TOWARDS UNDERSTANDING POLYETHYLENE TEREPHTHALATE HYDROLYSIS AND AMINOLYSIS IN TIRE CORDS

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Dedicated to My Family...

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ABSTRACT

TOWARDS UNDERSTANDING POLYETHYLENE TEREPHTHALATE HYDROLYSIS AND AMINOLYSIS IN TIRE CORDS

Polyethylene Terephthalate (PET) is the most common thermoplastic in the industry. It is synthesized *via* polycondensation reaction between ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT). PET has variety of application areas and it is widely used in tire industry due to its high physical strength and chemical resistance. However, it is subjected to different types of degradations during synthesis and processing. PET tire cords suffer especially from hydrolytic degradation during vulcanization where green tire is turned into standard tire with sulfur crosslinking with the help of accelerators. The degradation of PET is catalyzed by the released tertiary amines from the accelerators as a result of thermal decomposition. Quaternization was chosen as a method to address the problem which should block the tertiary amines' catalytic activities. TMP was chosen as an agent of methylation/quaternization. TMP was investigated for its methylation ability and chemical properties. Results show that both alkyl and aromatic amines can be quaternized/methylated by TMP. Then the study was focused to poly-2-vinyl pyridine containing latex (VP-latex), a coating used as an adhesion promotor in PET tire cords, which contain pyridine moiety that can potentially react with the TMP as a side reaction. First methylation of 2-vinyl pyridine units in VP-latex was investigated, then, its involvement in hydrolytic degradation was investigated *via* degradation studies.The results showed that VP-latex was not catalyzing the hydrolytic degradation of PET and it was inert to TMP.

ÖZET

LASTİK KORDLARDAKİ POLİETİLEN TEREFTALAT HİDROLİZİNİN VE AMİNOLİZİNİN ANLAŞILMASINA DOĞRU

Polietilen tereftalat endüstride en yaygın kullanılan termoplastik polimerdir. PET, etilen glikolün tereftalik asit ya da dimetil tereftalat ile olan polikondanzasyon tepkimesiyle sentezlenir. PET'in çeşitli uygulama alanları vardır. Yüksek fiziksel güç ve kimyasal direnç sebebiyle lastik endüstrisinde yaygın olarak kulanılır. Fakat, işlenmesi ve sentezi sırasında çeşitli bozulmalara maruz kalır. Ham lastiğin hızlandırıcılar yardımı ile sülfürün çapraz bağlanarak standart lastiğe dönüştürüldüğü pişirme sırasında PET lastik kordları özellikle hidrolitik bozunmaya uğrarlar. Bu bozunma, hızlandırıcıların ısıl bozunması sonucu serbest kalan tersiyer aminler ile katalize edilmektedir. Kuaternleşme üçüncül aminlerin katalitik aktivite sorunun çözmek için yöntem olarak seçildi. TMP bir metilleme/kuaternleşme ajanı olarak seçildi. TMP'nin metilleme kabiliyeti ve kimyasal özellikleri araştırılmıştır.Sonrasında PET lastik kordlarında yapışkanlık arttırıcı bir kaplama olan ve TMP ile istenmeye yan reaksiyon verebilecek poli-2-vinil piridin içeren lateks (VP-lateks) ile çalışmalar yapıdı. VP-lateks içindeki 2-vinil pridin ünitelerinin metillenmesi ve PET hidrolitik degradasyona etkisi araştırılmıştır

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv
ABSTRACT v
ÖZET vi
LIST OF FIGURES ix
LIST OF TABLES xi
LIST OF ACRONYMS/ABBREVIATIONS xii
1. INTRODUCTION 1
1.1. Historical and Economical Background 1
1.2. Properties and Application Areas 2
1.2.1. Physical and Chemical Properties 2
1.2.2. Application Areas 3
1.3. Synthesis of Polyethyene Terephthalate 4
1.3.1. Melt Polymerization 4
1.3.2. Solid State Polymerization 7
1.4. Polyethylene Terephthalate Degradation 8
1.5. Tire Application of PET Fibers and Aminolysis 10
2. AIM OF THE STUDY 17
3. EXPERIMENTAL 18
3.1. Methylation of Tertiary Amines 18
3.1.1. 3.1.1. Synthesis of N,N-diethyl-N-methylethanaminium and its counterion 18
3.1.2. 3.1.2. Synthesis of 1-methylpyridin-1-ium and its counterion . . 18
3.1.3. 3.1.3. Methylation of 2-vinyl pyridine unit in VP-latex 18
3.2. Degradation Experimentation of PET 19
3.2.1. Degradation of PET in Melt Polymerization Set-up 19
3.2.2. Degradation of PET in Extruder System 19
3.3. Gel Permeation Chromatography (GPC) Analysis 20
3.4. Intrinsic Viscosity (IV) Analysis 20
3.5. Carboxylic End Group (CEG) Analysis 20

4. RESULTS AND DISCUSSION 21
4.1. Methylation Studies Using TMP 21
4.2. The Potential Effect of 2-VP Latex on PET Degradation 25
4.3. Methylation Studies of 2-VP Latex with TMP 29
5. CONCLUSION 32
6. FUTURE WORK 33
REFERENCES 34

LIST OF FIGURES

Figure 1.1. Global annual demand of PET from 1986 to 2012. 2

Figure 1.2. Repeating Unit of Polyethylene Terephthalate. 2

Figure 1.3. Preparation of bis-(2-hydroxyethyl) terephthalate (BHET) by either Esterification or Transesterification. 5

