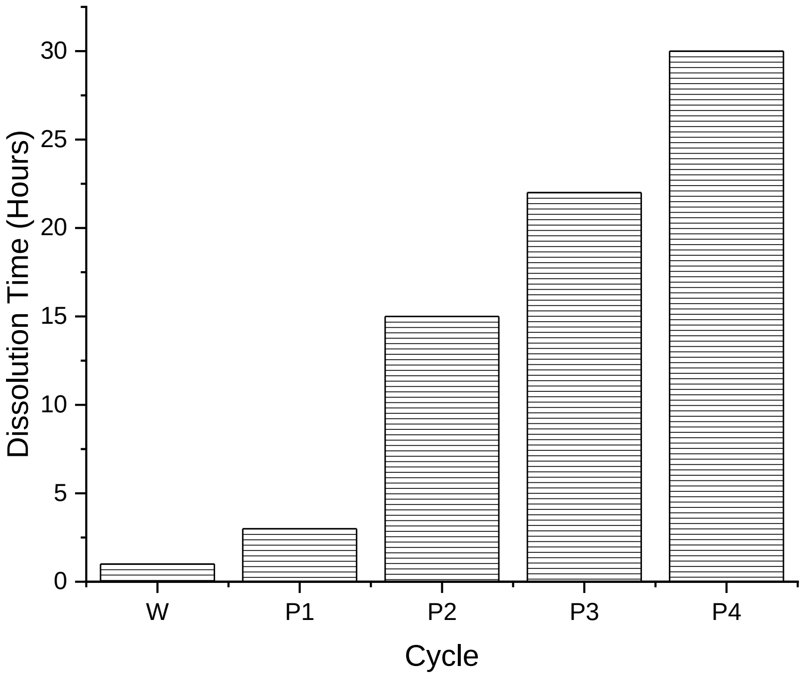


Figure 6. Comparison of dissolution time for recycled HDPE

Extrusion

Once vacuum dried and crushed, the powdered HDPE was extruded into thin filaments using a EX2 Filabot extruder. In order to determine the correct operating conditions for the HDPE sample, a series of extrusions was carried out. In the first test, the powdered HDPE

(Waste) was extruded at 190^0 C without any additives and was labelled as E1. In the second test, the extrusion was carried out at 190^0 C with additives. In this step, the antioxidants were mixed with the polymer prior to feeding the polymer to extruder. The powdered HDPE and antioxidants were put in a glass beaker and mixed with spatula. The mixing process was done for 15 min. This was labelled as E2. In the third test, the extrusion was carried out at 190 C where the additives and HDPE were simultaneously added to the hopper of the extruder. The sample was labelled as E3. In the fourth test, the extrusion was carried out at 230 C by mixing the additives prior to feeding the hopper of extruder. The extruded sample was labelled as E4. In the fifth test, the extrusion was carried out at 230 C where the additives and HDPE were simultaneously added to the hopper of the extruder. This sample was labelled as R1. After comparing the mechanical performance of the 5 tests from tensile test, procedure followed for R1 was standardized was further recycles.

Tensile test

An Instron Tensile tester was used to test the mechanical performance of the waste and recycled HDPE. The tensile strength for recycled samples were tested until failure of the specimen. The shredded filaments from each cycle of extrusion were used to prepare specimens for tensile tests using a melt press.

Figure 7 shows a stress-strain curve for waste HDPE. The stress-strain curve for waste HDPE first follows the Hooke’s law where stress linearly increases with increase in strain. Once the yield point (point on the stress strain curve where first non-linear pattern is observed) is reached, the plastic deformation of the specimen begins. This is where necking of the specimen takes place. This region can be identified by a decrease in stress of the specimen. However, even after necking, the stress continues to increase. This is a typical behavior of a stress strain curve for HDPE. The elongation for a virgin HDPE exceeds 1000 %[23]. However, the maximum elongation at break for waste HDPE was observed to be 230%.

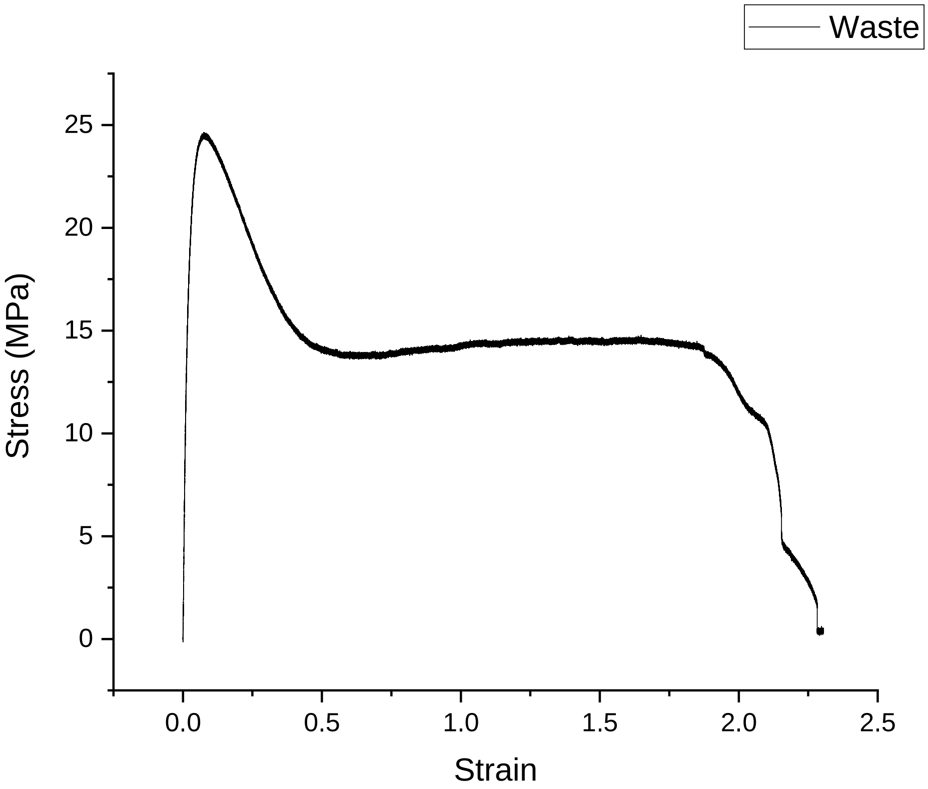


Figure 7. Stress-strain plot for waste HDPE specimen

Similarly, tensile tests were carried out for specimens HDPE (W), E1, E2, E3 and R1. Three specimens were tested after each cycle. Figure 8 shows the comparison of these specimens. It can be clearly seen that after extrusion of HDPE of just one cycle, the elongation has significantly reduced. For all the extrusions cycles carried out, the yield point of the samples has increased as compared to the waste HDPE specimen. The yield point is highest for extrusions carried out at temperature of 230 C which is E4 and R1 cycle. In R1 cycle, the additives and polymer were simultaneously added to the extruder which ensured better mixing of the additives. However, the shape of stress strain curve was retained only for one of the extrusion cycles. Also, R1 cycle showed maximum elongation and modulus as compared to all other cycles. In R1 cycle, the additives and polymer were simultaneously added to the extruder which ensured better mixing of the additives. Hence, this was one of the reasons to choose simultaneous addition of additives during the extrusion of HDPE for further cycles.

