Development of Solvent-Based Recycling Technique for Polyethylene Terephthalate from Waste Plastic

by

Nor Sharizat Arieff bin Kamaruzamal

Dissertation submitted in partial fulfilment
of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2014

UniversitiTeknologi PETRONAS,
Bandar Seri Iskandar,
31750 Tronoh,
Perak DarulRidzuan.

CERTIFICATION OF APPROVAL

Development Solvent-based Recycling Technique for Polyethylene Terephthalate from Waste Plastic

by

Nor Sharizat Arieff bin Kamaruzamal

Dissertation submitted in partial fulfilment
of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Approved by,

26/12/2013

____

(Dr. Iqbal Ahmed)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2013

ABSTRACT

This paper will cover the development of solvent-based recycling technique of polyethylene terephthalate (PET) taken from post-consumer drinks containers which have the labeling number of 1. These bottle containers are further processed to be made as small pellet with sizing of less than 2 mm (length) × 2 mm (width). This sample will then be treated with selected solvent in order to dissolve it from solid PET to liquid PET. Later on, this liquefied PET will be recovered through a dissolution/re-precipitation technique to make it as a pure PET polymer. This polymer is then will be tested with various chemical analysis methods in order to identify its purity so that the success of this project can be justified.

ACKNOWLEDGEMENT

In the name of ALLAH S.W.T, the most merciful and compassionate, praise to Allah, He is The Almighty, eternal blessing and peace upon the glory of the universe, Prophet Muhammad S.A.W, and his family and companions.

The author wish to express his appreciation and gratitude towards his project supervisor, Dr. Iqbal bin Ahmed, for all of his assistance, guidance and encouragement throughout the course of this project work. His support and supervision have helped the author in completing the project smoothly.

The author also would like to thank the lab technicians for their assist and guidance.Last but not least, a special credit goes to the author's parents, family members and friends for their unconditional support regarding my studies. Their confidence in author's ability has provided immense inspiration.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Study

The amount of rubbish produce by the world population is increasing each day. In Malaysia, it is estimated that 1.8 million tonnes of garbage produced by Malaysian each year. It means that, every person in Malaysia produced 1.3 kilogram (kg) of rubbish daily. This amount seems to be increasing as in 2001, the amount of rubbish produced in Malaysia was 17 000 tonnes daily while in 2005, the amount increased to 19 000 tonnes per day. Department of Solid Waste Management estimated the amount of rubbish produced by Malaysian will increase to 30 000 tonnes per day as the year of 2020 approach (Billy, 2011).In order to manage this problem, the government has implemented two famous methods in handling the rubbish.

The first method of managing the garbage is allocating certain area for the purpose of landfill. The garbage that has been collected throughout a certain region will be dumped in this so called landfill and then it will be left there to be decomposed through natural decomposition since most of the garbage are organic materials resulted from our food remains. This method seems promising as it does not consume any fuel and capable of saving the government budget. But, in the other hand, this method still has its own downside where there is limited space available to be made as a landfill. As of 2012 there are about 289 locations in Malaysia that have been allocated for landfill and the number increasing annually (Syed Ali, 2012). Apart from that this method also leads to air and water pollution throughout entire nation. Thus, in lieu of this situation, the government has made numerous studies to overcome this problem and has leaded us to the next waste management method.

The second method which generally practiced in Malaysia is incineration of the rubbish. In order to carry out this procedure, the garbage that has been collected will be taken into a processing site where the garbage will be burnt. This method could solve the problem of limited space for landfill but in contrast it will need the usage of fuel for the purpose of the incineration which will increase the cost of waste management. Other than that, this method seems more dangerous if compared to the latter as it will release the greenhouse gasses which later on will give impact on the global warming. Thus, the search of the solution of waste management problem is a must.

One of the contributing factors to this problem is the existence of the non-degradable materials; such as plastics. It seems like impossible to exclude plastic from this situation as plastic is widely used as container; even the garbage itself is bundled in a plastic bag. According to a statistical research conducted by (BERNAMA, 2011); one of the leading national news agency in Malaysia; it is observed that the highest composition of garbage is made up of organic material (45%), followed by plastic (24%), paper-based product (7%), steel (6%), and glass (3%).

From this statistic, it merely shows that if we manage to come out with a solution on how to handle plastic-based product, we merely solved the global waste problem. Thus, this paper will focus on developing a technique which will able to recycle major plastic composition; which is polyethylene terephthalate (PET); by using a suitable solvent.

1.2 Problem Statement

In order to successfully conduct this experiment, there are few problems that had and might have been identified throughout the entire process. The problems arise are listed in the following sections.

1.2.1 Problem Identification

(1) One of the major problems in this study is that PET is very well-known with its highly inert characteristic. It is unreactive towards most of common solvents. This characteristic is the reason why PET is made as the world largest bottle container.

According to (Oku, Hu, & Yamada, 1996), PET is highly insoluble in aqueous solution.

(2) Another problem identified is PET needs to be reacted at a high temperature. This situation will leads to a higher cost of processing in industrial scale.

(3) Lastly, the problem that might be encountered if the procedure is successful is the separation of the product from its solvent and their purity.

1.2.3 Significant of the Project

Currently, there is no specific study that significantly shows that PET can be recycled through solvent-based method without damaging the molecular structure of PET.

If this study is a success, it marks a great breakthrough in the history of solid waste management as it will use a environment friendly technique with a very low cost of procedure.

1.3 Objective and Scope of Study

1.3.1 Objective

1. Increase the surface area of reaction of PET.
2. Determine the most suitable solvent that can be used to dissolve PET.
3. Determine the lowest possible temperature that is suitable for PET reaction with the solvent.
4. Develop a technique to separate dissolved PET from its solvent.
5. Determine the most suitable technique to check the purity of the resulted PET.

1.3.2 Scope of Study

The scope of study will mostly falls under Chemical Engineering programme and Reaction Engineering will be mainly focused on. This project will deals with a lot of analytical equipment as it is crucial to determine the composition of the product which will determine the success of this experiment.

1.4 Relevancy of the Project

This project is highly relevant to current global situation where solid waste disposal problem is at stake. If the author manages to conduct this project successfully, most of the world problem in waste disposal might be solved.

This project is still relevant as it related to the author's course of study as it mainly deals with Chemical Engineering. If this project is a success it will bring the author and the university itself to a higher recognition.

