Preparation of Recycled Polyamide by Using Dissolution/Precipitation Method

by

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Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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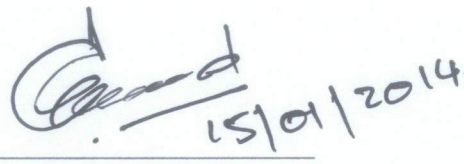
Approved by,



(Dr. Iqbal Ahmed)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

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 specified sources or persons.

(MOHD IQBAL BIN ABD AZIZ)

ABSTRACT

Dissolution/precipitation method is the one method to recycle polyamide or known as nylon. The dissolution method is done by using solvent that can dissolve the nylon from the used nylon materials. The solvent that had been used in this experiment is formic acid, methanol and ethanol. For the precipitation process, methanol is used for changing back the nylon into precipitate form. The result shows that the formic acid can dissolve the nylon in the form of liquid after dissolution process had been done. The formic acid also has been mix with methanol or ethanol to reduce the effect of degradation of properties in nylon. The result from FTIR also shows that the recycled nylon still in form of nylon. This shows that the recycling of nylon can be done by using this method.

ACKNOWLEDGEMENT

Alhamdulillah, thanks to the Almighty, Allah s.w.t, this project is finally completed and all results were successfully obtained. All process flows were run smoothly according to the work timeline.

With the exposure to the reality of researching, it is very good understood that researching process is not as easy as it looks. Researching through his study has provided me tools and skills to be successful researcher. Even though there are problems encountered along the way in completing this project, with the help of my supervisor Dr. Iqbal Ahmed, such problems were managed to be handled wisely. With his assistance and guidance, much information and understanding of this project were successfully obtained and developed through experimental works and literature research. My utmost gratitude goes to her for spending lots of time monitoring all FYP students worked under her supervision.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The polyamides especially nylon has been used in many products such as carpet, fishing net, tyres, etc. The product that has nylon based materials also known as high quality product because the structure of nylon increase the quality of product and also can increase the life span of the product. Because of much type of products have been produced by industry, most of them also have been thrown when their life span have been expired. To overcome this problem, the products that have been thrown need to recycle to ensure that the thrown items are not affecting the environment of our world (Al Salem, et al., 2009).

Many techniques can be done for recycling the nylon. There are three type of technique of recycle (Mihut, et al., 2001). Those techniques are:

1. Depolymerization
2. Extraction of polyamides
3. Melt Blending

For depolymerization, the technique will recycle the nylon by coverts the waste into products that having a quality equivalent to the "virgin" polymer. This method is quite efficient by break down the long polymer chains into their original monomers that can be repolymerized to the previous form (Mihut, et al., 2001).

For the second method, which known as extraction of polyamides that involves recovering of individual components of a polymeric mixture without necessarily breaking them down to the monomeric form like a previous method. This category also includes various extraction and separation methods (Mihut, et al., 2001).

For the third method of recycling, the melt blending method which consists of preparing a thermoplastic mixture by melt- blending the entire waste product. This technique is quite reasonable technique because it ensures the simplicity and low cost method. This method also can result to produce low quality melt-blended plastics with limited uses (Mihut, et al., 2001).

The purpose of this research is to identify the extraction of polyamides by using dissolution/precipitation technique. This technique will use with an appropriate solvent, reprecipitation by addition of non-solvent and finally recovery of the polymers through washing and drying. The technique also depends on the solvent use that will affect the structured of recycled polyamide either become low quality than before or same as the '"virgin" polyamide.

1.2 Problem Statement

Waste of polymer has become globally massive concern. It is because of the mass production of polymer based material that has good sustainable material for daily life used. Nylon is one of the polymers that widely used in industry and also one of the polymers that had been thrown by people after the material is already old to use it.

To overcome this problem, many techniques have been developing to recycle the nylon for reducing the waste of polymer in this world. Every method of recycling the nylon has their advantage and disadvantage. In this paper, the method of dissolution/precipitation has been choosen to study the result of this technique in recycling the nylon.

The technique of dissolution/precipitation is already done by the previous research for recycling the polyamides. In this method, it is hard to obtain the recycled polyamides that have comparable properties with the "virgin" polyamides. Usually, this method will lead the polyamides to reduce its physical properties because of the degradation of the polyamide chain (Mihut, et al., 2001). The technique also found that the selection of solvent will play a major role to change the physical properties of recycled polyamides. Therefore, this study is conducted to investigate to what extent the selected solvents are able to extract and recover the properties of the recycled polyamides.

Previous research found that formic acid can dissolve the nylon but the degradation happen after the nylon is dissolve in the solvent (Benhui, 1994). This will make the recycled nylon not comparable with the "virgin" nylon.

From the previous experiment, the ratio of the solvent with the polyamide is very important to determine the solubility of polyamide in the solvent (Nakajima and Tanaami, 1973). The best ratio will give the result to the solubility of the polyamide that will be recycled from the used nylon materials. More the solubility of the polyamides in the solvent, more the polyamides can be recycled from the used nylon materials. Therefore, this study also includes searching the right ratio of solvent to dissolve the polyamide in the solvent.

1.3 Objectives

There are some objectives that need to be achieved in this project. This project consists of two objectives. Those objectives are:

1. To extract the nylon from used nylon materials by using dissolution method.
2. To find the right ratio of solvent for extract the nylon from the used nylon materials.

1.4 Scope of study

For this project, there are some scopes that need to be focused during the recycled the polyamides. Below are the scopes that need to be done during the experiment:

1. Prepared the recycled polyamides by using the dissolution/precipitation method.
2. Determine the right ratio of solvent for dissolving the nylon for recycling the nylon.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review

Polyamides are polymers that contain an amide group, -CONH-, as a recurring part of the chain also known as nylon for common people usually. According to Monika, Ramaiah, et al., (2004) in article about nylon fibers, the nylon also was known as the first truly synthetic fiber to be commercialized during 1939. It is a polyamide fiber that derived from diamine and dicarboxylic acid. With variety of diamines and dicarboxylic acids can be produced, there are very large number of polyamide materials are available to produce nylon fibers. Nylon 66 (polyhexamethylene adiamide) and nylon 6 (Polycaprolactam, a cyclic nylon intermediate) are the two most common version in market. Raw materials for these are variable and sources used commercially are benzene (from coke production or oil refining), furfural (from oat hulls or corn cobs) or 1,4-butadiene (from oil refining). Below is the chemical reaction for producing the nylon 6 and nylon 66.

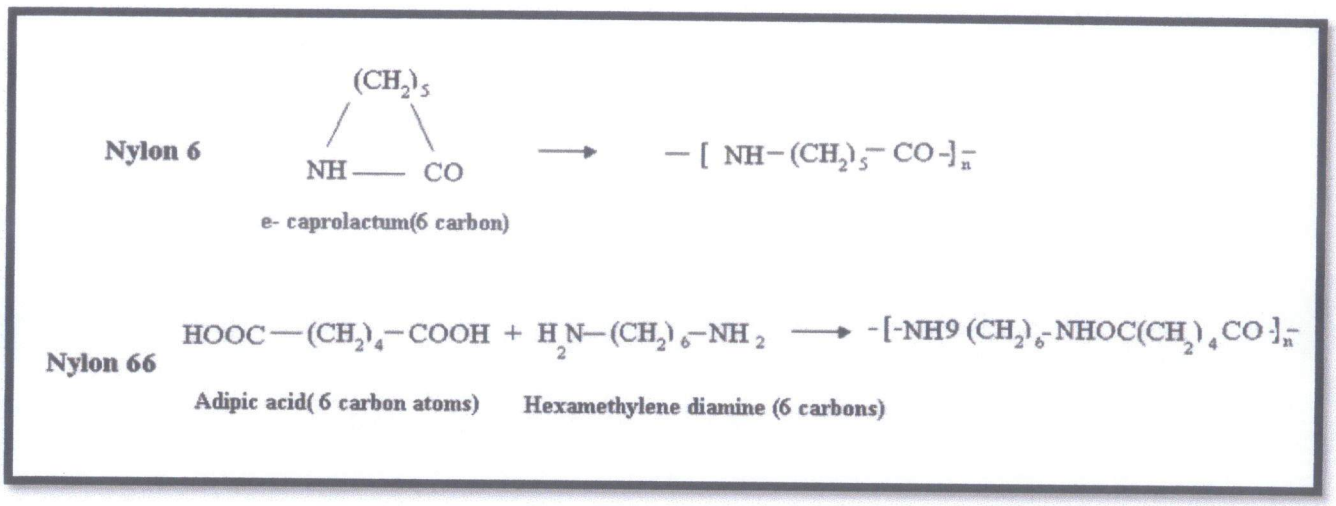

Figure 1: Chemical reaction of nylon 6 and nylon 66 (K. Monika, et al. 2004)

The nylon mostly used in many things especially in industry because of the good structure of the nylon that can improve the quality of synthetic polymer. "Nylon is the first commercialized synthetic fiber, which is used throughout the world such as wearing apparel, brush bristles and carpet." (Transport properties of electrospun nylon 6 nonwoven mats, 2003). The nylon also have been widely used in synthetic fiber because of its have good mechanical properties.