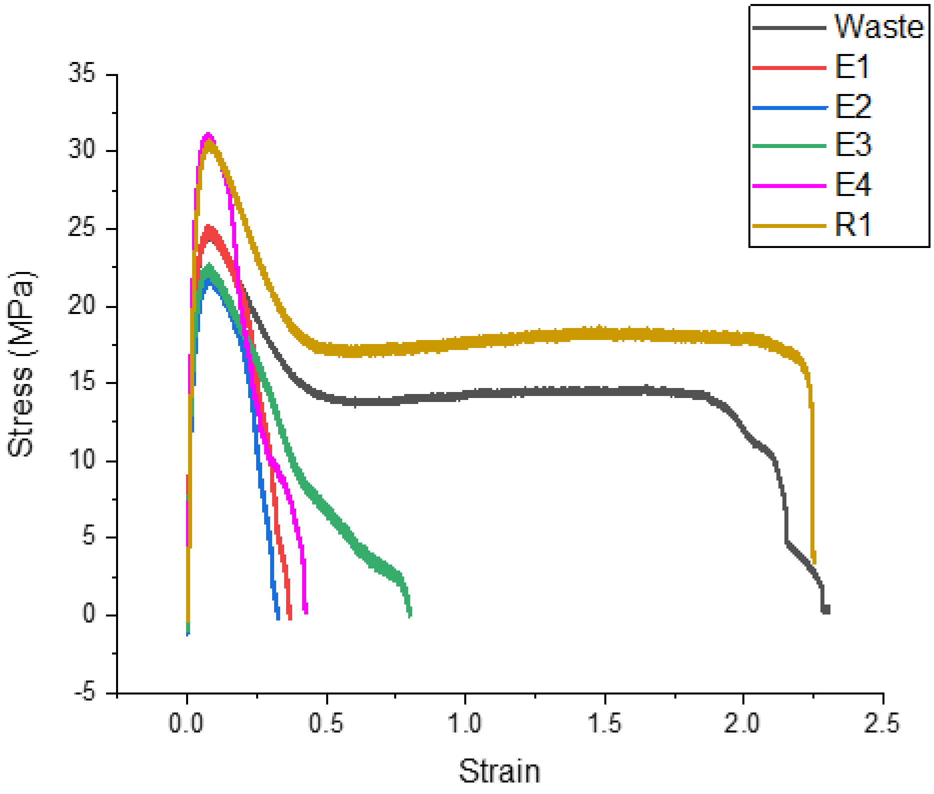


Figure 8. Comparison of stress-strain plot for optimum process conditions

Once the method of antioxidant addition to the extrusion process was fixed, 5 cycles of dissolution, reprecipitation and extrusion was carried out. After each cycle of extrusion, the mechanical performance of the HDPE specimens was tested. After each extrusion cycle, it is observed that the yield point of the specimen has increased gradually. This can be seen in figure 9. Moreover, the modulus has also increased gradually. This increase in modulus further strengthens the idea that with each cycle of extrusion, the crosslinking percent in the polymer is increasing. Such increase in modulus and yield point contributes towards enhanced material strength. However, it is also observed that with each cycle the maximum elongation at break is also decreasing. This gives us an idea of decreasing ductility of the material. The stress-strain plots of the waste and recycled HDPE is shown in figure 9.

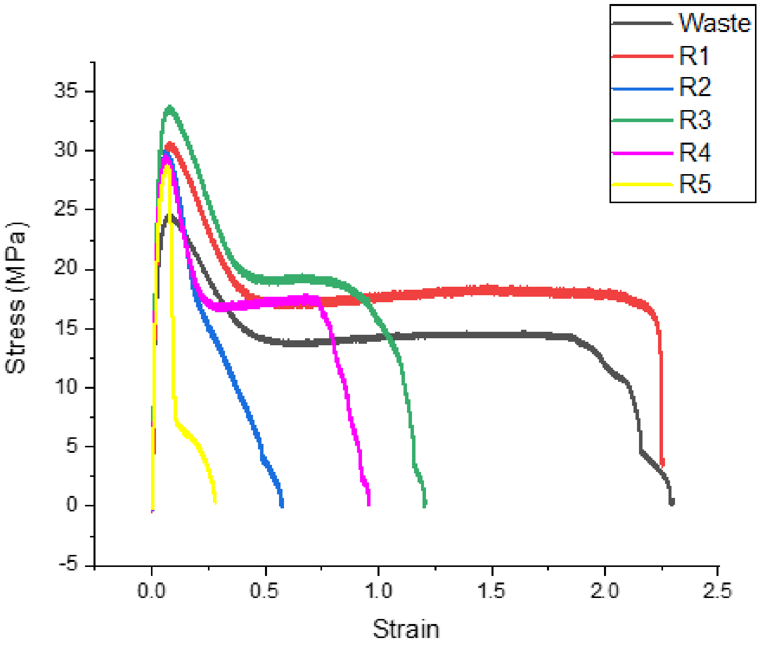


Figure 9. Comparison of stress-strain plot of waste and recycled HDPE specimens

Also, the elongation at break is not constant for all the three specimens. It can be seen that lowest elongation for the specimens could be as low around 50%. Such variability in elongation means that some parts of the polymer chain are showing crosslinking whereas some parts of the chain have been prevented from crosslinking due to additives. This could be due to the non-uniform mixing of additives during the extrusion process. This variability has been represented in the box plot as follows.

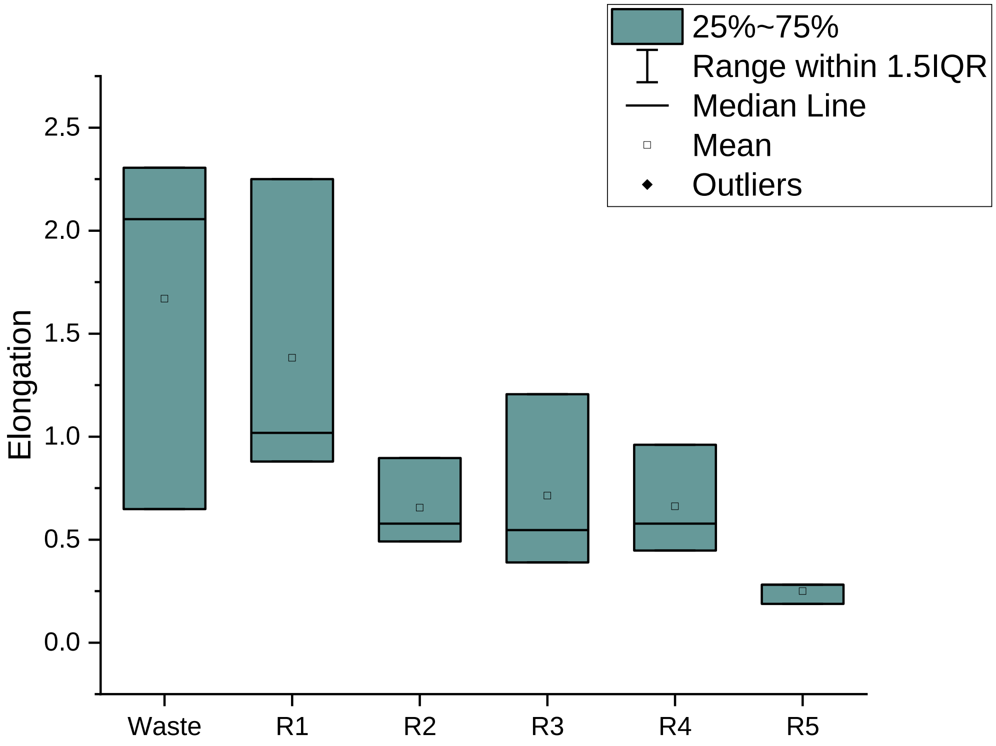


Figure 10. Box plots for comparison of elongations for specimens from each recycle