1.5 Feasibility of the Project within the Scope and Time Frame

This project will merely focus on the development of solvent-based recycling technique for polyethylene terephthalate (PET) from waste plastic. This project involves with the determination of suitable solvent that will be reacted with PET, recovery of PET from the solvent, and chemical analysis of resulted PET.

Judging from the objective and planned methodology in carrying out this experiment, it is believed that 8 months period allocated to finish this project is highly feasible.

CHAPTER 2

LITERATURE REVIEW

2.1 Polyethylene Terephthalate (PET)

Polyethylene Terephthalate (PET) was first introduced to the world in the year of 1941 by John Rex Whinfield, James Tennant Dickson and the company which they collaborate with; the Calico Printers' Association of Manchester (Wikipedia, 2013). In the production of polyester film, PET is well known as Mylar. This term was registered in 1952 but the people have already used it since June 1952. Currently, the trademark is owned by Dupont Teijin Film US which is believed to be partnered with a Japanese company (Teijin Limited, NA). However, the first patent of PET that has been used as bottle packaging was registered in the year of 1973 by Nathaniel Wyeth (Wyeth, 1973).

There are so many names that have been used to identify PET; one of them is known as Dacron (Wikipedia, 2013). In the polyester family, it is regard as thermoplastic polymer resin. Due to its excellent barrier material, it can withstand most of the gasses from coming in and out of the packaging and this is the reason why PET is made as soft drink packaging. In certain cases, PET is sandwiched with additional polyvinyl alcohol layer to increase its impermeability towards oxygen gas.

Most of PET that has been produced in the world is mainly for the purpose of synthetic fiber which account nearly at 60% while for packaging purpose it is estimated to be 30% of global demand. It is found that in the world polymer production, polyester makes up about 18% of its production and is considered as the third-most-produced polymer (Lancashire, 2011). PET is mostly referred to as polyester in the context of textile application whereas for packaging application the term "PET" is widely used.

There are so many ways PET polymer can be produced. Processing and thermal history play the biggest role in determining the structure of PET whether it can be made as amorphous (transparent) or as a semi-crystalline polymer. The crystal structure and particle size might be the important in order to determine what kind of appearance of PET might shows. For example, if the particle size is less than 500 nm the semi-crystalline material might appear white or opaque or transparent. The production of its monomer can be made possible with two methods via esterification reaction of terephthalic acid and ethylene glycol with water as its byproduct, or through transesterification reaction of ethylene glycol with dimethyl terephthalate with methanol as byproduct. In order to synthesize its polymer, this monomer has to undergone polycondensation reaction; which is immediately done after esterification/transesterification process; with water as its byproduct(Northwestern University, 2012).

In industrial practice, after terephthalic acid is combined with ethylene glycol, PET pellets are formed. In order to ensure the produced PET pellet is easy to be extruded and molded into any desired shape and form, the pellets are heated into a molten liquid. According to PET Resin Association (PETRA, 2012),

"...when the two raw materials of PET are combined under high temperatures and low vacuum pressures, long chains of the polymer are formed. As the mixture becomes thicker, the chains grow longer. Once the appropriate chain length is achieved, the reaction is stopped. The resulting spaghetti-like strands of PET are then extruded, quickly cooled, and cut into small pellet."

The structure of PET polymer consists of the monomer ethylene terephthalate with repeating $C_{10}H_8O_4$ as represented in the Figure 1.

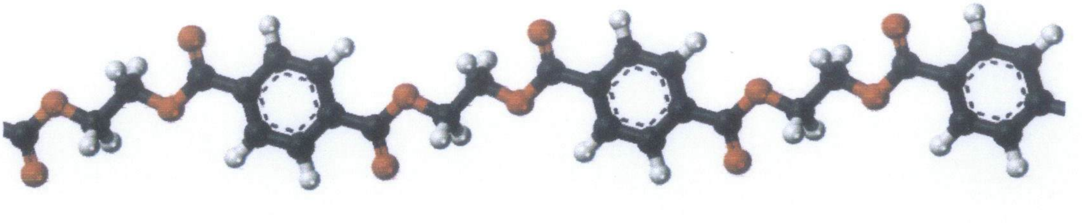


Figure 1: Short section of PET polymer chain (Wikipedia, 2013)

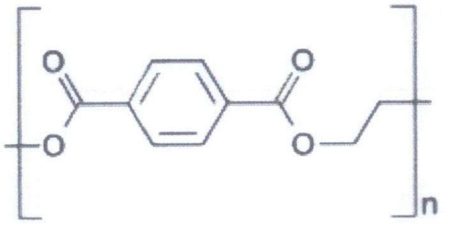


Figure 2: Polyethylene terephthalate monomer (Wikipedia, 2013)

PET is known to have a colourless and semi-crystalline resin in its natural state. Apart from that, due to its high mechanical strength, PET is often made as a high resistance tape. For example, PET always been used as carrier for magnetic tape or backing for pressure-sensitive tapes. Following are the tabulated references of PET's important criteria:

Table 1 : General properties of PET (A.K. Van Der Vegt)

General Properties	
Young's Modulus	2800 – 3100 MPa
Tensile Strength	55 – 75 MPa
Elastic Limit	50 – 150%
Notch Test	3.6 kJ/m^2
Glass Transition Temperature, T_g	67 – 81 °C
Linear Expansion coefficient	7×10^{-5}/K
Water Absorption (ASTM)	0.16

Table 2 : PET resistance towards chemicals (AZoM, 2013)

Chemical Resistance	
Concentrated Acids	Good
Diluted Acids	Good

Alcohols	Good
Alkali	Poor
Aromatic Hydrocarbons	Fair
Greases and Oils	Good
Halogens	Good
Ketones	Good

Table 3 : Physical Properties of PET (AZoM, 2013)

Physical Properties	
Density	1.3 – 1.4 g/cm^3
Flammability	Self-Extinguishing
Limiting Oxygen Index	21 %
Refractive Index	1.58 – 1.64
Resistance towards UV	Good

2.2 Solvent

Definitively, solvent is a substance which has the ability to dissolve a solute. It might come in many state by usually solvent exist in liquid form, however solvent may also come in solid and gas form. For household usage, solvents are always used to remove stain or any other material that stick rigorously to other object; as for example paint thinners, nail polish removers, glue solvent, etc.

In this experiment, solvent is the main essence in determining the success of this project. This is because in chemical recycling of PET (which will be discussed in depth in the next section) solvent is essential to dissolve the solid PET pellets. Thus, there are a lot of parameters that need to be taken into consideration in order to choose the exact solvent that is able to dissolve PET.In order to determine solubility of one substance into one solvent, there is a need to know about the solubility parameter.

