

Abstract

CHEN, JU. Advanced modification of PET. (Under the direction of Dr. Stephen Michielsen).

PET is the most common polyester used world wide. Many researches have studied the modification of PET. Grafting is a common method used in modification. Since there are not many reactive sites in the chemical structure, it is hard to graft PET with other functional groups. As a result, it would be easier if PET could be pretreated before grafting. This research focuses on this issue. Sodium hydroxide and amines were applied to degrade PET fabrics in order to make PET gain reactive sites on the surface. Amine pretreatments gave good performance that improved grafting of a dye-bound polymer to PET fabric. Firstly, ethylenediamine was used to modify PET fabric. The results showed that ethylenediamine provided an improvement in the grafting with the dye-bonded PAA. To apply this modification at higher temperature, hexamethylenediamine was applied in the modification instead of ethylenediamine. The results confirmed that hexamethylenediamine worked at higher temperature. It rose the effective treating temperature from 75°C to 90°C. Furthermore, a statistical analysis was applied in experiment design to find the optimized of treating conditions for both chemicals.

Advanced Modification of PET

by
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1. Introduction

Modification of PET material is important, because PET is unreactive so that it difficult to attach other functional groups without modification. To increase its hydrophilic properties and enlarge the application field of PET material, proper modification is needed. Lots of research has been done on the modification of PET materials. Normal methods use sodium hydroxide or amines. These two methods are also applied in PET recycling because they degrade PET well. In addition, prior work has proved that modification with amines can produce hydrophilic PET fabrics within 10 minutes at room temperature.

In the literature review section, the technical background of surface modification has been given to find a proper method to modify PET fabric. Grafting is the preferred method. Next information about grafting is presented to show the features of grafting.

At the very beginning of this research, sodium hydroxide was applied to PET fabrics, and their weight change was measured to obtain the degree of degradation.

Amines were the next choice for this research. First of all, PET fabrics were modified with ethylenediamine with different temperature and time combinations, in order to determine the range of applicability. The next step was coloring treated PET fabric with dye bonded to PAA (polyacrylic acid), actually there was a chemical reaction between ethylenediamine and the dye bonded with PAA. To test the results of fabric treating, leaching test was performed with UV-Vis device. The procedure of

leaching test was obtained from LAAMScience. To make it more suitable for PET fabric, some changes were needed.

In order to be able to modify PET at higher temperatures, hexamethylenediamine was used as well. The same treating methods were performed, and the same leaching test was also used.

2. Literature Review

2.1 PET

2.1.1 Basic Information about PET

Polyester is a category of polymers which contain the ester functional group in the main chain. Poly(ethylene terephthalate) (PET) is the most common type of polyester in the world.

PET consists of repeat units of ethylene terephthalate, $C_{10}H_8O_4$, which is shown in Figure 2.1.

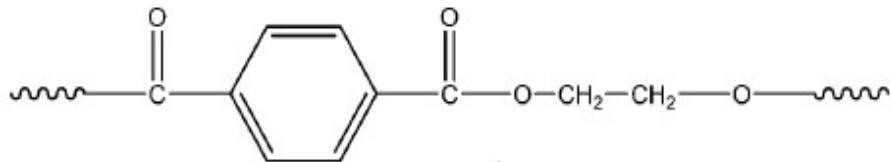


Figure 2.1 Chemical Chain of Polyester

2.1.2 Advantages and disadvantages of PET

Polyester has many advantages over natural fibers, such as improved wrinkle resistance, durability and high color retention. It also has good electrical insulation property, sunlight resistance, and good rubbing resistance.

When considering its chemical properties, polyester also has many advantages over natural fibers. It has good resistance to chemical reagents, especially weak acids and weak bases. Polyester is resistant to strong acid at room temperature, but weaker resistance to strong base. But there are disadvantages too. Polyester has poor dyeing performance, which usually requires harsh dyeing

conditions, such as high temperature and the application of disperse dye with a carrier.

2.1.3 Modification of PET

In modification of polyester, both physical and chemical methods have been investigated and applied. These methods proved to be effective to enhance those disadvantages. Physical methods mainly focus on changing the morphology of fibers. Chemical methods are more complicated. The following are some examples about common modification applied in polyester.

In order to increase the moisture capacity of polyester fiber, a hydrophilic monomers or oligomers of polyethylene glycol could be used to make co-polymers with polyester.

To improve the fire resistance properties of fibers, phosphorus, halogen and antimony compounds can be used.

Due to the high molecular weight of the polymer and the positive consumer properties, polyester usually has low pilling resistance. [1] These would contribute limitations for the possibility of applying them in fabrication of textile articles. To cover the pilling issue, chemical modification using a polyfunctional compound as a modifier has been examined.

To improve the dyeing properties of fibers, dyes substantive monomers, such as sulphonate, could be used to make copolymer. Chemical modification is another

way. Sodium hydroxide and amine have been used to hydrolyze PET in order to improve it.

2.2 Modification by Grafting

Literally, grafting means chemically bonding substances to the material. In materials study, surface grafting is a commonly used technology in order to alter the properties of materials.

2.2.1 Brushes

Polymer chains are formed from grafting, since they are attached to the substrate by their chain end. (Figure 2.2) When the density of grafted chains is increased to a high level, a brush like layer can be formed on the surface. These brushes provide the possibility of modification and functionalization. Grafting density, chain length, and chemical composition of the chains are three major parameters controlling the properties of brushes. [2]

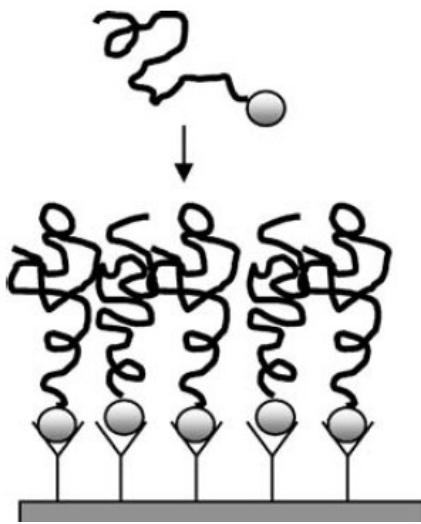


Figure 2.2 Polymer chains forms brushes like layer [2]

Brushes have four categories, which are separated from each other depending on the types of polymer chains. The four categories are homopolymer brushes, bidisperse polymer brushes, mixed polymer brushes and block-copolymer brushes. They are illustrated in Figure 2.3. For mixed polymer brushes and block-copolymer brushes, their morphology and wettability can be changed in response to variation of environment. [2]

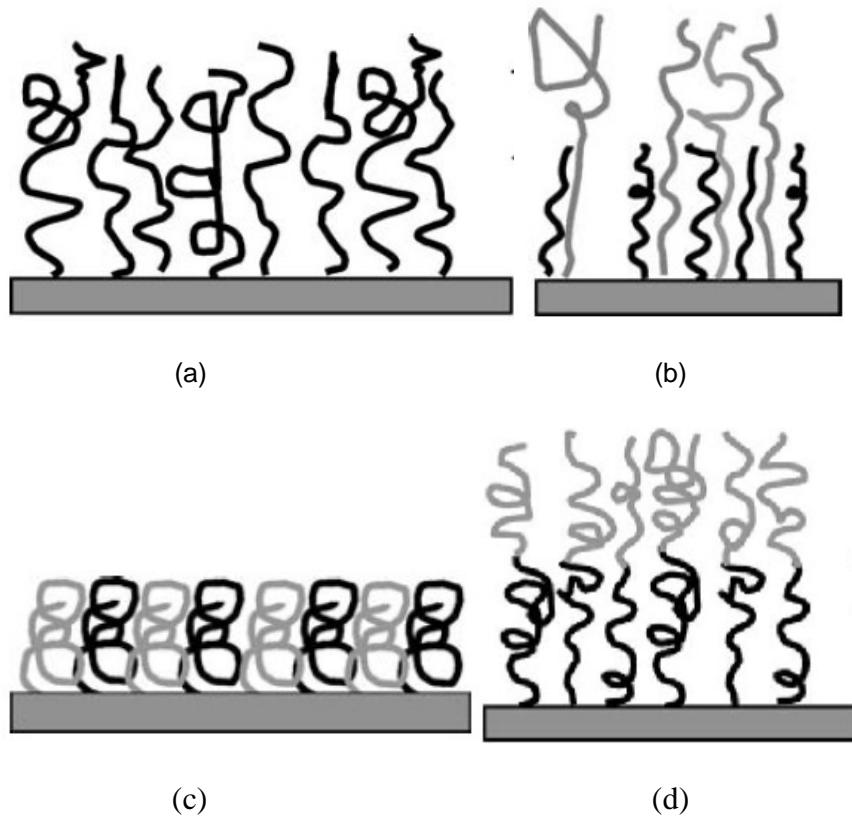


Figure 2.3 a) homopolymer brushes; b) bidisperse polymer brushes; c) mixed polymer brushes; d) block-copolymer brushes [2]

Different parameters of brushes determine various fundamental properties, such as regulation of wettability, colloidal stability, adhesion, friction, biocompatibility, conductivity or adsorptivity, and surface patterning. [2]

2.2.2 Categories of Grafting

Grafting could take place in these two ways: “grafting to” and “grafting from”. “Grafting to” means grafting end-functionalized polymer chains to the substrate, while “grafting from” means grafting reaction proceeding by polymerization from the surface. They all need materials having reactive sites on the surface.

“Grafting to” method is proceeded by chemical reaction to graft the functional groups onto the surface of polymer, and then polymer could gain this functional chain on surface. Compared with grafting from approach, the grafting to method has an advantage that the surface polymer can be treated before attaching to the surface. [2] Because of this interesting pre-treating process, additional steps are added in the continuous manufacturing process. From the perspective of saving resources and profit consideration, it should be easy to operate and require an acceptable time.

“Grafting from” is a method that initiator covalently attaches to the solid substrate of polymer. When applying this grafting from method, almost all known mechanisms for polymer synthesis can be involved in. This kind of approach usually needs a long time to finish the polymerization. Compared with grafting to approach, this one is more complicated, time-costly, and hard to control.

2.2.3 Specific Grafting Methods

When the issue comes to grafting methods, many studies have been done previously. Generally speaking, there are two types of methods; one is direct coupling reaction of existing polymer molecules to the surface and graft polymerization of monomers to the surface. [3] These two are illustrated below in Fig 2.4.

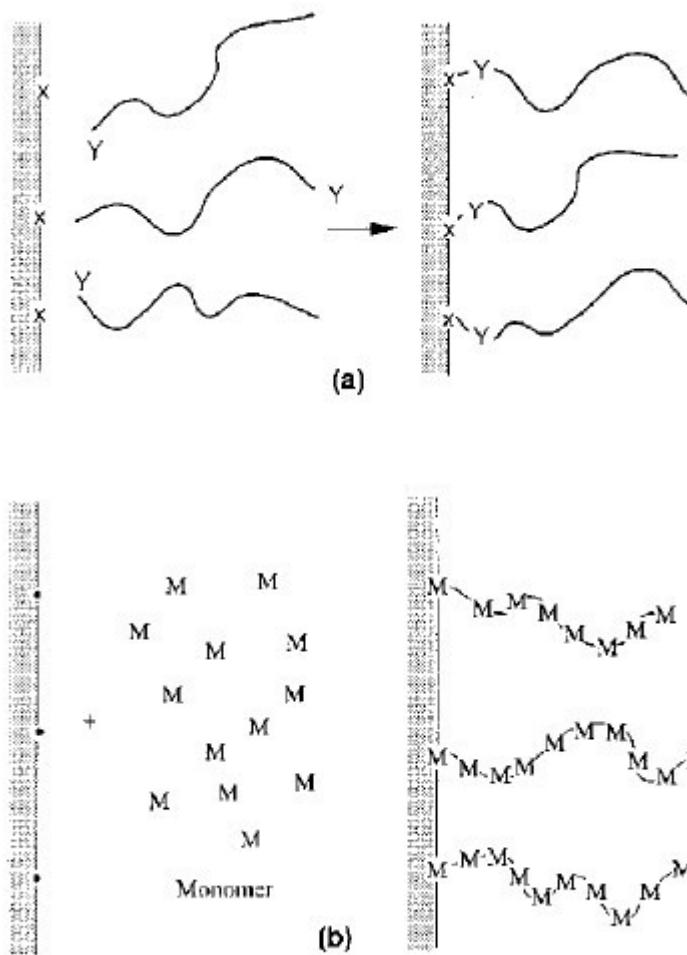


Figure 2.4 a) Direct coupling of polymers to the surface, b) Graft polymerization of monomers [3]

Chemical coupling reaction could take place when this situation is satisfied: polymer surface has been modified to have reactive groups in order to attaching other components. [3]

1. Plasma-induced grafting

Plasma has many advantages; it causes little harm to environment; it is dry and clean. First of all, how does plasma work? Plasma reactor performs by applying electrical energy to disrupt a gas into five parts: electrons, free radicals, ions, photons, and metastable species. The ones participating in plasma treatment are free radicals and electrons by colliding with polymer surface and rupturing covalent bonds.[4] Treatment with plasma usually imparts dehydrogenation, unsaturated bond formation, trapped stable free radicals formation, generation of polar groups, and increased surface roughness. [5]

Since reactive sites are created, the polymer surface gains the potential to combine with oxygen and moisture in air to form oxygen functionality including hydroperoxide.[5] As a result, the surface becomes more hydrophilic. Previous research about treating PET with plasma has been done. It indicates that it's possible to graft AA onto PET nonwoven fabric by He/O₂ plasma treatment, and AA grafting improves wettability a lot, which can be concluded by the experiment results of moisture regain and dyeability with a basic dye. [4]

2. Radiation-Induced Grafting

Radiation induced grafting is a relatively simple method. Compared with other conventional material processing, radiation induced grafting needs no catalysts or additives to initiate the reaction. This is the main characteristic of radiation induced grafting. High energy radiation is used for this kind grafting: gamma ray, UV or electrons. The grafting techniques include pre-irradiation, as

well as the mutual or the simultaneous method. [6] By ionizing irradiation, trapped radicals and peroxides or hydroperoxides are formed on the surface of polymer, which provides reactive sites for initiating grafting copolymerization reactions.

