AN EXPERIMENTAL STUDY OF NYLON RECYCLING AND ITS MODIFICATION USING HALOGEN BASED METAL HALIDES

by

DAVID WONG SIONG MING

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

AN EXPERIMENTAL STUDY OF NYLON RECYCLING AND ITS MODIFICATION USING HALOGEN BASED METAL HALIDES

by

David Wong Siong Ming

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(Dr. Iqbal Ahmed)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

____
(DAVID WONG SIONG MING)

ACKNOWLEDGEMENTS

First of all, the author would like to express his sincere thanks to the supervisor, Dr. Iqbal Ahmed, for his dedicated and continuous encouragement and guidance throughout the final year project. He has always been helpful and supportive. The author is also grateful for his tolerance of careless mistakes and his commitment to future success.

In addition, the author would like to thank all the lab technicians, especially Ms. Norhasneyza and Mr. Paris for their invaluable guidance throughout the project. Their kind supports have been helpful in order to guarantee the success of the project.

The author would like to express utmost gratitude to Chemical Engineering Department of Universiti Teknologi Petronas for giving each student a golden opportunity to expose them to research work environment. The author would like to thank Dr. Anis and Dr. Nurhayati Melon for their effort to ensure the final year project proceeds smoothly. This has provided an insight to the students whether they would like to venture into the research field of work later after graduated.

Lastly, the author would like to acknowledge his sincere indebtedness and gratitude to everyone who has assisted and guided him directly or indirectly throughout the final year project.

ABSTRACT

Drastic increase of the plastics demand over the last decade was in conjunction with the increasing population globally and their need to adopt better living conditions. While the consumption is increasing, the amount of plastics waste is piling up at the same time due to less efforts done for recovery of used plastic products and thus, causing plastic pollution. Post-industrial and domestic plastics were disposed mainly by landfill disposal and energy recovery with incinerators. Instead of disposing, recycling of plastics product is deemed more suitable. Chemical recycling of polyamide is studied in this project using formic acid and lithium chloride solvent system. Waste nylon product available in market is collected and identified using Fourier Transform Infrared Ray (FTIR) spectroscopy and melting point temperature determination. The percentage recovery of the recycled nylon is at the range of 98 % - 99 % after filtration. The presence of lithium chloride in the solvent system helps in altering the mechanical properties by bonding of lithium ions with the amide groups during dissolution, which has enhanced the tensile yield strength of the recycled nylon by 14.09 %.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND NOMENCLATURES

DME - Dimethyl Ether
FTIR - Fourier Transform Infrared Ray
L.O.P. - Longitudinal Operating Pressure
PA - Polyamide
PET - Polyethylene terephthalate
UTP - Universiti Teknologi Petronas

CHAPTER 1
INTRODUCTION

1.1 Background Study

Plastic products proliferation has caused a huge impact towards the modern civilization. These plastic products are almost inseparable in our daily life due to its incredible versatility and huge application in many end products. We use plastics products every day and put them away when we are done using them. However, the major problem here is we could never really put these plastic products “away”. Andrady and Neal (2009) and Scheirs (1998) mentioned that neither landfill disposal nor energy regeneration through incineration is a good resolve as these plastics products do not decompose easily and generate toxic fumes when burnt. Besides that, in recent research reports, Crompton (2007) stated that chemical additives and non-polymeric materials such as residual monomers, oligomers, low molecular weight fragments, catalyst remnants and polymerisation solvents can be present. Crompton also mentioned that these components are related to causing problems to human health. Zarfl and Matthies (2010) also revealed that food chain may be affected, for example, plastic is breaking down into many smaller pieces entering the food chain and releases chemicals into the fish that eat them. This has alarmed the environmentalists and raised concerns among more and more people nowadays. This situation is what we called plastic pollution. It is one of the biggest man-made catastrophes we have ever brought to ourselves in the history of human civilization. A resolve to this would be recycling of the used plastic products. Plastic recycling process could eliminate in part this problem and is chosen because recycling is the best option to conserve the raw material and decrease cost and contamination comparing to reuse, reduction in source material and so on. Therefore, in this research, an experimental study of nylon recycling with metal halides will be conducted and the characteristics of the recycled nylon will be studied.

1.2 Problem Statement

Some of the major nylon products are carpet, textile, fishing net and engineering plastics such as bullet proof vest and airbag. These nylon products are usually thrown away without recycling in the past after they are dumped or have degraded to a certain extent that their useful lives have ended. Fortunately, nylon products are more recyclable with a better economic feasibility nowadays thanks to the continuous advancement in nylon recycling technology. This has encouraged more researches to be done regarding to recycling nylon products. The most frequent nylon products being used are nylon 6 and nylon 66. However, most of the recycled nylon will have degraded physical properties if compared to virgin nylon. Therefore, the problem statement of this experiment is:

"What are the effects of chemical recycling of nylon waste product using formic acid solvent system with lithium chloride on the mechanical properties of recycled nylon?"

1.3 Objective

The objective of this research is to study and analyse the mechanical properties of recycled nylon using formic acid solvent system with lithium chloride and compare them with recycled nylon without additives.

1.4 Feasibility Study within Scope and Time Frame

This project is feasible within the scope and period of time allocated. The literature review and background study of the project can be done by using both local and online resources through UTP Information Resource Centre. Online journals and documents can be obtained through the website which UTP IRC has subscribed. Besides that, in conducting the experiment, UTP is a perfect ground with all the equipment such as the glassware and chemicals readily available for different kinds of experiment conditions and requirements. The characterization of the experiment is going to be done using the available facilities inside UTP as well. Therefore, all the executing procedures should be planned properly in order to achieve the ultimate objective of this project in the end. In conclusion, this research project is feasible within the time frame and also the scope of the study.

1.5 Scope of Study

In this research, the scopes of study are:

1. Effect of chemical recycling using formic acid solvent system with lithium chloride on the mechanical properties of recycled nylon.

A few characterizations to be done are:

1. Fourier Transform Infrared Spectroscopy (FTIR)
2. Tensile strength and strain

CHAPTER 2
LITERATURE REVIEW

2.1 Nylon

Nylon is generically known as polyamides. Nylon was firstly discovered by Wallace Hume Carothers, director of the DuPont Experimental Station in Wilmington, Delaware, in 1930s (Trossarelli, 2010). Wallace Carothers managed to create a synthetic silk which is renowned as miracle fibre today, and that is nylon. Until today, nylons are the first engineering plastics and still represent the most important class of these types of material("Nylon 6 and Nylon 6,6," 2009). The common nylon products are designated as nylon 6, nylon 6,6, nylon 6,12, nylon 11 and nylon 12. These nomenclatures refer to the number of carbon atoms that separate the recurring amide groups (-CONH-). Meanwhile, among the commonly used nylon products, Nexant Inc. (2009) surveyed and concluded in their report such that nylon 6 and nylon 6,6 are the most popular types to be used for polyamide commercial products, accounting for more than 90 per cent of nylon used in the global market. According to R, Desai, and Patel (2012) in their study, they have concluded that these amide groups have very strong hydrogen bonding capability and crystallinity in the polyamides, PA, giving them ultimate solvent resistance and mechanical properties. This is the reason why nylon is the first engineering plastics being used today.