Figure 1.4. Polycondensation of BHET. 6

Figure 1.5. Cyclic Reaarragement Intermediate. 8

Figure 1.6. Reactions of Vinyl Ester End Group and AA Formation. 9

Figure 1.7. Cyclic Reaarragement of 2-hydroxyethyl End Group and AA Formation. 9

Figure 1.8. Hydrolytic Degradation. 10

Figure 1.9. Mechanism of Thermo-Oxidative Degradation. 11

Figure 1.10. Textile Cord and Body Ply Preparation. 12

Figure 1.11. Curing (Vulcanization) Process. 12

Figure 1.12. Network Formation. 13

Figure 1.13. Reaction Mechanism of Rubber Curing with Sulfenamide. 14

Figure 4.1. Mechanism of Hofmann Elimination. 21

Figure 4.2. ^{1}H-NMR Spectrum of Triethylamine ($CDCl_3$). 22

Figure 4.3. ^{1}H-NMR Spectrum of N,N-Diethyl-N-Methylethanaminium and a Counterion (DMSO-d_6). 22

Figure 4.4. ^{1}H-NMR Spectrum of Pyridine ($CDCl_3$). 23

Figure 4.5. ^{1}H-NMR Spectrum of Synthesis of 1-Methyl Pyridin-1-ium and a Counterion (DMSO-d_6). 23

Figure 4.6. TGA Spectrum of TMP. 24

Figure 4.7. Repeating Unit of VP-Latex. 25

Figure 4.8. Schematic Representation of Degradation Study. 26

Figure 4.9. ^{1}H-NMR Spectrum of VP-latex (Toluene-d_8). 30

Figure 4.10. ^{1}H-NMR Spectrum of Precipitate (Toluene-d_8). 31

Figure 4.11. ^{1}H-NMR Spectrum of Solution (Toluene-d_8). 31

LIST OF TABLES

Table 1.1. Physical Properties of Polyethylene Terephthalate. 3

Table 1.2. The Global Demand and Future Prediction of PET by Application.(Unit in thousand tons). 4

Table 1.3. IV Values of PET According to Application Areas 4

Table 3.1. The Weight Percent Amounts of Additives. 19

Table 3.2. Types of PET and The Weight Percent Amounts of Additives. . . 20

Table 4.1. Temperature Effect on CEG, IV and M_w. 27

Table 4.2. Effect of Different Weight-Percent Ratio of VP-latex on CEG,IV and M_w. 27

Table 4.3. Effect of Different Types of Additives on IV and M_w. 28

Table 4.4. Effect of Different Weight-Percent Ratio of VP-latex on IV of SSP PET. 28

Table 4.5. Effect of Shear Force in the Set-up on IV 29

LIST OF ACRONYMS/ABBREVIATIONS

BHET	Bis(2-hydroxyethyl terephthalate)
CEG	Carboxylic End Group
DMT	Dimethyl Terephthalate
EG	Ethylene Glycol
GPC	Gel Permeation Chromatography
IV	Intrinsic Viscosity
M_w	Weight Average Molecular Weight
PET	Poltehtylene Terephthalate
RF	Resorcinol/Formaldehyde
RFL	Resorcinol/Formaldehyde/Latex
SBR	Styrene Butadiene Rubber
SSP	Solid State Polymerization
T_g	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis
T_m	Melting Temperature
TMP	Quaternization Agent
TPA	Terephthalic Acid
VP	Vinyl Pyridine

1. INTRODUCTION

1.1. Historical and Economical Background

In the polymer industry, two essential processes are present to manufacture. These are chain-growth polymerization to form polyolefines and step-growth polymerization to synthesize polyamides and polyesters [1].

Polyesters are synthesized with step-growth polycondensation reaction between difunctional carboxylic acids or esters and alcohols [2].

The history of polyesters begins with Carothers' works and his aliphatic polyesters towards the end of 1920s. However, it did not seem to be a proper synthetic replacement for natural fibers due to inadequate physical properties [3]. J. R. Whinfield and J. T. Dickson introduced first aromatic polyester, polyethylene terephthalate (PET or PETE) in 1941 [2–4]. Imperial Chemical Industries began to manufacture PET fiber with the name Terylene and it is called Dacron which Dupont started to produce in 1953 [2].

PET became preferred alternative material for various application areas due to its superior chemical and physical properties such tensile strength, thermal stability, chemical resistance and clarity. Global consumption and production of PET increased incomparably since its discovery and commercialization. The annual demand of PET from 1986 to 2012 are presented in the Figure 1.1. Additionally, it is assumed that increment rate in production will be around 10% in following years. [3]

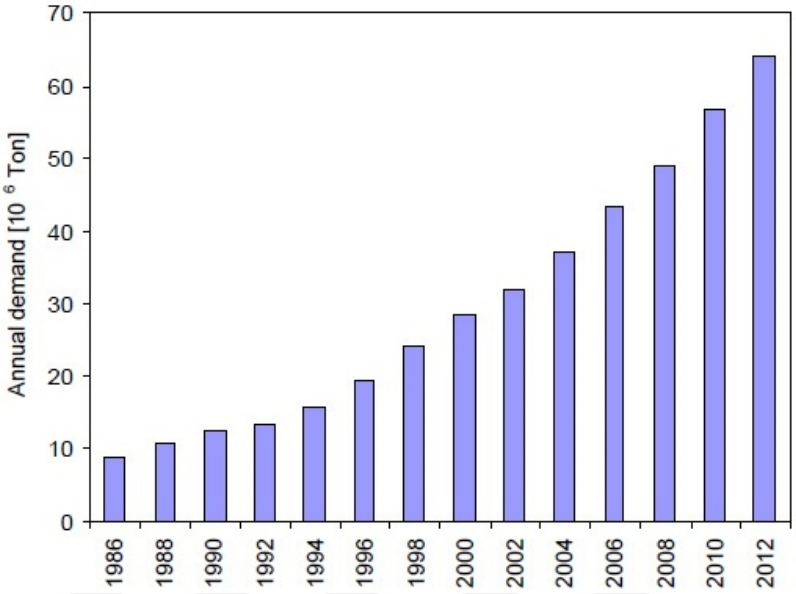


Figure 1.1. Global annual demand of PET from 1986 to 2012.