Currently, there are two (2) theories developed by scientists on solubility parameter. One of them is known as Hildebrand solubility parameter. This theory is developed by a scientist named Dr. Joel Henry Hildebrand. In this theory, Hildebrand believed that the degree of interaction between materials can be estimated with numerical notation. This numerical estimation is obtained through the square root of a substance's cohesive energy density represented by following formula:

$$\delta = \sqrt{\frac{\Delta Hv - RT}{Vm}}$$

By definition, cohesive energy density is the heat of vaporization divided by molar volume. There is an inclusive of heat of vaporization in this equation because it is the same as the amount of energy needed to totally remove unit volume of molecules from their adjacent molecules to an infinite separation. Solvency behavior is indicated with the square root of the cohesive energy density. Dr. Hildebrand concluded that materials with similar solubility parameter δ, have the ability to react with each other and will result in miscibility or solvation. According to Hildebrand's theory, the solubility parameter for PET is as following:

Table 4 : Hildebrand Solubility Parameter for PET (Vadenburg, 1999)

Substance	δ	δ (SI)
Polyethylene Terephthalate (PET)	10.1	20.5

Referring to information provided by Table 4, there arefew solvents which solubility are more or less the same as PET's are taken into consideration. Those solvents are tabulated in the following tables. Later on these solvents will be tested on its reactivity with PET to see whether it might dissolve the sample or not. The solvents shown in the table is for example.

Table 5 : Few solvents which will be taken into consideration (Burke, 2008)

Substance	δ	δ (SI)
Dichloromethane (DCM)	9.93	20.2
Diacetone alcohol	10.18	20.0
Methylene Chloride	9.93	20.2
Ethylene Dichloride	9.76	20.2
Butyl Cellosolve	10.24	20.2
Pyridine	10.61	21.7
p-xylene	8.85	18.2

Toluene	8.91	18.3
Kerosene (Turpentine)	-	16.6

Other theory in solving solubility parameter was created by Charles M. Hansen in the year of 1967.Inhis written thesis, his theory stated that a material has the capability to be dissolved in other materials to form a solution based on the idea of "like" dissolves "like". A molecule is defined as to like one another if the structure of its bond is bonding in similar way (Hansen, 1967). This theory is called Hansen Solubility Parameter.

If compared with the one developed by Hildebrand, this theory seems to be a little bit more complex since there is a need in giving three Hansen parameter to each molecule which bearing the unit of $MPa^{0.5}$. Those parameters are listed as follow:

- δ_d – amount of energy from dispersion forces between molecules
- δ_p – amount of energy from dipolar intermolecular force between molecules
- δ_h – amount of energy from hydrogen bonds between molecules

To better understand the Hansen parameter, one can imagine that these three parameters as co-ordinates of a point in three dimensional (3D) spaces also famously known as Hansen Space. Hansen suggested that the closer the two molecules are to each other in this space, the more likely they tend to dissolve to each other.

In order to determine likeability of the two molecules to each other; which usually represented by the solvent and the polymer; a value named interaction radius (R_0) is given to the substance that being dissolved, which exclusively the polymer itself. R_0 is important to be taken into account as it indicates the radius of the sphere in Hansen Space and its center is the three Hansen Parameters. Following formula is used in order to calculate the distance (Ra) between Hansen Parameters in Hansen Space:

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + \left(\delta_{p2} - \delta_{p1}\right)^2 + (\delta_{h2} - \delta_{h1})^2$$

From this equation, Ra is then been compared with R_0 which gives out the following equation

$$\frac{Ra}{R_0} = RED$$

RED gives a meaning of the relative energy difference of the system. If:

- RED < 1, the two molecules have the tendency to dissolve with each other and produce miscible solution
- RED = 1, the two molecules will partially dissolve to each other
- RED > 1, the two molecules will not dissolve and they will produce a heterogeneous solution

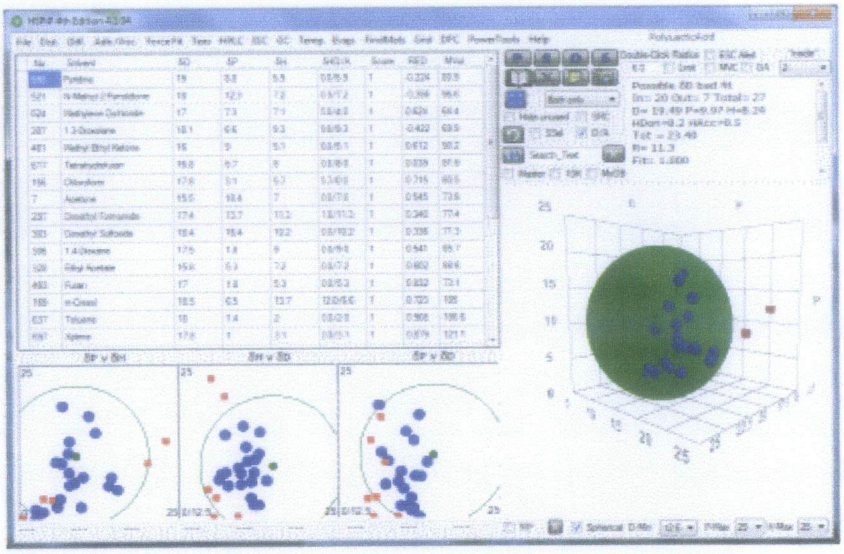


Figure 3: Hansen Solubility Parameter in Practice (HSPiP, 2013)

Table 6 : Hansen Solubility Parameter for PET (Accu Dyne Test, 2009)

	δ	δ_d	δ_d	δ_d	R_0
Polyethylene Terephthalate (PET)	20.8	18.7	6.3	6.7	6.5

According to Table 6, there might be RED calculations for various solvent in order to determine the most suitable solvent that can be used to dissolve PET. This calculation will further discuss in the following chapters.

Apart from these aforementioned solubility parameters, there is a table provided by CEM Corporation; a pioneer company in microwave chemistry industry; regarding polymer solubility, solvents, and related dissolution temperatures. Following is the table provided by the company:

Table 7 : Solvents suitable to dissolve PET at its minimum dissolution temperature (CEM, NA)

Polymer	Solvent(s)	Minimum Dissolution Temperature (^oC)
Polyethylene Terephthalate (PET)	DMF	80
	m-cresol	100
	HFIP	40

2.3 Chemical Recycling Technique

Recycling of PET using chemical reagents is not something new. This practice has already been implemented in various industries for many years. Yet, this technique still is not common in industrial scale since they are still using conventional method of recycling PET where PET plastics is melted by heat and molded into new shape and design.