While most of the plastics products are made for commodity purpose such as PET (Polyethylene terephthalate) for food and beverage packing industry, engineering plastics has gain more attention in recent years. Among the various types of engineering plastics, one of the greatest creations in the last century is nylon. Thanks to its versatility, high moldability and resistance to high temperatures and harsh chemicals, nylon has become one of the most commonly used key polymers today. It has wide applications especially in carpet, textile, automotive and fishery industries.(R et al., 2012)

Figure 2.1 illustrates the plastics consumption all over the world and their specific function or purpose of usage.("World plastics consumption long term, 1960-2020," 2012)

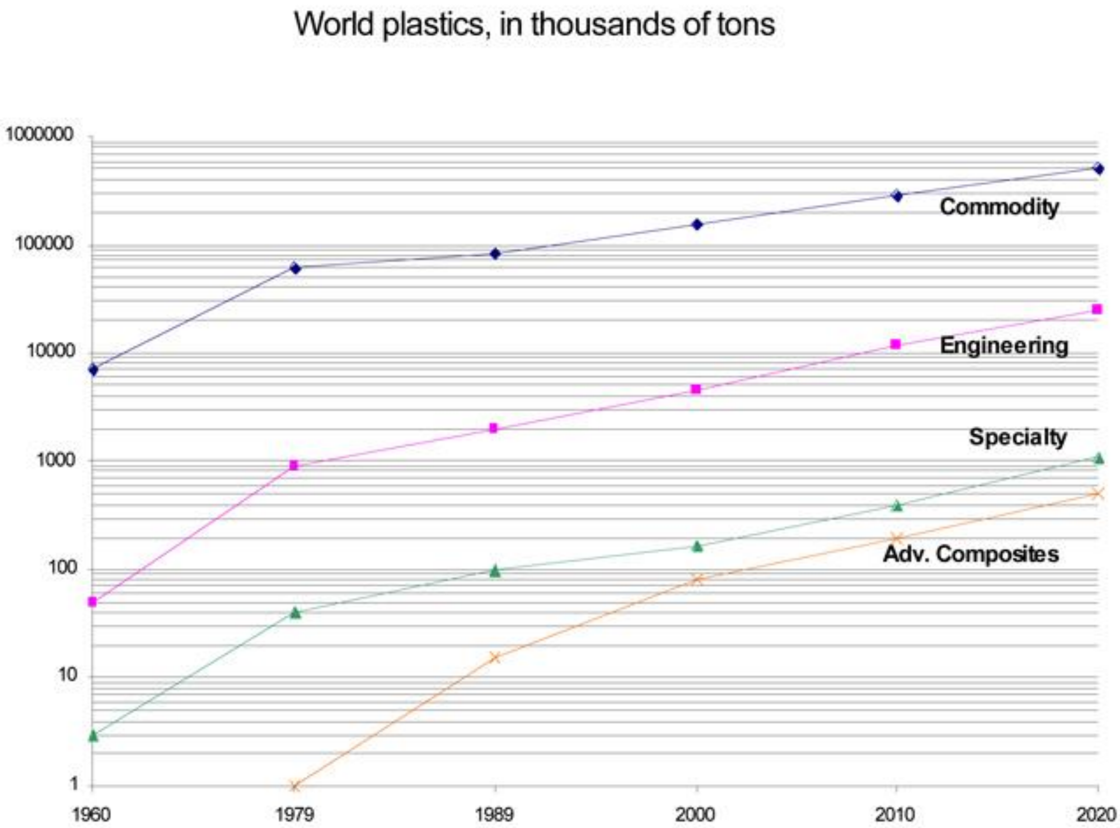


Figure 2.1: Global plastics consumption from 1960- 2020

Figure 2.2 indicates that both polyamide 6 and 66 are having major applications in engineering plastics products (EP-black coloured section) in the recent years and future forecast until the year 2020. ("PCI Nylon: Positive Signals from the European Nylon Symposium 2012," 2012)

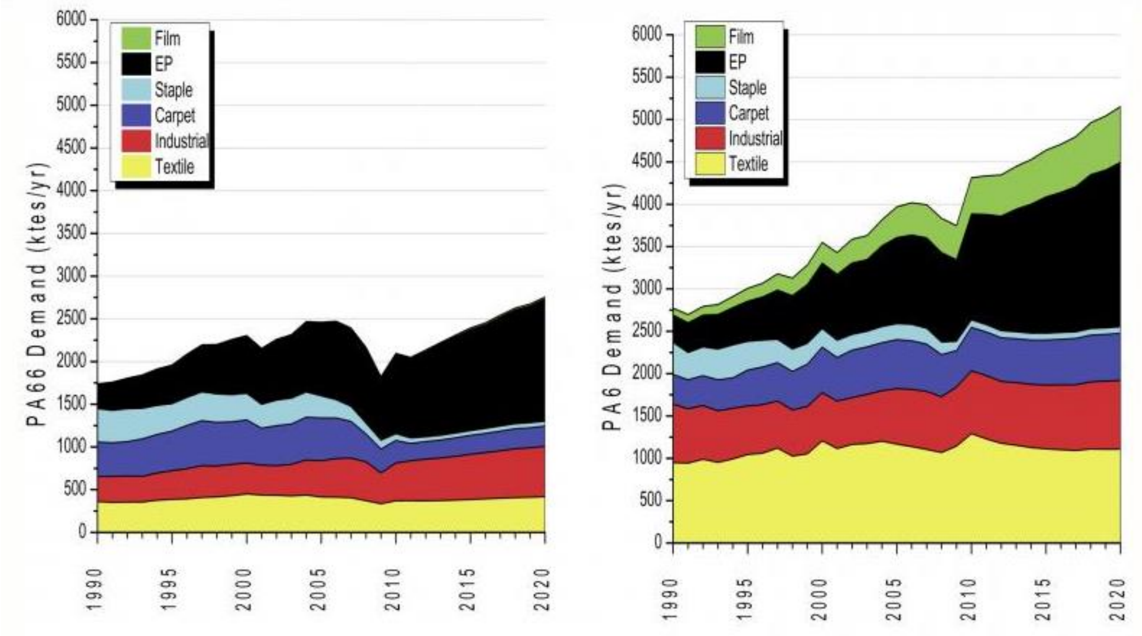


Figure 2.2: Future growth in global PA consumption and trends of usage

2.2 Chemistry of Nylon

Basically there are two reactions that are used to produce polyamide engineering polymers:

- Polycondensation of a dibasic acid and a a diamine
- Polymerization of an amino acid or lactam

Within these two types, a wide variety of polyamides are known having different physical and chemical properties depending on their structure. **Figure 2.3** and **Figure 2.4** show that the two major types of polyamides which contribute to the major commercial application, PA 6 and PA 66, are made by the ring opening polymerization of caprolactam and polycondensation of hexamethylenediamine and adipic acid respectively (Palmer, 2002).

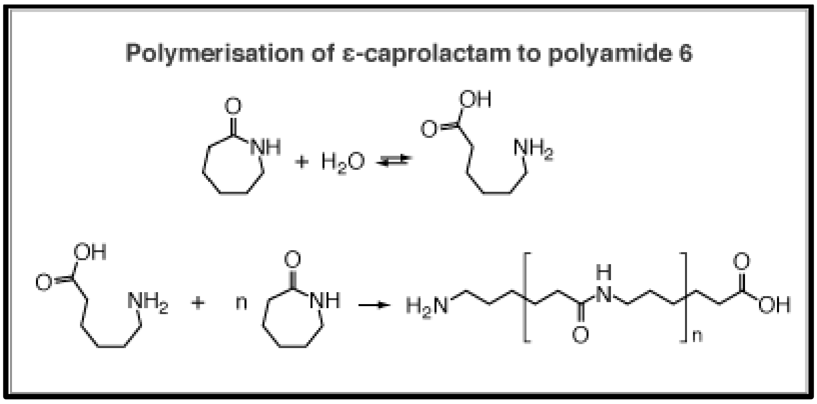


Figure 2.3: Ring-opening polymerization of ε-caprolactam with water to form nylon 6

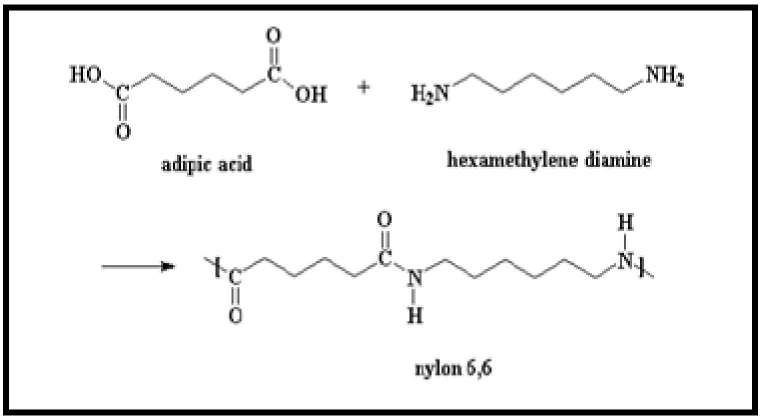


Figure 2.4: Condensation polymerization of hexamethylenediamine and adipic acid to produce nylon 6,6

In many applications that require high mechanical properties, heat resistance and chemical resistance, nylon 66 is preferred to nylon 6. Nylon 66 has enhanced mechanical properties mainly due to its tighter molecular structure caused by stronger hydrogen bonding. **Figure 2.5** illustrates the molecular structure of nylon 6 versus nylon 66 yielding enhanced properties. (Bagwala, 2012)