1.2. Properties and Application Areas

1.2.1. Physical and Chemical Properties

Polyethylene terephthalate is previously described as a thermoplastic and partially aromatic polyester and aromatic molecules typically are able to interact with each other which is called π - π stacking. This stacking ability of *para*-substituted aromatic part and short ethylene group in repeating unit (Figure 1.2), limit mobility of the chains and this results in high crystallinity. Superiority in physical and chemical properties is the outcome of the high crystallinity [2, 5].

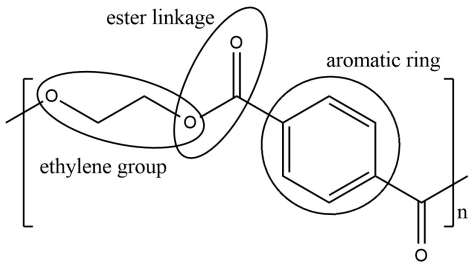


Figure 1.2. Repeating Unit of Polyethylene Terephthalate.

PET has acceptable thermal stability, remarkable impact resistance and high tensile strength with sound chemical resistance. A numeric overview on properties of PET is shown in Table 1.1 [5].

Table 1.1. Physical Properties of Polyethylene Terephthalate.

Property	**Value**
Glass Transition Temperature (Tg) (^{o}C)	69 - 115
Melting Temperature (Tm) (^{o}C)	250 - 265
Crystallization Temperature (Tg) (^{o}C)	150 - 190
Break Strength (Mpa)	50
Tensile Strength (Young's Modulus) (Mpa)	1700
Yield Strength (%)	4
Impact Strength (Jm^{-1})	90
Permeability to Hydrogen at ($25cm^3.cmcm^{-2}s^{-1}Pa^{-1}$)	$0.4x10^{-13}$
Permeability to Nitrogen at ($25cm^3.cmcm^{-2}s^{-1}Pa^{-1}$)	$0.04x10^{-13}$
Permeability to Oxygen at ($25cm^3.cmcm^{-2}s^{-1}Pa^{-1}$)	$0.03x10^{-13}$

1.2.2. Application Areas

PET is a polymer of great versatility. Its range of application areas has grown vastly in recent decades [5].Essentially, PET exists as fiber-grade and bottle-grade in the global market. As fiber, it is the most important material for manufacturing synthetic fibers.They are either filament (long fiber) or staples (short fiber).

Tire cord and technical textiles are made from filament, staples are turned into vowen textiles. Thanks to the gas barrier strength, good clarity and high chemical resistance, PET is a preffered material for bottles. Roughly, 60% of PET production is used as fibers and 30% of it is transformed into bottles. The remaining 10% includes packaging resin, film and other particular component for industry. Table 1.2 shows global PET demand in accordance with its application areas [6].

Table 1.2. The Global Demand and Future Prediction of PET by Application.(Unit in thousand tons).

	1990	**1995**	**2000**	**2005**	**2010**
Fiber	8 900	11 700	18 800	24 200	33 300
PET Resin (for bottles)	1 100	3 100	7 100	11 900	18 900
Film	1 000	1 100	1 400	1 400	1 700
Others	700	800	1 100	1 900	2 200
Total	11 700	16 700	28 400	39 400	56 100

Generally, the grade of PET is determined by molecular weight (M_w) and intrinsic viscosity (IV). Table 1.3 shows application areas according to IV.

Table 1.3. IV Values of PET According to Application Areas

Application Areas	**IV (dL/g)**
Textile	0.40 - 0.70
Technical	0.72 - 0.98
Biaxially Oriented Film	0.60 - 0.70
Sheet Grade for Thermoforming	0.70 - 1.00
Water Bottle	0.70 - 0.78
Carbonated Soft Drink Grade	0.78 - 0.85

1.3. Synthesis of Polyethyene Terephthalate

1.3.1. Melt Polymerization

Polyethylene terephthalate is produced from ethylene glycol (EG) and dimethyl terephthalate (DMT) or terephthalic acid (TPA) as previously mentioned. Synthesis of PET is a stepwise process. The process is comprised of two essential steps. Initially, first step is called prepolymerization where bis(2-hydroxyethyl terephthalate) BHET and oligomers are formed. Subsequently, polycondensation takes place by transester-

ification between the monomers in melt phase in order to produce PET with high moleculer weight [2–7].

In prepolymerization step, there are two possible; direct esterification between ethylene glycol (EG) and terephthalic acid (TPA) or transesterification between ethylene glycol (EG) and dimethyl terephthalate (DMT). Excess of ethylene glycol (EG) is used in both pathways. There are fundamental differences between these two routes which are represented in Figure 1.3 [2–7].