Various graft polymerization approaches have been developed, including direct graft polymerization of vinyl monomers already containing desirable functional groups, graft copolymerization of two or more different types of monomers onto a polymer backbone, and graft polymerization of a precursor-monomer that can be subsequently modified. [6]

2.3 Chemical modification of PET

2.3.1 Modification of PET by NaOH

PET has weak resistance to strong bases. When treated with sodium hydroxide, PET can be broken down into its monomers, terephthalic acid and ethylene glycol, through a hydrolysis reaction with sodium hydroxide: [7]

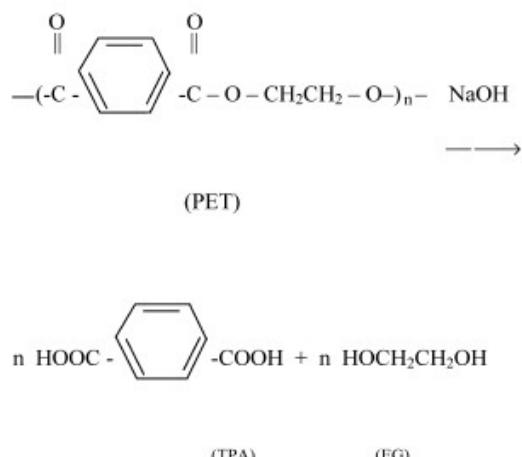
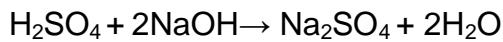
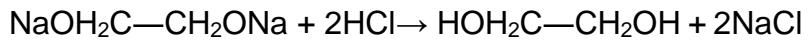
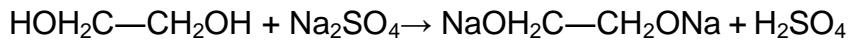


Figure 2.5 Process of chemical reaction between NaOH and PET [7]

Chemical reactions involved during EG recovery operation: [7]



This hydrolysis reaction takes place on the PET surface, while this reaction is not violent at all. Because of the degree of crystallinity and cross-linking in the PET, this hydrolysis reaction usually happens in a low speed. Temperature is a parameter that has a strong effect on reaction degree and rate as well. Studies have been done to observe the morphology change of PET at different sodium hydroxide treating time. The results are shown in Figure 2.7. [8] Previous work has found that although one hour treating time is enough to increase hydrophilicity of polyester, treatment less than 8 hours treating time did not induce notable change in polyester fiber surface,[8] which directly reflected in dents that appear on the fiber surface as shown in Figure 2.6.

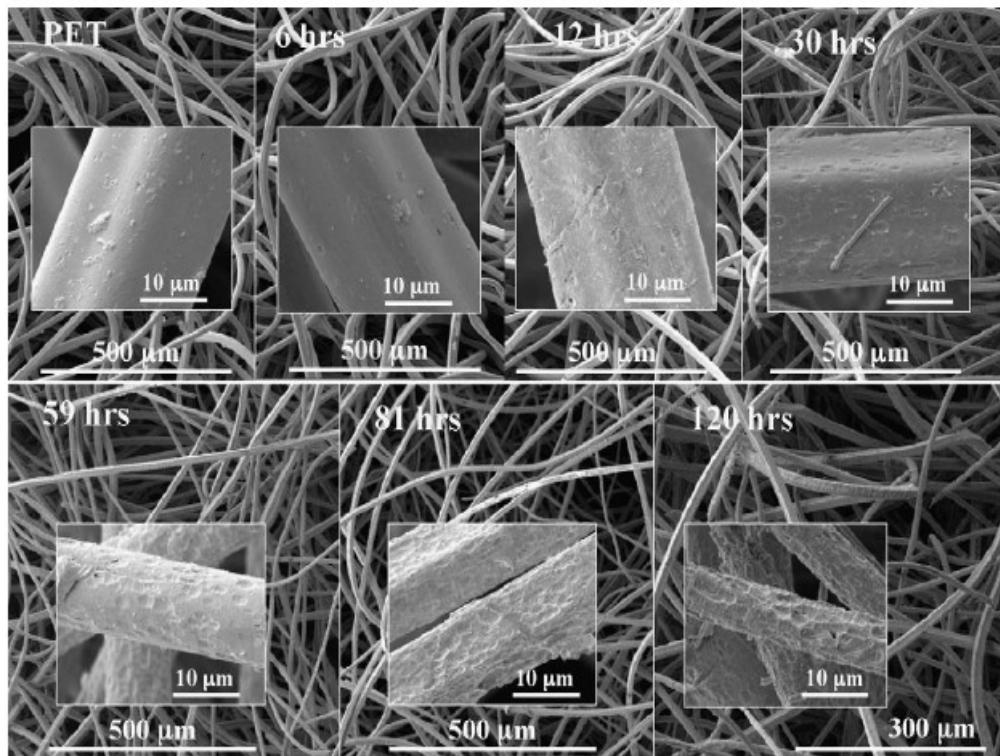


Figure 2.6 Scanning electron micrographs of PET matrices before and after NaOH treatment for various times (0, 6, 12, 30, 59, 81, and 120h). The matrices were not deformed or significantly weakened in their mechanical strength despite the increased surface roughness and decreased fiber diameter with increasing treatment time. [8]

As shown in Figure 2.6, more and more roughness appeared on the fiber surface with increase in treating time. The degree of crystallinity and cross-linking on the PET fiber determine rate of degradation. At the regions that have lower crystallinity and cross-linking, higher degree of hydrolyzation happens because this region is more likely to react with hydroxyl ions.[8] As treating time increases, this PET fiber surface gets degraded more and more, and the fiber surface gets rougher.

Because of hydrolysis, the direct effect is weight loss and the reduction in fiber diameter of PET fiber. This decrease in diameter would cause an increase in the surface curvature of the fibers and a decrease in available surface area. As a result, there should be an optimum conditions for NaOH modification. To study the kinetics of PET hydrolysis by NaOH, previous works have shown the hydrolysis kinetics. (Figure 2.7)

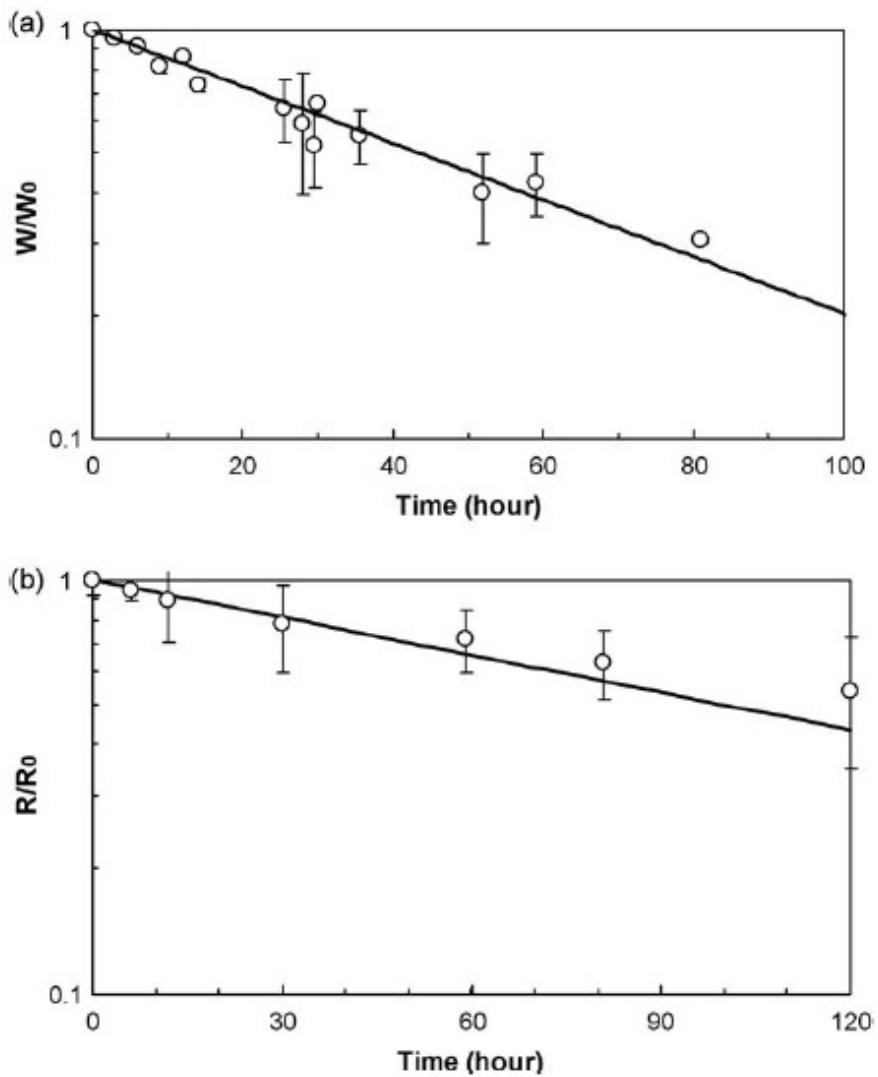


Figure 2.7 Kinetics of PET hydrolysis in 1N NaOH at 70°C. (a) Weight loss kinetics with a decay rate constant of 0.0147h^{-1} . (b) Exponential degradation kinetics of fiber radius with a decay rate constant of 0.0073h^{-1} . Error bars represent standard deviations. [8]

By this kinetics analysis of PET hydrolysis with NaOH, fiber diameter can be predicted.

2.3.2 Chemical Modification of PET by Amines

Chemical reaction between PET and amines is similar to aqueous sodium hydroxide. Polymer undergoes nucleophilic substitution during aminolysis.[9]

As we know, PET fibers usually have low surface energy and limited chemical reactivity, resulting in poor wettability and weak adhesive bonding. Amine groups can help PET increase its wettability, and also provide reactive sites for potential formation of covalent chemical bonds with polymeric materials as in a composite.[9] Amine groups can chemically react with epoxides, isocyanates, and methylol compounds, forming chemical bonds with epoxies, polyurethanes, and phenol-and resorcinol-formaldehyde resins.

Chemical reaction of amines and PET can be illustrated as follows:

1. Reaction of an amine with PET

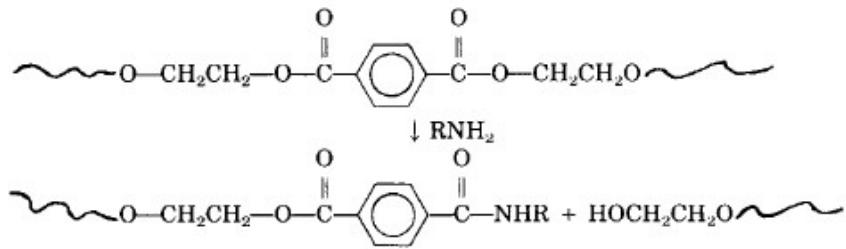


Figure 2.8 Process for reaction of an amine with an ester group of PET [10]

Amine groups were attached to PET through this chemical reaction, then they were expected to react with carboxyl groups coming from the dye bound PAA to form a covalent bond. These are the chemical reactions used to finish the grafting of PET.

2. Reaction of a multifunctional amine with PET

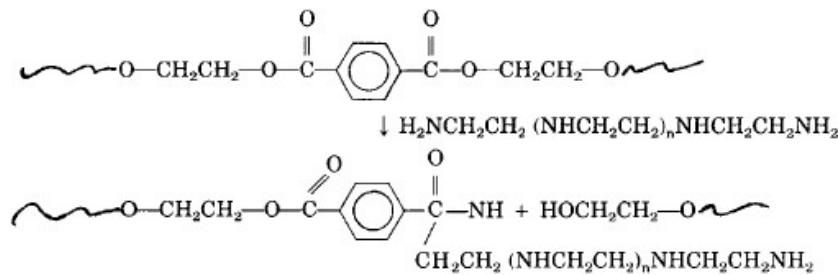


Figure 2.9 Process for reaction of a multifunctional amine with PET [10]

In the real experiments, in order to enable the reactions to take place at higher temperature, multifunctional amines were applied. The principle of their reaction is shown in Figure 2.9. The reason choosing multifunctional amine is they have higher boiling point which makes it possible that the reaction can happen in high temperature without any amine missing.

As shown in Figure 2.9, only one amine group participates in attachment with the chain scission to form an amide group, while the rest of the amine groups should be incorporated into the PET structure. This incorporation is vital to fiber wettability properties. Considerable research has been done to study how amine groups change wettability. The experiment result indicated that most of the change in wettability can be achieved in 10 minutes. [7] When the amount of grafted amine groups reach a certain level, the wettability of treated PET didn't change with the increase of amine groups, which can be illustrated below in Figure 2.10:

WETTABILITY OF TTEPA-TREATED PET YARN

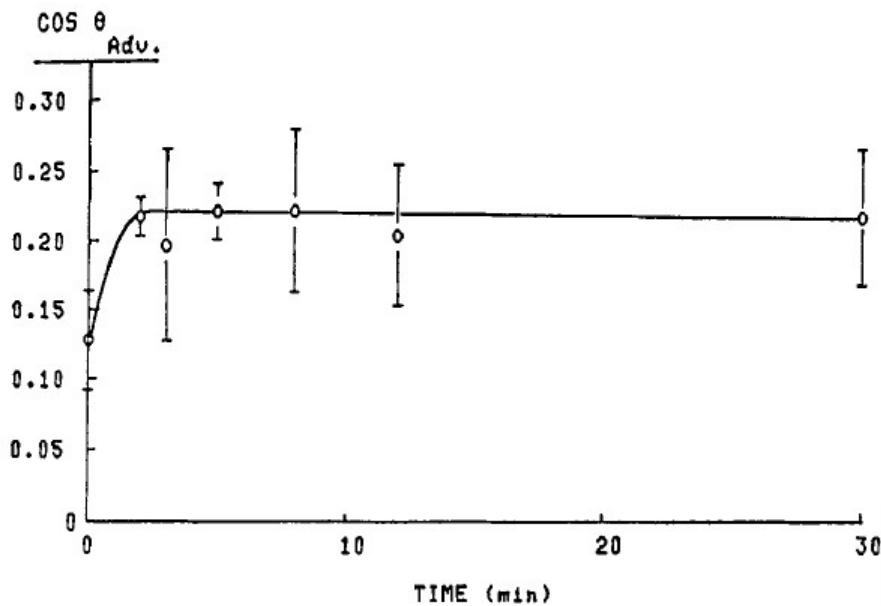


Figure 2.10 Wettability of filaments from a TTEPA-treated polyester yarn as a function of reaction time at 85°C. [10]

3. Information about the dye-bonded PAA

In this research, the target is to adhere dye-bonded polymer onto surface of PET fabric, the polymer is poly (acrylic acid), which chemical structure is shown below in Figure 2.12.