"Worldwide Textile Mill consumption of Nylon is averaging 3.5 million tons yearly since the 90's and new investments in China announced recently, will drive the number even higher." (Silva, Recycled Polyamides, a literature review and research opportunities). This shows that the demand on the consumption of using nylon in industries is quite high. With this consumption level, the amount of waste of nylon also will increase and also can affect the environment of earth. The recycling technique for the wasted nylon need to implement to overcome this problem before the worst scenario come because of the demand for the synthetic polymer become higher from time to time.

"Recycling of polyamides is of great interest because of their excellent performance, their valuable application, but also because of their significant cost." (A model study for the recovery of polyamides using the dissolution/precipitation technique, 2000). The research about the recycle of the polyamides is still undergoing for the

development of new technologies for some company. For example, Wont Co. has programmed the development of new technologies to recycle efficiently a significant percent of the total PA (polyamides) consumption. This shows that the development of the research is quite remarkable effort due to concerning the recycling of polyamides.

In review paper by Mihut et al. has study about the recycling of nylon from carpet waste has found about the three method of technique in recycling the polyamides especially in carpet waste. Those three methods are depolymerization, extraction and separation methods and melt blending. Those three techniques are quite popular among the recycling for the polyamides waste.

According to Mihut, et al., for method of depolymerization, polymer chains are broken down into their monomeric constituents during polymerization. The depolymerization of nylon 6 is a first order which takes place in initiation and de-propagation steps in endothermic reaction. This process also requires high temperature since it is in endothermic reaction and need to achieve it by using superheated steam. Temperature above the boiling point of caprolactum which is around 267°C are typically used to create heterogynous system (a liquid polymer melt and a gas-phase caprolactum product). Removing the caprolactum monomer from the reactor along the steam will shift the equilibrium towards further monomer formation.

According to Mihut, et al., for method of extraction, it will attempt to separate and recover the polyamides from the other carpet components without converting them back to the original monomers. Most of them utilize organic solvents at certain temperature can separate different carpet components in sequential steps. The solvent that have to use need to have high selectivity in dissolving only the nylon fibers. This is the key of choosing the right solvent for doing the dissolving the nylon. The better purity of the separate nylon obtained from the process can be achieved by using higher selectivity of solvent. However, extraction tends to reduce the quality of recycled polyamides due to degradation which occurs throughout the process.

Therefore, a few studies are done to test several solvents in order to determine the degree of recovery of the polyamides properties. Kelkar et al. (1991) used copper chloride to recover the properties of recycled polyamides. From the results obtained and analysis made (density measurement, FTIR and x- ray diffraction) the structure of polyamide changes on doping with copper (II) chloride.

Benhui (1994) has conducted an experiment to dissolve polyamide in formic acid solution and mixture of methanol and calcium chloride. From the results obtained, the characteristic of recycled polyamide is significantly reduced. The melting point of the sample obtained is about 91K lower than the pure one. This show, the hydrogen bonds in polyamides are severed which later on lead to the decreasing of intermolecular interaction of the compound as well as decreasing the crystallinity of polyamides.

A more recent study has been performed by Papaspyrides and Kartalis (2000), to recover the properties of the recycled PA6 and PA 6 6 by using dimethylsulfoxide solution. The recovered polyamides are then tested to determine its molecular weight, end group, grain size, thermal analysis and etc. The recovery process achieved a significant impact when the solvents used manage recover PA properties almost as the virgin one.

According to Mihut, et al., for method of melt blending, the recycled of polyamides is done including by including the wasted product like carpet by melting or extruding it to form a blended mixture that subsequently used in the production of injection molded polymers and thermoplastics. This technique also known as low cost process because there is no expensive method required especially to separate and depolymerization the polyamides. However, the method is quite expensive in term of process because the amount of energy use for this method is highest compare to the other method. This method also depending on waste product components melt-blending that can come out result that usually with low quality melt-blended plastics with limited uses.

For this project, the technique of extraction of polyamides is been choose to recycled the nylon. This method is quite efficient and can come out with a good result that

depends to the solvent used in the experiment. The high selectivity need to be used to get the better result in the future. For this technique, the polyamides will undergoes recovery by using dissolution/reprecipitation method. This recovery technique quite useful for strengthen again the polyamides by using metal halide.

For previous paper, Kelkar and Bhat have demonstrated the investigation of structural and mechanical properties of copper chloride doped nylon 6 film and found that doping up to 1.25% of copper chloride increase the crystallization of nylon-6 in the α-crystalline form in the structure of polyamides. The changes also depend on the dopant concentration. For the elastic and viscoelastic properties, the study the structural and mechanical properties of copper chloride doped nylon 6 film found that the glass transition temperature of the doped films increase in the dopant concentration. When the low concentration of doping (up to 1.25%), it will obviously that the salt acts as a plasticizer. When the higher concentration of doping (up to 12.5%) is used, it will act vice versa.

In study on the mechanism of nylon 6,6 by dissolving process using calcium chloride($CaCl_2$) with methanol(MeOH) as the solvent by Benhui found that the complexation of a Lewis acid ($CaCl_2$) and a Lewis base (nylon 6,6) can be used to probe intermolecular interactions such as hydrogen bonding in polymers, to modify the polymer properties and mediate its solubility and processing. This is because due to the chemical properties of the two solvent that help the nylon 6,6 to modify the polymer properties. The melting point of $CaCl_2$–nylon 6,6 complex was found to be reduced by 91K relative to the pure nylon 6,6 polymer. The methanol also acts as catalyst because the behavior of methanol is somewhat similar to a catalyst.

In study on dissolution of nylon in the solvent, Akio Nakajima and Kazuoo Tanami (1973) have found some composition range that can dissolve the nylon those solvent. Below is the list of the solvent that have been test by them in their research.

Metal halide	Solvent composition (g halide/dl alcohol)		
	Methanol	Ethanol	*n*-Butanol
LiCl	15—40	10—20	Insoluble
$CaCl_2$	7—30 (50—12)[a]	5—25 (48—10)[a]	Insoluble
$CaCl_2 \cdot H_2O$	10—50 (40—8)[a]	10—40 (28—7)[a]	Insoluble
$CaCl_2 \cdot 2H_2O$	15—75 (31—5)[a]	10—65 (32—5)[a]	Insoluble
$CaCl_2 \cdot 4H_2O$	30—100 (19—6)[a]	15—90 (27—4)[a]	Insoluble
$CaCl_2 \cdot 6H_2O$	50—150 (14—5)[a]	50—125 (10—4)[a]	Insoluble
$ZnCl_2$	25—120	20—100	Insoluble

[a] Numbers in parentheses denote the mol ratio of alcohol to Ca in the solvent systems in which Nylon 6 is dissolved.

Figure 2: Composition of solvent with metal halide (A Nakajima, K. Tanaami, 1973)

Metal halide are used to mix with the solvent to dissolve the nylon 6 with temperature of 30°C. Almost all the solvent with the metal chloride are dissolved the nylon 6 by using methanol and ethanol. The n-butanol is not suitable for dissolving the nylon that have shown in the figure above.

There are many method that can make the nylon dissolve before recycling the nylon. The solubility of nylon in solvent is important because this will increase the amount of recycled of nylon after dissolving it. The dissolved nylon will be undergoes precipitate method to complete the recycling method.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Sample preparation

To recycle a nylon, some used nylon material need to be collected before conduct the experiment. Some material need to be tested to recycle the nylon. For this experiment, fishing line was chosen as used nylon material for this experiment. This is because the fishing line have high percent of purity of nylon compared to other used material that containing nylon.

Figure 3: Fishing line with nylon as based material

The fishing line is collected from fishing area that has been thrown by the people. Before start the experiment, the fishing lines were washed and then cut it into small pieces. This is to make sure that the impurities are removed from the fishing line. Then the fishing lines or polymer will cut by scissor to increase the surface area of the polymer to dissolve in the solvent.

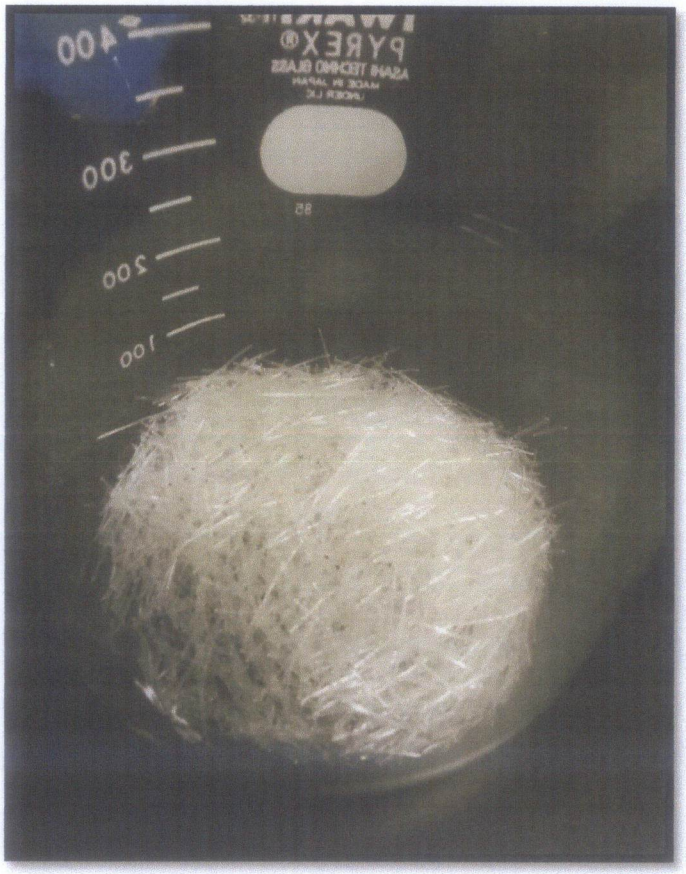

Figure 4: Pieces of fishing line

Figure 4 shows that the fishing line is cut into pieces. By cutting the fishing line will help the polymer to react faster when dissolving it into solvent. The polymer will react fast compare to the polymer that have not cut because of the difference of surface area.