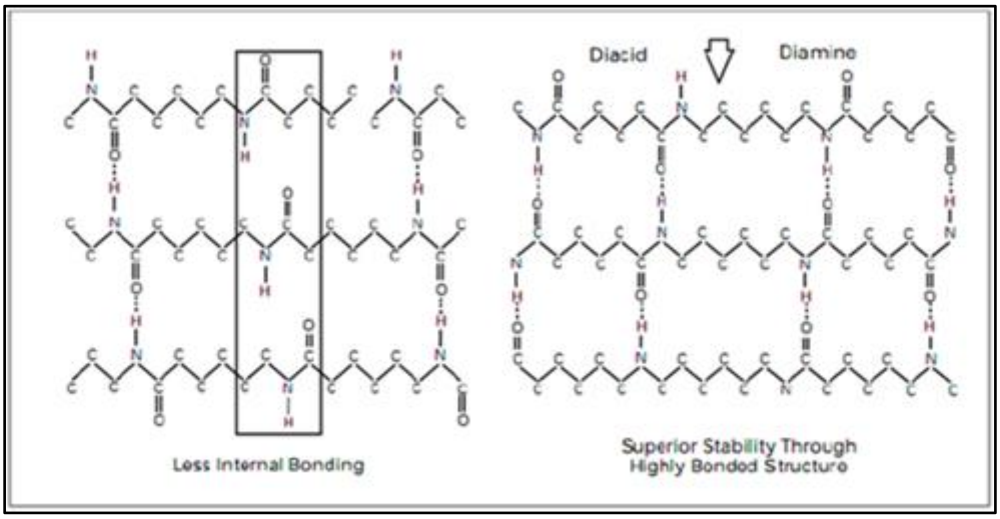


Figure 2.5: The molecular structure of nylon 6 and nylon 66

Table 2.1 below shows the typical physical characteristics of Nylon. (Palmer, 2002)

Table 2.1: Typical Physical Characteristics of Common Nylon

		Typical Physical Characteristics of Nylon					
ASTM test*	Property**	6,6	6	11	12	6,9	6,12
D792	Specific Gravity	1.14	1.13	1.04	1.02	1.09	1.07
D570	Water absorption 24 hr, wt%	1.2	1.6	0.3	0.25	0.5	0.25
	Equilibrium at 50% rh	2.5	2.7	0.8	0.7	1.8	1.4
	Saturation	8.5	9.5	1.9	1.5	4.5	3
D2117	Melting point (^{o}C)	255	215	194	179	205	212
D638	Tensile yield strength, Mpa	83	81	55	55	55	61
D638	Elongation at break, %	60-90	50-150	200	200	125	150
D790	Flexural modulus, MPa	2800	2800	1200	1100	2000	2000
D256	Izod impact strength, J/m	53-64	55-65	40-68	95	58	53
D785	Rockwell hardness, R scale	121	119	108	107	111	114
	Starting acid or lactam	Adipic acid	Caprolactam	Aminoundecanoic acid	Dodecanolactam	Azaleic acid	Dodecanedioic acid
*Test methods and standards may vary depending on the manufacturing region in worldwide supply network							
**Actual properties will depend on the type of polymer being used							

2.3 Recycling System

Since nylon is a highly precious polymer and due to its high consumption as predicted in Figure 2.2, the industry is forced to develop ways to reuse or recycle the nylon scraps whenever possible. This also complies with the requirement of sustainable energy consumption. Scheirs (1998) stated that most nylon (PA 6 and PA 66) is used on carpet industry and the recycling of carpet was first patented by DuPont in 1944 and until today, the recycling of carpet industry is still tough and very challenging. Recycling systems mostly used in the last decade have been reviewed. The recent recycling of waste nylon polymers can be done with many approaches. **Table 2.2** tabulates four main approaches being practised in recent years (Achilias et al., 2012; Karayannidis & Achilias, 2007; Scheirs, 1998):

Table 2.2: Four major recycling systems applied worldwide

Major Recycling System	Description
Primary Recycling	• In-plant recycling of the scrap material • Recycles only clean uncontaminated single-type waste
Mechanical Recycling *(Secondary Recycling)*	• Separate polymers from contaminants • Sorting and separation of wastes, size reduction and melt filtration • Product properties degradation • Maintain polymer average molecular weight by intensive drying , degassing vacuum, use of chain extender compounds, etc.
Chemical Recycling *(Tertiary*	• De-polymerization and re-

Recycling)	polymerization - Ammonolysis - Hydrolysis
Energy Recovery *(Quaternary Recycling)*	- Plastics energy content recovery during incineration - Emit toxic fumes

2.4 Chemical Recycling

Nylon de-polymerization and re-polymerization, or commonly known as chemical recycling system, has been applied in order to reproduce virgin nylon from the commercially used nylon products. Although mechanical recycling continues to play the major role in recycling nylon waste products, it is, however, not the most economical and a long term solution to the total resource recovery issue (Shukla, Harad, & Mahato, 2006). Shukla et al. (2006) also mentioned that the recycling of polymeric waste to the monomer are usually done in a high temperature and high pressure environment with the presence of catalysts and this has complicated the process control, equipment design and monomer recovery process.

The two methods commercially used for depolymerisation of nylon are hydrolysis and ammonolysis while currently preferred route in use at the DuPont Company is ammonolysis (Kasserra, 1998). At temperatures between 300^{o}C and 350^{o}C and a pressure of about 68 atmospheres, the reaction of nylon 66 and nylon 66/nylon 6 mixtures with ammonia in the presence of an ammonium phosphate catalyst gives a mixture of monomeric products (McKinney, 1994).

2.4.1 Formic acid solvent system

Formic acid is chosen as the solvent because it has the ability to replace the strong hydrogen bonds that hold the nylon. The formic acid used in the experiment will have an initial concentration of about 90% by weight(Araujo et al., 2011). The dissolution will be done at a temperature in the range of 0-80^{o}C for a period of 1 to

20 hours (Shukla et al., 2006). This polymer solution will become homogenous later. The solution is then filtered for nylon precipitates or granules and treated with hot water to remove the residual formic acid (Shakaib, Ahmed, Yunus, & Idris, 2013). This is because formic acid will disrupt the process of condensation polymerization later if it is not removed and the formic acid is recovered later and can be reused.(Lehmann, Neunhoeffer, Roselius, & Vitzthum, 1973; Roberts & Griffith, 1997; Waibel, Schonemann, Krukonis, Lawrence, & Caulfield, 2011)

2.4.2 Lithium Chloride

The effect of lithium chloride to nylon has been reported by Shenoy, Saini, and Nadkarni (1983) such that the introduction of lithium chloride is able to decrease the melting point and increase the glass transition temperature and melt viscosity. Besides that, a research done by Mantia and Acierno (1981) further confirmed that the glass transition temperature is increased by about $25^{o}C$ with addition of 4% lithium chloride. Mantia and Acierno (1981) also revealed that lithium chloride is more effective in altering the properties of the nylon. He also mentioned that the effect was due to the formation of a pseudo-cross-linking between lithium ions and the carbonyl-oxygen groups of the polyamide. Therefore, in this experiment, the effect of adding 3% of lithium chloride by weight on the recycled nylon is studied and compared with recycled nylon without any additives. Addition of lithium chloride is also believed to reduce the tensile modulus but improve the tensile elongation at rupture. (Wyzgoski & Novak, 1987)

2.4.3 Nylon dissolution in methanol/calcium chloride solvent system

The method discussed in this section will be using methanol and metal halides salt dissolution system. Nylon dissolves partially in methanol when heated to reflux but it can dissolve completely when metal halides such as calcium chloride is added into the solvent(Sun, 1994). Besides that, Sun (1994) also mentioned that the methanol is functioning as a bridge to allow the calcium ions to complex with the amide groups. **Figure 2.6** explains the process of the complexation in 4 simple steps:

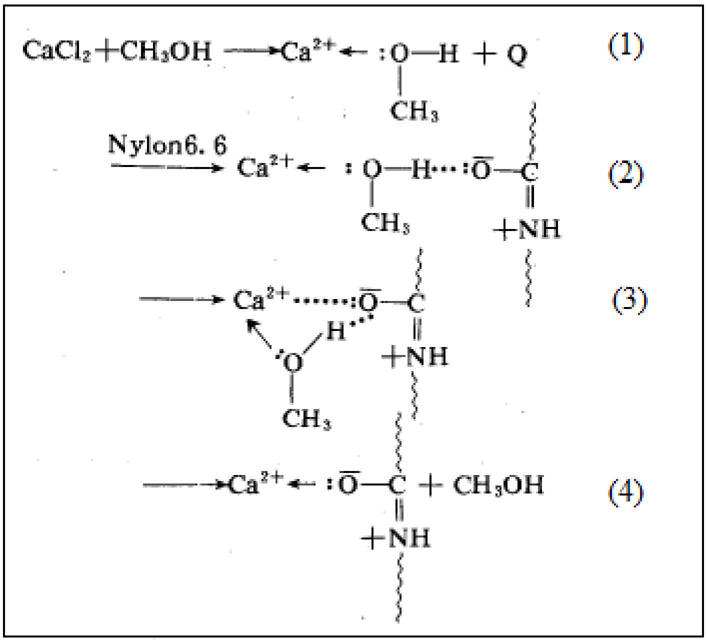


Figure 2.6: Complexation of calcium ions with the amide groups through methanol

1. (1) Complexation between calcium ions with methanol O-H groups releasing heat.
2. (2) Calcium chloride-methanol complex molecules come close to nylon 6,6 molecules.
3. (3) Bonding between calcium cation and oxygen atom of a carbonyl group (C=O) due to higher complexing capability than the hydroxyl group.
4. (4) Calcium chloride-nylon 6,6 complex are formed.

This polymer solution will then become homogenous after heating to reflux for some time. Precipitates of nylon can be obtained by a few methods such as adding appropriate liquid (anti-solvent) or by cooling the polyamide solution (Booij, Hendrix, Frentzen, & Beckers, 1998). Booij et al. (1998) also stated that the shape of the polyamide precipitates can be controlled by varying the rate of cooling. The precipitates can then be separated by conventional filtration. The 4 stages of complexation explained above provides an insight as to how the lithium chloride will complex with the amide group of the nylon dissolved in formic acid.

Table 2.3 summarises the critical literature review over the years pertinent to nylon recycling technology and research.

Table 2.3: Critical Literature Review

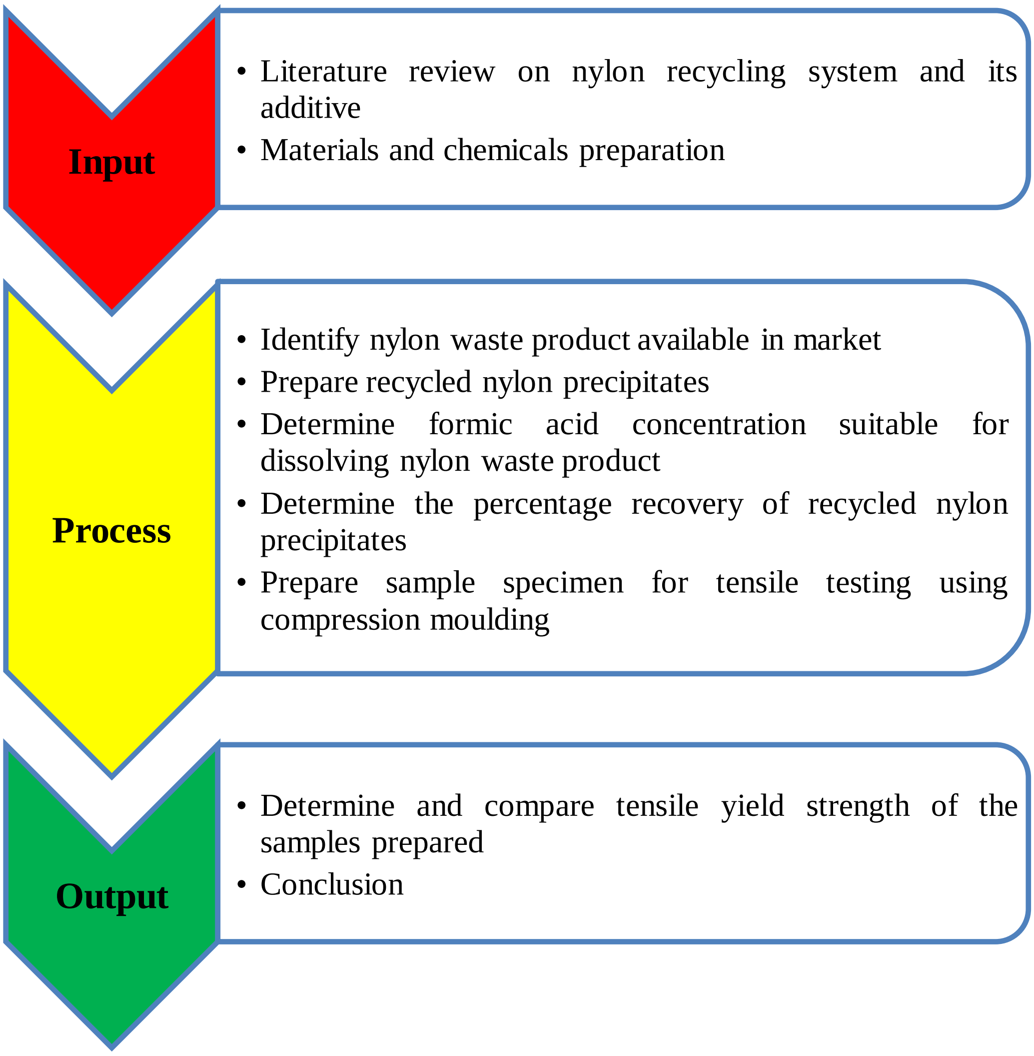
Journal/Article Title	Author(s)	Outcome(s)
Nylon Extraction from Commingled Materials	Waibel et al. (2011)	• Nylon is extracted from commingled materials • Formic acid is used as solvent • Nylon polymer is selectively precipitated using dimethyl ether (DME) as anti-solvent • High purity is achieved and can be performed at ambient temperatures • Nylon precipitates collected in the form of discrete, free flowing particles
Depolymerization of Nylon 6 Waste Fibers	Shukla et al. (2006)	• Formic acid, hydrochloric acid and sulphuric acid are used as solvents • Distilled water is used as anti-solvent • Nylon dissolved under reflux with the solvent used and precipitates were produced when anti-solvent is added • Recycled nylon properties degraded and the degree of degradation varies with respective to different acid concentration
Process for Recovering and Recycling Polyamide from Carpet Waste	Booij et al. (1998)	• Nylon production waste was recycled using aliphatic alcohol as solvent such as methanol, preferably at 155 ^{o}C to about 165 ^{o}C for PA66 and 135 ^{o}C to 140 ^{o}C for PA6

		- Pressure used at 0.5MPa to 1.5 MPa - PA6 and PA66 precipitate at different temperature - Controlled cooling can be used to selectively collect either Polyamide 6,6 granules or Polyamide 6 granules.
Study on the Mechanism of Nylon 6,6 Dissolving Process using $CaCl_2$/MeOH as the Solvent	Sun (1994)	- Nylon 6,6 dissolved in methanol-calcium chloride solvent - Recycled calcium chloride-nylon 6,6 complex has reduced melting point; 91K lower than pure nylon 6,6 polymer - Calcium ions free methanol solvent can be recovered completely
Method of Reconstituting Nylon by Solution in Formic Acid and Distillation with Hydrocarbon	(Simon, 1961)	- Formic acid is employed to dissolve nylon from textile wastes - Nylon recovered is degraded and discoloured - Nylon absorbs formic acid tenaciously and separation of the formic acid from the recycled nylon requires high temperature - Nylon from textile wastes without degradation and discolouration can be achieved by using a binary azeotropic mixture of formic acid and certain hydrocarbons such as n-hexane, n-heptane, cyclohexane, hexane, cyclohexene, benzene and toluene

CHAPTER 3

METHODOLOGY

3.1 Project Activities Overview



Input

- Literature review on nylon recycling system and its additive
- Materials and chemicals preparation

Process

- Identify nylon waste product available in market
- Prepare recycled nylon precipitates
- Determine formic acid concentration suitable for dissolving nylon waste product
- Determine the percentage recovery of recycled nylon precipitates
- Prepare sample specimen for tensile testing using compression moulding

Output

- Determine and compare tensile yield strength of the samples prepared
- Conclusion

Figure 3.1: Process Flow Chart for the project

3.2 Specific Project Activities

3.2.1 Research and Literature Review

A critical analysis and review had been done in order to understand the background information related to this project. Intensive study was done prior to commencement of this project. Since the project involves mainly experimental work, experimental studies will be done sufficiently in order to understand the configuration or setup of the laboratory work and also the effects of different variables on the outcome of the project. Later, qualitative and quantitative analysis such as FTIR and tensile test will be done. The procedure for the analysis will be studied and practised. The results of the experiment will then be compared with findings from the previous readings or research work, theoretically and practically.