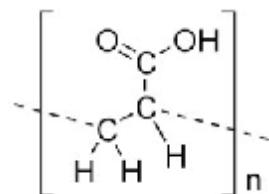


Figure 2.12 Chemical Structure of Poly (acrylic acid)

PAA has many reactive sites in its structure, and the amount of reactive sites depends on the repeat unit of polymer. Poly (acrylic acid) is ideal for grafting

because it's a highly functional polymer and it allows for increased sites on the surface of fabric.

On the other hand, the dye-bonded PAA makes use of PAA as the reactive site. No matter what dye was bonded, PAA should be the one attaching to the surface of PET fabric. In another word, COOH groups should be the reactive sites in this dye-bonded polymer.

4. Reaction with dye-bonded PAA and Amine Modified PET fabric

As it shown that PET gain NH groups after being treated with amines, which makes it possible to react with COOH groups of the dye-bonded PAA. By this reaction, the dye-bonded PAA could be attached onto the surface of PET fabrics, and let it gain the color and properties of this dye.

3. Experiment

3.1 Approach of this research

The approach of this research was to treat 100% polyester nonwoven fabrics with ethylenediamine, then graft a proprietary dye-bound PAA (polyacrylic acid), DYE-BONDED PAA, to the fabric with the help of ethylenediamine. In another words, ethylenediamine is applied to build a bridge for polyester and the proprietary dye-bound polymer. Ethylenediamine contains two NH₂ groups at the end of its chemical structure, one of which covalently bond to the COOH group in polyester, the other bond to the COOH group in the dye-bonded PAA with the same covalence. Ethylenediamine modifies the nonwoven fabric surface by creating additional sites for the dye-bound polymer to covalently bond to. In addition, the real antibacterial function compound, the special source DYE-BONDED PAA is not easily grafted to surface of polyester, because polyester's chemical structure and properties, there is no site on polyester to allow it react with the dye-bound polymer. To create new sites, ethylenediamine is applied to break polyester's chemical chain and bond to it to build a bridge for them. Sodium hydroxide was used during the initial attempt, although, ethylenediamine proved to work better. Hexamethylenediamine was applied later to improve performance beyond that obtained for ethylenediamine.

The target of this research was to advance modification of polyester nonwoven to get a product with antibacterial function, and these advantages as well: easy processing and low cost.

3.2 Experimental Materials

3.2.1 Sodium Hydroxide

Sodium hydroxide was obtained from Sigma-Aldrich, St. Louis, MO with a concentration of 50% by weight. It was chosen to break polyester's long chain in the reaction between sodium hydroxide and polyester.

3.2.2 Ethylenediamine

Ethylenediamine ($C_2H_8N_2$) was obtained from Sigma- Aldrich, St. Louis, MO as extra pure (99%) grade. Its molecular weight is 60.1 g/mol and its boiling point is 117°C. The chemical structure of ethylenediamine is shown below in Figure 3.1. Ethylenediamine was selected because of its basic structure and its amine ends.



Figure 3.1 Chemical structure of ethylenediamine

3.2.3 Hexamethylenediamine

Hexamethylenediamine ($C_6H_{16}N_2$) was obtained from Sigma-Aldrich in solid form. (Sigma-Aldrich, St. Louis, MO) It has higher boiling point of 204-205°C and is water soluble. The chemical structure of hexamethylenediamine is shown below in Figure 3.2. It was selected because it has amine ends as well but has higher boiling point.

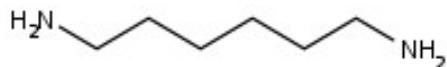


Figure 3.2 Chemical structure of hexamethylenediamine

3.2.4 Dye-bonded PAA

Dye-bonded PAA is a proprietary dye-bound polymer based on poly(acrylic acid). LaamScience, Inc. (Morrisville, NC) kindly provided DYE-BONDED PAA as a 10% solution in water.

3.2.5 Hanks' Balanced Salt Solution (HBSS)

Colorless HBSS was obtained from Cellgro. (Cellgro, Manassas, VA) It contains calcium and magnesium. It was used in the determination dye leaching of treated fabric following the procedure described in section 3.5.2, below.

3.2.6 Methanol

Methanol (CH_3OH) was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO). It was used as an alternate solvent to determine dye leaching of treated samples.

3.2.7 Ninhydrin

Ninhydrin (2,2-dihydroxyindane-1,3-dione) was obtained Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO). It's used to detect ammonia or primary and secondary amines. When reacting with free amines, a deep blue or purple color (Ruhemann's purple) is produced. So ninhydrin was selected to detect amines in order to judge the products of reaction between EDA and polyester.

3.2.8 Fabric Used

There were two kinds of 100% polyester fabrics used in the whole study.

One of the PET fabric is a knit structure, the other is nonwoven fabric with basic weight of 24gsm.

3.3 Attempts with Sodium Hydroxide

Polyester has moderate resistance to strong alkali. So sodium hydroxide was used to introduce COOH groups into chemical chain of polyester through chain scission. COOH groups can provide sites for the next stage in grafting.

3.3.1 Experiment preparation

1. Preparation for chemical reaction

100% polyester knit fabrics were used. First, polyester knit fabric was cleaned with water before treatment. Polyester fabric was cut into 1×3 cm, and a 0.5 mol/L NaOH solution was prepared with water. A control sample is required so a non-treated polyester knitting fabric was also cleaned, but left untreated.

The molecular weight ratio of DMTMM (MW 276.72 g/mole) and Azure A (291.8 g/mol) is nearly 1:1, as a result, weight 0.1g DMTMM and 0.1g Azure A.

3.3.2 Procedures

Before treatment, every sample was weighed and recorded as w_0 . NaOH solution was heated to 90°C, and keep the temperature with sensor. The stirring speed of the heating pot was set at 600 rev/minute. Three samples were placed into

the solution at the same time, allowing them to be treated with NaOH for 10 seconds (marked as group A).

After 10 seconds treating time all three samples were immediately removed and immersed in water for 5 minutes, the water was replaced and the washing step was repeated 3 times. PH paper was used to test fabric's pH value in order to make sure there was no NaOH left on the samples.

When finishing above treating steps, the sample was dried and weighed. The weight of treated samples, record as w_1 .

This treatment was repeated with the other 5 different time sets: 20 seconds (group B), 30 seconds (group C), 40 seconds (group D), 50 seconds (group E), and 60 seconds (group F). Every step was followed exactly as the 10 seconds-treated samples.

3.3.3 Testing

First 0.1g DMTMM was dissolved in 10ml water. Then 0.1g Azure A was dissolved in 200ml water. When these two solutions were ready, the DMTMM solution was added into Azure A solution and stirred for 10 seconds. Then, the group F samples were dropped into the mixed solution, and left stirring for 2 hours; the stir speed is set as 660 rev/min.

During this time, clean water was heated until its temperature reaches 80°C, and kept at this temperature with a sensor of heating pot. When the 2 hours stirring of the group F samples finished, the fabric was removed and rinsed in the hot water

with a stirring speed of 660 for one hour until no ore color came off. Finally, the sample was dried.

These steps were repeated the control samples.

3.4 Application of Amine

3.4.1 Exploration with Amine

1. Exploration with Hexamethylenediamine

Previous work has shown that hexamethylenediamine has strong erosion effect on polyester. It can break polyester's chemical structure. As a result, before designing an experiment for the final production, hexamethylenediamine was used to react with pure polyester fabric and the occurrence of reaction was judged from the fabric's weight loss before and after treatment.

To gain a consistent high temperature, an oil bath was used to heat the hexamethylenediamine. A test tube was used as the container for hexamethylenediamine. Polyester knit fabric was cut into 5×5 cm pieces, washed in water and air-dried before treatment. Control sample was a non-treated fabric. Including control group there were five groups in total, they were divided by treating time (Table 3.1).

Table 3.1 Distinguish between Hexamethylenediamine Groups

Treating Time	control group	1 minute	2 minutes	3 minutes	5 minutes	10 minutes
Group #	A	B	C	D	E	F

After all preparation, the oil bath was heated to 86°C. Because hexamethylenediamine is solid in its glass bottle, the bottle was heated with a heat gun to melt it. Then it was removed with a pipette. The volume was just enough to cover the samples. The test tube was placed into the oil and fixed with a clamp. The hexamethylenediamine was heated until a clear ring appeared above the liquid, which indicated that the chemical was at the right temperature and was ready for the following step.

Next a fabric sample was weighed (w_0) and immersed in hexamethylenediamine for 10 minutes. During these 10 minutes, clean water was prepared. At the end of 10 minutes, the sample was removed immediately and dropped it into clean water. The samples were washed for 10 minutes, the water was changed and the washing was repeated for 3 times. After washing the samples, they were dried and weighed to get w_1 .

Each group was run the same way, except that groups B, C and D were reacted with same solution without changing to fresh hexamethylenediamine. The reason was to save chemical and for convenience. Group F was the first group reacted with hexamethylenediamine, then group E, then groups B, C and D.

2. Exploration with Ethylenediamine (EDA)

(1) Exploration with Different Concentration

Since the weight loss using hexamethylenediamine to treat polyester fabric was large, and the requirement of our target is a slight reaction, ethylenediamine

(EDA) was used to replace hexamethylenediamine. In this section, difference between groups and group name are listed in Table 3.2.

Table 3.2 Group name & Concentration differences between EDA treated groups

EDA Concentration	Control group	1 minute	2 minutes	3 minutes	5 minutes	7 minutes	10 minutes
99%	A ₁	B ₁	C ₁	D ₁	E ₁	F ₁	G ₁
10%	A ₂	B ₂	C ₂	D ₂	E ₂	F ₂	G ₂

All the steps were the same as with hexamethylenediamine, except use the extra pure EDA (concentration of 99% in weight) instead and an additional time, 7 minutes, was used. In addition, by compared with low concentration (10% in weight), it's found out that lower concentration of EDA solution was enough to letting the reaction to reach the level as required.

To observe the effect of concentration, 10% and 1% of EDA in weight were used to treat polyester fabric as well. In this comparison, 10% concentration group was treated for 10 seconds, while 1% concentration group was treated for 1 minute. Both groups were treated exactly following the steps of prior work of 99% EDA. The results showed small difference, so concentration of 1% was applied for the upcoming detailed study.

(2) Detailed Study with Concentration of 1%

In this detailed low concentration study, treating time and temperature were studied. Four times and four temperatures were set to finish a combination. (Table 3.3)

Table 3.3 Time and Temperature set for 1% EDA

Concration: 1% EDA in weight				
Treating Time	10 seconds	30 seconds	1 minute	3 minutes
Temperature	60°C	75°C	90°C	130°C

Pad/dry/cure process was used. Polyester samples were previously cleaned with water, and then padded once using a laboratory scale pad made by Werner Mathis AG CH#8155 Pad. The samples were directly dried and cured in a Werner Mathis AG LTF#134489 oven for those specifically set temperature and time combinations. The pad and oven used are shown below in Figure 3.4 and Figure 3.5.



Figure 3.4 Werner Mathis AG CH#8155 Pad



Figure 3.5 Werner Mathis AG LTF#134489 Oven

3. Existence of Amine groups

The purpose of treating polyester fabric with either hexamethylenediamine or EDA is to build sites to graft the dye-bonded polymer onto polyester. So the existence of amine group on the surface of polyester fabric would be vital for the success of the whole experiment. Ninhydrin was used here to test the existence of amine groups.

(1) Testing of Exploration with Different Concentration

The samples used here were obtained from the last EDA exploration part. Both 99% and 10% EDA treated fabrics were tested here. One sample from each

group was selected and one non-treated polyester fabric was prepared to be the control group.

To prepare the reagent, 0.25g ninhydrin was dissolved in 126ml acetone to make the solution with concentration of 0.25% by weight. The calculation is following: need 100g acetone, and density of acetone is 0.7925g/ml, so volume of acetone equals to $100\text{g} \div 0.7925\text{g/ml} \approx 126\text{ml}$.

After preparation of reagent, all samples were dipped into ninhydrin solution for 10 seconds. They were air-dried. Because of the high vapor pressure of acetone, air-drying just takes a short time.

To observe the existence of amine groups, UV lamp was used to light them to observe the purple color. If there was purple color on the fabric, we could judge that there are amine groups which were introduced by the reaction of EDA and polyester.

(2) Testing of Detailed Study with Concentration of 1%

One sample from every combination was selected and the ninhydrin test was performed exactly as described in section 3.4.1.3(1).

3.4.2 Application of Ethylenediamine

From the last exploration section, it was found that by reacting with EDA, polyester does obtain amine groups, which offers sites to react with COOH groups of DYE-BONDED PAA in order to graft DYE-BONDED PAA onto surface of polyester fabric. So, 100% polyester nonwoven fabric was used in the grafting.

There were two steps in this section: EDA treatment, and DYE-BONDED PAA attachment. The Pad/Cure/Dry process was applied as the treating method in both

steps. In EDA treatment step, temperature of Werner Mathis AG LTF#134489 oven was set as 75°C, while in DYE-BONDED PAA attachment step, temperature of the oven was set as 170°C.

1. Preparation

(1) Reagent and Sample Preparation

A 400ml EDA solution with concentration of 1% in water was prepared. To improve the hydrophilicity of PET, 0.8g Triton-100 surfactant was added to the EDA solution and dissolved in it. Generally speaking, 0.2g Triton-100 is a proper dosage for 100ml liquid.

Two 200 ml DYE-BONDED PAA solutions were prepared with concentrations of 10% and 5% of the dye-bonded polymer solution in water giving final concentrations of 1% and 0.5% of DYE-BONDED PAA. No surfactant is needed because DYE-BONDED PAA already contains a surfactant.

Next 100% polyester nonwoven samples were cut to the proper size (around 10*15 cm), separated into two groups, one for dyeing with 10% DYE-BONDED PAA solution, the other for dyeing with 5% DYE-BONDED PAA solution, and marked as group A and group B.

(2) Designed Treatment Conditions

For EDA treatment, treating temperature was 75°C; four treating times were set in order to observe the effect of time: 10seconds, 30seconds, 1minute, and 3minutes. For DYE-BONDED PAA attachment, treating temperature was 170°C, treating time was 1 minute.

To make sure sample's weight pick-up was 100% after pad, pressure of the laboratory scale pad was set at 3 bars with a rolling speed of 1.6 m/minute.

2. Treating Process

EDA treatment used method of Pad/Dry/Cure. The oven was preheated to 75°C. Two samples picked from group A and group B were padded once with 1% EDA solution, and then placed into the oven for 10 seconds. This was repeated with the rest samples for other three treating times.