Dissolution

Solvent is prepared before conduct the experiment. Preparation of solvent is very important to make sure that the nylon will dissolve in the solvent completely. There are some solvent that has been prepare to dissolve the nylon by mix it with the fishing line. Below is the list of the solvent that need to be prepared for this experiment.

1) Solvent 1: Methanol (MeOH) with calcium chloride (CaCl).

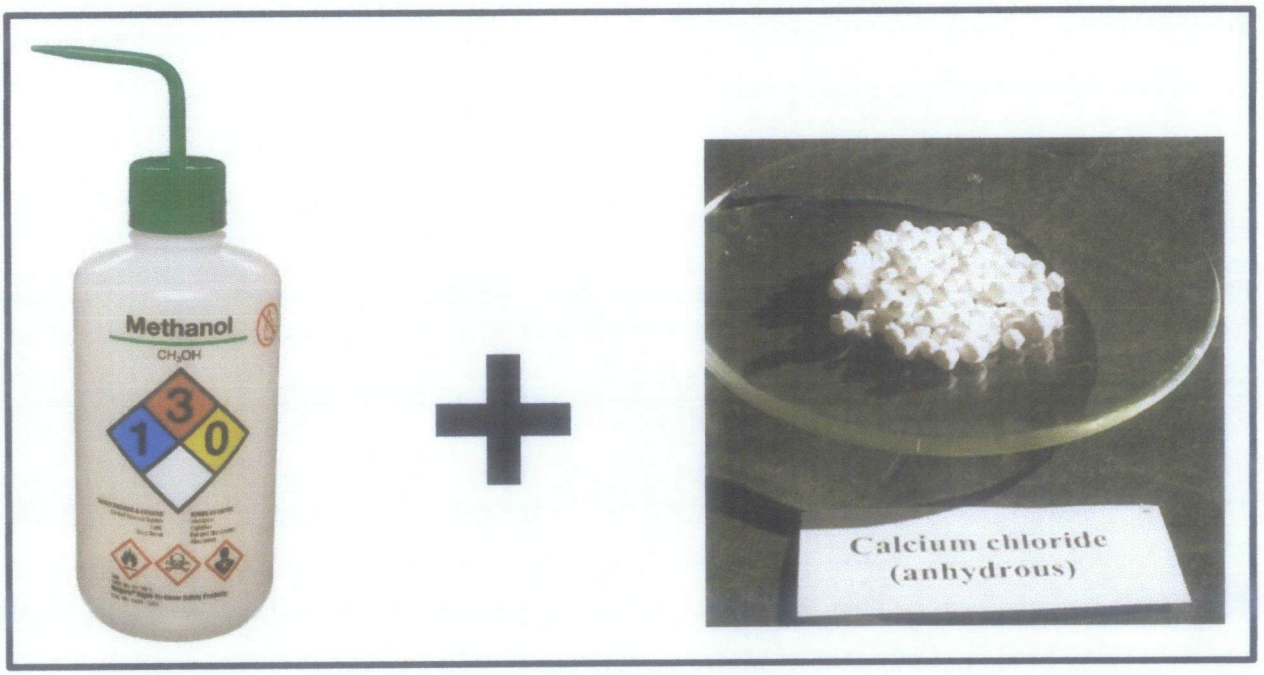

Figure 5: Component of Solvent 1

Figure 5 shows the component that have in the first solvent. The methanol was mix with the calcium chloride by using certain ratio. In this solvent, methanol was used 80 percent of weight percent (%wt) and calcium chloride only used 2%wt. For the remaining percent, 18%wt was reserved for polymer in dissolving it in this solvent.

2) Solvent 2: Methanol (MeOH) with calcium chloride (CaCl)

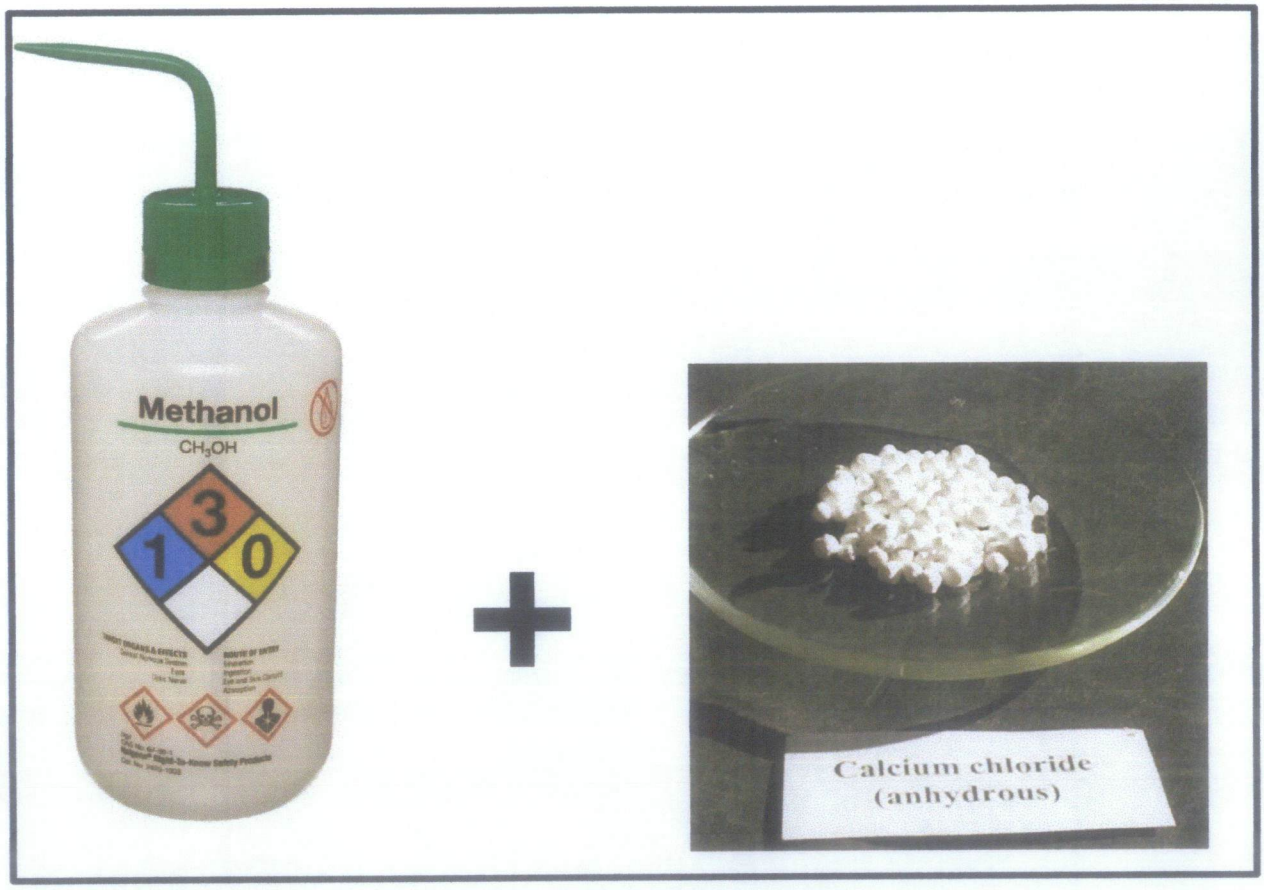

Figure 6: Component of Solvent 2

Figure 6 shows for component for the second solvent, the methanol and calcium chloride also was used for preparing the solvent. This second solvent was prepared with difference ratio compared to the first solvent. The second solvent was consist of 88%wt of methanol and 2%wt of calcium chloride. Even though the solvent have same component with first solvent, the reaction will be difference because of difference ratio of those component will give difference result in solubility of the polymer in the solvent (A. Nakajima and K. Tanaami, 1973). For the remaining weight percent, the polymer was reserved for 10%wt.