3.2.2 Nylon Waste Product Collection and Identification

Plastics products are readily available in the market everywhere. However, most of the commercial products such as common known nylon thread used for scouting and carpet are actually not made of nylon. Most of them do not dissolve in formic acid. They are mostly mixed with other types of polymer such as polyester and polyethylene-terephthalate to serve the purpose of the product. To identify and confirm the types of polymer used, FTIR analysis and melting point temperature of the waste product are determined. FTIR analysis is done using the FTIR spectrometer as shown in **Figure A1**. Above all, the polymer must be able to dissolve in formic acid.

3.2.3 Determination of Formic Acid Concentration Suitable for Dissolving Nylon

The initial concentration of formic acid (Baker PCS Reagent) is 90% by weight. 3 grams of nylon waste product is dissolved in 25ml of formic acid. Distilled water is added into the solution while stirred on a hot plate. The distilled water is added continuously until a cloudy solution is observed. The amount of distilled water added is recorded and the concentration of the formic acid is calculated using the formula $m_1v_1=m_2v_2$. The formic acid is then added into the solution again until a clear solution is observed. Record the amount of formic acid added. Repeat the experiment to obtain an average value of the dissolving concentration and crystallizing or precipitating concentration.

3.2.4 Nylon Recycling/Nylon Precipitates Preparation

Dope solution with different weight percentage of nylon scraps and lithium chloride, 99%, Merck 105679, is prepared with the nylon scraps cut into smaller fragments and dissolved at room temperature and pressure in the formic acid. The dope solution is stirred on a hot plate until all the nylon scraps dissolve completely and homogenous solution is observed. Adequate amount of distilled water acting as anti-solvent is then added in order to obtain precipitates of nylon. The precipitates is filtered, removed and washed with hot water to remove the residual formic acid. The pH value is tested and recorded. The collected precipitates are dried later in a drying oven at $60^{o}C$ for at least 6 hours. After that, the dried precipitates are granulated using a Panasonic branded blender so that the size and shape of the precipitates are more evenly distributed. The precipitates prepared are shown in **Figure A2.** The percentage recovery of recycled nylon is calculated.

Percentage recovery = Weight of precipitates / Total weight dissolved x 100 %

3.2.5 Compression Moulding/Tensile Test

The granulated precipitates are then made into the dog bone specimen with dimensions according to the standard plastic tensile strength test ASTM-D638 using CARVER compression moulding machine as shown in **Figure A3**. The specimen used was in dumbbell shape with the dimension of 163 mm x 19 mm X 4 mm as shown in **Figure A4**. For tensile test, it was conducted under the parameter condition set by the standard ASTM D-638 under the room temperature and humidity with Testometric Tensile Tester M350-10kN as shown in **Figure A5**. The loading speed set was 5 mm/min. A constant 10N preload was applied for 5 seconds at the initial of the testing, the purpose was to tighten the gripper and prevent slipping from happening during the testing. For each specimen group, 3 - 5 sample tests were conducted.

3.3 Gantt chart and Key Milestones

Table 3.1: FYP 1 Project Gantt Chart and Key Milestones

FYP 1	January			February				March				April		
Details\Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FYP Title Selection	🟥	🟥												
Preliminary Research Work and Literature Review		🟥	🟥	🟥	🟥	🟥								
Submission of Extended Proposal							▲							
Proposal Defense								🟥	▲					
Detailed Literature Review										🟥	🟥	🟥		
Experiment setup and familiarizing										🟥	🟥	🟥		
Sample material preparation										🟥	🟥	🟥		
Preparation of Interim Report										🟥	🟥	🟥	🟥	
Submission of Interim Report (Draft)													▲	
Submission of Interim Report (Final)														▲

▲ **Key Milestone**

🟥 **Progress**

Table 3.2: FYP 2 Project Gantt Chart and Key Milestones

FYP 2	May		June				July				August				
Details\Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Project Work Continues	🟥	🟥	🟥	🟥	🟥	🟥	🟥								
Submission of Progress Report								▲							
Project Work Continues								🟥	🟥	🟥	🟥	🟥			
Pre-SEDEX											▲				
Submission of Draft Report												▲			
Submission of Dissertation (soft bound)													▲		
Submission of Technical Paper													▲		
Oral Presentation														▲	
Submission of Project Dissertation (Hard Bound)															▲

▲	Key Milestone
🟥	Progress

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Material Identification

An effort is done to identify the possible nylon products available in the market. Most of the nylon waste product found could not dissolve in formic acid. This was mostly due to that the plastic or polymer products were usually mixed with other types of polymer during processing and moulding such as polyester, polypropylene and polyethylene terephthalate. Mixed polymers product does not dissolve easily and sorting and separation of the polymeric material requires proper equipment which is a limitation at laboratory work scale. Therefore, among the tested nylon waste product, only badminton strings and nylon fishing line were successfully identified and confirmed as nylon product and they could perfectly dissolve in the formic acid. The nylon wastes are further identified and confirmed by doing the Fourier Transform Infrared Ray (FTIR) spectroscopy analysis and melting point temperature determination.

The FTIR analysis provides us an insight on the presence of the critical functional groups related to the nylon. **Table 4.1** below illustrates the respective wavenumber of the important functional groups in nylon as well as the experimental wavenumber obtained. The wavenumber (peak) obtained from **Figure 4.1** shows that the desired functional groups are all present when compared to literature in **Table 4.1**. This proves that the waste material is nylon product. To further identify the types of nylon structure, the melting point temperature is determined.

Figure 4.1 shows the IR Spectrum and wavenumbers at peak of the recycled nylon waste product.

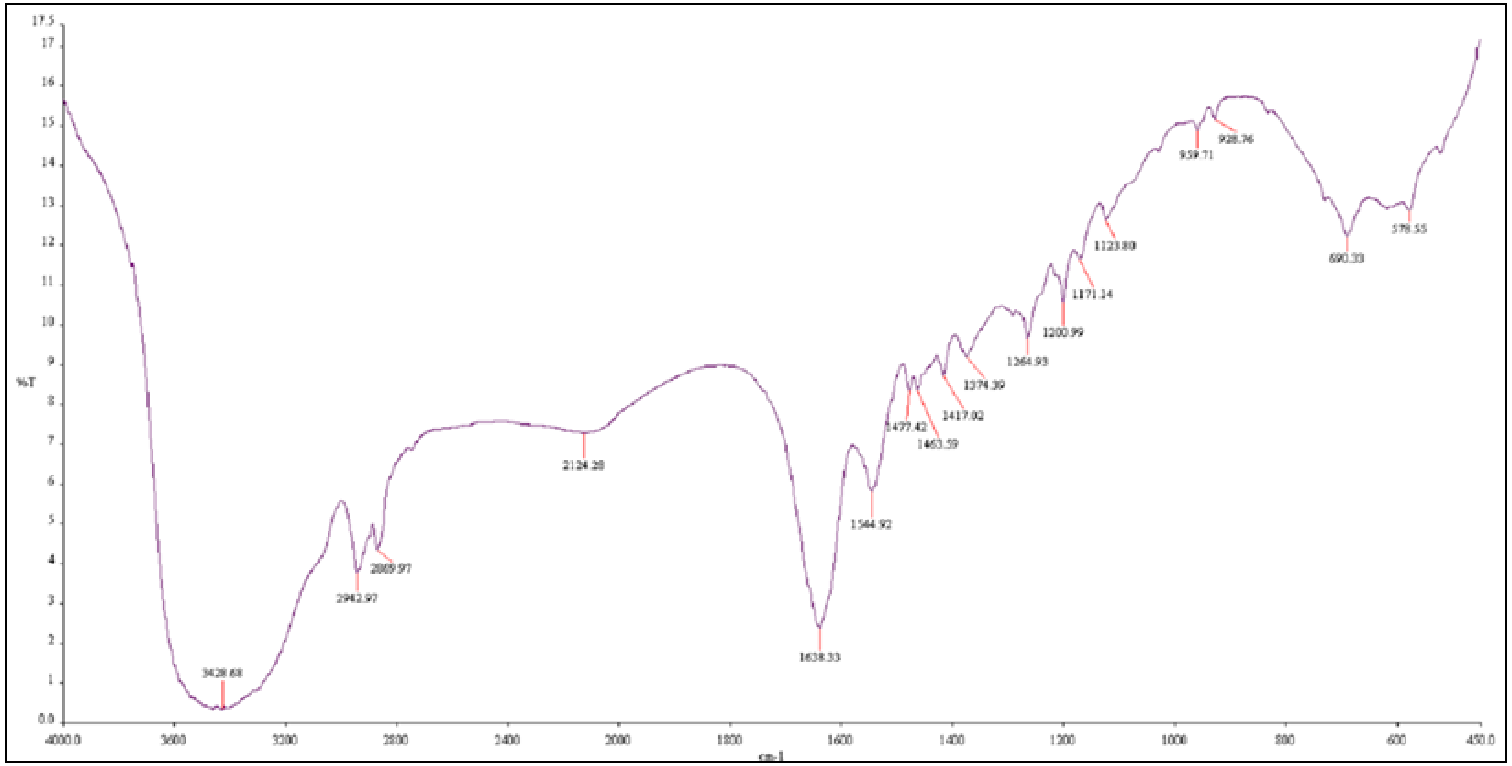
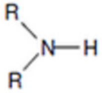
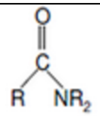