There are many ways PET can be chemically recycled. One of them is called hydrolysis. In this method, PET is reacted with water; whether it is acidic, neutral, or alkaline environment; which consequently leads to total de-polymerization to its monomers which is the terephthalic acid (TPA) and ethylene glycol (EG). This technique is getting wide interest due to the introduction of new factory which able to synthesize PET directly from TPA and GE. However, this procedure might involved with high temperatures and pressure up to 220 – 250 °C and 1.4 – 2.0 MPa respectively, as well as long reaction time for de-polymerization process (Karayannidis & Achilias, 2007). This condition considered as disadvantage towards industrial practitioners as it will increase the cost of production.

However, the methods that are able to reach commercial maturity are glycolysis and methanolysis. In glycolysis, ethylene glycol (EG) is inserted in the PET chain which resulted in bis(hydroxyethyl) terephthalate (BHET). BHET is actually a substrate for PET synthesis and other oligomers. This method is conducted at a range of temperature of 180 – 240 ^{o}C which will take the time of reaction up to 0.5 to 8 hours. Catalytic effect might be found on PET glycolysis if zinc compound is used under 245 ^{o}C (Karayannidis & Achilias, 2007).

In the other hand, methanolysis is a process where PET is degraded with methanol at a very high temperatures and high pressures by producing dimethyl terephthalate (DMT) and EG as main product. DMT later on is further purified with distillation process where all physical contaminants are removed. After that, this purified DMT will be used as a raw material for the production of PET (Karayannidis & Achilias, 2007). However, this method needs the temperature as high as 180 – 280 ^{o}C and pressures from 2 – 4 MPa in order to ensure methanolysis of PET flakes is performed (Paszun & Spychaj, 1997).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Project Activities

Referring to the information obtained from the literature review, most of the project activities are planned according to the required outcomes. These project activities will focus on solving the problem encountered throughout the entire experiment. In order to better plan the experimental methodology, this project is divided into certain stage that might assist in developing its activities. The stages are represented as follows:

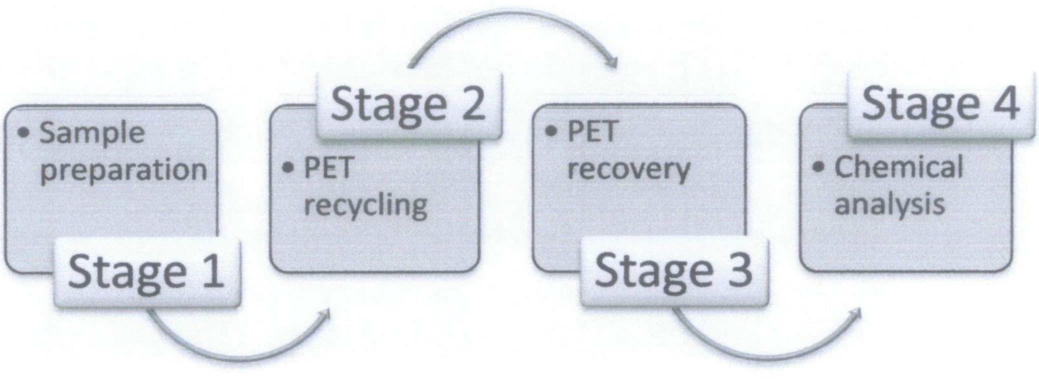


Figure 4: Stages involved throughout experimentation

3.1.1 Stage 1 (Sample Preparation)

In this stage, PET sample is needed to be prepared according to recommended pellets size which is at least 2mm length × 1 mm width. This characteristic must be achieved since surface reactivity of PET is the major rate-determining stage (Oku, Hu, & Yamada, 1996). Thus, to ensure this property is achieved, following procedure must be accomplished.

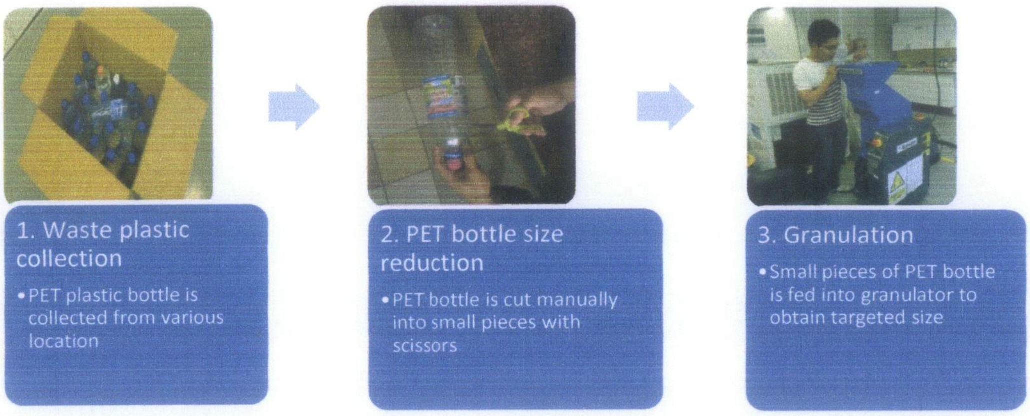


Figure 5: PET pellets preparation

3.1.2 Stage 2 (PET Recycling)

This stage is the most important stage as it will determine the entire course of this project. It will involve with identification of the exact solvent that is suitable to dissolve PET pellets in order to recycle the PET. Most of the project timeline will be consumed in this stage as there are a lot of solvents that needed to be taken into consideration since until now there is no exact literature which has proven a solvent which can dissolve the PET pellet according to the required conditions. Thus, in order to achieve the property needed, following procedure has been developed.

1. Take a weight ratio of PET to the solvent to 1: 99 (in this case take 1 g of PET against 99 g of solvent)
2. Mix the PET with the solvent in a conical flask.
3. Set up the apparatus as shown in the Figure 6.