3) Solvent 3: Formic acid (FA)

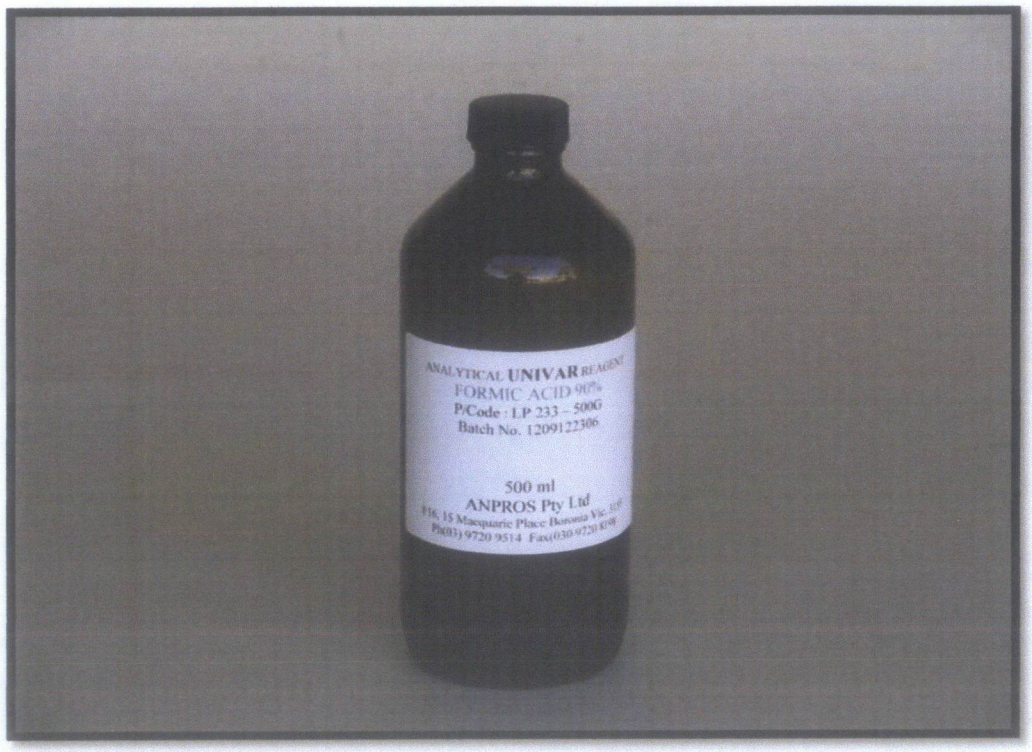

Figure 7: Component of Solvent 3

Figure 7 shows that solvent 3, formic acid was used to prepare the solvent. Formic acid was used only 90%wt for dissolving the polymer. For the remaining 10%wt was reserved for polymer to be mix with the solvent 3.

4) Solvent 4: Methanol (MeOH) with formic acid (FA)

Figure 8: Component of Solvent 4

Figure 8 shows the component for this solvent 4, methanol and formic acid are used for prepared the solvent. The methanol was used only 45%wt and formic acid only 45%wt. Those mixture will be used for dissolving the polymer. The remaining 10%wt will be reserved for polymer.

5) Solvent 5: Methanol (MeOH) with formic acid (FA)

Figure 9: Component of Solvent 5

Figure 9 shows that the component for solvent 5, the same component with solvent 4 is used for prepared the solvent. The ratio of methanol with formic acid also same with the formic acid compared to solvent 4. For solvent 5, polymer will be used in smaller quantity compared to quantity of polymer that will be used in the solvent 4. For solvent 5, methanol only used 49%wt and formic acid only used 49%wt for prepared the solvent. The remaining 2%wt is reserved for polymer.

6) Solvent 6: Ethanol with formic acid (FA)

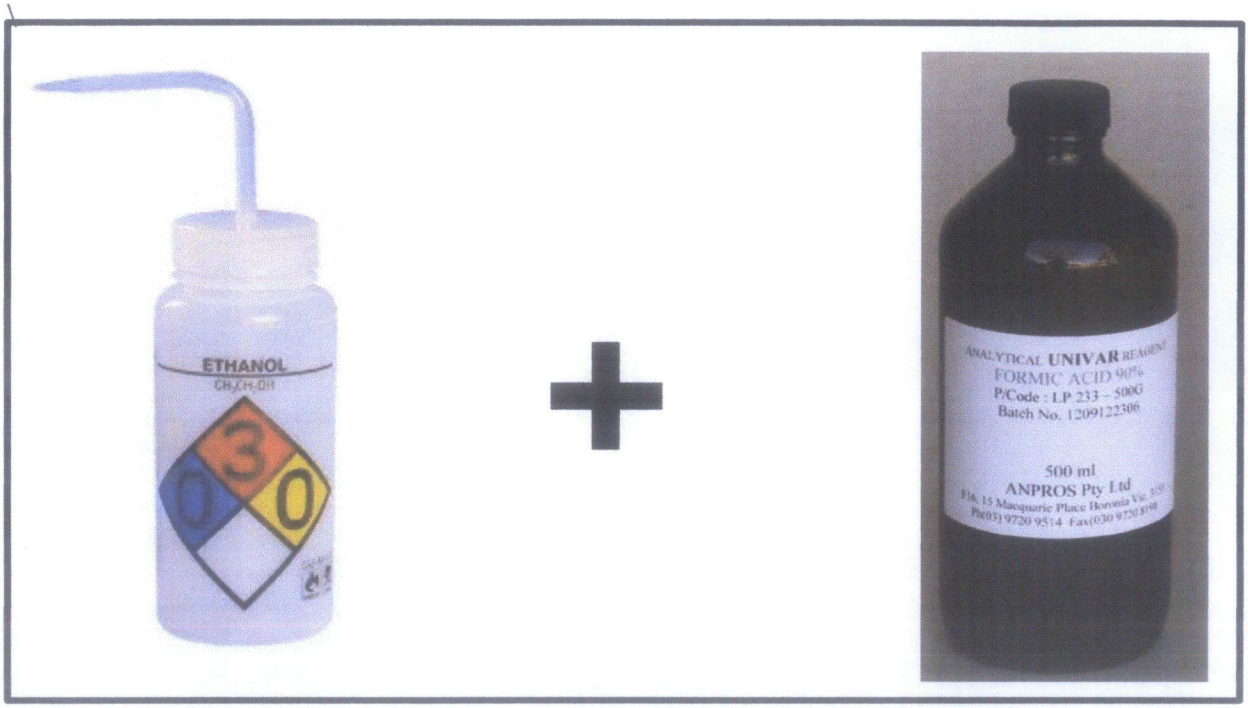

Figure 10: Component of Solvent 6

Figure 10 shows that the component for solvent 6, ethanol and formic acid is used for preparing the solvent. The ethanol was used only 49%wt and formic acid used only 49%wt. For the remaining 2%wt was reserved for polymer in proceeding the dissolution method.

Below is the overview of following ratio that has been prepared for the solvent and polymer:

Table 1: Ratio of solvent

No of mixture	Solvent	Solvent Ratio (wt%)
1	MeOH, CaCl	MeOH(80%), $CaCl_2$(2%)
2	MeOH, CaCl	MeOH(88%), $CaCl_2$(2%)
3	FA	FA(90%)
4	FA, MeOH	FA(45%), MeOH(45%)
5	FA, MeOH	FA(49%), MeOH(49%)
6	FA, Ethanol	FA(49%), Ethanol(49%)

Those solvent will be mix with the polymer to dissolve the nylon. For dissolving the nylon, every mixture will be conduct in the same temperature by using hot plate. Below is the table that will show the temperature of every solvent:

Table 2: Temperature of each mixture

No of Mixture	Mixture (wt%)	Temperature (°C)
1	MeOH(80%), $CaCl_2$(2%), Polymer(18%)	50°C
2	MeOH(88%), $CaCl_2$(2%), Polymer(10%)	50°C
3	FA(90%), Polymer(10%)	50°C
4	FA(45%), MeOH(45%), Polymer(10%)	50°C
5	FA(49%), MeOH(49%), Polymer(2%)	50°C
6	FA(49%), Ethanol(49%), Polymer(2%)	50°C

Those mixtures will continuously stir until the nylon dissolve completely in the solvent. This is to make sure that the nylon is recycled with the maximum amount from the used nylon material.

Another set experiment also has been conduct by using different temperature. This experiment will for mixture of formic acid in 90°C. Below is the table that will show the mixture of solvent that will use for dissolving the nylon.

Table 3: List of mixture for operate in 90°C

No of Mixture	Mixture (wt%)	Temperature (°C)
7	FA(55%), MeOH(35%), Polymer(10%)	90°C
8	FA(45%), MeOH(45%), Polymer(10%)	90°C
9	FA(45%), Ethanol(45%), Polymer(10%)	90°C

Those mixtures also will continuously stir until the nylon dissolve completely in the solvent.

Precipitation:

After the nylon is dissolve from the mixture, the remaining precipitate is filter from the mixture and takes the homogenous solution to undergo the precipitation process. The precipitation process will determine the amount of nylon that can be recycled during experiment. The amount of recycled nylon is depends on the solubility of nylon in the solvent during dissolution method.

The precipitation method also depends on the condition of the mixture during undergoes the dissolution process. Some solvent that cannot dissolve the nylon will not undergoes this precipitation process and also mixture that have become solid during dissolution process.

The mixture that undergoes this process will precipitate the nylon by using other solvent to make attract the solvent from the mixture. This will attract the solvent from the nylon and make the nylon become precipitate immediately.