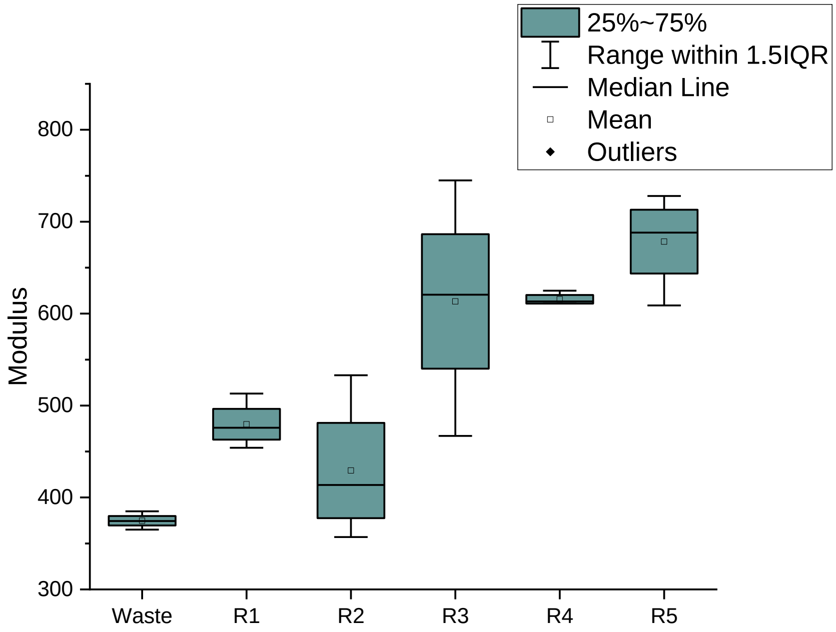


Figure 11. Box plots for comparison of moduli for specimens from each recycle

Table1 compares the mechanical performance of the recycled polymer after different cycles.

Table 1. Mechanical properties of waste and recycled HDPE

Cycle	W	1	2	3	4	5
Avg. Modulus (MPa)	375	480	430	613	615	678
Max. Tensile strength (MPa)	30	30.7	30.6	36.5	29.7	29.8
Max Elongation (%)	230	225	90	120	96	28

The crosslinking phenomena could be explained by the free radical mechanism. When the polymer pellets are dumped into the hopper of an extruder, the temperature of the polymer increases and melts the polymer. When the polymer melt is gradually passed through the screw of the extruder, it tears apart the polymer chains resulting into free alkyl radicals. Some of these free radicals either form a vinyl group or a branched chain or cross-link or oxidize into carboxylic acids or ketones. In order to suppress these reactions, antioxidants irganox 1010 and irgafos 168 was used. From the data of the tensile tests, it can be seen that even with use of these antioxidants, the polymer starts to form long chain branches, short chain branches or crosslinks. During each extrusion cycle, some amount of chain scisson, branching, cross-linking takes place. This amount of degradation can be decreased with proper mixing of antioxidants with the polymer. The mixing of additives with the polymer powders in this study was not perfect.

FTIR

The analysis was done to determine the oxidative stability of the polymer in the form of carbonyl index which could correspond to mixture of ketones, aldehydes or carboxylic acids. Figure 12 shows an IR spectrum for waste polyethylene.

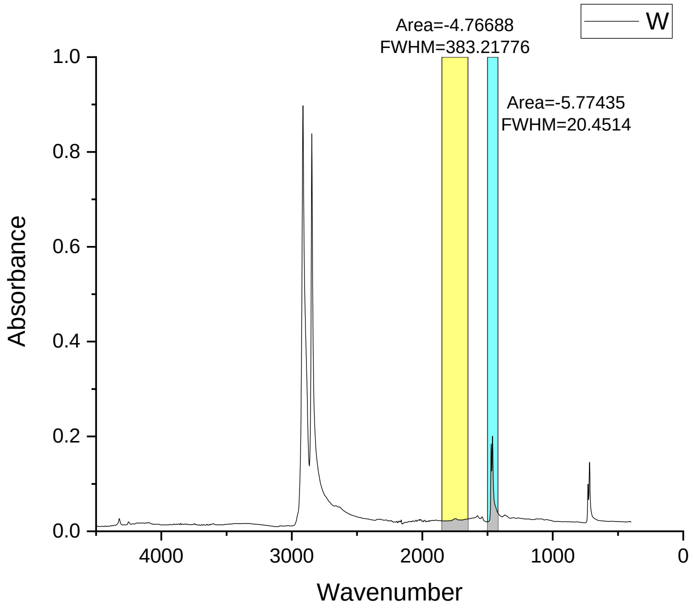


Figure 12. FTIR spectra for waste HDPE specimen

The carbonyl index (CI) was determined using the SAUB method described by Almond et al.[24] This method uses the region between 1850 to 1650 cm^{-1} and 1500 to 1420 cm^{-1} to estimate the formation of non-volatile carbonyl oxidation products. The region between 1850-1650 cm^{-1} belongs to the carbonyl stretch (C=O) whereas region between 1500-1420 cm^{-1} belongs to the methylene stretch (CH$_2$).

$$CI = \frac{\text{Area under band 1850 to 1650 cm} - 1}{\text{Area under band 1500 to 1420 cm} - 1}$$

The CI for waste and recycled HDPE is depicted in the figure 13. With increase in the number of cycles, it can be seen that there has been a gradual increase in CI. For samples R1, R2, R3, and R4, a slight decrease in CI is observed. This could be due to the dissolution, filtration and precipitation procedure of the sample. It is possible that part of the polymer chains which were oxidized during extrusion were filtered out after the dissolution process. In cycle R2 and R5, a slightly sharper increase in CI has been observed as compared to the gradual increase in CI of other recycled samples. This is because during extrusion cycle of R2 and R5, the extruder was slightly clogged resulting in slower extrusion and hence higher residence time. As the polymer was exposed to high temperature for longer period of time, sample R2 and R5 were prone to higher oxidation and hence exhibiting higher CI. This can also be confirmed with stress-strain analysis which showed lower elongation as compared to other recycled samples. In order to avoid this clogging in future cycles, the extruder was first pre- heated upto 270 C and allowed to stay at 270 C for 10 min. This would eliminate any kind of polymer that was stuck in the extruder. The extruder temperature was then lowered down to 230 C before starting the extrusion process.

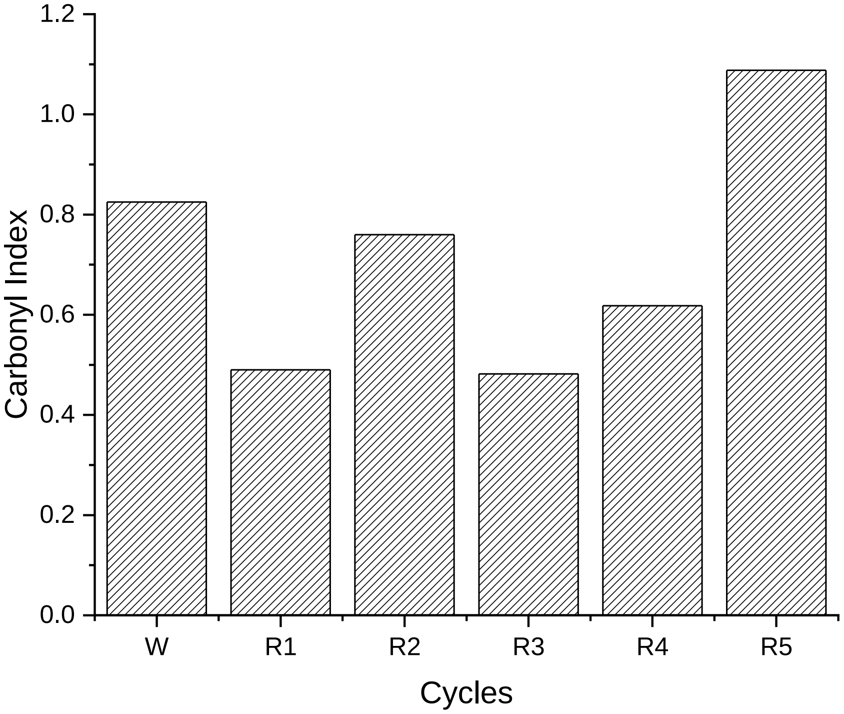


Figure 13. Comparison of carbonyl index for waste and recycled HDPE specimens

The FTIR analysis was further used to determine vinyl unsaturations in the polymer. This was determined using the method described by Stark et al.[25] The vinyl index (VI) is calculated from the ratio between intensity peak at 1715 cm^{-1} and the intensity peak at 2912 cm^{-1}. This is expressed as follows:

$$\mathrm{VI} = \frac{\mathrm{I}908}{\mathrm{I}2912}$$

From figure 14, it can be observed that the VI decreases for most of the cycles. This decrease in vinyl concentration is indicative of vinyl groups reacting with other polymer chains.[26, 27] This reaction gives rise to short chain branching or long chain branching or crosslinking. This reaction is also accompanied by chain scission reaction to small extent. From the data gathered so far, it seems that cross linking reaction is the more dominant reaction as compared to chain scission.

However, in some cases, increase in VI has been observed. This is indicative polymer chain scission in the extruder. This could be observed in cycle R2 and cycle R5. Higher residence time could be the reason for chain scission to be the dominant reaction.

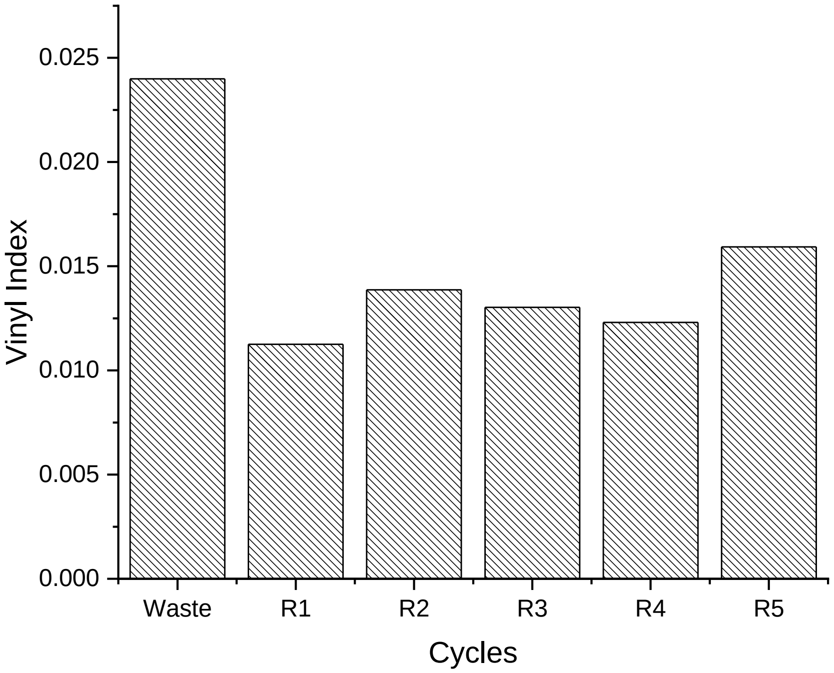


Figure 14. Comparison of vinyl index for waste and recycled HDPE specimens

Differential Scanning Calorimetry

The fusion behavior and crystallinity of the waste and recycled polymer were determined from the thermograms obtained from DSC. The thermogram obtained from for a waste HDPE specimen is shown in figure 15. The crystallinity of a polymer can be calculated if the heat of fusion of perfectly crystalline polymer is known. The heat of fusion is the amount of heat needed to transform a crystalline or semicrystalline polymer to an amorphous state. The percentage crystallinity of a polymer can be expressed as follows:

$$\text{Crystallinity} = \left(\frac{\Delta H_{exp}}{\Delta H_f}\right) * 100$$

ΔH_{exp} is the heat of fusion waste or recycled HDPE

ΔH_f is the heat of fusion of perfect crystal of HDPE= 293 J/g

ΔH_{exp} can be calculated by measuring the under the curve of the thermogram.

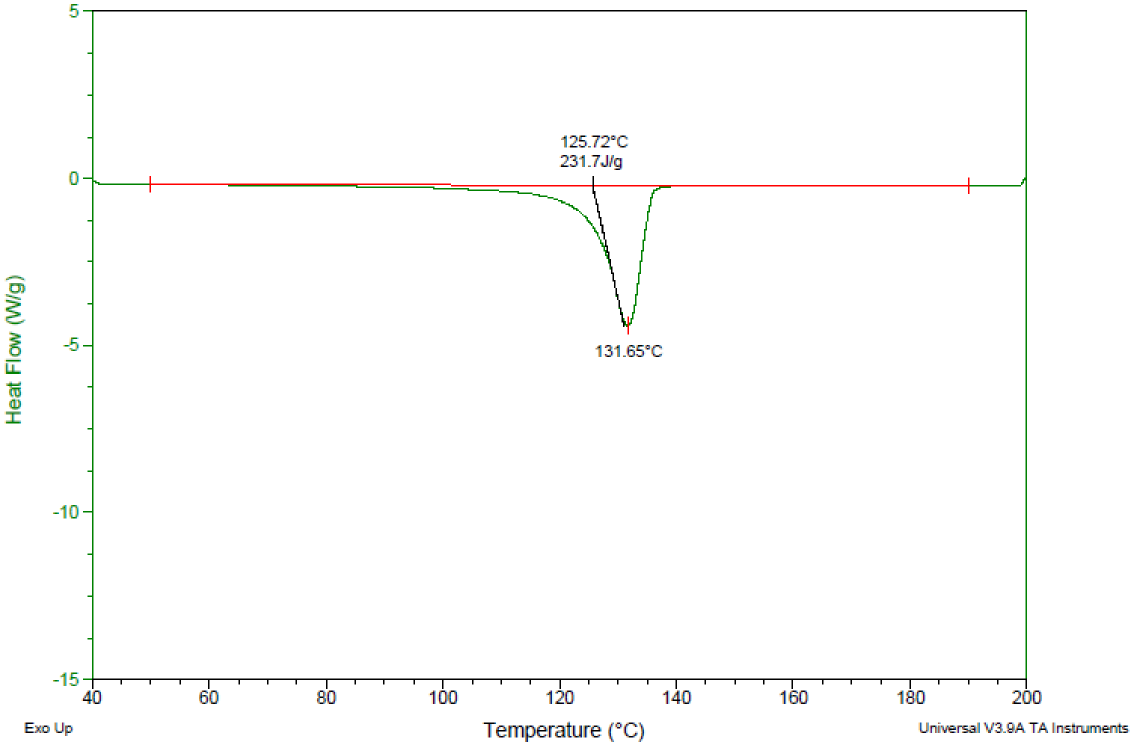


Figure 15. Thermogram for waste HDPE specimen

Using this method, the crystallinity was calculated for the waste and recycled samples. From table 2, it can be observed that there has been significant drop in the crystallinity of recycled HDPE samples. This suggests that there has been a change in the chemical structure of the polymer. The comparison of data from the tensile tests and dissolution time hints towards the crosslinking of the polymer. The thermograms obtained from the DSC and decrease in crystallinity provide further evidence that crosslink density has increased with each recycle.