When removing from the oven, group A samples were padded once with 10% DYE-BONDED PAA solution, then place them into preheated oven for one minute. The temperature was 175°C. Treated group B samples just like group A, except using 5% DYE-BONDED PAA solution.

The samples were placed into an envelop to prevent light exposure.

3.4.3 Optimization of EDA Treating Conditions

The purpose was to get an optimized treating condition, which have to satisfy the requirement of saving time and resources. The key of attaching DYE-BONDED PAA to polyester is success of reaction between EDA and polyester. As a result, conditions of EDA treatment were focused in this optimization. With the help of JMP, combinations of temperature, time and concentration were provided, which were shown in Table 3.4.

Table 3.4 Optimization of EDA treating conditions

Temperature of oven (°C)	Concentration of EDA (%)	Treating Time (seconds)
70	1	5
70	1	15
70	3	5
70	5	5
70	5	10
70	5	15
75	1	10
75	3	10
75	3	10
75	3	10
75	3	10
75	3	15
75	5	5
80	1	5
80	1	15
80	3	5
80	5	5
80	5	10
80	5	15

Each sample was treated as described in 3.4.2. For example, the first row combination means PET samples were treated with 1% EDA water solution in a temperature of 70°C.

3.4.4 Improvement with Hexamethylenediamine

Hexamethylenediamine was also applied in an effort to obtain better results. It was used directly following the optimization section. The only change was set three temperatures as 70°C, 80°C and 90°C. the changes were showed in Table

3.5. In addition, to observe the performance of hexamethylenediamine in higher temperature, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C and 170°C these eight temperatures were also used in hexamethylenediamine treating process. But the concentration of hexamethylenediamine solution was only set as 3%, and the treating time was only set as 5seconds for these higher treatment temperatures.

Table 3.5 Optimization of Hexamethylenediamine treating conditions

Temperature of oven (°C)	Concentration of EDA (%)	Treating Time (seconds)
70	1	5
70	1	15
70	3	5
70	5	5
70	5	10
70	5	15
80	1	10
80	3	10
80	3	10
80	3	10
80	3	10
80	3	15
80	5	5
90	1	5
90	1	15
90	3	5
90	5	5
90	5	10
90	5	15

Samples were treated with EDA water solution following steps exactly the same as part 3.4.3, except using Hexamethylenediamine instead of EDA. These treated samples were also saved in envelops.

3.5 Experimental Testing Method

DYE-BONDED PAA was chemically bonded to polyester fabric. As a result, if DYE-BONDED PAA wasn't firmly bonded to the fabric, it would leach into surrounding medium. LAAM Science Inc provided a procedure to assess spectrophotometrically the amount of dye leaching from treated nylon. This method was modified to fit the experiment described above.

1. Materials and equipment

A Cary 3E spectrophotometer (Figure 3.6), Vortex; 20ml Glass vials; Methanol; Coated fabric; Pipette; Fabric scissors; Ruler; Forceps were used.

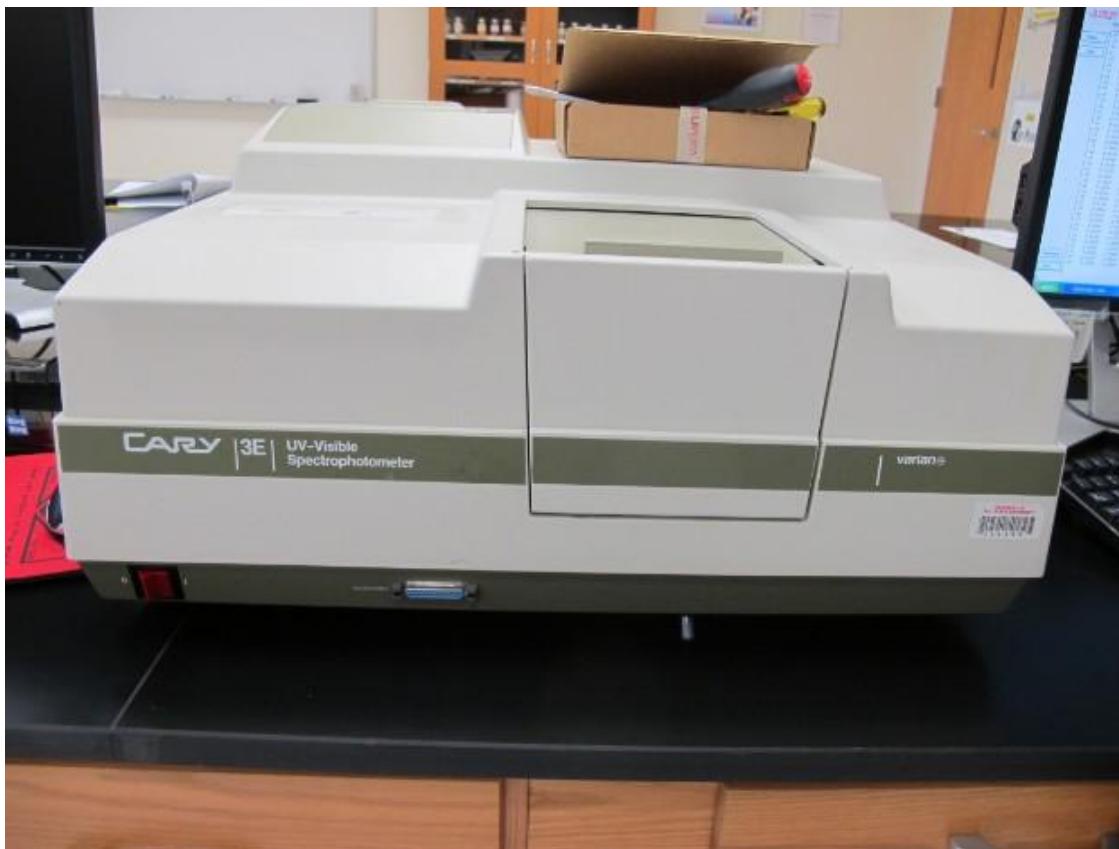


Figure 3.6 Cary 3E Spectrophotometer

2. Procedure

All of the coated samples as well as the non-coated raw material were collected. The fabric weight of the raw material (in gsm), was determined and recorded in the worksheet.

Leach testing uses duplicate samples, so two 4×4cm square swatches of both the coated and non-coated fabrics were cut. Then, each swatch was cut into at least 4 pieces, and placed into a 20ml glass vial with forceps.

Each vial was labeled. The non-coated fabric swatches were labeled as No.1 and No.2, these are controls. Next 4ml methanol was added into each vial. The vials were vortexed for 5 minutes at speed of 500 while ensuring that the swatches in the vials were covered by the solution. When time was up, the vials were immediately removed from the vortex and the fabric was removed from each vial with forceps.

The Cary 3E spectrophotometer was turned on and the Sample Reader in the computer was started. Wavelengths 565nm and 720nm were entered into the read mode in setup section. Two glass cuvettes were filled with 3ml of methanol as blanks. For each leachate solution from the vials, one cuvette was filled.

The two methanol blanks were placed into the Cary 3E spectrophotometer and the absorbance was measured by clicking “Blank”. Next the outside cuvette was removed and replaced with leachate solution and the absorbance read.

The Δ_{abs} of all the samples was calculated by subtracting absorbance at 720nm from absorbance at 565nm.. If the result was larger than 0.0011, the dye had leached from the fabric.

3.6 Statistical Analysis

JMP was used to analyze the data from 3.4.3 and 3.4.4 sections and to build a mathematical function for optimization.

4. Results and Discussion

4.1 Sodium Hydroxide Treatment

Sodium hydroxide is a base used to increase hydrophilicity of PET. PET fabrics were immersed into heated sodium hydroxide solution for 10 seconds. Through the weight loss of PET samples, we can tell the reaction degree.

Sodium hydroxide works on PET fabric by degradation. The change can be measured directly by its weight loss. To make sure the measured weight loss is correct, it's necessary to clean fabric before this strong base treatment.

Figure 4.1 illustrates the weight loss before and after treatment, which shows that the weight loss increases with treatment time.

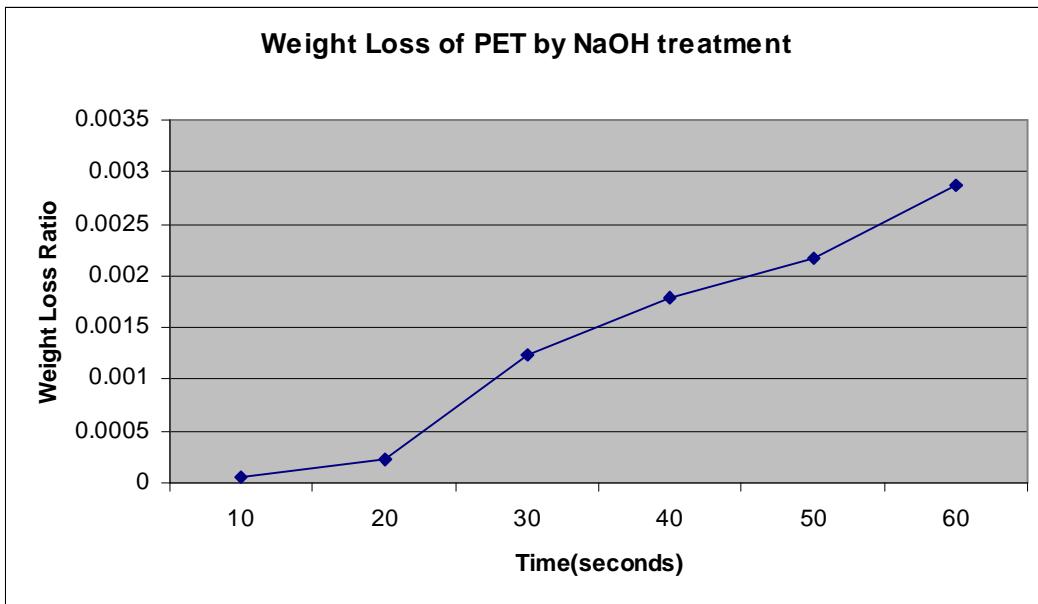


Figure 4.1 Weight Loss Ratio of PET by NaOH treatment. Ratio $r = (w_1 - w_0) / w_0$. w_0 = the weight of PET fabric before NaOH treatment, w_1 = the weight of PET fabric after NaOH treatment.

In this one minute region, the slope of oblique line is not large. From 0 to 15 seconds, slope is the smallest value, which means degradation in 15 seconds was weak and it didn't increase much with time. After 15 seconds, slope of line increased substantially. From the chart, the weight loss was smaller than 0.3%. This degree of degradation is enough for the target application.

4.2 Exploration with Hexamethylenediamine

Sodium hydroxide does work on PET modification, it's a strong base that is dangerous for human. The concentration of sodium hydroxide was 0.5mol/L. Amine is another chemical used to modify PET material. To check the performance of amines, hexamethylenediamine was applied to modify PET fabrics.

Neat hexamethylenediamine was used. There are five different treating times, which were 1, 3, 5, 7, and 10 minutes; long treating time showed very strong effect, all those samples treated for 10 minutes were fully degraded. As a result it was not possible to measure their weight. One 7 minute sample also disappeared in hexamethylenediamine. So these two groups were given up to gain data of weight loss. But their degradation showed the strong effect of hexamethylenediamine.

Other samples also showed large weight loss. This was negative for physical properties of PET fabric. For example, the fabric would be weak in tearing strength.

4.3 Exploration with Ethylenediamine

In the last section, hexamethylenediamine showed so strong effect on degradation of PET fabric that two groups were given up. To obtain the exact effect of amines, such as the effect of concentration and reaction situations, a weaker amine should be used to modify PET fabrics. As a result, ethylenediamine was chosen because its shorter chain.

4.3.1 Exploration with different concentrations

Two concentrations were applied to treat PET fabrics: 10% and 1% EDA by weight in water. 10% EDA show a good trend here as seen in Figure 4.2, as we see, it took less time than NaOH to reach a larger weight change. But this level of degradation is much heavier than what we desire for grafting, around 0.01% weight loss to allow for grafting.

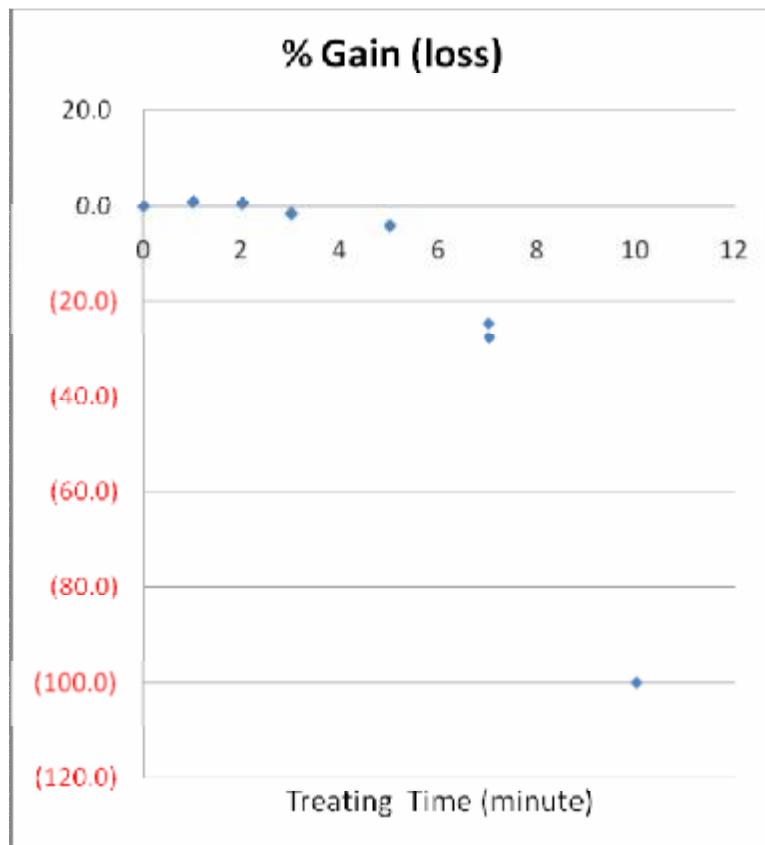


Figure 4.2 Weight gain/loss ratio of 10% EDA treated PET fabrics

Based on the results of 10% EDA treated samples, 1% EDA was also applied in experiment to see what will happen.