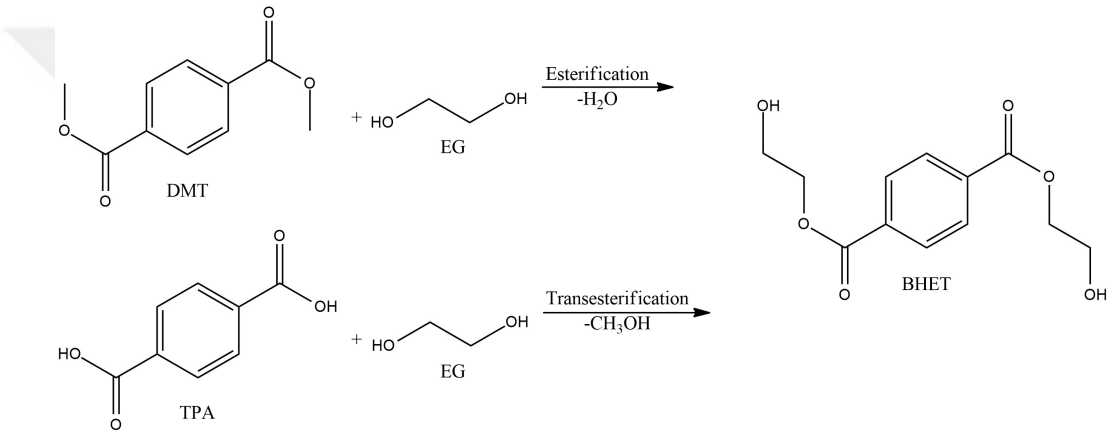


Figure 1.3. Preparation of bis-(2-hydroxyethyl) terephthalate (BHET) by either Esterification or Transesterification.

In transesterification reaction, methanol is removed as a by-product. The reaction undergoes at a temperature ranging from 170^{o}C to 210^{o}C. Commonly, catalyst for transesterification is chosen from oxides or acetates of metals such as titanium, zinc, manganese, cadmium, lead, calcium and manganese and it is used between 0.05% to 0.1% by weight of dimethyl terephthalate (DMT) [2–7].

In esterification reaction, water is eliminated as by-product. Temperature of the reaction medium should be around 220^{o}C -260^{o}C. Catalyst may not be used for the esterification because the carboxylic group of terephthalic acid catalyzes this step. However, number of these carboxylic acid groups are reduced as reaction proceeds. Thus, the mentioned metal catalysts can be used. Homogenous mixture of the reactants is advantageous but contrary to dimethyl terephthalate (DMT), terephtalic acid (TPA)

does not melt at the polymerization temperature but dissolves in ethylene glycol (EG). [2, 5]

In the second step, polycondensation of BHET and oligomers from the first step begins with increasing temperature around 270^{o}C – 300^{o}C and continues with the removal of ethylene glycol as *by*-product under vacuum at 0.5 – 1 torr. Likewise in prepolymerization, removal of *by*-product facilitate progress of the reaction according to Le Chateulier's Principle. Commonly, antimony oxide (Sb_2O_3) is the most favorite catalyst because no negative effect has been reported so far. Also, germanium oxide (GeO_2) appears as a more effective catalyst especially when higher clarity is targeted. However, it could not become a common catalyst due to its high cost. The reaction is represented in Figure 1.4 [2, 5].

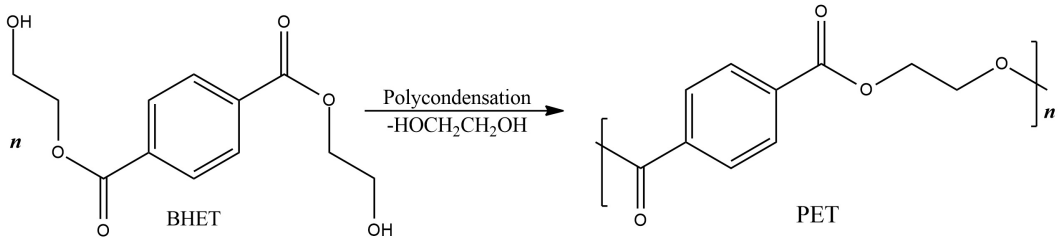


Figure 1.4. Polycondensation of BHET.

Industrially, the manufactured PET should ensure some level of qualification depending on the application area. Commercially, the qualifications are represented by molecular weight and intrinsic viscosity as described earlier. The requirements are not only higher values of these data but also color of the polymer. In polycondesation, reaction time and temperature are two main elements which shape the molecular weight of the polymer. As the polymer is held for longer hours at higher temperatures, higher moleculer weight can be attained. On the other hand, under these conditions thermal degradation starts to interfere with the polycondensation reaction in molten state. Degradation products negatively effect the polymer properties. Solid state polymerization method is applied to reduce the degradation and produce PET with the demanded high M_w and IV [3–5].

1.3.2. Solid State Polymerization

In melt polymerization, molecular weight of 25000 – 30000 g/mol is obtained where the IV is between 0.5 and 0.7 dL/g. In solid state polymerization (SSP), M_w's achieved are higher than 30000 g/mol and IV's are higher than 0.7 dL/g which are used for bottle and fiber industry application respectively [5].

In SSP, as its name suggests, contrary to melt polymerization, the reaction proceed in solid state. Reaction temperature is around 220^{o}C – 230^{o}C which is lower than the melting point (T_m) of the polymer and higher than the glass transition temperature (T_g). Polymerization continues with a slow reaction rate at temperature between T_g and T_m. Reaction time can differ from 5 hrs to 25 hrs. Vacuum is applied to remove *by*-products such as water, EG and acetaldehyde [2, 4, 5].