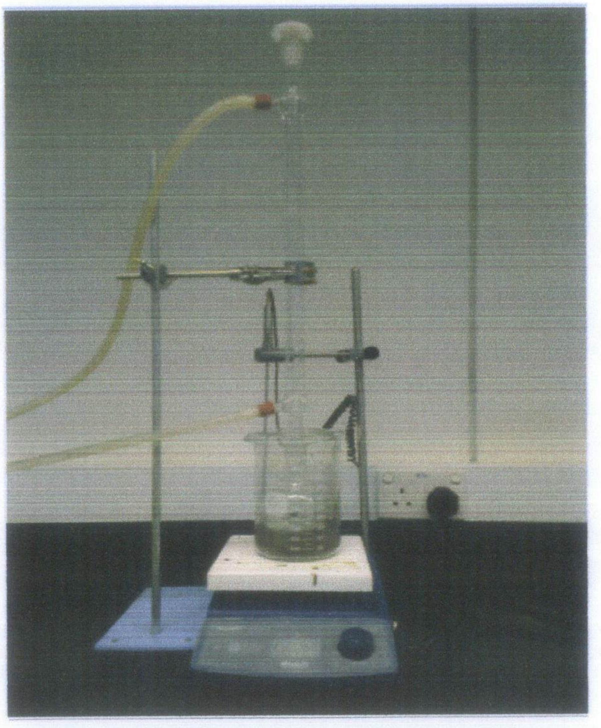


Figure 6: Set Up of the Apparatus

4. Heat the mixture to 90 °C for 15 minutes, simultaneously; stir the mixture with magnetic stirrer. Increase the temperature at 10 °C intervals every 15 minutes until the temperature reach 150°C. Stop the experiment if PET pellets are dissolved in the solution.
5. Record the observations for every temperature interval.
6. Repeat the experiment using other solvents.

Observation is made based upon the solubility of the PET pellets. This can be made by making a physical observation and weighing method. The physical observation method can be tabulated as follows:

Table 8 : Sample of table for physical observation of PET solubility

Polymer	**Solvents**	**Temperature (°C)**	**Appearance**
PET			Soluble/Not Soluble

To observe the solubility of PET through weighing technique, following procedure must be followed:

1. Weigh the amount of PET before it is mixed with solvents.
2. Filter the mixture of PET and the solvent with filtering paper.
3. Weigh the amount of PET after the reaction is completed.
4. Find the difference between initial values with final value. If there is any decrement in the final values, it means some amount of the PET pellet is soluble in the solvent.
5. Record the findings in the following table:

Table 9 : Sample of table of observation of PET solubility through weighing technique

Temperature	Initial amount of PET (g)	Final amount of PET (g)	Difference in weight (g)	Amount soluble in the solvent (g)

3.1.3 Stage 3 (PET Recovery)

After the PET pellets has been dissolved in the suitable solvent, there is a need in recovery the PET from the solvent as it need to be made as pure as possible and be shaped in small pellets. Later on, in industrial practice, these pellets can be melted and molded into required shape and purpose. Thus, to recover the dissolved PET, dissolution/re-precipitation technique is applied according to following procedure(Goje, 2005):

1. Set up the apparatus as shown in the figure.

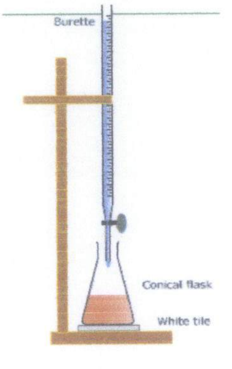


Figure 7: Set up of titration method (alevelchem, NA)

2. Slowly introduce boiling neutral water of 150 mL into the hot filtrate by maintaining 80 °C of filtrate.
3. After 150 mL of boiling neutral water is fully titrated into the filtrate, quickly filter the mixture and collect the PET grains produced.

3.1.4 Stage 4 (Chemical Analysis)

After the PET pellets are successfully dissolved in selected solvent, now it is the time to check the purity of the recovered PET polymer either it is highly pure or not. This stage is essential as it will determine whether this method of PET recycling is successful and economically viable. In order to conduct this purification test, there are few methods available to be implemented but the selection of the method is depending on the availability of the equipment available in this institutions. Following are the suitable chemical analysis methods that can be conducted:

1. Fourier Transform Spectroscopy (FTIR)
2. Atomic Absorption Spectroscopy (AAS)
3. High Performance Liquid Chromatography (HPLC)
4. X-Ray Diffraction (XRD)

3.2 Key Milestone

In order to identify a progress of certain project, there must be a benchmark that can be used to measure the project's current achievement. Thus, for this experiment the key milestone that can be observed to identify its progress is made into stages as listed in previous topic. Thus, the key milestones are as follow:

Table 10 : Key milestone of project's progress

KEY MILESTONE	REMARKS
Stage 1 Sample Preparation	Completed
Stage 2 PET Recycling	Completed
Stage 3 PET Recovery	Completed
Stage 4 Chemical Analysis	Completed

The project might goes smoothly as planned in the Gantt chart; however, there were some hindrance throughout the entire process since there are some difficulty in obtaining the chemicals and equipment. However, current progress is so promising that it is believed this project can be finished before the deadline is up.

3.3 Gantt Chart

STAGE	FYP 1													FYP2												
	Weeks																									
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Finalizing topic of project																										
Background Research																										
Stage 1 (Sample Preparation)																										
Stage 2 (PET Recycling)																										
Stage 3 (PET Recovery)																										
Stage 4 (Chemical Analysis)																										

3.4 Tools Required

Throughout the entire project, there is a list of tools which are needed to ensure the project achieve its success. This list is made up by identifying all objective and the purpose of the tools that can be used to achieve it. The list is as follows:

Table 11 : List of tools required in this experiment

NO.	OBJECTIVE	TOOLS REQUIRED	PURPOSE	REMARKS
1	Prepare small pellets of PET from waste plastic bottles.	Scissors	To reduce the size of the PET bottle plastic into required size of pellet.	All items are obtained
		Granulator		
2	Determine the most suitable solvent that can be used to dissolve PET.	Conical flask	To arrange the equipment according to the designated setup so that PET recycling procedure can be carried out.	All items are obtained
		Retort stand and clamp		
		Magnetic stirrer		
		Two-neck round bottom		
		Measuring cylinder		
3	Determine the lowest possible temperature that is suitable for PET reaction with the solvent.	Hot plate	To heat and detect the temperature of the mixture and the solvent.	All items are obtained
		Thermometer		
		Thermocouple		
4	Separate dissolved PET from its solvent.	Burette	To recover dissolved PET from the solvent.	All items are obtained
		Beaker		
		Filter paper		
5	Investigate the purity of the recovered PET.	FTIR	To check the purity of the recovered PET.	In booking process
		AAS		
		HPLC		
		XRD		

CHAPTER 4

RESULT AND DISCUSSION

Referring to the key milestone that has been mentioned in previous chapter, it is shown that current progress of this project is still at Stage 2 where the process mainly deals with the recycling of the PET polymer. In this stage, the PET pellets obtained from the waste bottle plastics are treated with various solvent with the objective of liquefaction of the PET pellets at lowest temperature possible.However, the experiment is not able to be conducted using preferred solvent; solvents which having nearest solubility parameter to the PET; as there is a limitation in the resources of the solvents. After certain period of time, this problem can be solved as the solvents can be obtained and ordered from other institutions.