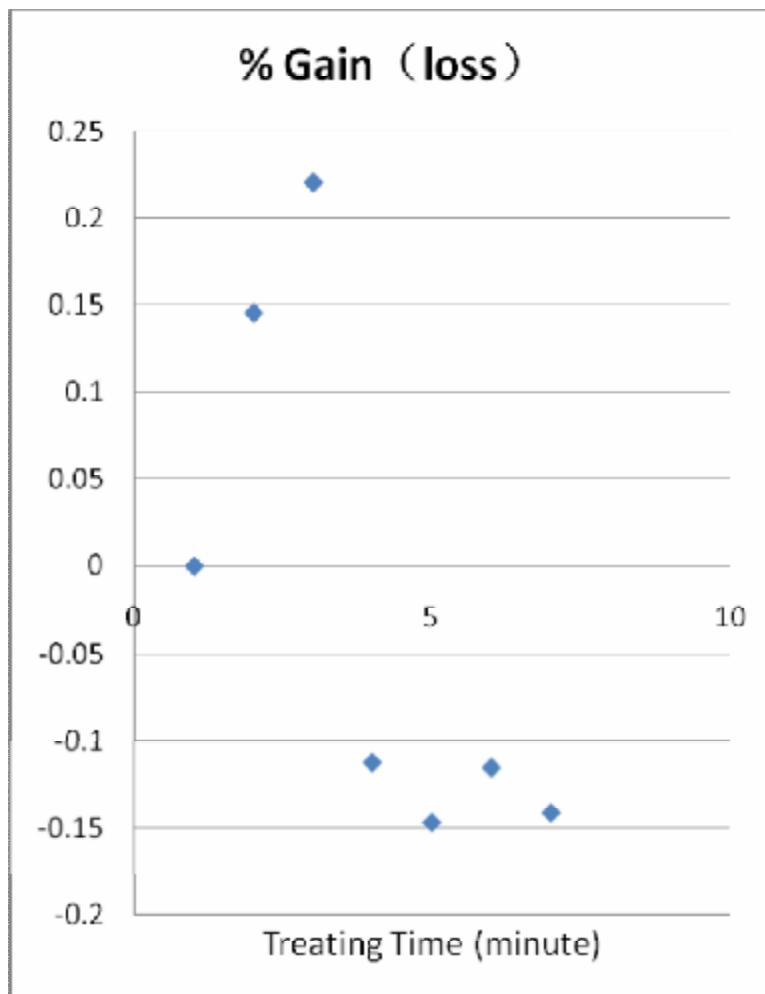


Figure 4.3 Weight gain/loss ratio of 1% EDA treated PET fabrics

1% EDA is not as effective as 10% EDA, but it reaches the target weight loss in one minute. This fulfilled the requirement of time saving. And with time increase, there is no big improvement in degradation. From safety and environmental considerations, lower concentration of EDA is preferred to use. As a result, concentration of 1% was selected to apply in proceeding following steps.

4.3.2 Existence of Amine groups

Amines also work on degradation of PET, and they offer NH₂ groups for PET long chain, which has few reactive sites to covalently attach other polymers.

Because amines provide reactive sites for PET, and this reaction wouldn't take very long to increase the hydrophilicity of PET effectively. As a result, amines were tried.

To see the results of this hydrolysis reaction, there is an easy way. The purpose of this reaction was making PET gain amine groups, so the existence of amines could help us to determine what happened. To avoid the effect of residual hexamethylenediamine, samples were washed before ninhydrin spray, which is a dye that indicated the presence of amine groups.

The results showed that all samples present light purple color. It indicates that there are amine groups on the surface of PET fabrics. There are many possible reasons for this: amine groups have been successfully covalently attached to PET chain; amine groups adhere to the PET fabric surface. The prior situation was the result of chemical reaction, this result is the one expected to happen. The latter one is just physical adherence, and this situation could be explained as hexamethylenediamine residue making color changes. In addition, these two situations can exist at the same time.

Although there are complicated situations that might happen, the first situation is the most likely to happen one. From color tone of all samples, the darkest sample

means there are the most amine groups on PET fabrics. Short time is enough, those samples with less than 3 minutes treating time showed enough color change.

4.3.3 Quick wash of EDA treated PET samples

1% EDA was applied in the whole experiment to modify PET fabrics. Because prior results showed that 3 minutes was enough, so when operating the whole grafting experiment, 3 minutes was the longest treating time used in this section. Four time sets were applied in EDA treating process.

To obtain the performance of amines grafting, samples were quick washed with methanol for three times. The following graphs illustrate the results of quick wash.

1. 10% dye-bonded PAA

In this section, concentration of 10% dye-bonded PAA solution was used to color the modified PET fabrics. Before coloring, PET samples were modified with 1% EDA solution. There were four different treating time for grafting as shown in Figure 4.4. For coloring process, all samples were heated in an oven for 1 minute without considering the different grafting time.

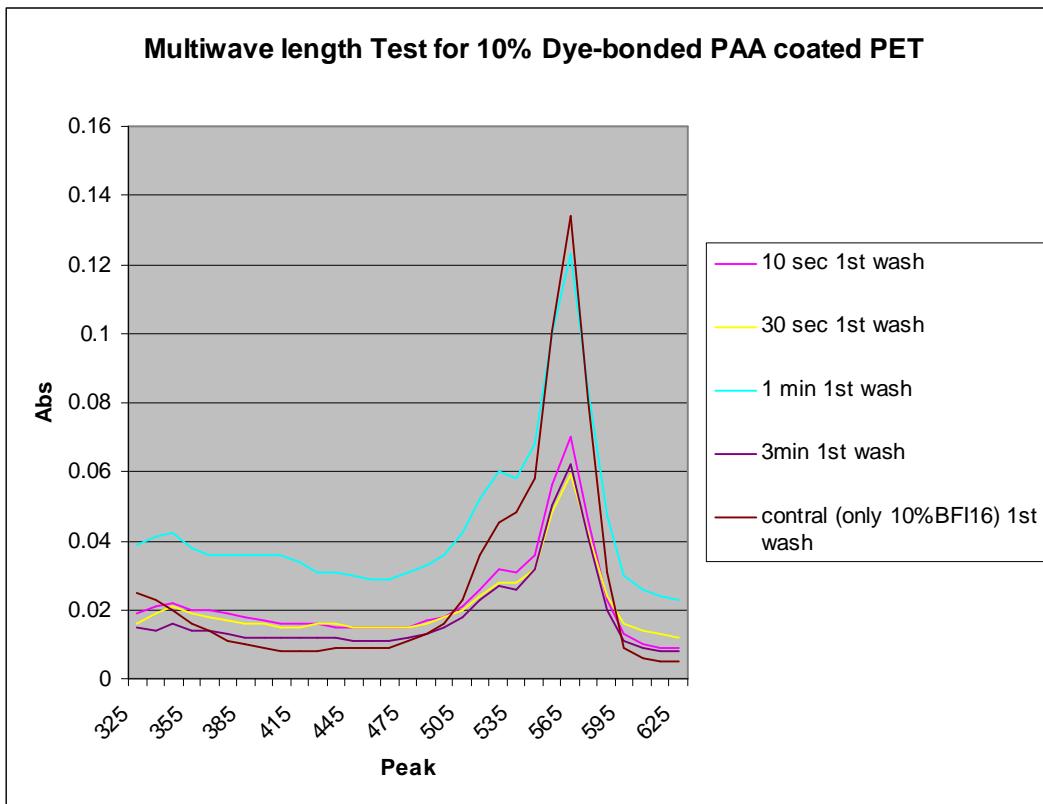


Figure 4.4 Absorbance of the first PET samples quick wash on 10%DYE-BONDED PAA colored PET fabrics.

From the multiwavelength spectrum, it's easy to tell the peak is around 565nm. It's known that the absorbance peak of the dye used to produce DYE-BONDED PAA is 565nm. These two peaks match each other. So this picture of multiwavelength can be seen as the one of DYE-BONDED PAA.

The peak value of four samples can be placed in this order: control sample > 1 minute group > 10 seconds group > 3 minutes group > 30 seconds group. It's hard to see any trend here, because there is no clear relationship between

absorbance peak value and EDA treating time. As a result, the effect of EDA and the results of hydrolysis are not easy to judge.

Considering the base line of every absorbance curve, they didn't share the same one. This causes a problem in comparison. This may because the accuracy of the UV-Vis device. The device in our lab is not sensitive enough to measure absorbance accurately at low levels. The minimum value which can be monitored should be larger than 0.05. Those values smaller than 0.05 are not reliable to tell any conclusions. While the data in every absorbance curve are mostly smaller than the minimum value. From the accuracy consideration, those small values should be seen as zero.

In summary, there is not strong clue to tell the effect of EDA treating. The only thing that can be sure was that EDA did cause something to happen on the fabrics.

This graph was illustrated by the first quick wash methanol solution. Although methanol is strong solvent for organic matter, one time quick wash was not enough to wash all remainder EDA off. So three times quick wash were operated, then the sum of their absorbance was used to draw a graph. The following Figure 4.5 was the sum of all absorbance value of three times quick wash solution.

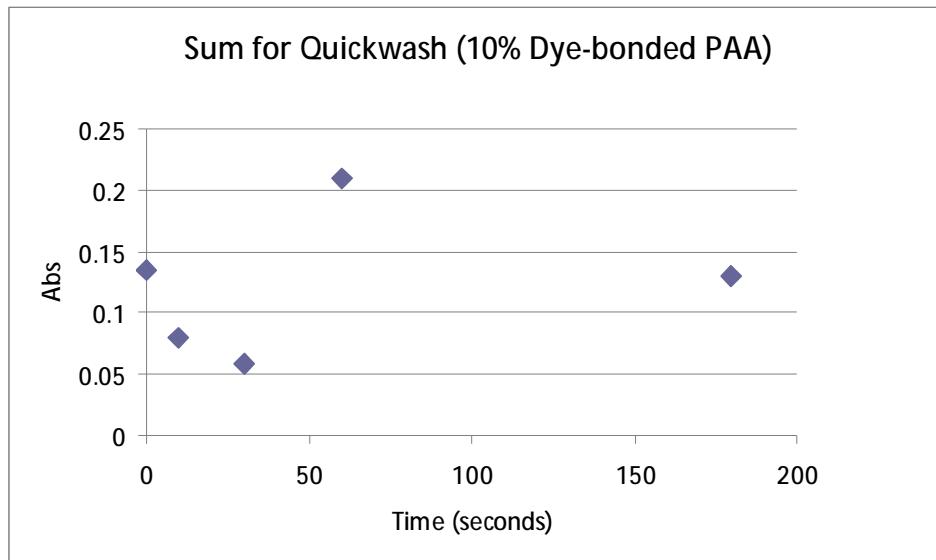


Figure 4.5 Sum of absorbance for three times quick washes on 10%DYE-BONDED PAA colored PET fabrics.

There is an interesting thing should be noticed, the sum of absorbance of control groups is even smaller than those one minute treated sample and 3 minutes treated samples. It's unusual because control group were none EDA treated samples, which were colored with DYE-BONDED PAA directly without EDA treating process. PET fabrics are known as the material hard to dye with this material. So this control group data set is seen as unusual.

2. 5% Dye-bonded PAA

Concentration of 5% EDA solution was also used to treated PET samples before getting colored.

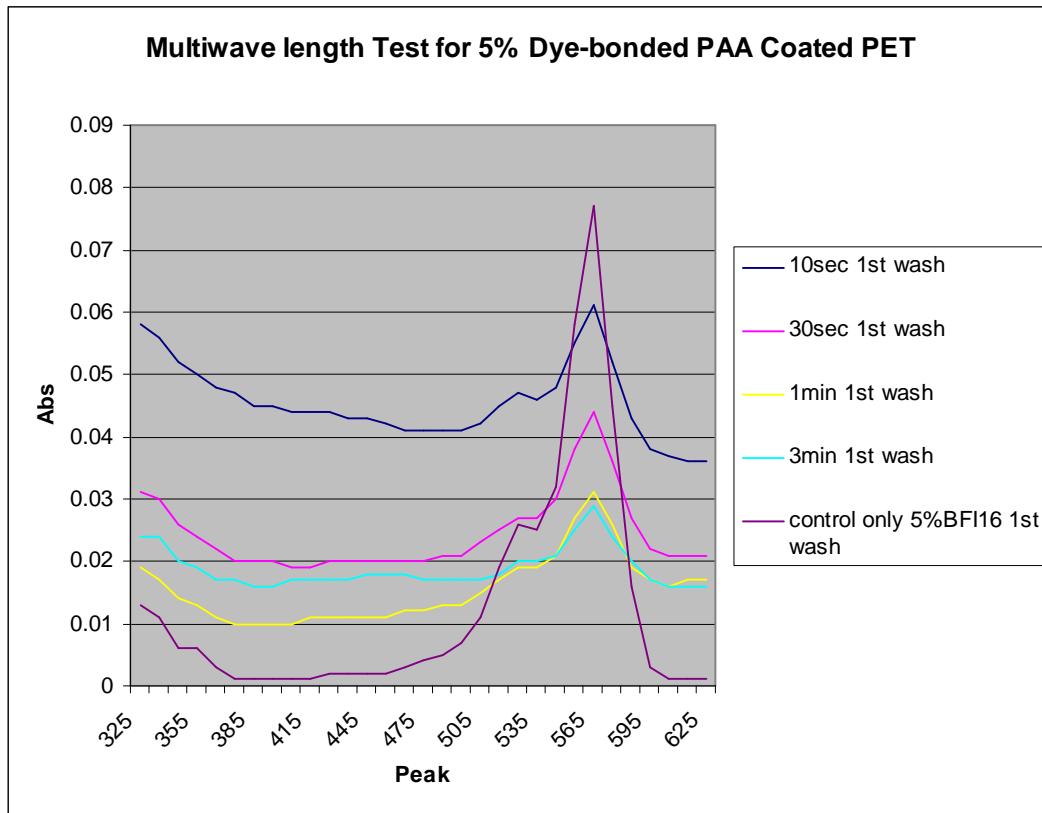


Figure 4.6 Absorbance of the first PET samples quick wash on 5%DYE-BONDED PAA colored PET fabrics.

From the spectra, it's easily to tell the peak is around 565nm. It's the same with Figure 4.4. So these curves also represent the absorbance of DYE-BONDED PAA. Concentration didn't change the wavelength where peak value showed up.

The peak value of four samples can be placed in this order: control

sample > 10 seconds group > 30 seconds group > 1 minute group > 3 minutes group. Compared with Figure 4.4, their peak values were placed with a different order. The only same thing is that the largest value was the same. It's hard to see any trend here, because there is no clear relationship between absorbance peak value and EDA treating time. As a result, the effect of EDA and the results of hydrolysis are not easy to judge.