Products of polycondesation with an IV of around 0,5 dL/g are quenched with water and then chopped into chips. These chips may be then used in SSP. Precrystallization of the oligomers (often referred as amorphous-or intermediate IV-PET) is required prior to SSP since the chips are highly amorphous and sintering occurs Tg. Treating the intermediate IV PET above its Tg increase segmental chain mobility and results in higher crystallinity and T_g. Additionally, precrystallization helps to reduce moisture [4, 5].

In SSP diffusion and reaction of chain ends in amorphous region is responsible for the further polymerization. The crystalline regions are highly ordered and end groups in this region are not available due to diffusion problems. Thus they do not take part in the SSP reactions [2, 4, 5, 8].

As a result, thermal degradation and degradation product content are minimized. PET attains high molecular weight.The disadvantages of melt polymerization is eliminated and intrinsic viscosity is improved to 1.0 dL/g or even higher values [2, 4, 5, 8].

1.4. Polyethylene Terephthalate Degradation

In daily usage, PET is a physcially durable and chemically stable material. However, degradations are unavoidable side reactions which occur during processing and synthesis of PET at high temperatures [5, 9, 10]. While multiple bond breakage takes place as common outcome of degradations, more carboxylic end groups are generated. Thus, track of degradation reactions can be monitored with number of CEG in the polymer [5, 11, 12].

Thermal, thermaoxidative, hydrolytic are main mechanisms for the degradation [5, 9, 11, 13].

Degradation mechanisms are highly active when the polymer is in the molten state where temperature is around 270^{o}C - 300^{o}C. However, hydrolytic degradation starts even at lower degrees right above glass transition temperature (T_g) where the effects of thermal degradation do not emerge yet [5, 9, 11, 12].

Thermal degradation is activated and accelerated by high temperatures without the presence of oxygen. First step in the mechanism of thermal degradation is breakage of ester bond in the chain and the production of carboxylic acid and vinyl ester end groups [2–5, 13, 14].

The mechanism of scission cannot be explained as homolytic cleavage because radicalic inhibitors do not block or retard the advance of the degradation. Instead of radicalic path, six-membered cyclic intermediate formation is used to describe the beginning of the chain scission as depicted in the Figure 1.5 [9, 13, 14].

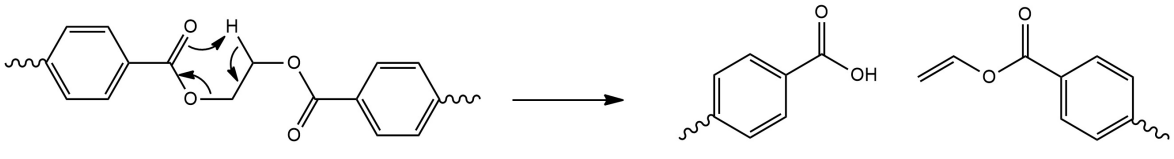


Figure 1.5. Cyclic Reaarragement Intermediate.

Vinyl alcohol is the product of transesterification reaction of vinyl ester end group. Vinyl alcohol is an unstable molecule and turn into acetaldehyde (AA). There are several transesterification reactions of vinyl ester and they are respresented in Figure 1.6. 2-Hydroxyethyl end groups also generate acetaldehyde with a similar rearrangement as shown in Figure 1.7. Since CEG and AA is generated as a result of thermal degradation. The degree of thermal degradation can be followed by monitoring AA concentration [2–5, 13, 14].

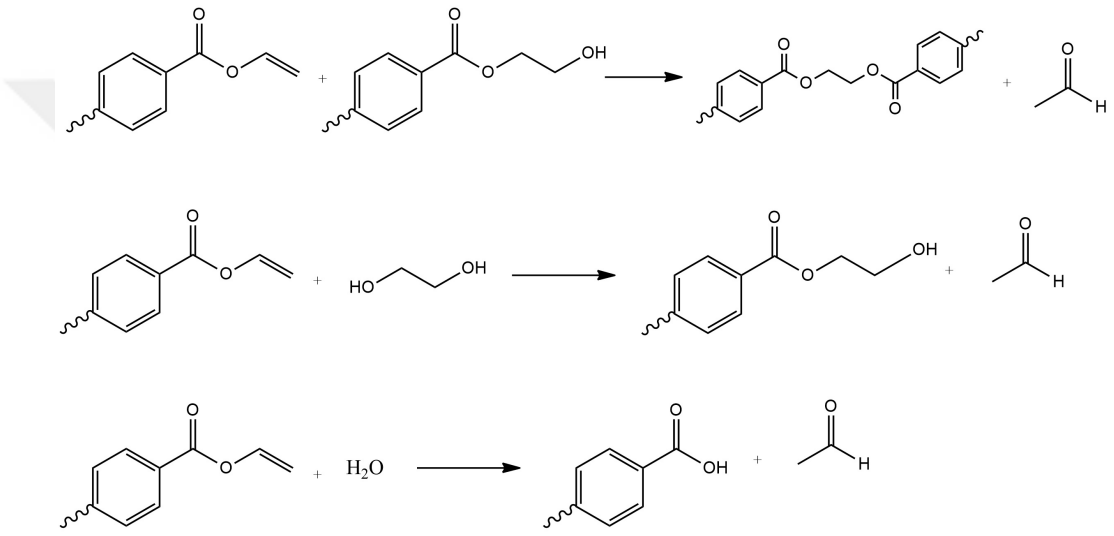


Figure 1.6. Reactions of Vinyl Ester End Group and AA Formation.