Table 2. Crystallinity of waste and recycled HDPE

Cycle	Crystallinity
Waste	79.08
P1	72.08
R1	65.18
R2	69.11
R3	65.53
R4	66.82
R5	60.61

Flow sweep

The Discovery Hybrid rheometer (DHR) was used to conduct the flow sweep test. The flow sweep test helps us to gather necessary rheological data for characterization of the polymer. This rheological data helps us to understand how the polymer would behave in polymer processing techniques such as extrusion, injection molding or blow molding. This test shows the variation of viscosity and shear stress with change in shear rate at a constant temperature. It helps us to understand the flow of polymer or resistance to flow of polymer melts or solutions. Figure 16 shows a flow sweep test for the waste HDPE at 190 C for shear rate between 0.01 s^{-1} and 23 s^{-1}. It can be observed that viscosity remains almost constant from shear rate 0.01 to 0.1 s^{-1} and then drops off gradually which is a shear thinning behavior (decrease in viscosity of fluids when subjected to shear) of non-Newtonian fluid (change in viscosity when subjected to shear stress).

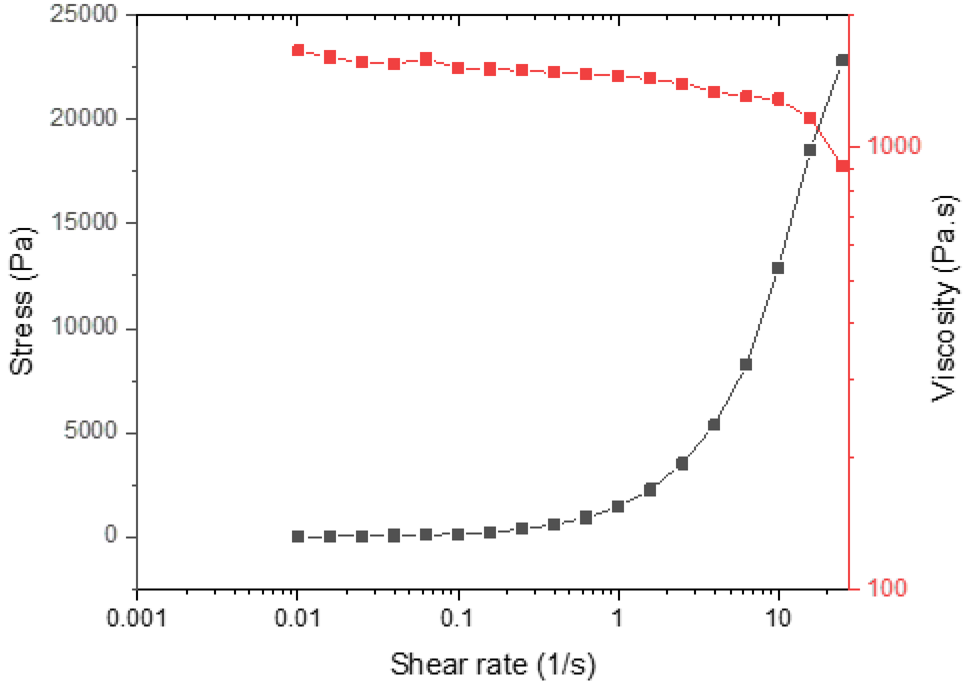


Figure 16. Flow sweep for waste HDPE specimen

This test can also be used to simulate a melt flow index (MFI) tester. An MFI tester is machine which gives a measure of the flow of a polymer in a melt state. It basically measures the amount of polymer flowing through a die of specific size under a standard pressure at a specified temperature. The MFI of a polymer is expressed as the amount of polymer flowing through the die in 10 min (g/10 min) under a certain load. During this test, certain amount of shear stress and shear rate is exerted on the polymer which is important rheological data for the polymer. Shenoy et al. described a method to generate rheological data from MFI test.[20] Conversely, in this study, the rheological data obtained from the flow sweep test conducted on DHR has been used to determine the MFI for the polymer. The melt flow index has an inverse correlation to molecular weight of the polymer. [28]

$$MFI \propto \frac{1}{Mw^{x}}$$

Mw is the molecular weight of the polymer

x is an exponent which varies depending on the branching and crosslinking of the polymer.

Figure 17 shows variation of MFI with change in load.

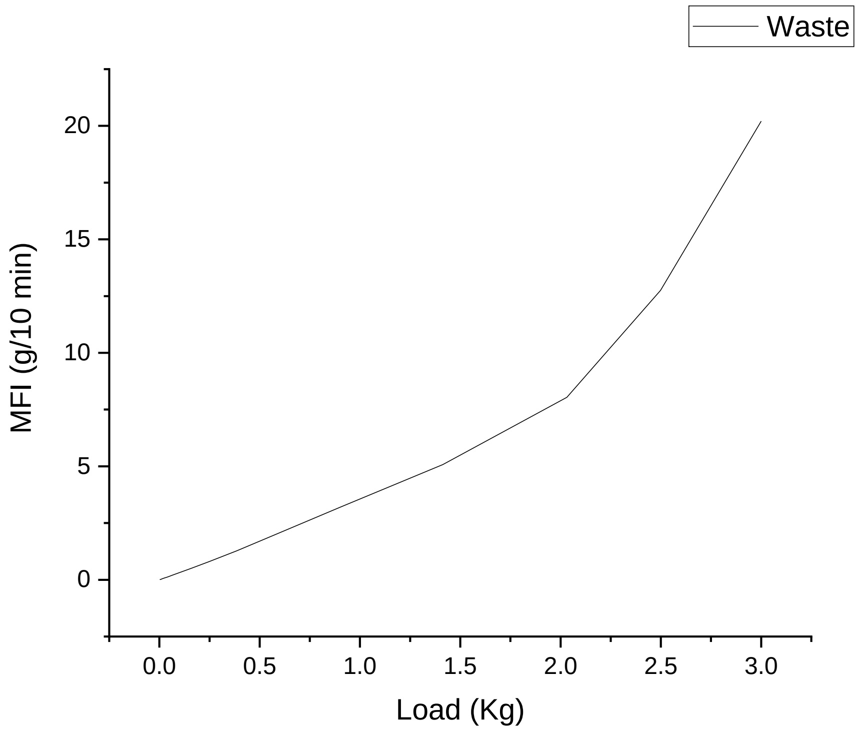


Figure 17. MFI variation with load for waste HDPE specimen

Similar to the waste HDPE samples, flow sweep tests were conducted on the recycled samples. It can be observed that the viscosity of each of the recycled samples is slightly higher than the waste HDPE sample except for R3. Similar correlation has been observed in MFI for the recycled samples. This decrease in viscosity or decrease in MFI can directly correlated with the molecular weight of the polymer. This increase or decrease in the molecular weight of the polymer is due to the crosslinking or chain scission reactions in the extruder. Depending on the conditions, one or the other reaction is dominant during the extrusion process. The viscosity is observed to be highest in sample R2 which is followed by sample R5. In both the samples, the residence time was slightly higher as compared to the other samples due to clogging in the extruder. Hence, we can see a greater increase in viscosity of the polymer. This suggests crosslinking reaction in the extruder. However, FTIR data (vinyl index) suggests chain scission mechanism in R2. Therefore, it seems that sample R2 showed a high degree of crosslinking as well as chain scission. For sample R3, a decrease in viscosity and an increase in MFI has been observed. This indicates that the chain scission mechanism was more dominant in case of R3. The pre-heating of the extruder could have led to a dominant chain scission mechanism. However, this hypothesis could not be confirmed as no confirmation were provided by FTIR or any other characterization test.