3.2 Project Activities, Key Milestones and Gantt chart

Below is the management Gantt chart for this study in semester 2:

Table 4: Gantt Chart

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report										11th Nov 2013						
3	Project Work Continues																
4	Pre-EDX												2th Dec 2013				
5	Submission of Draft Report										9th Dec						
6	Submission of Dissertation (soft bound)											16th Dec 2013					
7	Submission of Technical Paper											16th Dec 2013					
8	Oral Presentation											23th – 27th Dec 2013					
9	Submission of Project Dissertation (Hard Bound)											2nd Jan 2014					

Mid-Semester Break

Suggested milestone

Process

3.3 Project Activities and Key Milestones

Following is the project activities involve in this study:

Table 5: Project activities

Key Milestone	Project Activities
Week 2-12	-Performing the experimental procedure for the study -Updating progress report -Updating technical report -Preparation for oral presentation -Meeting with SV
Week 8	-Submission of progress report -Meeting with SV
Week 12	-Submission of project dissertation (softcopy) -Meeting with SV
Week 13	-Submission of technical paper -Meeting with SV
Week 14	-Oral presentation
Week 15	- Submission of project dissertation (hardcopy)

3.4 Tools

These are the chemicals that will be used in this project:

i) Methanol (MeOH)
ii) Formic acid (FA)
iii) Calcium Chloride ($CaCl_2$)
iv) Ethanol 95 vol. %

These are the list of glass ware:

i) Beaker
ii) Two neck round bottle
iii) Filter paper
iv) Conical flask
v) Condenser

These are the equipment or tools that will be used in this project:

i) Hot plate with magnetic stirrer
ii) Digital weighing scale
iii) FTIR

CHAPTER 4

RESULT AND DISCUSSION

4.1 Data Gathering and Analysis

Dissolution process:

Following is the result from the dissolution process that has been obtained during the experiment. The result only can be determined by observation. Below are the details of the result from the experiment:

Table 6: Observation of each mixture during experiment

MIXTURE	SOLVENT WITH POLYMER RATIO (wt%)	Temperature(°C)	OBSERVATION
1	MeOH(80%), CaCl2(2%), Polymer(18%)	50°C	The nylon is partially dissolve in the solvent. Very viscous solution is obtained. Dry up the solvent after heat up for a long time.
2	MeOH(88%), CaCl2(2%), Polymer(10%)	50°C	The nylon completely dissolve in the solvent. Very viscous solution is obtained.

3	FA(90%), Polymer(10%)	50°C	The nylon completely dissolve in the solvent. Slightly viscous solution is obtained.
4	FA(45%), MeOH(45%), Polymer(10%)	50°C	The nylon not dissolve in the solvent.
5	FA(49%), MeOH(49%), Polymer(2%)	50°C	The nylon not dissolve in the solvent.
6	FA(49%), Ethanol(49%), Polymer(2%)	90°C	The nylon is dissolve in the solvent.
7	FA(55%), MeOH(35%), Polymer(10%)	90°C	The nylon is dissolve in the solvent. Immediately become partially precipitate after dissolve.
8	FA(45%), MeOH(45%), Polymer(10%)	90°C	The nylon is dissolve in the solvent. Immediately become precipitate after dissolve.
9	FA(49%), Ethanol(49%), Polymer(10%)	90°C	The nylon is dissolve in the solvent. Immediately become precipitate after dissolve.

Precipitation process

Mixture 1:

Mixture 1 cannot undergoes precipitation method because the polymer in the mixture is not completely dissolve in the solvent. The solvent in the mixture also easily dry up the solvent during dissolution process and make the mixture became solid during the process.

Mixture 2:

Mixture 2 also cannot undergoes precipitation process because the mixture is already became viscous solution during the dissolution process. After left it for a while, the viscous mixture became solid.

Mixture 3:

Mixture 3 can undergoes the precipitation process because the nylon in the mixture is dissolve completely and the mixture also still in form of liquid after the dissolution process was finished. The nylon undergoes the precipitation method by using methanol (MeOH) for attracting the solvent in the mixture and let the nylon become precipitate in powder form.

Mixture 4, Mixture 5 and Mixture 6:

Mixture 4 cannot undergoes the precipitation process because the nylon in the mixture is failed to dissolve by the solvent in the mixture.

Mixture 7, Mixture 8 and Mixture 9:

Mixture 7 can undergoes the precipitation process because the nylon in the mixture is dissolve completely and the mixture also still in form of liquid after the dissolution process was finished. The nylon undergoes the precipitation method by using methanol (MeOH) for attracting the solvent in the mixture and let the nylon become precipitate in powder form.

Discussion:

From the observation of the result, all of the mixtures have shown that nylon can be dissolve with solvent of methanol and formic acid. But the solubility of the nylon depends on the ratio of the solvent to dissolve the nylon in the mixture.

Mixture 1: MeOH(80%), CaCl2(2%), Polymer(18%) in 50°C

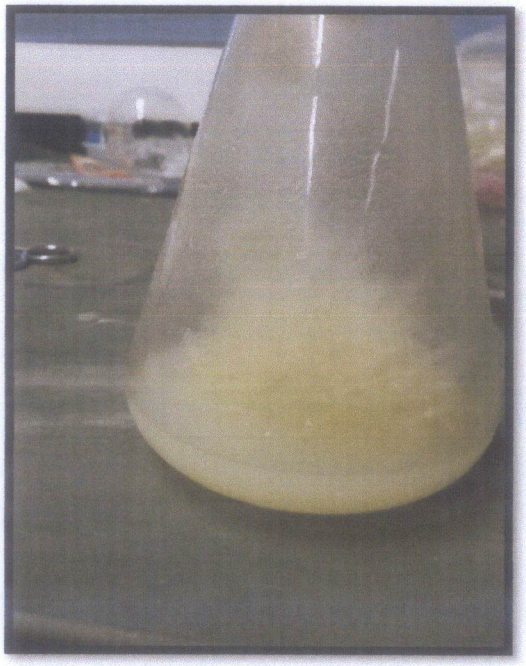

Figure 11: Observation from mixture 1

Figure 11 shows that the mixture gives the result that the nylon partially dissolves in the solvent. This shows that the ratio of the mixture is not suitable to dissolve the nylon. The quantity of the polymer also is quite bigger compare to the rest mixture. So, the nylon in the polymer is too hard to dissolve in the solvent. The dissolution process also had been proceed until all the solvent dry up and became solid completely. It is because the solvent was easily evaporate during the dissolution process. Figure 11 below shows that the nylon already became solid completely after undergoes dissolution process.

Figure 12: Observation of mixture 1 after dissolution process

Figure 12 shows that the recycled nylon become solid after dissolution process. The condition of mixture 1 after dissolution method was not suitable for proceeding the precipitation process.

Mixture 2: MeOH(88%), CaCl2(2%), Polymer(10%) in 50°C

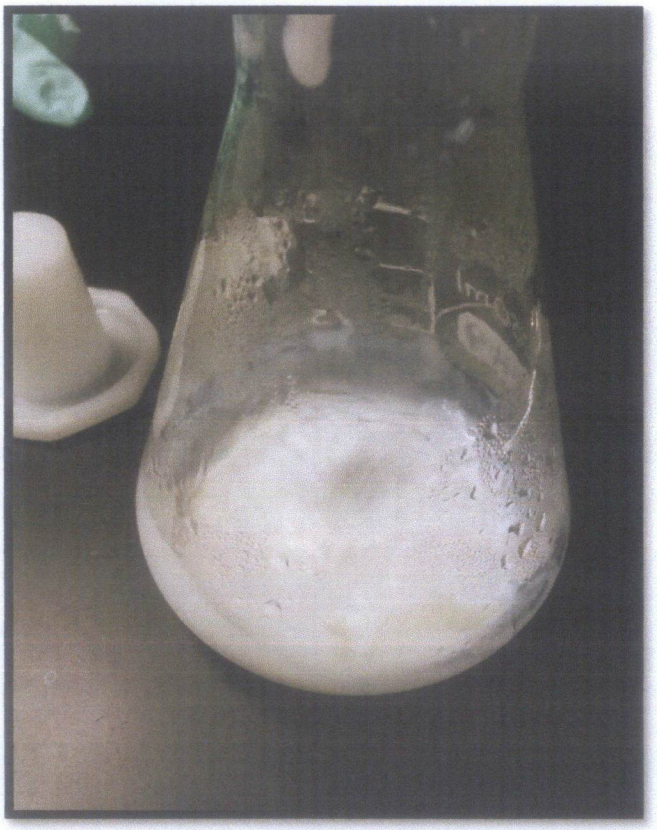

Figure 13: Observation from mixture 2

Figure 13 shows that the nylon in the mixture dissolves completely and become viscous solution after nylon dissolving in the solvent. During the dissolving reaction, the solvent keep evaporate to the air. It is because the methanol in the solvent has high volatility during the heating of mixture. After the mixture done dissolving the nylon, the solvent has decrease from the mixture and then become viscous solution. After left it for a while, the viscous mixture became solid. The nylon is predicted to become different from the virgin nylon because the $CaCl_2$ in the mixture will change the chemical bond of the nylon and will combine with the polyamide chain. This will give different polymer compare to the original nylon. So the experiment will be not proceed with MeOH/CaCl solvent because the nylon will bond with the CaCl.