Considering the base line of every absorbance curve, they didn't share the same one as well. The curves of 30 seconds group, 1 minute group, and 3 minutes group are fully below 0.05. Most data of control group and 10 seconds group are smaller than 0.05. These small values could be seen as zero as well. The difference between Figure 4.4 and Figure 4.6 build the conclusion that the accuracy of the UV-Vis device didn't fulfilled the sensitivity requirements.

In sum, there is no strong clue to tell the effect of EDA treating. The conclusion that can be sure was that EDA did cause something happened on the fabrics.

The following Figure 4.5 was the sum of all absorbance value of three times quick wash solution. All three times quick wash absorbance were added together to gain these sum.

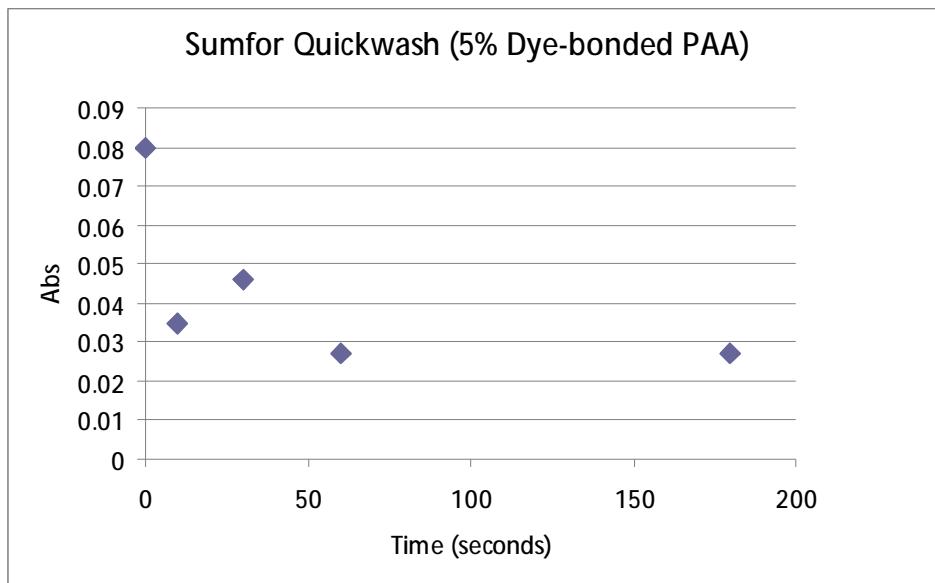


Figure 4.7 Sum of absorbance for three times quick washes on 5% dye-bonded polymer colored PET fabrics.

In this chart, control samples showed a normal performance here, it was larger than other four groups. Compared with figure 4.5, the sums of 1 minute group and 3 minutes are smaller than 10 seconds group. There is a trend here in Figure 4.7, control groups has the largest absorbance, with time increase, absorbance increase first, when it reaches a peak, then starts to decrease and keep on a value. If it's correct, this trend means time is an important parameter for EDA treating. Time played a positive role here. Short time advanced EDA treating, when it's over the peak value, time still helped a lot in EDA treating but the good performance kept the same. Longer time means more power and more resources, as a result, it's not valuable that spending such long time in EDA treating to gain a good performance.

From all four figures above, it's not easy to find any clue in the relationship between EDA treating and treating time. On the other hand, the test method was just quick wash that is not accurate enough because that there is no exact standard on leaching methods to follow. Any small difference in wash time could be the reason that causing no trend here. To make sure of the accuracy of tests, a standard leach test method is needed. And the device is another matter affecting the results of test.

4.4 Leach Test

The following Leach Tests were all followed by LAAMScience Leach Test Procedure.

There were some modifications to the LAAMScience Leach Test Procedure to ensure the absorbance difference was located in a proper range in order to make it easy to compare with conversion factor to judge whether the dye leaches or not.

The conversion factor is calculated with basic weight of material. Since the PET materials used in the experiment has basis weight of 24gsm, its conversion factor is basic weight divided by 24 equals to 1.

The additional information about LAAMScience Leach Test Procedure is that it was built by researchers from LAAMScience Inc.. They applied this procedure in testing their nylon product. This procedure shows a good performance in nylon product leaching test. Since PET is different from nylon when applied in grafting, this procedure might not fit for this research of PET grafting. As a result, some changes should be made to make the procedure fit for PET research.

4.4.1 Leach Test with Methanol

There were some changes here. To enlarge the value of absorbance difference, the volume of methanol solution has been decreased to 4ml, rather than 12ml which was specified in the procedure. When preparing samples treated with methanol, the water bath has been removed because the solvent effect of methanol is so strong that no water bath is needed. The washing time was reduced to 5 minutes. The remainder of the procedure was kept the same.

Table 4.1 Leach Test with Methnol following LAAM Science Procedure. The conversion factor nonwoven of Nylon is 1.4583, basic weight of nylon nonwoven is 35gsm; conversion factor of PET nonwoven is 1, basic weight of PET nonwoven is 24gsm.

Absorbance Difference							
Fabric	Vial No.	Sample No.	Abs at WL1(565nm)	Abs at WL2(720nm)	$\Delta\text{abs} = \text{WL1} - \text{WL2}$	divided by 1	baseline 0.0011
PET treated with 5% DYE-BONDED PAA	control	1	0.203	0.003	0.2	0.2	L
		2	0.214	0.007	0.207	0.207	L
	10 sec	1	0.187	0.021	0.166	0.166	L
		2	0.171	0.01	0.161	0.161	L
	30 sec	1	0.174	0.011	0.163	0.163	L
		2	0.139	0.003	0.136	0.136	L
	60 sec	1	0.239	0.006	0.233	0.233	L
		2	0.105	0.007	0.098	0.098	L
	180 sec	1	0.178	0.003	0.175	0.175	L
		2	0.219	0.006	0.213	0.213	L
PET treated with 10% DYE-BONDED PAA	control	1	0.715	-0.001	0.716	0.716	L
		2	0.655	0.004	0.651	0.651	L
	10 sec	1	0.41	0.008	0.402	0.402	L
		2	0.47	0.002	0.468	0.468	L
	30 sec	1	0.502	-0.001	0.503	0.503	L
		2	0.591	-0.001	0.592	0.592	L
	60 sec	1	0.463	-0.002	0.465	0.465	L
		2	0.649	0	0.649	0.649	L
	180 sec	1	0.622	0	0.622	0.622	L
		2	0.786	0.001	0.785	0.785	L

In Table 4.1, control groups mean those PET samples were colored with 5% or 10% dye-bonded PAA solution in water without treating with amine. The vial numbers show the treating time of amine modification. For example, 10 sec means

PET samples were treated with EDA solution for 10 seconds, and then colored with dye-bonded PAA solution.

To judge whether they pass the leaching test or not, the result of “divided by 1” of each group should be compared with 0.0011. Only if it’s smaller than 0.0011, does it pass this leaching test. The results showed that, no samples pass the leaching test. The concentration was too high to pass it.

As mentioned before, the device in our lab was not sensitive enough to measure values smaller than 0.05. To cover this disadvantage of device, concentration of each samples was increased to a large range that device is able to measure. That’s the purpose of doing such modification in the procedure.

Comparing the 10% dye-bonded PAA colored samples to the 5% dye-bonded PAA colored samples, the absorbance of the prior group was larger, which means there was more color leach off. The reason would be that more dye-bonded polymer was applied to color samples, and the reactive sites on PET fabrics are limited so that not all dye-bonded polymer could be attached on the surface. For both groups, this situation would be likely to happen because the chemical reaction between EDA and PET are at so slight level that not enough reactive sites were built for grafting.

The data of 5% group shows that control group has the highest absorbance, which means there is the most amount of color agent in its wash-off solution. In another word, PET fabrics in control group had the most serious leaching issue. This performance proved that for PET fabrics, dye-bonded polymer is hard to attach to PET without help from surface modification.

In addition, all treated samples in both groups had smaller absorbance than control groups, which indicate that the modification by EDA did have some effect to increase the dying property of polyester. Modification by EDA increases the amount of DYE-BONDED PAA adhering to the surface of PET fabrics.

These 5% dye-bonded PAA colored data showed that the 30 seconds group performed best because it had the smallest amount of leachate absorbance. The 10 seconds group and 1 minute group had similar performance, which means their modification reaches to levels that are similar to each other. The 3 minute group had an absorbance similar to the control group, which means modification with 3 minutes treating time didn't help much on grafting. These indicated that there is a best point in treating time to achieve the best result, and this best point is around 30 seconds. Longer time didn't perform well.

Those 10% dye-bonded PAA colored data shared the same performance of control group with those 5% dye-bonded PAA colored data. It's the largest absorbance as well. And the 3 minutes group also showed the worst performance in the treated samples. The absorbance of 3 minutes group is even larger than control group. 10 seconds groups showed the best performance here, while the other two groups didn't have large differences in absorbance. These data indicated that longer treating time didn't refer to the best modification, and there is also a best point here, around 10 seconds.

4.4.2 Leach Test with HBSS

To make a comparison, the unmodified leaching tests were operated with HBSS as described by the LAAMScience procedure.

Table 4.2 Leach Test with HBSS following LAAMScience Procedure. The conversion factor nonwoven of Nylon is 1.4583, basic weight of nylon nonwoven is 35gsm; conversion factor of PET nonwoven is 1, basic weight of PET nonwoven is 24gsm.

Absorbance Difference							
Fabric	Vial No.	Sample No.	Abs at WL1(565nm)	WL2(720nm)	$\Delta\text{abs} = \text{WL1} - \text{WL2}$	divided by 1	baseline 0.0011
PET treated with 5% DYE-BONDE D PAA	control	1	0.02	0.002	0.018	0.018	L
		2	0.028	0.003	0.025	0.025	L
	10 sec	1	0.053	0.004	0.049	0.049	L
		2	0.033	0.004	0.029	0.029	L
	30 sec	1	0.028	0.003	0.025	0.025	L
		2	0.026	0.003	0.023	0.023	L
	60 sec	1	0.027	0.011	0.016	0.016	L
		2	0.029	0.006	0.023	0.023	L
	180 sec	1	0.024	0.007	0.017	0.017	L
		2	0.027	0.008	0.019	0.019	L
PET treated with 10% DYE-BONDE D PAA	control	1	0.041	0.009	0.032	0.032	L
		2	0.057	0.018	0.039	0.039	L
	10 sec	1	0.048	0.004	0.044	0.044	L
		2	0.082	0.021	0.061	0.061	L
	30 sec	1	0.068	0.01	0.058	0.058	L
		2	0.048	0.008	0.04	0.04	L
	60 sec	1	0.039	0.01	0.029	0.029	L
		2	0.028	0.008	0.02	0.02	L
	180 sec	1	0.059	0.006	0.053	0.053	L
		2	0.032	0.004	0.028	0.028	L

The result of “divided by 1” was also compared with 0.001 to judge the test results. And it indicates that there are no samples that pass this leaching test.

Every absorbance difference is larger than 0.0011. From the perspective of LAAMScience Leaching Test, dye-bonded polymer was not bonded well to the fabric surface. But the interesting thing is that absorbance value of control groups are even smaller than treated samples.

Compared 10% dye-bonded PAA colored samples and 5% dye-bonded PAA colored samples, prior group have more color leaching off. This situation is the same with the discussion in section 4.4.1.

The data of 5% group shows that all data from treated samples illustrated a decreasing trend. It means more color leaches off with time increases. But the control group shows a smaller absorbance value than 10 seconds and 30 seconds group, so combined all five data, it's hard to get any conclusion here.

When considering the 10% dye-bonded polymer colored data, the situation was almost the same. The difference was that 1 minute group showed the smallest absorbance. Without considering control group and 1 minute group, the other shows a trend that absorbance decreases with time increase.

4.4.3 Absorbance Difference

To compare those two-group data easily, the following Figure 4.8 was illustrated to show the relationship.

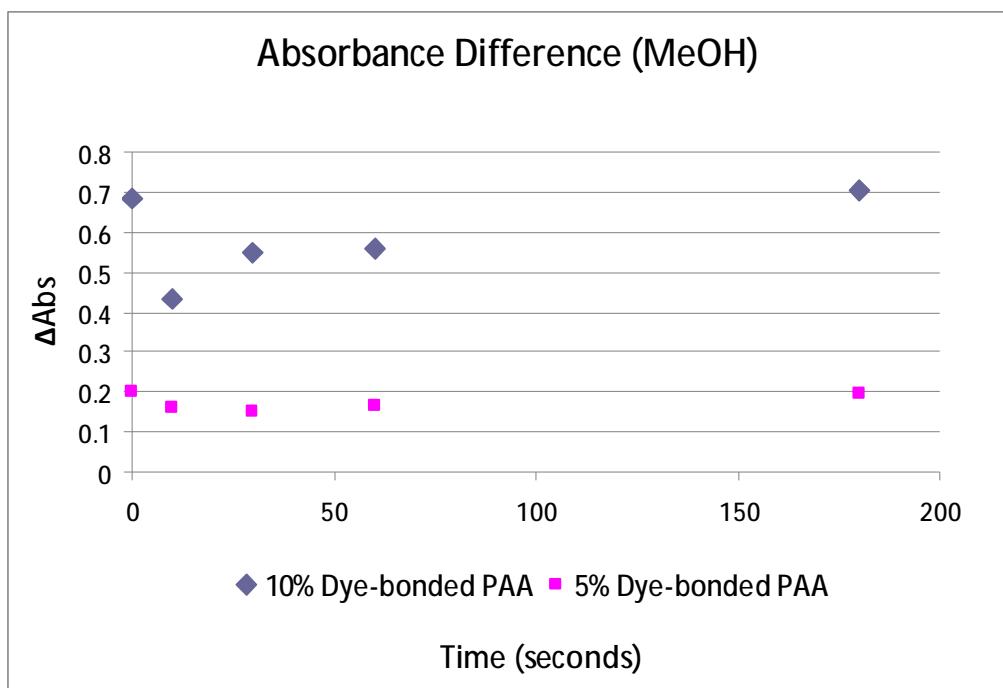


Figure 4.8 Absorbance Difference between 565nm and 720nm by solvent of Methanol

If the dye-bonded PAA is attached to PET fabric, then, comparing the 10% dye-bonded PAA colored one to the 5% dye-bonded PAA colored one, and representing their absorbance value as A and B, respectively, their absorbance should follow this mathematic function: $\frac{1}{2} A > B$.