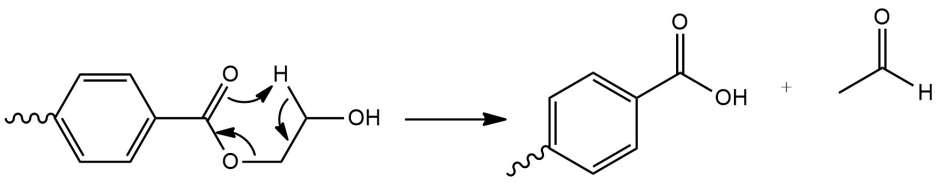


Figure 1.7. Cyclic Reaarragement of 2-hydroxyethyl End Group and AA Formation.

Acetaldehyde amount in the polymer is critical for food packaging industry. It should be lower than 25 mmol/kg because it causes contamination by diffusing into food and beverages [3–5].

Esterification is a reversible reaction and this reverse reaction and this reverse reaction is called hydrolysis. It produce carboxylic acid and alcohol back out of ester

in the presence of water [2, 11, 13].

PET undergo severe hydrolysis reaction which is called hydrolytic degradation in the presence of moisture at elevated temperature.In acidic or basic enviroment, hyrolysis accelerates significantly. Thus, hydrolysis reaction is cataylzed by carboxylic acid and this makes it an autocatalytic reaction because each chain scission produces addtional carboxylic end group [2, 5, 9, 13, 14].

The hydrolytic degradation is active at lower temperatures compared to thermal and thermaoxidative degradation and it is the most problematic one among them due to exceedingly high reaction rate. Reaction rate is 10000 times higher than thermal degradation at around 100^{o}C - 120^{o}C in the presence of moisture [9, 11, 13, 14]. The scheme of hydrolysis is shown in Figure 1.8 .

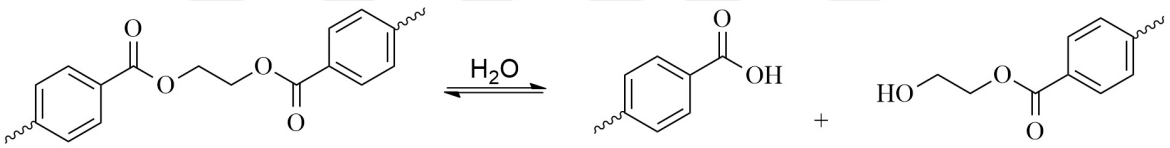


Figure 1.8. Hydrolytic Degradation.

Third route is thermo-oxidative degradation. As the name implies, it is a combination of thermal degradation and oxidation. In the presence of oxygen, the degradation mechanism is significanly different than the classical thermal degradation. Instead of rearrangement intermediate, radicalic mechanism is followed. The oxygen molecule abstracts the hydrogen at the alpha position and initiates the mechanism [2,5,9,13,14]. The mechanism is shown in detail in Figure 1.9

1.5. Tire Application of PET Fibers and Aminolysis

Polyethylene terephthalate (PET) fibers have high value of tensile strength and modulus with high dimensional stability and fatigue resistance. Accordingly, PET is widely chosen as reinforcing fiber for rubber especially as carcass fabric in tires [15–17].