Mixture 3: FA(90%), Polymer(10%) in 50°C

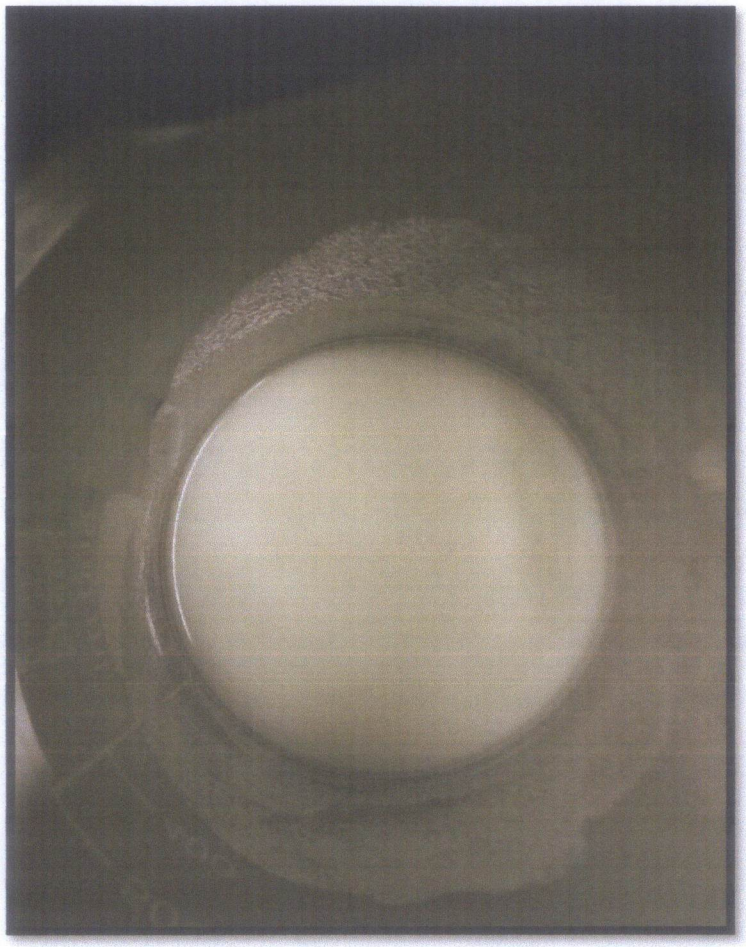

Figure 14: Observation from mixture 3

Figure 14 shows that the nylon in the mixture dissolves completely and the mixture becomes slightly viscous. The formic acid dissolves the nylon smoothly after several minutes heating the mixture 3 while continuously stir the mixture. After dissolving the nylon, methanol is add until the nylon became precipitate to form nylon. The precipitation process also can be proceed to mixture because the mixture 3 still in liquid form. In precipitation method, methanol is used to precipitate the nylon in the mixture 3. The methanol is solvent that can attract the formic acid and make the nylon detached from the formic acid. This will make the nylon immediately to form precipitate and the nylon

became powder form. Below is the figure shows that the nylon is precipitate in powder form.

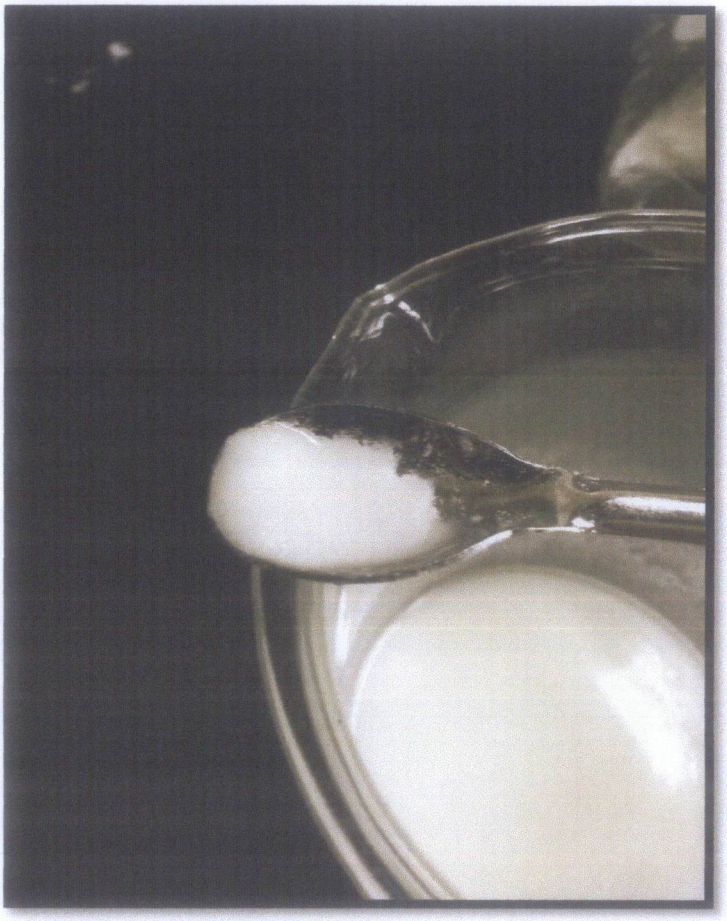

Figure 15: Nylon precipitate in powder form

The figure 15 shows the nylon is precipitate in powder form after undergoes precipitation process. This shows that the nylon is suitable to dissolve with formic acid and the formic acid also not easily vaporize during the dissolution process compare to the methanol. The ratio of the formic acid and the nylon also is quite good compare to the other mixture. The recycled nylon is predicted close enough with original nylon but the physical properties is still unknown because the nylon still not been test.

Mixture 4: FA(45%), MeOH(45%), Polymer(10%) in 50°C

Figure 16: Observation from mixture 4

Figure 16 shows that the nylon in the solution of mixture 4 is not dissolve in the solvent. This shows that the methanol was already dissolve with formic acid. The formic acid cannot dissolve it because of present of methanol that have same amount with the formic acid in the solvent.

Mixture 5: FA(49%), MeOH(49%), Polymer(2%) in 50°C

Figure 17: Observation from mixture 5

Figure 17 shows that mixture 5 cannot dissolve the nylon by using those solvent. The component of mixture 5 is same with the mixture 4 because the mixture 5 is perform to test the influence of quantity of nylon in the solvent. Result shows that quantity of nylon is not the reason for solubility of the nylon in that mixture. This shows that the combination of formic acid with methanol cannot dissolve the nylon even though the quantity of polymer has been decrease from the ratio. It conclude that the methanol will attract with formic acid and make the nylon not dissolve in the mixture.

Mixture 6: FA(49%), Ethanol(49%), Polymer(2%) in 50°C

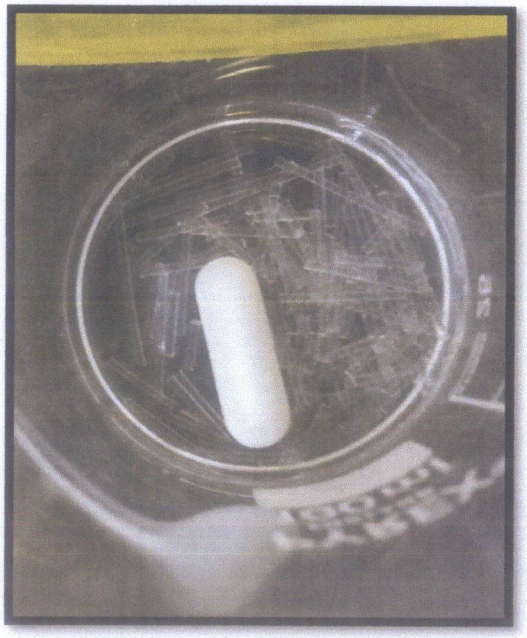

Figure 18: Observation from mixture 6

Figure 18 shows that the nylon is not dissolve the mixture 6. The component of mixture 6 is predicted that have same reaction compared to mixture 5. The ethanol was attract with the formic acid and make the nylon cannot dissolve in the mixture. The ethanol is predicted to have same behavior as methanol. Therefore, the nylon cannot in the mixture because of reaction of ethanol with formic acid. This case is have same result with mixture 5.

Mixture 7: FA(55%), MeOH(35%), Polymer(10%) in 90°C

The result shows that the nylon can be dissolve in this mixture because the amount of formic acid was greater than methanol. The excess amount of formic acid will help the nylon to dissolve in the solvent. The dissolve nylon can be proceed with precipitation process. Below is the figure that shows that the nylon become precipitate in powder form after perform the precipitation process.

Figure 19: Nylon from mixture 7

Figure 19 shows that the recycled nylon become precipitate after precipitation process happen. Presence of formic acid is important to dissolve the nylon.

Mixture 8: FA(45%), MeOH(45%), Polymer(10%) in 90°C

The result shows that the nylon can be dissolve in this mixture. This is because the nylon is heat up exceed to the boiling point of methanol. During the experiment, the methanol become vapor and the nylon immediately dissolve in solvent because of the amount of methanol is reduce because of the vaporization of methanol. With help of condenser, the methanol become liquid again and drop into the solvent again. The methanol automatically change the dissolved nylon into precipitate after drop into the solvent. Figure below shows that the nylon become powder form after the precipitation process occur.

Figure 20: Nylon from mixture 8

Figure 20 shows that the recycled nylon become precipitate after precipitation process happen. This shows that the formic acid is the main reason that the nylon dissolve in the solvent. The amount of methanol in the solvent will dilute the formic acid and expected to reduce the degradation of the recycled nylon.

Mixture 9: FA(45%), Ethanol(45%), Polymer(10%) in 90°C

The result also shows that the nylon can be dissolve in this mixture. This is because the nylon is heat up exceed to the boiling point of ethanol. This case is similar with the mixture 8 reaction that the nylon will dissolve after the ethanol was vaporize. The nylon also become precipitate after the ethanol is condensate by condenser. Figure below shows that the nylon become powder form after the precipitation process occur.