The larger the difference between them, the more dye-bonded polymer is attached to the 5% dye-bonded PAA group. This is because once all of the amino graft sites are filled, any additional dye-bonded PAA cannot graft and will wash off.

Four data from each treated group followed this function. This indicated that there was dye-bonded PAA attached to the PET fabrics.

5% concentration of dye-bonded polymer was able to indicate a difference on absorbance, as a result, this smaller concentration could be enough to finish the following research. And because of the high cost of dye-bonded polymer, lower concentration would be preferred.

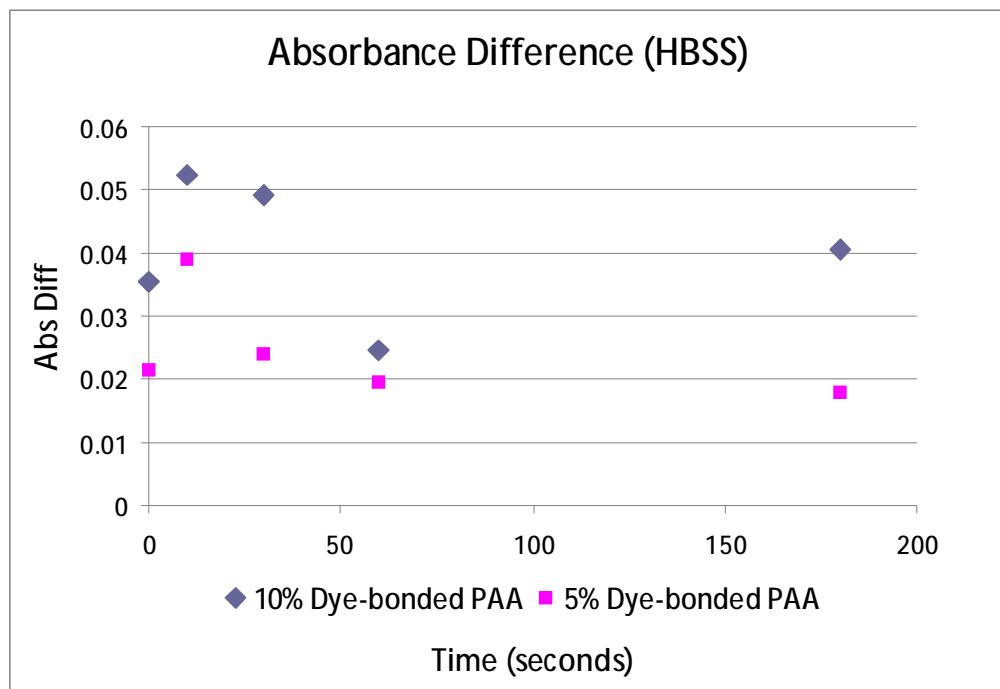


Figure 4.9 Absorbance Difference between 565nm and 720nm by solvent of HBSS

Figure 4.9 illustrates the comparison between those two groups exactly following LAAMScience Procedure. Without considering the control samples, none of rest treated samples obey the inequality of $1/2A > B$.

4.5 Optimization

As EDA improved dying of PET, no matter what kind of adherence happened on PET fibers, we would like to apply it in the antimicrobial nonwoven material production. Based on the prior work, the concentration of EDA was kept at 3% by weight in water. The results showed that temperature of 75°C was enough to provide a good performance when EDA was used to treat the fabric, and the proper treating time was around 10 seconds. With this information, an optimization was needed to finish to build a mathematical function to find out the best point in treating conditions. A statistical software package JMP was used to generate the experiment design.

Table 4.2 Experiment Design by JMP

Optimizaiton		
Temperature(°C)	Concentration (%)	Time (second)
70	1	5
	1	15
	3	5
	5	5
	5	10
	5	15
75	1	10
	3	10
	3	10
	3	10
	3	10
	3	10
	3	15
	5	5
80	1	5
	1	15
	3	5
	5	5
	5	10
	5	15

Table 4.2 was the result JMP offered to us. It gives a series combination of concentration, temperature and time to find out the optimization point with data of all combinations. A central composite design with five center points was selected to study, temperature (70° C , 90° C), concentration (1%, 5%), time (5,15), and an additional factors of dye-bonded PAA (5%,10%). The output y is the absorbance difference.

4.5.1 Data for optimization with EDA

Table 4.3 Data for optimization of EDA

Diff Absorbance				
Temp (°C)	Conc (%)	Time (seconds)	5% DYE-BONDED PAA	10% DYE-BONDED PAA
70	1	5	0.0465	0.0455
	1	15	0.043	0.042
	3	5	0.05	0.044
	5	5	0.039	0.05
	5	10	0.05	0.034
	5	15	0.0405	0.054
75	1	10	0.069	0.0285
	3	10	0.022	0.0465
	3	10	0.0535	0.024
	3	10	0.014	0.06
	3	10	0.07	0.043
	3	10	0.0565	0.021
80	3	15	0.0375	0.0335
	5	5	0.0565	0.1065
	1	5	0.0665	0.0415
	1	15	0.0665	0.065
	3	5	0.0805	0.0345
	5	5	0.0565	0.083
	5	10	0.079	0.071
	5	15	0.0605	0.0525

Data of optimization were recorded in Table 4.3. Temp stands for the temperature used in EDA modification. Conc stands for the concentration of EDA water solution. Time means the treating time of EDA modification. The remaining two columns record the data of final absorbance difference for those samples colored with 5% and 10% dye-bonded PAA.

There is no control group in optimization section. All these data were input into computer and analyzed with JMP.

4.5.2 Statistical Analysis for combined 5&10% dye-bonded PAA

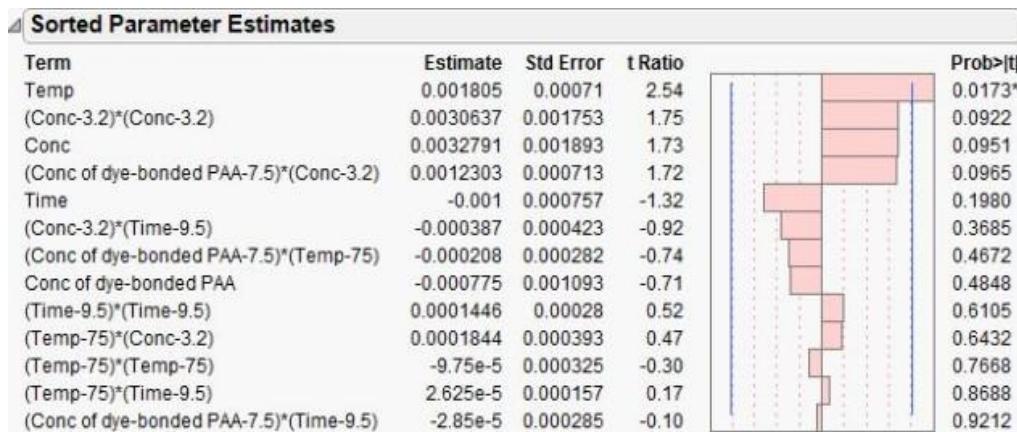


Figure 4.10 Sorted Parameter Estimates for optimization function of EDA

From the sorted parameter estimates, it's easy to tell that temperature has the most effect, the other parameters including time and concentration don't have so much effect.

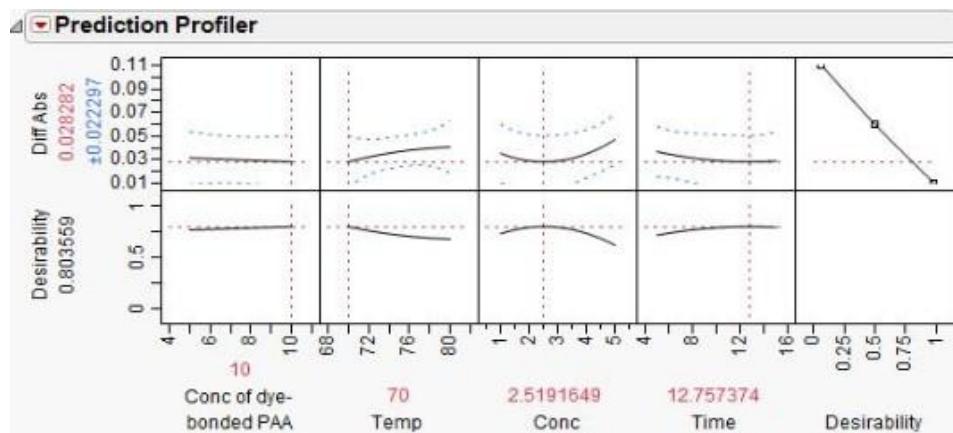


Figure 4.11 Desirability Function for EDA

By desirability functions, JMP provided a maximized desirability on the minimization in absorbance. The optimized reaction situations were: temperature of 70°C, EDA concentration of 2.5%, and treating time of 13 seconds.

4.6 Improvement with Hexamethylenediamine

EDA showed a weak effect on PET fabric modification. To intensify this hydrolysis, hexamethylenediamine was used instead of EDA to finish this modification. Although these two compounds are both amines, hexamethylenediamine has longer chain than EDA, which makes it possible to modify in higher temperature.

To simplify the research procedures, hexamethylenediamine was used in the optimization of EDA, except that the temperatures were replaced with 70°C, 80°C and 90°C in hexamethylenediamine treating process. Because hexamethylenediamine has higher boiling point than EDA, higher temperature was also used. The reason is that hexamethylenediamine won't evaporate while treated with higher temperature. Eight higher temperatures, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C and 170°C, were also applied. For these eight high temperatures, concentration was chosen to be 3% in weight, and treating time was chosen to be 5 seconds, which was the best performed combination in EDA optimization.

4.6.1 Data for optimization with hexamethylenediamine

The hexamethylenediamine modification experiment was done following the experiment design for EDA except the temperature of modification was changed as 70°C, 80°C and 90°C. All experiment data were reported in following table 4.4.

Table 4.4 Data of optimization combinations

Temp (°C)	Conc (%)	Time (seconds)	Diff Absorbance	
			5% DYE-BONDED PAA	
			#1	#2
room	0	0	0.0128	0.0097
70	1	5	0.013	0.0128
	1	15	0.0132	0.0134
	3	5	0.0149	0.0139
	5	5	0.0132	0.0121
	5	10	0.0118	0.0128
80	5	15	0.0154	0.0136
	1	10	0.017	0.0121
	3	10	0.0126	0.0147
	3	10	0.0119	0.0132
	3	10	0.0122	0.0143
90	3	10	0.0129	0.0145
	3	10	0.0144	0.0169
	3	15	0.0127	0.0136
	5	5	0.0099	0.0109
	1	5	0.0093	0.0112
	1	15	0.0129	0.0118
	3	5	0.0081	0.0115
	5	5	0.0111	0.0111
	5	10	0.0083	0.0106
	5	15	0.0096	0.0112

Data of optimization were recorded in Table 4.4. Temp stands for the

temperature used in hexamethylenediamine modification. Conc stands for the concentration of EDA water solution. Time means the treating time of EDA modification. The remaining two columns record the data of final absorbance difference for those samples colored with 5% dye-bonded PAA.

The groups treated in room temperature are set as control ones, which were treated without amines but only coated by 5% dye-bonded PAA. Optimization analysis was done with the average of the two samples for each experimental run.

The difference between these two data from control group is too big, the reason causing this situation could be the location of sample cutting. No.1 control group is more reliable because it close to previous control group data (in Table 4.1 and Table 4.2) was 0.02 and 0.018.

By comparison with control group, 90°C group represents the best performance. There is only one sample in 90°C group showing larger absorbance value than control group. In another words, PET nonwovens treated with hexamethylenediamine at 90°C temperature makes the dye-bonded polymer attach to the surface of fabric.

By the way, most samples from 70°C and 80°C groups have larger absorbance value than control groups.

On the other hand, higher temperature was applied in modification to see what would happen in the temperature above 100°C. The experiment was design with fixed concentration and treating time (3% and 5 sec), all combinations were

shown in Table 4.5. Since these two parameters were fixed, Table 4.5 showed the relationship between temperature and absorbance difference.

Table 4.5 Hexamethylenediamine modification with higher temperature

Diff Absorbance					
Temp (°C)	Conc (%)	Time (seconds)	5% dye-bonded PAA		
			#1	#2	
70	3	5	0.0149	0.0139	
90	3	5	0.0081	0.0115	
100	3	5	0.0208	0.0215	
110	3	5	0.0186	0.0183	
120	3	5	0.0163	0.0142	
130	3	5	0.0158	0.0102	
140	3	5	0.0138	0.0151	
150	3	5	0.0189	0.021	
160	3	5	0.0196	0.0196	
170	3	5	0.0099	0.0133	

To make it easy for comparison, results from 70°C and 90°C group in Table 4.4 were put in Table 4.5 as well. From the results of higher temperature modification, higher temperature didn't help a lot here. Their results were not good as 90°C group. There is one thing need to notice that all these eight higher temperatures are higher than 100°C, the boiling point of water. If the reaction of hexamethylenediamine is catalyzed by water, then without water, the reaction should be slower. When temperature of oven over than 100°C, water would evaporate first, then there is no water catalyze the hexamethylenediamine reaction with PET. These would induce the high leaching of color in absorbance measurement.

4.6.2 JMP Analysis

In this section of JMP analysis, two different models were built. One model was built with the data from Table 4.4. The other model was built only with data from Table 4.5. The following figure 4.12 is the analysis result from Table 4.5.