From the MFI calculations, it can be observed that the MFI varies between 4.8 and 6 g/10 min at 1.6 Kg load for all the samples except sample R3. This can be observed in figure 19. Hence, it can be concluded based on the MFI data that no significant change in molecular weight has been observed over 5 cycles of recycle.

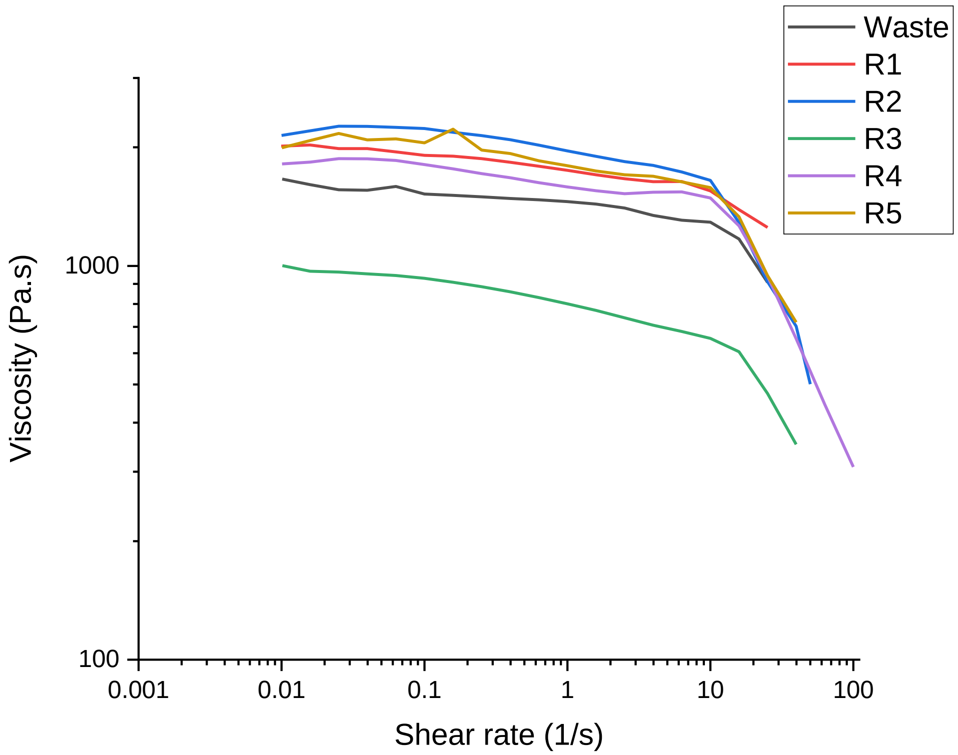


Figure 18. Comparison of viscosity as a function of shear rate for waste and recycled HDPE specimens

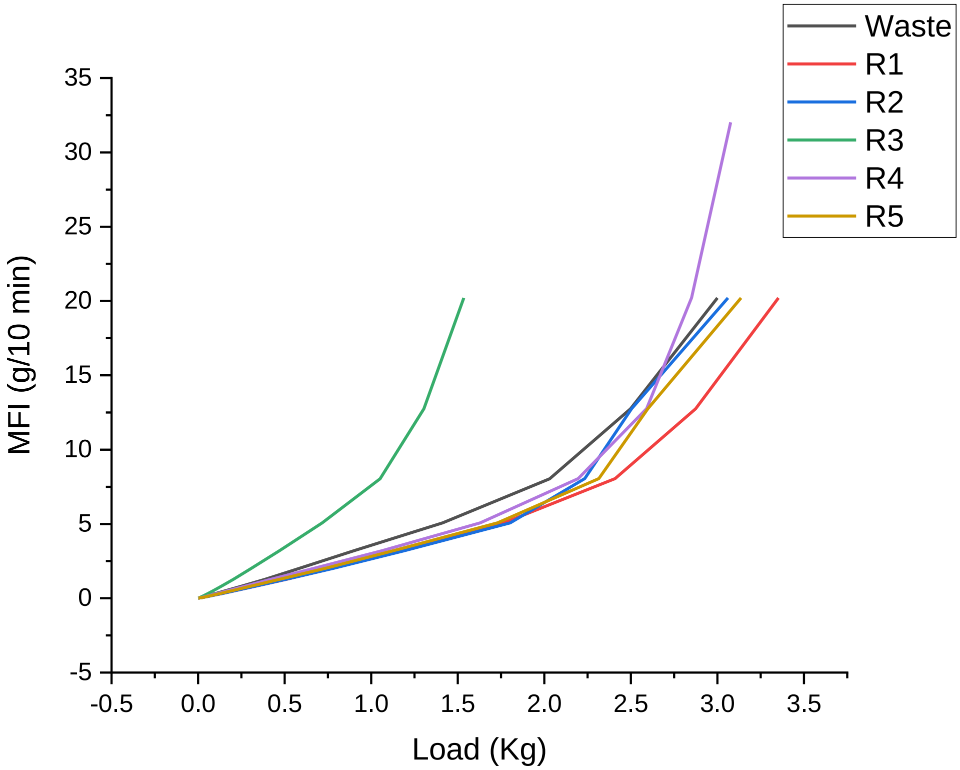


Figure 19. Comparison of MFI at varying loads for waste and recycled HDPE specimens

Frequency sweep

Since polymers have complex chemical structure and high molecular weight, it is difficult to predict the flow behavior of polymers with just one parameter like viscosity or MFI. In order to choose a method for polymer processing, it is essential to determine the viscoelastic properties of a polymer melt. The frequency sweep tests help us to understand the viscoelastic behavior of polymer melts and polymer solids. It is used to determine if the polymer behaves like a liquid or solid when subjected to shear. This test measures the storage modulus, loss modulus and complex viscosity of the polymer as a function of frequency at constant strain, temperature and oscillation amplitude. Higher the loss modulus of the material, more is the liquid like behavior of the material and similarly if the storage modulus for a polymer melt is high it will be more elastic and exhibits solid like behavior. If the polymer melt has higher storage modulus, it can lead to abnormal flow behavior and present complications during processing of the polymer.[29] Moreover, if the polymer melt is more elastic, the end product has more surface defects. [30]

To conduct a frequency sweep, it is necessary to determine a linear viscoelastic region. In the linear viscoelastic region, the material is stable as the storage modulus remains constant with respect to change in strain. The viscoelastic region can be determined by amplitude sweep. Beyond the viscoelastic region, the storage modulus starts to decrease represesnting that the material is not stable.

Figure 20 shows a frequency sweep for waste HDPE. It can be observed that the storage modulus tends to decrease or remain constant for frequency below 0.5 rad/s whereas the loss modulus increases linearly. This means that HDPE specimens are taking more time to relax and hence is more viscous at lower frequencies. This can also be confirmed from phase angle (tan δ - ratio of loss modulus and storage modulus) values for the specimens. Tha phase angle values are much higher at lower frequencies as compared to those at higher frequencies. However, phase angle is decreasing as it approaches higher frequencies. This means that the polymer melt is showing more elastic behavior as it approaches a higher angular frequency of 100 rad/s.