Figure 21: Nylon from mixture 9

Figure 21 shows that the recycled nylon become precipitate after precipitation process is occur. The present of ethanol also to dilute the formic acid for reduce the degradation of nylon during recycled process.

Result from Fourier transform infrared spectroscopy (FTIR) for Recycled Nylon

Below is the result from FTIR for recycled nylon by using mix of formic acid with methanol or ethanol. Those result will be compare with the virgin nylon-6 that contain in the fishing line. For the nylon-6, the characteristic of the band position in the FTIR (Socrates G., 2001):

Nylon-6: 1465cm^{-1} (~6.83μm), 1265cm^{-1} (~7.91μm), 960cm^{-1} (~10.42μm), 925cm^{-1} (~10.81μm)

1. Recycled nylon with FA (Mixture 3)

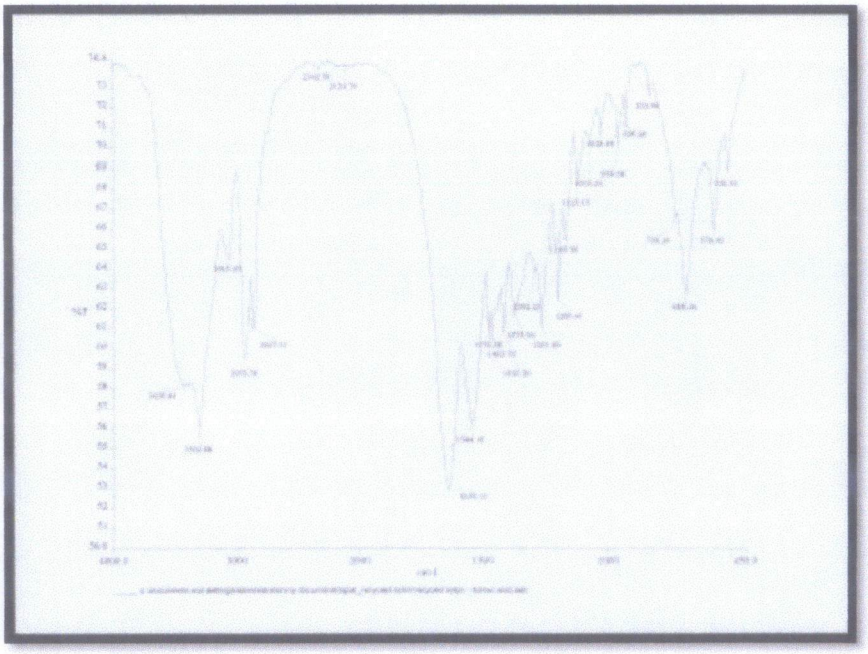

Figure 22: Recycled nylon with mixture 3

The figure 22 shows the band position for this mixture is 1462.72cm^{-1}, 1263.86cm^{-}1, 958.98cm^{-1} and 928.48cm^{-1}. Because of due to present of additive in the fishing line, the band position is not far from the original position. This shows that the recycled nylon is still consider as nylon because of the band position is not far from the original nylon.

2. Recycled nylon with FA 55%, MeOH 35% (Mixture 7)

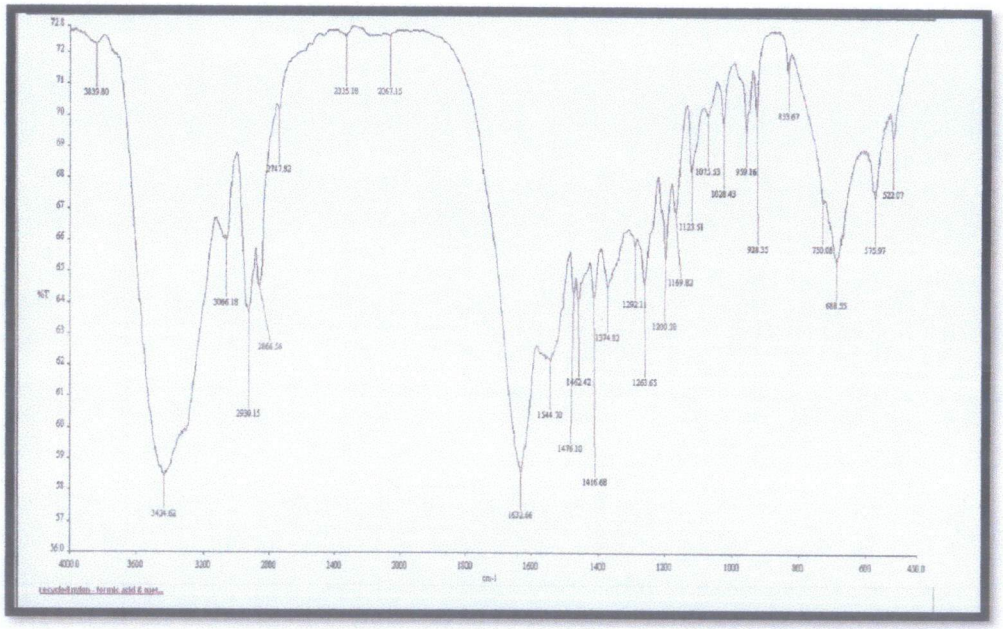

Figure 23: Recycled nylon with mixture 7

The figure 23 shows the band position for this mixture is 1462.42cm^{-1}, 1263.65cm^{-}1, 959.16cm^{-1} and 928.35cm^{-1}. The band position shows that the band position of this recycled nylon still not far from the original nylon. This shows that the recycled nylon still consider as nylon.

3. Recycled nylon with FA 45%, Ethanol 45% (Mixture 9)

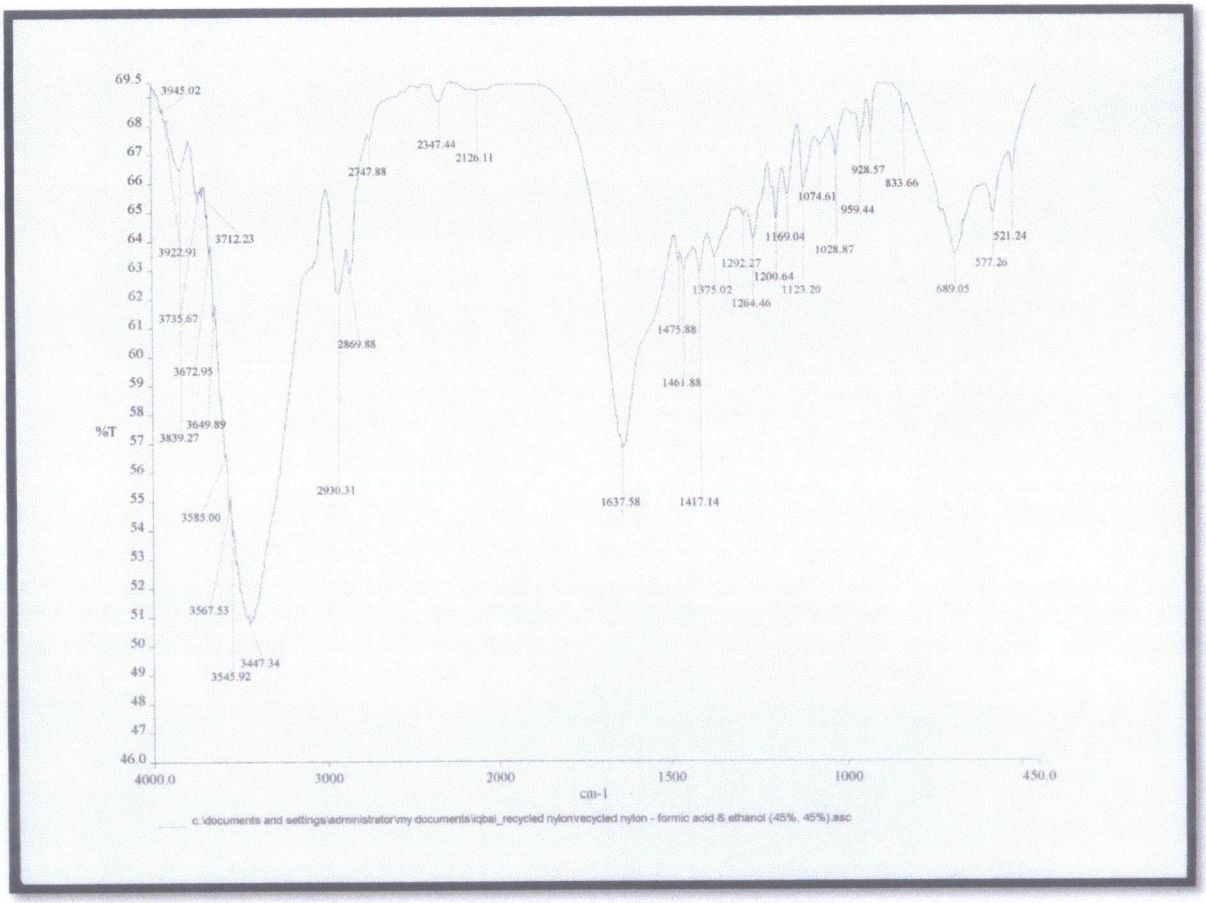

Figure 24: Recycled nylon with mixture 9

The figure 24 shows the band position for this mixture is 1461.88cm^{-1}, 1264.46cm^{-}1, 959.44cm^{-1} and 928.57cm^{-1}. This band position also shows that the recycled nylon also still not far from the original version. This shows that this recycled nylon still consider as nylon.