Following are the results of experiments that have been conducted in order to determine the reaction that takes place after the PET pellets have been treated with various solvents.

4.1 Experiment 1: PET solubility in Toluene

Table 12 : Results of PET being treated with Toluene

Sample	Solvents	Temperature (^{o}C)	Appearance
	Toluene	90	Not soluble
		100	Not soluble
		110	Not soluble
		120	Not soluble
		130	Not soluble
		140	Not soluble
		150	Not soluble

From the observation recorded in Table 12, it can be seen that PET is not soluble in toluene at any given temperature. The temperature needs to be stopped at 150 ^{o}C because it seems that there is an accumulation of pressure inside the conical flask and this step is essential in order to avoid any explosion due to high pressure. It is assumed that any higher temperature will give the same result where the PET pellets do not soluble in the toluene. This condition occurs because; according to the Hildebrand; only materials with the same solubility parameter will dissolve with each other (Burke, 2008). Following table will show the comparison of Hildebrand solubility parameter between PET and toluene:

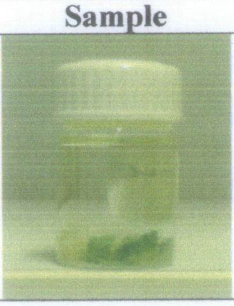
Table 13 : Comparison of solubility parameter between PET and Toluene

Substance	δ	δ (SI)
Polyethylene Terephthalate (PET)	10.1	20.5
Toluene	8.91	18.3

Referring to the table above, it can be observed that there is a huge difference in the solubility parameter of the two materials. Thus, it can be conclude that PET is not soluble in the Toluene.

4.2 Experiment 2: PET solubility in Kerosene (Turpentine)

Table 14 : Result of PET being treated with Kerosene

Sample	Solvents	Temperature (°C)	Appearance
	Kerosene	90	Not soluble
		100	Not soluble
		110	Not soluble
		120	Not soluble
		130	Not soluble
		140	Not soluble
		150	Not soluble

After the treatment of PET with the toluene has failed, the experiment continued by treating the PET with the kerosene. However, the result of this experiment is not much different with the previous one as it is observed that PET pellets which have been immersed in the toluene are not soluble at all. Judging from Hildebrand point of view in solubility parameter, it can be seen that there is also a huge different between the two materials which make them insoluble to each other.

Table 15 : Comparison of solubility parameter between PET and Kerosene

Substance	δ	δ (SI)
Polyethylene Terephthalate (PET)	10.1	20.5
Kerosene (Turpentine)	-	16.6

4.3 Experiment 3: PET solubility in treated Diesel

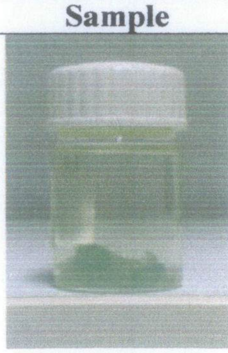
Table 16 : Result of PET being mixed with treated Diesel

Sample	Solvents	Temperature (°C)	Appearance
	Treated Diesel (11% H_2O_2)	90	Not soluble
		100	Not soluble
		110	Not soluble
		120	Not soluble
		130	Not soluble
		140	Not soluble
		150	Not soluble

Another approach has been taken into consideration in the pursuit of looking for the correct solvent to dissolve the PET where the PET pellet is mixed with treated Diesel. In this method, diesel has been combined with hydrogen peroxide which constitutes up to 11% of the total weight of the mixture. This is done because pure hydrogen peroxide is considered as weak acid (US Peroxide, 2009). Weak acid is aimed to be used because it is believed to have the ability to dissolve a material without damaging its molecular structure. However, judging from Table 16, it seems like, this so-called treated diesel does not have any impact on the PET pellets.

4.4 Experiment 4: PET solubility in Dichloromethane (DCM)

Table 17 : Result of PET being mixed with DCM

Sample	Solvents	Temperature (°C)	Appearance
	Dichloromethane (DCM)	20	Not soluble
		30	Not soluble
		40	Soften
		50	Soften
		60	Soften
		70	Soften
		80	Soften
		90	Soften
		100	Soften

After considering another factor of solvent which might affect the solubility of a substance in a solvent; which is the solubility parameter; DCM is taken into consideration due to its Hildebrand's solubility parameter value is near to the one of PET's. Following is the table that shows their respective solubility parameter:

Table 18 : Comparison of solubility parameter between PET and DCM

Substance	δ	δ (SI)
Polyethylene Terephthalate (PET)	10.1	20.5
Dichloromethane (DCM)	9.93	20.2

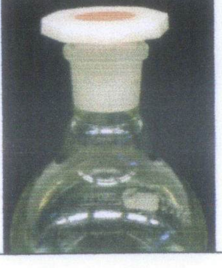
Referring to the Table 18, we can observe that the difference between DCM and PET is very little. According to Hildebrand and Hansen, both of these substances can dissolve to each other due to similarities in their solubility parameter. Thus, this experiment is conducted based on the fact mentioned by both of the renowned scientists.

However, after the experiment is conducted, it is observed that the mixture is not entirely dissolve. The PET become soften when the temperature reach 40 °C. The experiment is continued until the temperature reach 100 °C but still there is nothing changes in the texture of the PET except from being soften.

Another drawback from this experiment is that the boiling point of DCM is very low which is at 40 °C. Thus, to avoid the loss of containment of DCM into vapor, the setup is equipped with condenser which can provide vapor reflux into the boiling flux once again.