Figures 21, 22 and 23 show a comparison of storage modulus, loss modulus and phase angle of polymer melts of waste and recycled specimens. Specimens R2, R3 and R4 have a storage modulus slightly higher than the waste specimen whereas specimens R1, and R5 have lower storage modulus than the waste specimen. Similar trend has also been observed in loss modulus of the respective specimens. However, in order to get a clear picture of elastic and viscous behavior of the polymer, we need to consider the phase angle of the polymer. Phase angle comparisons suggest that R1 shows most viscous behavior as compared to other specimens. Specimen R5 is slightly more viscous than the waste HDPE specimen whereas specimens R2 and R3 show more elastic behavior as compared to the waste specimen. Overall, the rheological properties of waste and HDPE specimen as remained almost same over 5 recycles.

Moreover, the storage modulus for waste HDPE and recycled HDPE is same as the storage modulus for virgin HDPE tested by Lem et al.[31] The data from frequency sweep tests hints towards negligible change in rheological properties of waste, recycled HDPE and virgin HDPE.

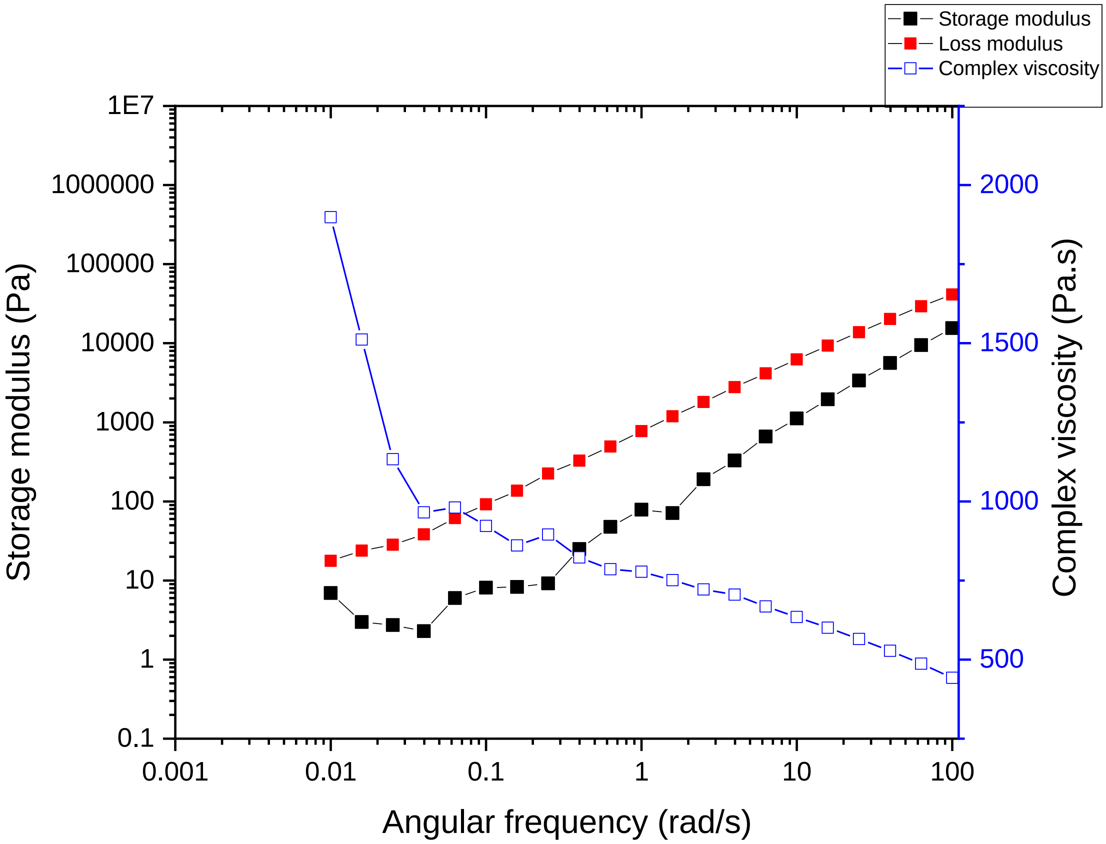


Figure 20. Frequency sweep for waste HDPE specimen

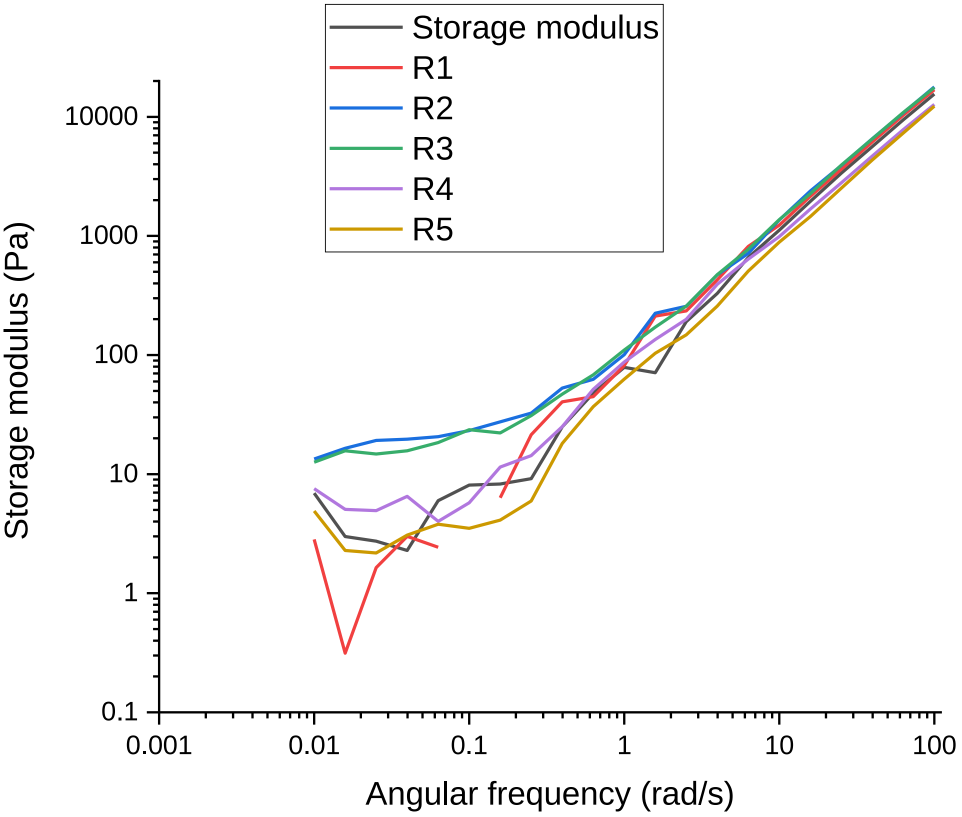


Figure 21. Comparison of storage modulus for waste and recycled HDPE specimens

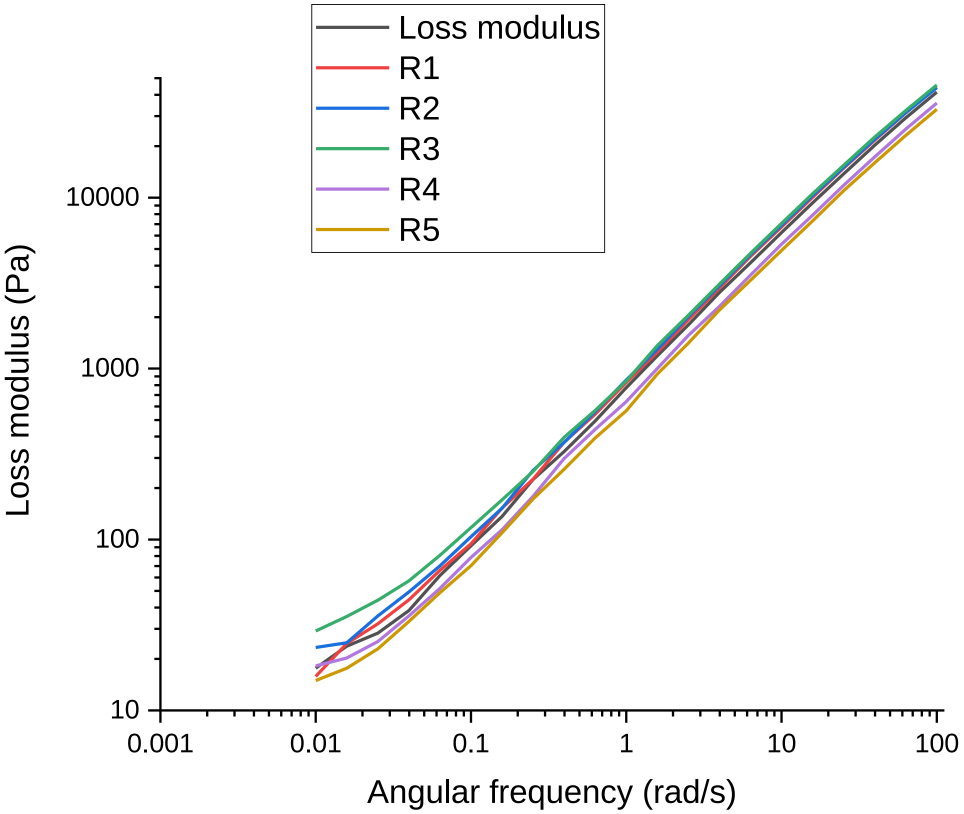


Figure 22. Comparison of loss modulus for waste and recycled HDPE specimens

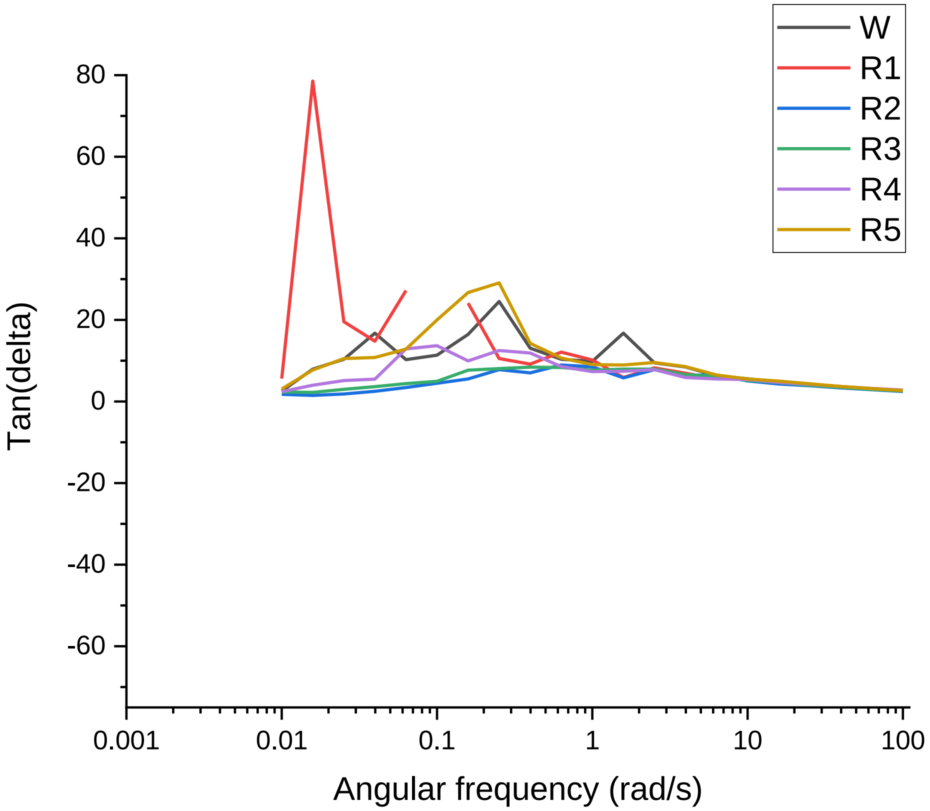


Figure 23. Comparison of phase angle for waste and recycled HDPE specimens

CHAPTER 5

CONCLUSION AND FUTURE WORK

In summary, this work discusses a method to recycle HDPE using dissolution, reprecipitation technique with the use of additives during the extrusion process. The processing conditions for dissolution, extrusion temperature, and mixing technique were optimized for the process. The recycled polymer specimens were characterized by FTIR and DSC. The rheological properties were examined using DHR and the mechanical properties of the recycled specimen were determined using a tensile tester. The carbonyl index showed a decrease of more than 25 % until the 4th cycle as compared to the waste specimen. However, after the 5th recycle, an increase of 32% was observed. Vinyl unsaturation showed a decrease of 33 % representing crosslinking in the polymer. This crosslinking was further confirmed by the dissolution time for polymers. The dissolution time for waste specimen was 1 hour whereas the dissolution time for specimen after 4th recycle was more than 30 hours representing that the dissolution time increased to 30 times the dissolution time for the waste specimen.