CHAPTER 5

CONCLUSION

5.1 Conclusion

Almost all of the result shows that the nylon can be dissolve in the solvent that has been prepared in the experiment. This shows that the recycling the nylon can be done by using formic acid with other solvent. The selection of solvent is very important because it also can give impact for the solubility of solvent during undergoes dissolution process. This shows that the first objective is already achieve by recycle the polyamide by using dissolution/precipitation method.

Even though the selection of solvent can give big impact to the solubility of nylon in the solvent, the right ratio of the solvent also is very important for recycle the nylon efficiently. The result shows that by diluting the formic acid can dissolve the nylon by operate it at high temperature. The presence of formic acid is very important to dissolve the nylon. From the result of FTIR, the band position of recycled nylon is not far from the original nylon. This shows that the recycled nylon is still consider as nylon.

By doing this experiment, many waste that have nylon can be save from being thrown by people. The nylon also nowadays is widely used and this recycling method will help to reduce to handle when the product become waste product. Furthermore, the nylon also known as polymer that hardly to handle in a waste treatment process.

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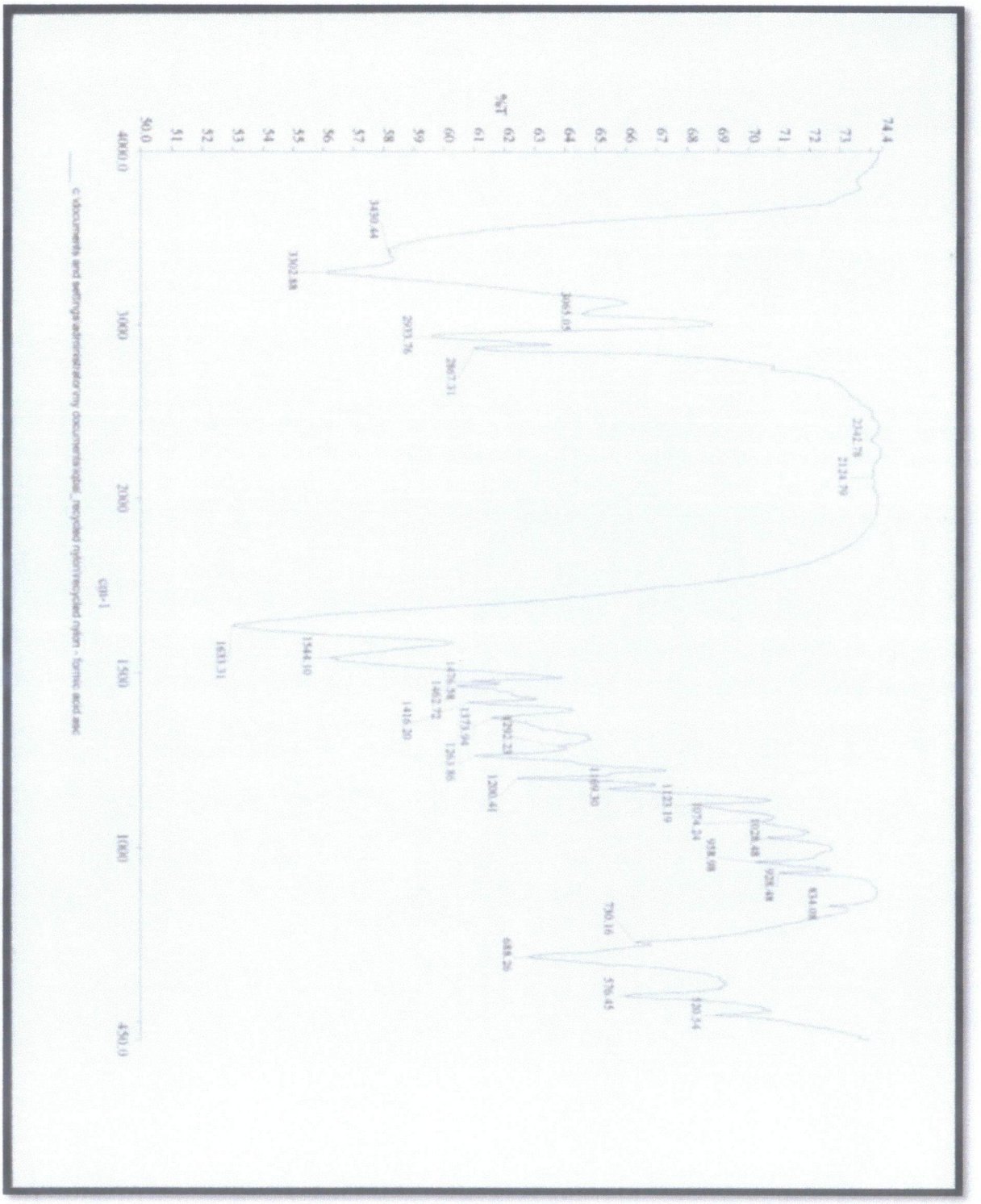
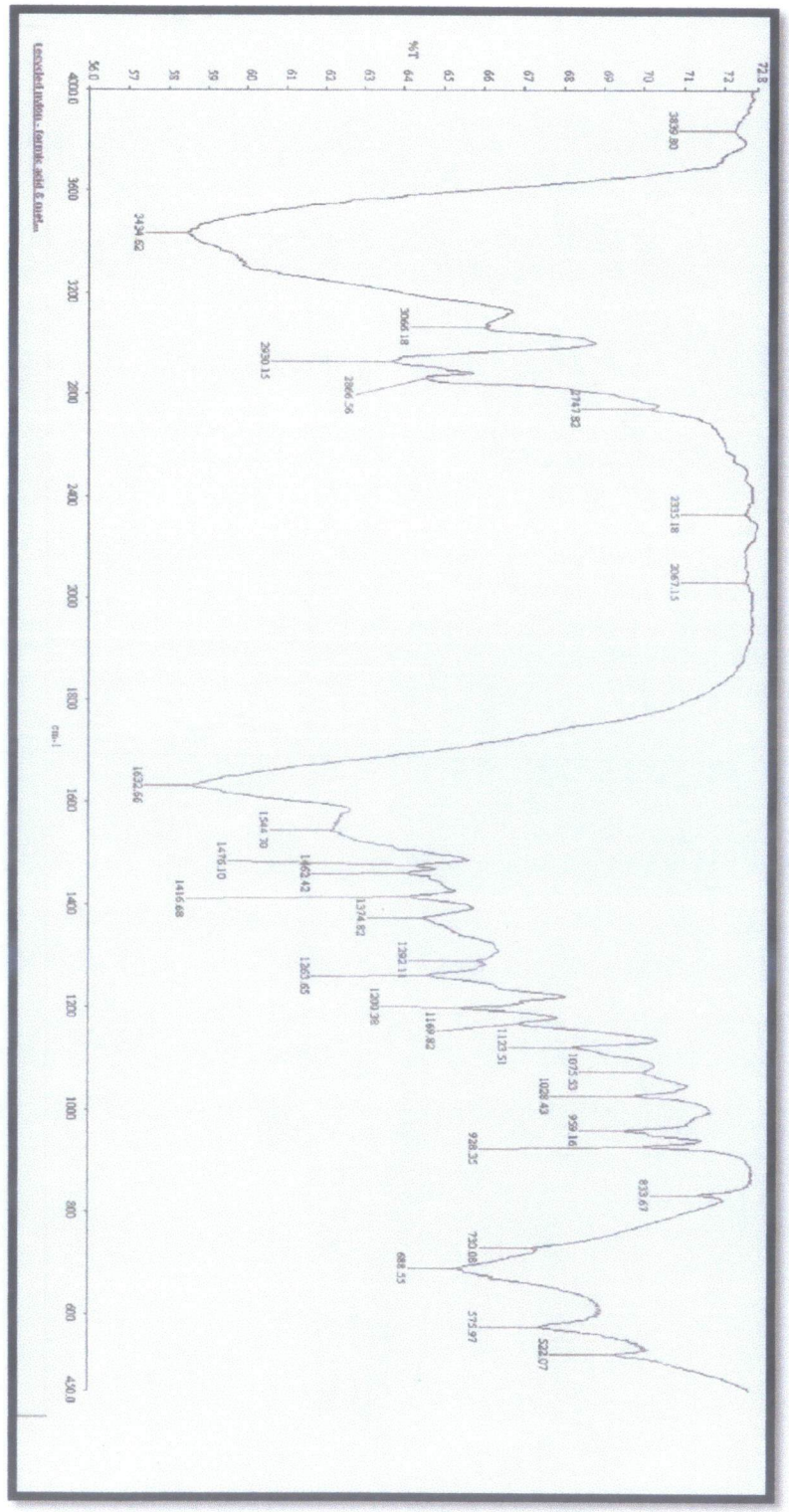
APPENDICES

Appendix 1: Result from FTIR for Recycled Nylon in Formic acid



Appendix 2: Result from FTIR for Recycled Nylon in MeOH with FA



Appendix 3: Result from FTIR for Recycled Nylon in Ethanol with FA