4.5 Experiment 5: PET solubility in Treated Toluene

Table 19 : Result of PET being mixed with DCM

Sample	Solvents	Temperature (°C)	Appearance
	Treated Toluene (10% Naphthalene)	90	Not soluble
		100	Not soluble
		110	Not soluble
		120	Soluble
		130	Soluble
		140	Soluble
		150	Soluble

		160	Soluble
		170	Soluble
		180	Soluble

In this experiment, the solvent that is used is toluene treated with naphthalene. First of all, toluene is used due to the fact that toluene is a solvent for Polyethylene (PE) polymer (Whiteley, Heggs, Koch, Mawer, & Immel, 2005). However, this solvent alone cannot withstand the strength of PET where PET does not even change its feature when combined with toluene as shown in Experiment 1.

Thus, in order to enhance the ability of toluene in dissolving PET, toluene is treated with naphthalene. This is because there is one research made by (Goje, 2005); he is able to dissolve PET with naphthalene. From his research, one of the drawbacks that he did not take into consideration is the high operating temperature of the reactor which it operated at 220 °C. Another downside of his experiment is that the size of the PET polymer he has been using is very small which the pellet is in powder form. In industrial practice, in order to achieve such pellet sizing, the cost is very high. Economically, this technique is not economic friendly.

Therefore, the toluene is mixed with the naphthalene based on weight percentage where 5 g of naphthalene is combined with 45 g of toluene. This mixture is then heated up until 90 °C and simultaneously the PET pellet is poured into the mixture. Every 30 minutes, the temperature is raised up to 10 °C until the PET pellet appeared to be dissolved. At 120 °C, the PET pellet seems to be dissolved instantaneously.

4.5.1 Re-precipitation of the dissolved PET

Since, the PET pellet is dissolved in the newly created solvent; we were able to move to the next stage which is the Stage 3 where PET is recovered from its dissolved solution. In this stage, the technique used to recover the PET is the precipitation technique. The solution is titrated with distilled water and instantaneously white precipitate is form (as shown in Figure 7). This situation is due to the fact that PET is highly insoluble in aqueous solution thus; at the end it produced PET precipitates.

Figure 8: Result of titration of PET-Treated Toluene solution with water

Figure 9: Solvent is recovered from the solution

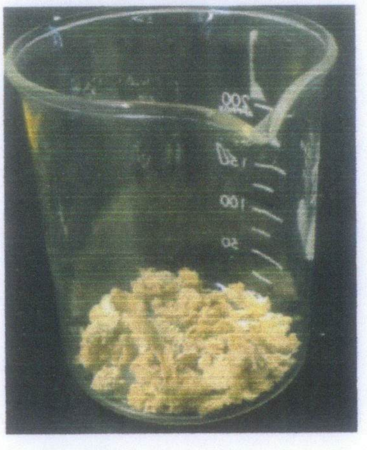
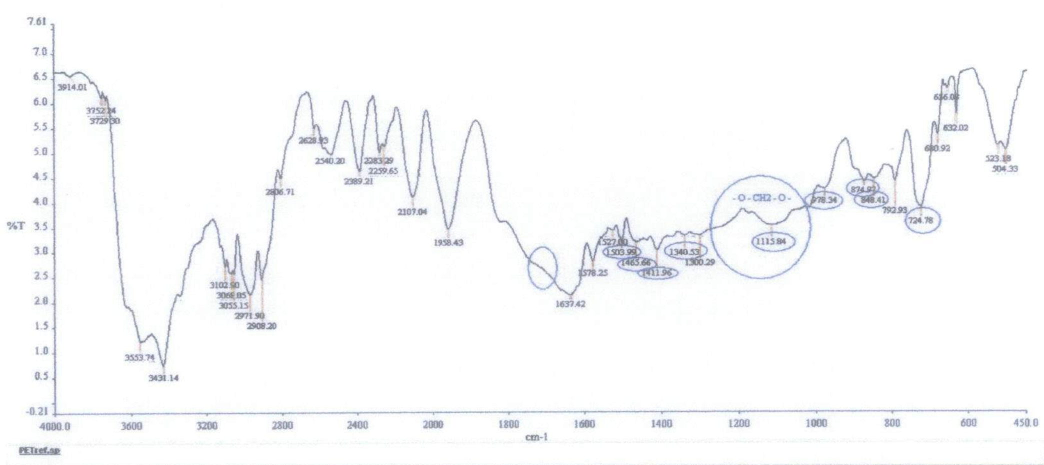


Figure 10: Recycled PET recovered in powder size

4.5.2 Chemical Analysis on Recycled PET

After the PET pellets are successfully dissolved in selected solvent, now it is the time to check the purity of the recovered PET polymer either it is highly pure or not. This stage is essential as it will determine whether this method of PET recycling is successful and economically viable. In order to conduct this purification test, there are few methods available to be implemented but the selection of the method is depending on the availability of the equipment available in this institutions. Thus, for this experiment, the equipment that is used for the chemical analysis is the FTIR. Following is the graph obtained for the recycled PET:



From the graph, we can observe that there is a shift in the value of IR spectrum of recycled PET if compared with the literature value of IR spectrum of virgin PET. For example, there should be a peak at 1408 and 1339 cm^{-1} which correspond to the deformation of C-H alkane. However, from the graph obtained, the peak can be seen at 1411 and 1340 cm^{-1} which there is a slight shift occurred. C-H bending, aromatic C-C stretching and C-H asymmetric stretching should all be occurring at 1453 cm^{-1}, 1505 cm^{-1}, and 2960 cm^{-1}. However, there is no sign of existence of aromatic ring that should appear at 1713 cm^{-1}. This condition might be due to the additives added to the PET sample. Overall, it can be estimated that the purity of the recycled PET is 85% as pure as virgin PET.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

There is a need in liquefying the solid PET pellets because it will make the process of recycling much easier since the PET plastic will be molded and shaped into any desired design. This experiment proceeds with the idea of liquefying the solid PET polymer by dissolving it in solvent because, conventional method of liquefying PET plastic by heating consumes a lot of energy; which consequently result in higher cost; since there is a need of fuel to produce the heat. During this stage, it is also aimed to dissolve the PET pellets at lowest temperature possible. The lower the temperature used, the lower the cost of production/recycling; especially if this method is applied in industrial scale.