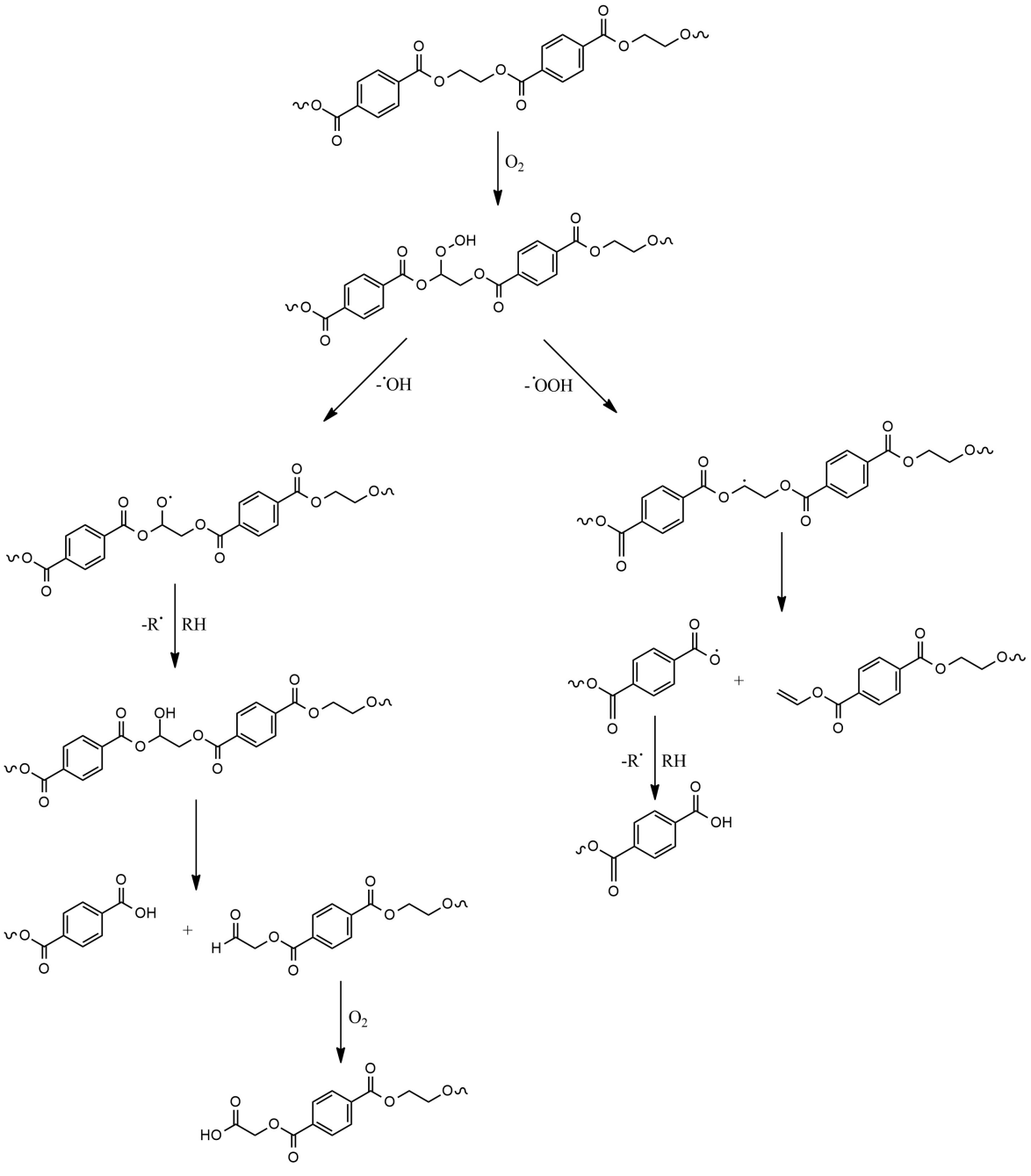


Figure 1.9. Mechanism of Thermo-Oxidative Degradation.

Tire cords are made of twisted PET fibers. They are placed between two sheets of rubber. This layer is called body ply which stabilize internal air pressure and put a resistance to impact from sidewall of the tire [18,19].Its manufacturing process is shown in Figure. 1.10.

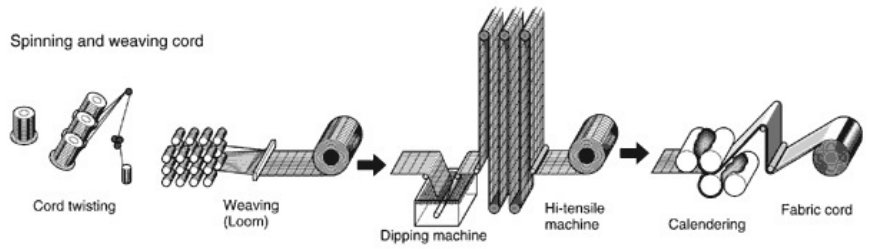


Figure 1.10. Textile Cord and Body Ply Preparation.

A passanger tire manufacture is started by wrapping multiple specialized rubber layers on a rotating drum. Green tire is the name of final product when all specific layers are assembled and green refers to uncured state of tire. In order to start curing, the tire is placed in a large mold at elevated temperature, the vulcanization reaction begins where the crosslinking of rubber with sulfur achieved [18, 19]. Curing step is depicted in Figure 1.11.



Figure 1.11. Curing (Vulcanization) Process.

Tire is a elastic and strong material of vulcanized rubber. Vulcanization is an essential procedure in order to manufacture rubber products with desired mechanical

properties.Vulcanization or curing is a term for croslinking in rubber industry . As a brief description, crosslinking is establisment of bridges between linear chains of polymers. In this case, the crosslinker is sulfur molecule [20, 21]. This network formation is represented in Figure 1.12.

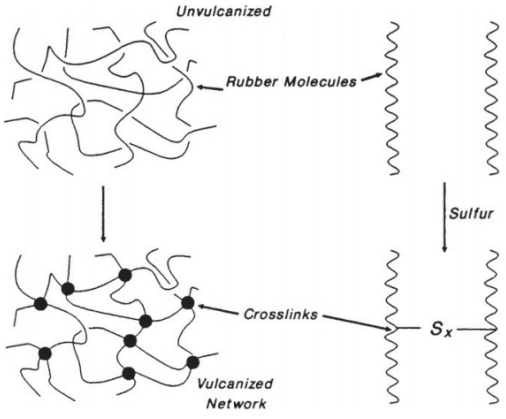


Figure 1.12. Network Formation.

The first commercially application of vulcanization is ascribed to Charles Goodyear in 1841. However, Thomas Hancock is the first person who patented the method several weeks earlier than Goodyear. They accomplished curing by heating natural rubber with elemental sulfur. Vulcanization was completed with 8 parts of elemental sulfur for each 100 parts of rubber at 140^oC at the end of 5h. The procedure is no longer commercially in use because curing accelerators reduce concentration of crosslinker to 0.5 parts and time to 1-3 mins [20, 21].

Tire is a product of highly detailed and specialized manufacturing and design. Thus, in vulcanization of rubber the degree of crosslinking should be under control [21]. There are two types of accelerators. Primary ones are responsible for the delay of premature vulcanization and strength enhancement with medium fast cure. Secondary ones provide very fast curing. They are generally used in combination [20]. Different accelerators were developed according to needs of curing process since Goodyear's method.

Polyethylene terephthalate (PET) tire cords undergo severe degradation during the vulcanization. This heavily strength reduction is attributed to aminolysis and hydrolysis of ester bonds rather than the thermal decomposition [12,15–17,22]. Amine derive *by*-products are generated from rubber-curing accelerators during vulcanization, are actively responsible for the aminolysis and have catalytic effect in hydrolysis [15–17, 22]. The relation between degradation and the amines was established by using different amounts and kinds of accelerators [22]. The degree of degradation increased with the increasing amount of accelerator [12, 15]. Accelerators which have do not liberate amine derivatives or generate ones with low chemical activity, cause significantly less damage [16, 22]. In tire manufacturing sulfenamides are still in use due to its delayed action and good vulcanization properties [21].The liberation of secondary amine from sulfenamide type accelerator during the introduction of sulfur to crosslink the rubber is depicted in Figure 1.13.