Figure 4.1: FTIR Spectrum of Recycled Nylon without Lithium Chloride

Table 4.1 shows the functional group present in the sample with respect to wavenumber.

Table 4.1: Experiment IR Spectrum and Respective Functional Group

Functional Group	Structure	Literature Absorption Range (cm^{-1})	Experimental Absorption Wavenumber (cm^{-1})
N-H Stretch of Amide		3500-3300	3428.68
H-C-H Stretches of Alkane	R_3C-H (R= H or C)	3000-2850 (multiple bands)	2942.97 and 2869.97
C=O Stretch of Amide	 (R-H or C)	1700-1625	1638.33

The FTIR spectrum results confirmed the identity of the sample being analysed is nylon. However, the types of nylon being used can only be determined with further analysis of melting point temperature. The sample is heated up in melting point equipment and the melting point temperature determined is 215^{o}C. Referring to the literature melting point discussed in **Table 2.1**, the nylon waste product being recycled is nylon 6.

4.2 Formic Acid Recovery

Formic acid can be recovered using distillation method to separate the water from it. (Simon, 1961) However, in this experiment, some attempts and trials are done to reuse the formic acid. First of all, 3 grams of nylon waste product is dissolved in the 90% by weight concentration formic acid at room temperature and pressure. Distilled water is added slowly into the solution using a burette and cloudy solution is carefully observed. First trial shows that when 25 ml of distilled water is added into the solution, cloudy solution is observed and the nylon precipitates can be seen. The nylon precipitates are filtered and another 3 g of nylon waste product is added into the 50 ml solution now. The solution is less milky after the precipitates are filtered. However, the nylon does not dissolve even after some time. Therefore, formic acid is added slowly and carefully into the solution again and observes when the nylon waste product dissolves and the solution becomes clear again. The experiment is repeated 3 times. The amount of distilled water and formic acid added each time to obtain cloudy and clear solution respectively is recorded and tabulated. The concentration of formic acid at each point of measurement is calculated.

Table 4.2 shows the concentration of formic acid when cloudy solution is observed. There are 4 trials altogether. However, the average value of concentration will be calculated using only trials 2, 3 and 4. This is because the first trial is done just to get an idea on the range of the formic acid at which the nylon will start to form precipitates.

Table 4.2: Concentration of formic acid at crystallization

Trial	Formic Acid (ml)	Distilled Water (ml)	Observation	Formic Acid Concentration (weight %)
1	25	25	Cloudy	45.00
2	50	40	Cloudy	50.00
3	100	76.7	Cloudy	50.93
4	149.5	118.8	Cloudy	50.15

First trial in getting cloudy solution is done in order to know the range at which concentration of formic acid the precipitates can be observed. Trials 2, 3 and 4 are done by adding distilled water carefully and slowly using a burette. Likewise, similar procedure is repeated but this time formic acid is added slowly instead of distilled water. **Table 4.3** shows the concentrations of formic acid when the cloudy solution turns into clear again when formic acid is added slowly.

Table 4.3: Concentration of formic acid at dissolution

Trial	Formic Acid (ml)	Distilled Water (ml)	Observation	Formic Acid Concentration (weight %)
1	50	25	Clear	60.0
2	85	40	Clear	61.2
3	149.5	76.7	Clear	59.48

The average concentration of formic acid at crystallization and dissolution are calculated as follow:

Formic acid concentration at crystallization

$$= \frac{50 + 50.93 + 50.15}{3}$$

$$= 50.36\ wt.\%$$

Formic acid concentration at dissolution

$$= \frac{60 + 61.2 + 59.48}{3}$$

$$= 60.23\ wt.\%$$

The concentration calculated is based on when 3 grams of nylon waste product is dissolved in the formic acid. However, it still provides an insight regarding to the amount of formic acid required to dissolve nylon completely. Therefore, it is safe to assume a concentration of 70% in practice to dissolve and recycle nylon waste product. **Figure 4.2** shows the cloudy and clear solution observed in experiment.

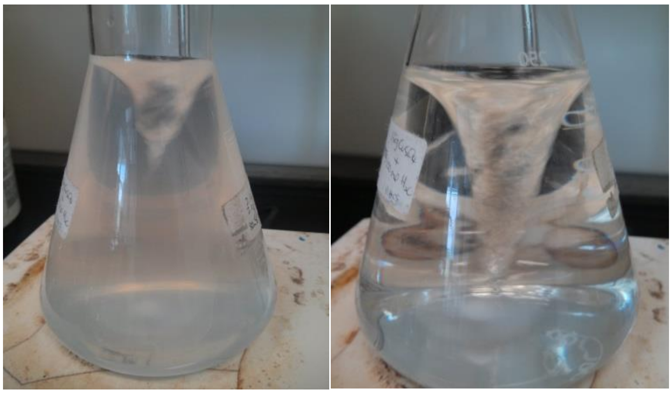


Figure 4.2: Cloudy solution and clear solution

4.3 Percentage Recovery of Recycled Nylon

The percentage recovery of recycled nylon is determined using simple mass balance calculation. Nylon dissolved in sample 1 and 2 are without lithium chloride while sample 3 and 4 with lithium chloride added. **Table 4.4** and **Table 4.5** tabulate the percentage recovery of recycled nylon for when no addtive is added and when lithium chloride is added respectively.

Table 4.4: Percentage recovery of recycled nylon (no additive)

Sample	Amount of nylon dissolved (g)	Amount of recycled nylon recovered at 1st filtration	Amount of recycled nylon recovered after 2nd filtration	Recovery at 1st filtration (%)	Recovery after 2nd filtration (%)
1	100g PA	95.59	98.66	95.59	98.66
2	100g PA	93.37	97.89	93.37	97.89
				Average	98.28

Table 4.5: Percentage recovery of recycled nylon (with LiCl)

Sample	Amount of nylon dissolved (g)	Amount of recycled nylon recovered at 1st filtration	Amount of recycled nylon recovered after 2nd filtration	Recovery at 1st filtration (%)	Recovery after 2nd filtration (%)
3	97g PA + 3g LiCl	96.53	99.03	96.53	99.03
4	97g PA + 3g LiCl	96.33	98.87	96.33	98.87
				Average	98.95

4.4 Tensile Test

Figure 4.3 and **Figure 4.4** show the force versus elongation graph plotted to study the mechanical behavior of both the recycled nylon with and without lithium chloride added. Based on the observation from the graph, it can be deduced that the material produced are brittle because there are no sign of yielding happening before fracture.