Up until this stage, it can be concluded that solvents which have huge differences with PET does not dissolve the polymer at all. Following is the summary of PET reaction towards few solvents:

Table 20 : Solubility parameter comparison between PET with few solvents

Solvents	Reaction	δ (SI)	PET, δ(SI)
Toluene	Not soluble	18.3	20.5
Kerosene (Turpentine)	Not soluble	16.6	
Treated Diesel	Not soluble	-	
DCM	Soften	20.3	
Treated Toluene	Soluble	-	

5.2 Recommendation

The result of the experiment might be inaccurate due to the inefficiency of the equipment used. The best equipment to be used in this experiment is high pressured reactor. Since the solvent that were used in this experiment are volatile, high pressure reactor is able to keep the pressure low and able to ensure the experiment run smoothly.

Since there is a need in the usage of FTIR for the purpose of the chemical analysis of the sample, thus, there should be a regular routine where he FTIR equipment is calibrated regularly. Any faulty in the machine; even the small ones; it will deviates the result of the experiment.

The solvent that were used in this experiment are only available in industrial scale. An industrial scale is a scale where it is standardized to be used in industrial practice. Thus, in order to ensure the right combination of the solvent and the PET, thus, there should be experiment conducted with different ratio of PET: solvent.

Somehow, due to lack of chemical solvent available in the institution, there is not enough experiment conducted to test solubility of PET in various solvent. Thus, in order to find solvent which is economic friendly and has high tendency in dissolving PET, the experiment should be conducted with many solvents instead of few as tested in this project.

REFERENCES

A.K. Van Der Vegt, L. G. (n.d.). van keten tot kunstof. In *Polymeren.*

Accu Dyne Test. (2009). *Surface Free Energy Components by Polar/Dispersion and Acid—Base Analyses; and Hansen Solubility Parameters for Various Polymers.* Retrieved November 8, 2013, from Accu Dyne Test: Only from Diversified Enterprise: http://www.accudynetest.com/polytable_02.html?sortby=sort_hansent

alevelchem. (NA). *AS Inorganic Chemistry - Titration.* Retrieved November 8, 2013, from A' Level Chemistry Web: http://alevelchem.com/aqa_a_level_chemistry/unit3.3/331/titration.htm

AZoM. (2013). *Polyethylene Terephthalate Polyester (PET, PETP) - Properties and Applications - Supplier Data by Goodfellow.* Retrieved November 7, 2013, from Azom - The A to Z Materials: http://www.azom.com/article.aspx?ArticleID=2047#_Applications

BERNAMA. (2011, June 22). *Lebih 12,000 Tan Sampah Dibuang Setiap Hari.* Retrieved November 5, 2013, from Bernama: Malaysian National News Agency: http://www.bernama.com/bernama/v3/printable.php?id=595884

Billy. (2011, April 4). *Rakyat Malaysia Buang 1.8 Juta tan Sampah Setahun - Hebat ke Tak Hebat?* Retrieved October 10, 2013, from Billy Info: http://billyinfo.blogspot.com/2011/04/rakyat-malaysia-buang-18-juta-tan.html#axzz2hKWwylAj

Burke, J. (2008, November 23). *The Hildebrand Solubility Parameter.* Retrieved November 7, 2013, from CoOL: Conservation OnLine: http://www.cool.conservation-us.org/byauth/burke/solpar/solpar2.html

CEM. (NA). *Polymer Solubilities, Solvents, and Dissolution Temperatures.* New York: CEM Corporation.

Goje, A. S. (2005). Recycling of Waste Poly(Ethylene Terephthalate) with Naphtalene and Neutral Water. In A. S. Goje, *Polymer-Plastic Technology and Engineering* (pp. Volume 44, Issue 8-9).

Hansen, C. M. (1967). *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient and Their Importance in Surface Coating Formulation.* . Copenhagen: Danish Technical Press.

HSPiP. (2013). *Hansen Solubility Parameter in Practice*. Retrieved November 8, 2013, from The Official Hansen Solubility Parameter Site: http://www.hansen-solubility.com/HSPiP.html

Karayannidis, G. P., & Achilias, D. S. (2007). Chemical Recycling of Poly(ethylene terephthalate). *Macromolecular Materials and Engineering*, 128-146.

Lancashire, R. J. (2011, August). *Unit - Chemistry of Garments: Synthetic (man-made) Fibres* . Retrieved November 6, 2013, from The University of West Indies: http://wwwchem.uwimona.edu.jm/courses/CHEM2402/Textiles/Synthetic_Fibres.html

Northwestern University. (2012, October 24). *Condensation Polymerization*. Retrieved November 7, 2013, from Materials World Modules: http://www.materialsworldmodules.org/resources/polimarization/4-condensation.html#Part7

Oku, A., Hu, L. C., & Yamada, E. (1996). *Alkali Decomposition of Poly(ethylene terephthalate) with Sodium Hydroxide in Nonaqueos Ethylene Gycol: A study on Recycling Terephthalic Acid and Ethylene Glycol.* Kyoto: John Wiley & Sons, Inc.

Paszun, D., & Spychaj, T. (1997). Chemical Recycling of Poly (ethylene terephthalate). *Ind. Eng. Chem. Res*, 1373-1383.

PETRA. (2012). *About PET*. Retrieved November 7, 2013, from PETRA: PET Resin Association: http://www.petresin.org/aboutpet.asp

Syed Ali, S. (2012, December 28). *Kawasan Pelupusan Sampah Negara Semakin Kritikal?* Retrieved November 5, 2013, from Kementerian Perdagangan Dalam Negeri, Koperasi dan Kepenggunaan: http://kpdnkk.bernama.com/newsBm.php?id=464735&

Teijin Limited. (NA). *Trademark*. Retrieved November 6, 2013, from TEIJIN: Human Chemistry, Human Solution: http://www.teijin.com/terms_conditions/trademark.html

US Peroxide. (2009, 21 10). *What is the pH of the H2O2 solution?* Retrieved 11 10, 2013, from US Peroxide - Technologies for clean environment: http://www.h2o2.com/faqs/FaqDetail.aspx?fId=26

Vadenburg, H. (1999). A simple solvent selection method to accelerated solvent extraction of additives from polymers. In *The Analyst* (pp. 1707-1710).

Whiteley, K. S., Heggs, T. G., Koch, H., Mawer, R. L., & Immel, W. (2005). Polyolefins. In K. S. Whiteley, T. G. Heggs, K. Hartmut, R. L. Mawer, & W. Immel, *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH.

Wikipedia. (2013, October 28). *Polyethylene Terephthalate*. Retrieved November 6, 2013, from Wikipedia: http://en.wikipedia.org/wiki/Polyethylene_terephthalate

Wyeth, N. C. (1973). *Patent No. 3733309*. United States of America.