Furthermore, the tensile tests performed on the waste and recycled specimens substantiated the crosslinking in the polymer. Due to the crosslinking, the elastic modulus of polymer increased up to 64% by the 4th recycle and up to 81% by the 5th recycle. The maximum elongation at break for all the specimens tested for the waste specimen was 230% which dropped down to 96% after the 4th recycle and 28% after the 5th recycle. Moreover, the elongation at break for all the specimens tested was not the same. Some of the specimens showed much lower elongations. This suggests that the degradation was minimized for some parts of the polymer. It can be surmised that the mixing of the additives with the polymer was not thorough and hence led to uneven degradation of the polymer. It was observed that the maximum elongation for the specimen after 1st recycle was almost equal to the waste specimen. Hence, it can be concluded that a consistent mixing of additives and polymer could minimize the degradation even further.

The flow sweep tests revealed the MFI data for recycled specimens. No drastic change in MFI was observed in the specimens of waste HDPE and specimens after the 5th recycle. This suggests that the amount of crosslinking and chain scission were almost the same. Consequently, suggesting that the molecular weight has not changed considerably over the 5 recycles. This is a crucial aspect of polymer rheology as it plays an important role in determining the polymer processing technique. In order to further confirm the rheological performance of the polymer, frequency sweep tests were carried out. This test revealed the storage modulus, loss modulus, and phase angle of the polymer. Similar to the MFI results, no considerable change was observed in the storage modulus and loss modulus of the waste specimen and specimens obtained after the 4th and 5th recycle. The phase angle values for the 5th recycled specimen were slightly higher than the waste specimen. A higher phase angle represents a better surface finish for the extruded polymer, suggesting that the recycled specimen would be even better than the waste specimen. Considering all the tests, the mechanical, rheological, and structural properties of the polymer were retained after the 1st recycle. Also, the recycled specimens after the 5th cycle showed good retention of rheological properties whereas slight deterioration in oxidative stability and chemical structure of the polymer was observed. However, the mechanical properties of the polymer were considerably compromised after 5th recycle representing improper mixing of the additives.

In the future, the study includes optimization of the mixing procedure of additives with polymer. Also, it must be considered that the solvent and non-solvent used in the research were completely discarded as the recovery of solvents using distillation was very time-consuming and not feasible. In order to make this process feasible (even in the lab), a distillation process must be set up. Furthermore, the design of the extruder can play an important role in the degradation of the polymer during processing. The extruder could be designed in such a way that the breaking of polymer chains can be minimized during the heating of the polymer. This could enhance the number of recycles with minimum deterioration of properties.

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