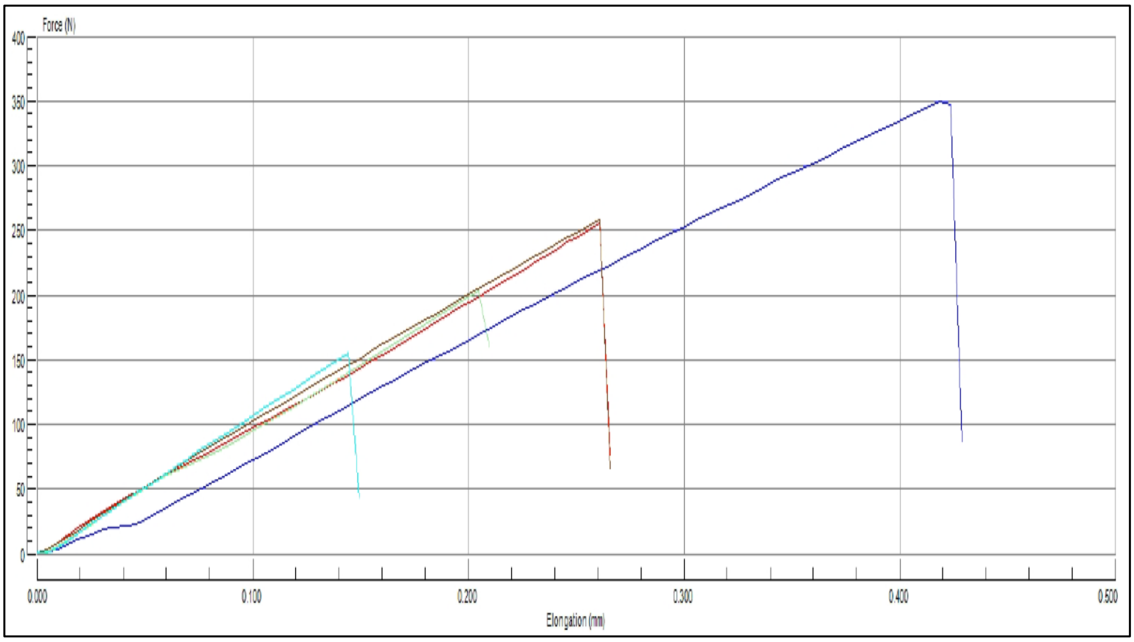


Figure 4.3: Force versus elongation curve (No LiCl)

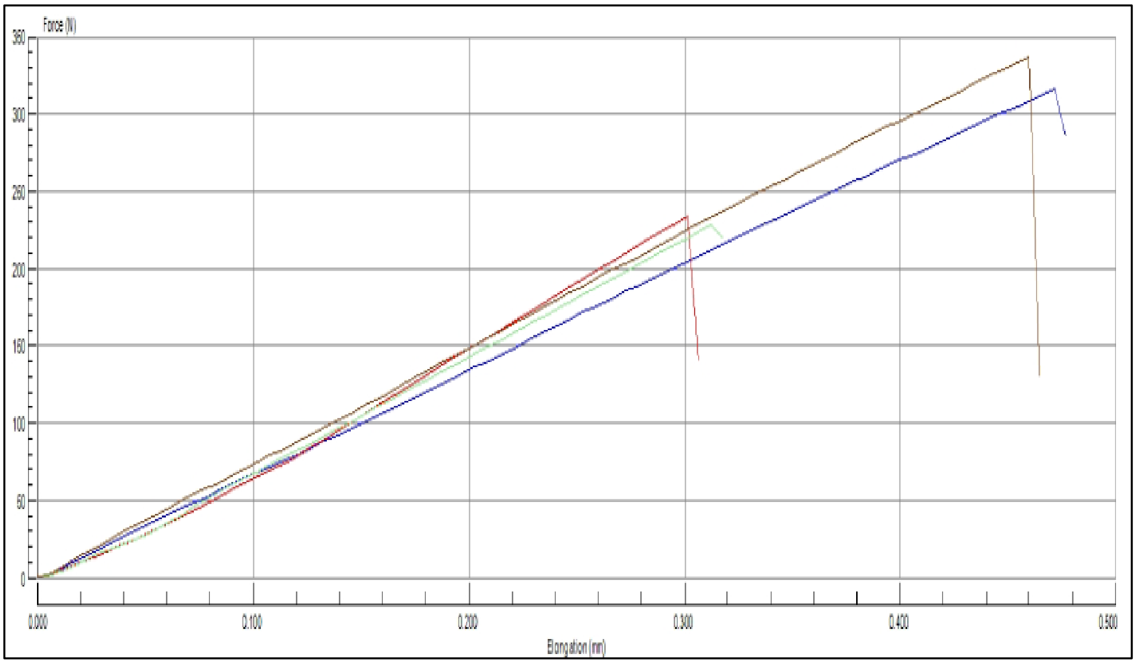


Figure 4.4: Force versus elongation curve (with LiCl)

The average tensile properties of both specimens are tabulated in **Table 4.6** and **Table 4.7** below:

Table 4.6: Tensile properties of specimen prepared without additive

Test No.	Stress at break (N/mm2)	Stress at 0.000mm (N/mm2)	Force at peak (N)	Elongation at break (mm)	Elongation at L.O.P. (mm)	Energy to break (N.m)	Stress at yield (N/mm2)	Force at break (N)	Young Modulus (N/mm2)	Stress at L.O.P. (N/mm2)	Energy to upper yield (N.m)	Strain at peak (%)
1	1.141	0.001	350.200	0.429	0.151	0.075	4.608	86.700	2022.662	1.588	0.072	0.260
2	1.007	0.001	255.000	0.266	0.147	0.034	3.355	76.500	1955.442	1.853	0.033	0.162
3	2.114	0.001	203.100	0.210	0.205	0.021	2.672	160.700	2098.256	2.672	0.020	0.127
4	0.867	0.001	257.800	0.266	0.094	0.035	3.392	65.900	2134.760	1.270	0.034	0.162
5	0.570	0.001	155.100	0.150	0.065	0.011	2.041	43.300	2327.370	0.879	0.011	0.090
Mean	1.140	0.001	244.240	0.264	0.132	0.035	3.214	86.620	2107.698	1.652	0.034	0.160

Table 4.7: Tensile properties of specimen prepared with lithium chloride as additive

Test No.	Stress at break (N/mm2)	Stress at 0.000mm (N/mm2)	Force at peak (N)	Elongation at break (mm)	Elongation at L.O.P. (mm)	Energy to break (N.m)	Stress at yield (N/mm2)	Force at break (N)	Young Modulus (N/mm2)	Stress at L.O.P. (N/mm2)	Energy to upper yield (N.m)	Strain at peak (%)
1	3.763	0.001	316.200	0.477	0.128	0.076	4.161	286.000	1288.199	1.108	0.075	0.293
2	1.864	0.001	234.000	0.307	0.302	0.034	3.079	141.700	1799.588	3.079	0.033	0.187
3	2.903	0.001	228.200	0.318	0.313	0.035	3.003	220.600	1609.912	3.003	0.034	0.194
4	1.724	0.001	336.300	0.465	0.317	0.079	4.425	131.000	1604.321	3.112	0.078	0.286
Mean	2.563	0.001	278.675	0.391	0.265	0.056	3.667	194.825	1575.505	2.575	0.055	0.240

From **Table 4.6** and **Table 4.7**, a bar chart is plotted to compare the tensile yield strength of the specimens tested. **Figure 4.5** shows the difference between the tensile yield strength of both specimen prepared with and without lithium chloride as additive.