Sorted Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
(Temp-124)*(Temp-124)	-5.977e-7	3.127e-7	-1.91	0.0729
Temp	-2.792e-6	9.401e-6	-0.30	0.7700

Figure 4.12 Sorted Parameter Estimates for optimization function of hexamethylenediamine with higher temperature (Table 4.5)

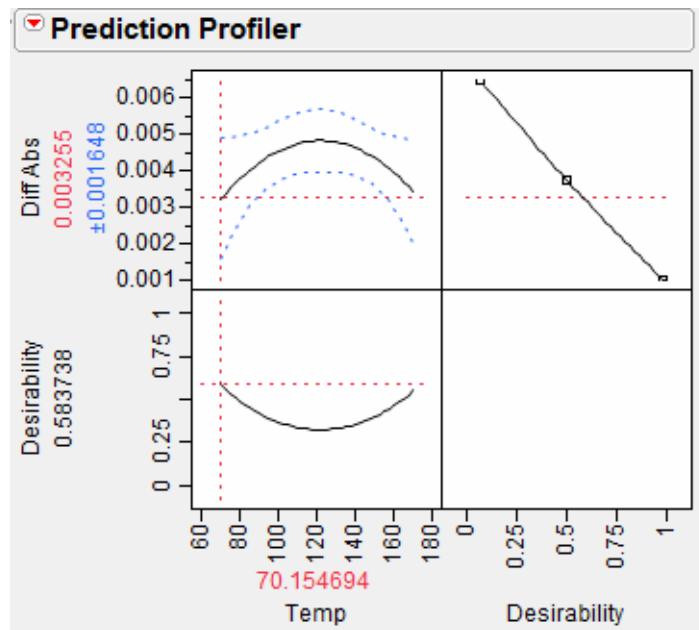


Figure 4.13 Desirability Function for hexamethylenediamine with higher temperature

There is no significant parameter different from others in the with higher temperature model. With desirability function building, the optimized temperature was 70 °C, while this analysis didn't obey the experiment result because experiment result showed that 90 °C provided the best performance. The worst temperature

given by analysis was 124 °C, while experiment showed the worst performance appeared around 100 °C. It seems that JMP analysis missed something here. As a result, another way was used in next part 4.6.3.

On the other hand, Figure 4.14 showed the analysis for Table 4.4.

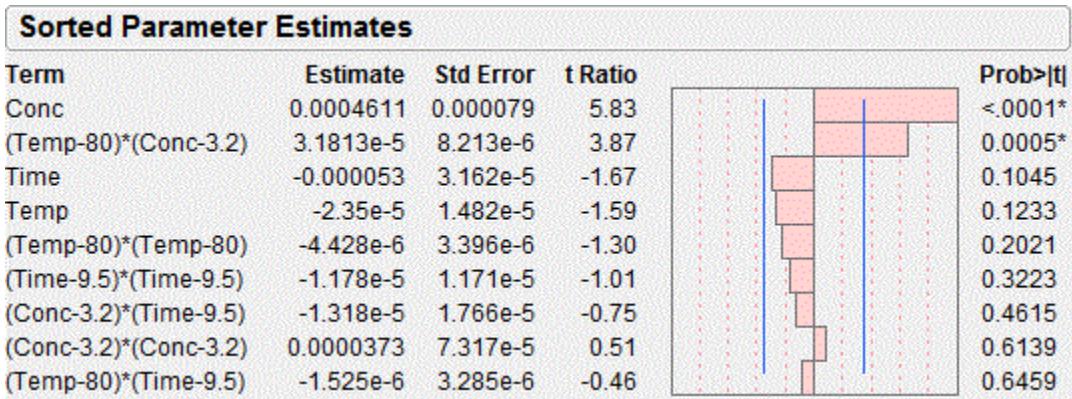


Figure 4.14 Sorted Parameter Estimates for optimization function of hexamethylenediamine (Table 4.4)

As the analysis showed, concentration has significant effect on absorbance difference. Parameter of treating and temperature didn't have too much effect on absorbance difference.

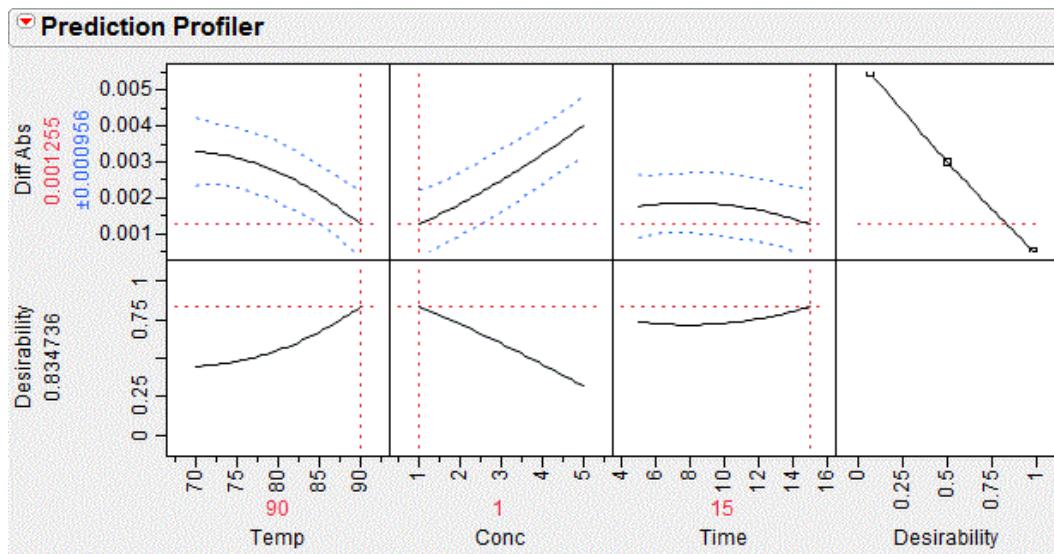


Figure 4.15 Desirability Function for hexamethylenediamine

When ignoring the higher temperature treatment, JMP analysis showed that temperature was the effective parameter. By building the desirability functions, JMP provided a maximized desirability on the minimization in absorbance. The optimized reaction situations were: temperature of 90°C, hexamethylenediamine concentration of 1%, and treating time of 15 seconds.

4.6.3 Analysis about Table 4.5 in Excel

Since JMP analysis about Table 4.5 didn't explain experimental data well, all data were draw in a scatter plot with Excel to find any explanation.

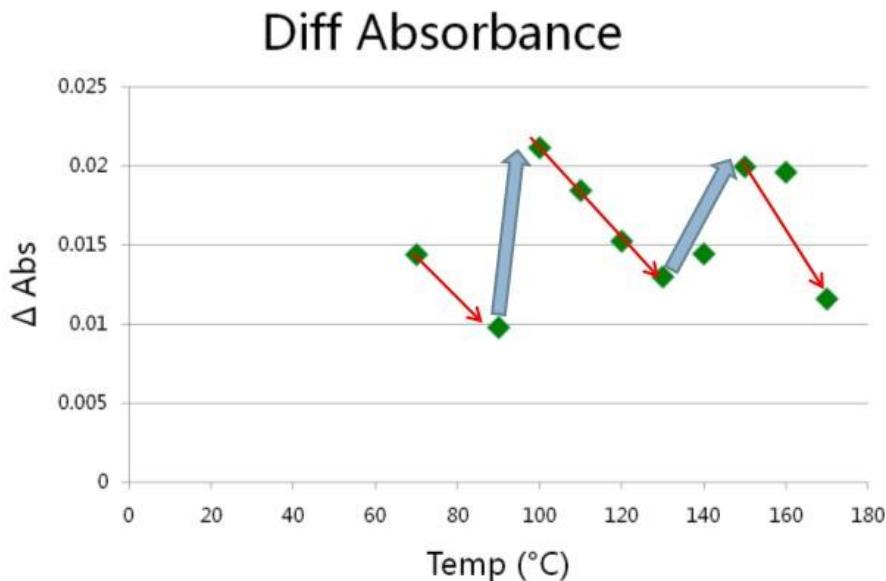


Figure 4.16 Analyses about Table 4.5

It seems that there is no trend until separate them as three parts. There comes with one assumption. When temperature below 100°C, temperature is a parameter that speeds the reaction, so 90°C works better than 70°C. As temperature goes higher, water starts to evaporate. Considering water may catalyze the reaction of hexamethylenediamine and PET, there is a skip that

absorbance difference increases. At this time, temperature still speeds the reaction, as a result, absorbance difference decreases. With temperature going up to around 130°C, there is another skip making absorbance difference return to high value. The possible explanation is that high temperature cause hexamethylenediamine start to evaporate (boiling point is 204°C). So the decrease of hexamethylenediamine makes absorbance difference increase. After this step, temperature still has positive effect to reaction. More work is needed to prove this model.

4.6.4 Leach Test with HBSS

In order to make a comparison and see what exact happen with HBSS applied leach test, HBSS was applied in leach test as well. Leach test was repeated with HBSS exactly following the LAAMScience procedure. The following Table 4.6 reports the data of leach test with HBSS.

Table 4.6 Leach Test with HBSS for optimization combination

Diff Absorbance				
Temp (°C)	Conc (%)	Time (seconds)	5% dye-bonded PAA	
			#1	#2
room	0	0	0.0120	0.0005
70	1	5	0.0034	0.0041
	1	15	0.0023	0.0034
	3	5	0.0042	0.0027
	5	5	0.0047	0.0044
	5	10	0.0037	0.0042
	5	15	0.0038	0.0040
80	1	10	0.0041	0.0041
	3	10	0.0027	0.0029
	3	10	0.0044	0.0034
	3	10	0.0040	0.0036
	3	10	0.0047	0.0038
	3	10	0.0049	0.0032
	3	15	0.0035	0.0037
	5	5	0.0044	0.0050
90	1	5	0.0011	0.0009
	1	15	0.0017	0.0009
	3	5	0.0049	0.0032
	5	5	0.0052	0.0051
	5	10	0.0052	0.0047
	5	15	0.0040	0.0035

It shown that the control group has the absorbance around of 0.01. The other three groups show that most samples have smaller absorbance than control group. The biggest absorbance of modified sample was 0.0052, which was almost half value of control group. By the comparison with control groups, all modified samples showed good performance of grafting.

In addition, higher temperature was applied in modification. The following shows the performance of it.

Table 4.7 Leach Test with HBSS for Higher Temperature Modification with Hexamethylenediamine

Diff Absorbance				
Temp (°C)	Conc (%)	Time (seconds)	5% DYE-BONDED PAA	
			#1	#2
100	3	5	0.0052	0.0044
110	3	5	0.0055	0.0043
120	3	5	0.0028	0.0025
130	3	5	0.0061	0.0063
140	3	5	0.0053	0.0059
150	3	5	0.0043	0.0036
160	3	5	0.0051	0.0033
170	3	5	0.0015	0.0046

Higher temperature did not show better performance. Most data were even bigger than those reported in Table 4.6. And all data in Table 4.7 were bigger than the one of control group. It means that higher temperature works, but is not an improvement.

Comparing the HBSS leach test and the methanol leach test, we can see that methanol has better performance. It shows the effect of modification temperature

clearly, while HBSS just showed that modification of amines was effective. As a result, it's indicated that methanol is the suitable solvent for the leach test of modified PET fabric.

5. Conclusion

Three different chemicals were applied in PET fabric modification. They are sodium hydroxide, ethylenediamine and hexamethylenediamine. They showed different effects on surface modification.

Sodium hydroxide was used to hydrolyze PET. It was found to be able to degrade PET successfully. But it needs too much time to finish degradation. In addition, sodium hydroxide is such a strong base that it could harm workers if it splashed on them when applied in production. From the safety consideration, sodium hydroxide was given up, and amines were chosen instead. On the other hand, weight loss of PET by sodium hydroxide modification didn't show significant evidence that it was enough degree of modification to achieve the next step of grafting dye-bonded polymer.

Amines have been applied in PET recycling because of its strong degradation on PET. Prior researchers have proved that the effective work about improving the hydrophilicity of PET could be achieved in 10 minutes and room temperature. This speed and temperature requirements are profitable for industry production.

Ethylenediamine is more effective than sodium hydroxide to modify PET fabric. After modification, poly(acrylic acid) bound dyes can be grafted. Comparison between EDA treated and non-treated fabrics showed that EDA modification increase the ease of grafting to PET fabric, which was proved by the absorbance reduction in the leaching test. Treated samples had smaller

absorbance values than non-treated samples. Modification temperature was around 75°C to achieve the treatment. Longer treating time was proved not to be any more effective than shorter ones. The proper treating was found to be around 15 to 30 seconds.

Although ethylenediamine is effective in PET modification, the reaction degree is slight. To intensify the modification, hexamethylenediamine was used instead of ethylenediamine. Compared with ethylenediamine, hexamethylenediamine maintains its reactivity at higher temperature.

PET fabric modified with hexamethylenediamine was also capable of being modified by polymer bound dye. The experimental results confirmed the assumption of hexamethylenediamine working more effectively than ehtylenediamine. From the absorbance gained from UV-Vis test, the 90°C treating temperature performed best, only one sample from this group had larger absorbance than non-modified fabric in UV-Vis test. Although 90°C represented good performance, the other two temperatures still had excessive leaching. In addition, the results from leach test with HBSS showed that there is no serious leaching issue. These appeared to lead to one possible explanation. The LAAMScience leach test procedure does not fit for PET fabrics. Methanol is the better solvent than HBSS to operate the leach test.

Optimization of treating situations were designed with JMP. And by the analysis result of JMP, the best combination for ethylenediamine was 70°C of treating temperature, 2.5% of amine solution concentration and 12.75 seconds of treating time; and the best combination for hexamethylenediamine was 90°C of

treating temperature, 1% of amine solution concentration and 15 seconds of treating time.

While applying the leaching test procedure from LAAM Science, there were many operations not suitable for PET fabrics. There were some changes have been done to improve the procedure and make it matching test of PET fabric. The new procedure used reduced time and eliminated the heating step because of the strong solvency of methanol. The original test required 60 minutes and 37°C for HBSS. After modification, only 5 minutes and room temperature were enough for methanol.

6. Recommendation for Further Work

The first thing that needs to be improved is how to operate the leach test. The one from LAAM Science was designed for nylon fabric, which is easier to modify with chemical grafting. So, there would be some steps not suitable for PET fabrics. In this research, some changes have been done in the old procedure according to one target, which is to make absorbance measurable by the device. But the disadvantage is that standards in the modified procedure are not precise enough. For example, the wash time was 5 minutes with methanol. Is it enough or too long? It should be studied.

Although ethylenediamine and hexamethylenediamine were proved to be effective on PET modification, they were expected to covalently attach to PET to the fiber surface. The results of leaching test with both HBSS and methanol showed that the new compound created from the modification was able to be removed in methanol but not in water. As a result, this is another thing that should be figured out. What exact chemical reactions happened here? What is the new compound? This newly generated compound should adhere to PET fibers without chemical bonds. As a result, this modification would inevitably fade away. So here comes with one question, how long will this modification last? By solving these questions, the lifetime of production can be decided.

The last suggestion is about safety. As we know, ethylenediamine and hexamethylenediamine are not safe chemicals. Ethylenediamine exposure can cause the skin to become irritated. While hexamethylenediamine is moderately toxic, it will also cause burns and severe irritation. So researchers should pay more attention on safety consideration. To cover this disadvantage, there are two ways, one is to control the amines volume, and the other is finding other safer chemicals.

7. References

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