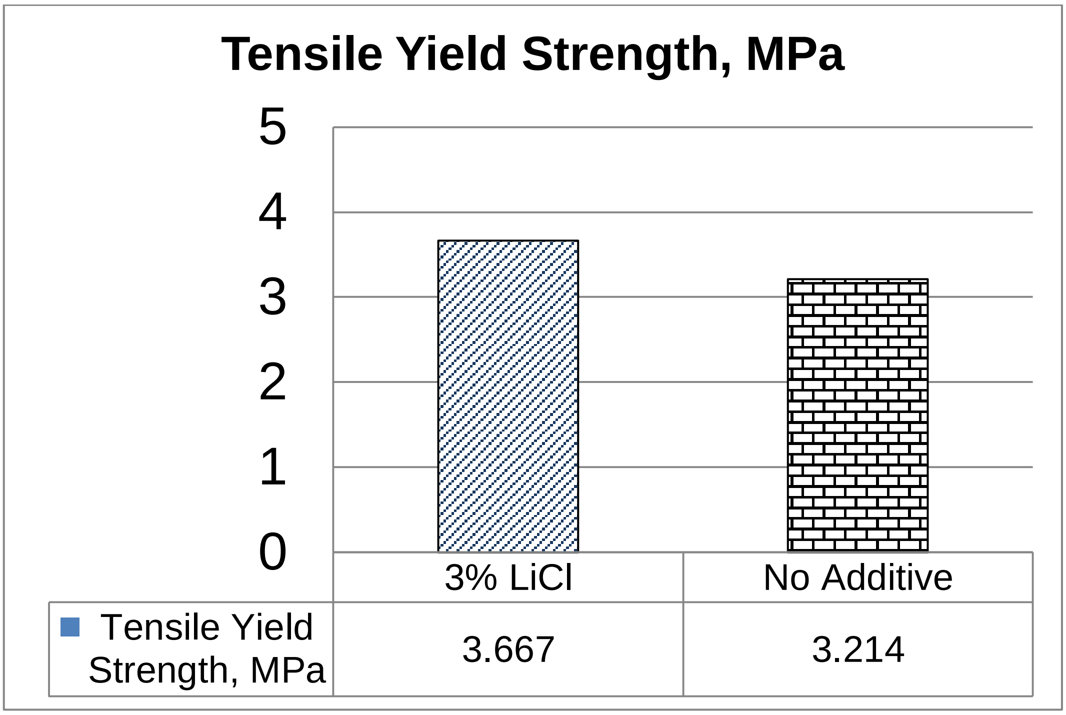


Figure 4.5: Comparison of tensile yield strength of both specimens

It can be deduced that the tensile yield strength of the specimen prepared with lithium chloride as additive exhibits a higher tensile yield strength in comparison to the specimen prepared without additive.(Mantia & Acierno, 1981) The tensile yield strength of the specimen prepared with lithium chloride is enhanced by 14.09%. This result is pertinent to the finding of the research done by Wyzgoski and Novak (1987).

Percentage of enhancement = (3.667 - 3.214) / 3.214 x 100%

= 14.09 %

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, the feasibility of nylon recycling in this project is appraised by evaluating the effect of chemical recycling of nylon waste product using formic acid/lithium chloride solvent system. The tensile yield strength of the recycled nylon is enhanced by 14.09% with the additive lithium chloride. Besides that, the percentage recovery of the nylon waste product after recycling can reach up to 98.28% and 98.95% for recycled nylon with and without lithium chloride respectively. Formic acid can be recovered and reused if proper distillation process is performed. Collection and sorting of nylon waste material requires effort from every single party so that maximum recycling and recovery of used nylon product can be recovered.

5.2 Suggested Future Work/Study and Recommendations

The experiment settings and configuration will be further studied and setup accordingly to manipulate the variables such as the amount and the type of metal halides used or variations of concentration of formic acid to be used to optimize the yield of the recycled nylon and also the economic recovery. The temperature and pressure conditions at which the nylon dissolves and crystallise can be studied as well to determine the effect of them on the morphology and microstructure of the recycled nylon. Addition of metal halides is not only expected to alter the mechanical properties, it can also function as stabilizer for the polymeric products produced in the market. This stabilizer will slow down the degradation of the nylon products due to UV light decay, thermal degradation and oxidation besides changing the mechanical properties of the recycled nylon such as tensile strength and flexural strength (Plischke & Danly, Dec. 23, 1988).

REFERENCES

1. Achilias, Dimitris S., Andriotis, Lefteris, Koutsidis, Ioannis A., Louka, Dimitra A., Nianias, Nikolaos P., Siafaka, Panoraia, . . . Tsintzou, Georgia. (2012). *Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA)*: In Tech.
2. Andrady, A. L., & Neal, M, A. (2009). Applications and societal benefits of plastics. *Philos. Trans. R. Soc. London, Ser. B: Biological Sciences, 384*(1526), 1977-1984.
3. Araujo, Edcleide, Leite, Amanda M. D., N., Vanessa Da, Medeiros, Paz, Rene Anisio, & Lira, Helio De L. (2011). *Comparative Study of Membranes Obtained from PA6 and PA66/National Clay Nanocomposites*: InTech.
4. Bagwala, Mufaddal. (2012, October 4). Review: Preparations, Properties and Applications of Nylon 6,6 Fibres.
5. Booij, Martin, Hendrix, Jan A.J., Frentzen, Yvonne H., & Beckers, Nicolaas M.H. (1998). Netherlands Patent No. 5,840,773.
6. Crompton, T.R. (2007). *Additive Migration from Plastics Into Foods: A Guide for Analytical Chemists*. Shrewsbury: iSmithers Rapra.
7. Karayannidis, G.P., & Achilias, D.S. (2007). Chemical recycling of poly(ethylene terephthalate) *Macromol. Mater. Eng.* (pp. 128-146).
8. Kasserra, H.P. (1998). Science and Technology of Polymers and Advanced Materials. In P. N. P. e. al. (Ed.), *Recycling of Polyamide 66 and 6* (pp. 629-635). New York: Plenum Press.
9. Lehmann, Gunter, Neunhoeffer, Otto, Roselius, Wilhelm, & Vitzthum, Otto. (1973). United States of America Patent No. 3,749,698.
10. Mantia, F. P., & Acierno, D. (1981). The glass transition behaviour of salted nylon 6. *Colloid and Polymer Science, 259*(7), 693-696. doi: 10.1007/BF01419312
11. McKinney, R.J. (1994). United States of America Patent No. 5,302,756.

12. . Nylon 6 and Nylon 6,6. (2009): ChemSystems Process Evaluation/Research Planning.
13. Palmer, Robert J. (2002). Polyamides, Plastics *Encyclopedia of Polymer Science and Technology*: John Wiley & Sons, Inc.
14. PCI Nylon: Positive Signals from the European Nylon Symposium 2012. (2012, March/7/2013). Retrieved from http://plasticker.de/Plastics_News_16329_PCI_Nylon_Positive_Signals_from_theEuropean_Nylon_Symposium_2012
15. Plischke, Lemoyne W., & Danly, Donald E. (Dec. 23, 1988). United States of America Patent No. 4,851,466.
16. R, Vaishali Vaghela, Desai, R. N., & Patel, P. K. (2012). Modification of Nylon 6,6. *International Journal of Scientific Engineering and Technology, 1*(2), 79-82.
17. Roberts, Christopher B., & Griffith, Aron T. (1997). United States of America Patent No. 5,994,417.
18. Scheirs, J. (1998). Polymer Recycling, Science, Technology and Applications. New York: John Wiley & Sons.
19. Shakaib, M., Ahmed, Iqbal, Yunus, Rosli M., & Idris, Ani. (2013). Morphology and Thermal Characteristics of Polyamide/Monosodium Glutamate Membranes. *Int. J. Polym. Mater., 62*(6), 345-350.
20. Shenoy, A. V., Saini, D. R., & Nadkarni, V. M. (1983). Rheology of nylon 6 containing metal halides. *Journal of Materials Science, 18*(7), 2149-2155. doi: 10.1007/BF00555009
21. Shukla, S. R., Harad, Ajay M., & Mahato, D. (2006). Depolymerization of Nylon 6 Waste Fibers. *Journal of Applied Polymer Science, 100*, 186-190. doi: 10.1002/app.22775
22. Simon, Jack. (1961). United States of America Patent No. 3,006,867.
23. Sun, Ben Hui. (1994). Study on the mechanism of nylon 6,6 dissolving process using CaCl2/MeOH as the solvent. *Chinese Journal of Polymer Science, 12*(1).
24. Trossarelli, L. (2010). The History of Nylon.
25. Waibel, Brian J., Schonemann, Hans, Krukonis, Val, Lawrence, David J., & Caulfield, Joseph N. (2011). United States of America Patent No. 8,071,656.

26. World plastics consumption long term, 1960-2020. (2012). Retrieved from http://www.pardos-marketing.com/hot04.htm
27. Wyzgoski, MichaelG, & Novak, GlenE. (1987). Stress cracking of nylon polymers in aqueous salt solutions. *Journal of Materials Science, 22*(5), 1715-1723. doi: 10.1007/BF01132397
28. Zarfl, C., & Matthies, M. (2010). Are marine plastic particles transport vectors for organic pollutants to the Arctic? *Marine Pollution Bulletin, 60*(10), 1810-1814.

APPENDICES

Figure A1: PerkinElmer FTIR Spectrometer

Figure A2: Recycled nylon precipitates grinded into powder

Figure A3: CARVER Compression Moulding Equipment

Figure A4: Dumbbell shaped sample specimen for tensile testing

Figure A5: Testometric Tensile Tester