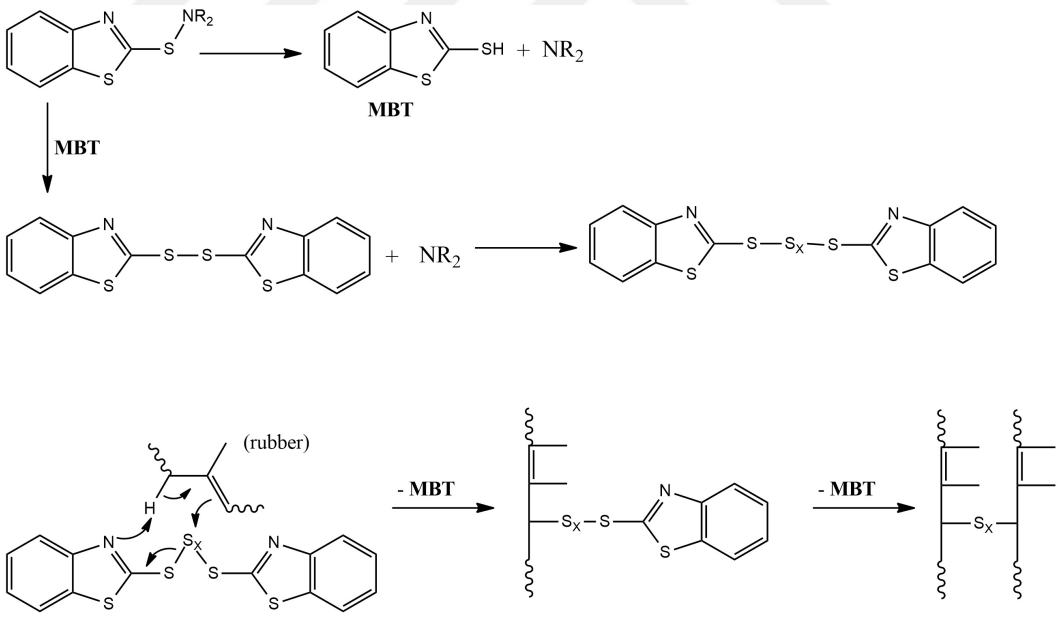


Figure 1.13. Reaction Mechanism of Rubber Curing with Sulfenamide.

Polyethylene terephthalate severely suffers from several types of degradations which are thermal, thermo-oxidative and hydrolytic degradation as described in previous section. In order to maintain the desired properties, the degradation should be prevented or impeded according to the particular mechanism of each degradation [9,13].

Recall that thermal degradation is the consequence of melt polymerization and processing at high temperature. Instead of homolytic cleavage, it evetuates with cyclic rearrangement as intermediate in the absence of oxygen. Additionally, water molecules cause hydrolysis of the polyester chains. Thus, stabilizers which are used to eliminate radicals have no effects on blocking these reactions [13].

Alkyl and aromatic phopshite esters were introduced as an early examples of stabilizers in order to compansate degradation. IV of molten polymer was maintained while there is a reasonable decrease of M_w during polymerization without the phosphite esters [13, 23]. In another study, triphenyl phopshate was found excellent in decreasing carboxyl content of PET and concentration of diethylene glycol which is another side product that indicates a degradation apart to acetaldehyde [13, 24].When triphenyl phosphate was added to the reaction at 260^oC maximum chain extension with minimum degradation was observed [13, 25].

Phosphorus containing stabilizers are still used in industry as an essential ingridient and their reputation is based on thermal stability, antioxidant feature and reactivity towards chain ends. In short, prevention of chain scission and end group decrease are main objectives of the stabilizers and this can be achieved by having a control on reactivity of the end groups. Other than the phosphite esters as general stabilizers, different additives are proposed with similar approaches [13].

In hydrolytic degradation, carboxylic end groups have catalytic effect on rate and thermal stability and resistance. Thus, additives which are called end-capping agents, are used to block polymer chain ends, particularly carboxylic acid chain ends by reacting with them [13]. Carbodiimides were found quite convenient compounds due to their high reactivity towards particularly carboxylic acid end groups. Reaction between carboxylic acid and carbodiimide results in amidation of carboxylic end group and formation of an isocyanate [13,26]. Furthermore, carbodiimides with low molecular weight can be volatile and have tendency to migrate out of the polymer [27]. In order to overcome these problems, polymeric carbodiimides were proposed [13, 26, 27].

In polycondesation, polymerization and degradation are in competation at high temperatures. Thus, solid state polymerization is chosen in order to produce polyester fibers with higher molecular weight and minimize degradations. However, it is costly in machinery and a time and energy consuming procedure. Instead of SSP due to its drawbacks, chain extenders are used to compansate the decrase in molecular weight during polycondensation and processing of PET. Chain extenders can be described as di or multi function molecules which reacts with carboxylic acid or hyroxyl end groups of PET [5, 13]. Diepoxides, diisocynates, dianhydrides, bis-oxazolines, carbodiimides, bis-dihydrooxazines are the most preferred chain extenders for PET [5, 28].

In the presence of primary and secondary amines, aminolytic degradation of PET formation starts with nucleophlic attack of nitrogen on the carbon of carbonyl group. In the presence of water, reaction proceeds to form amide and alcohol [9, 29, 30]. On the other hand, tertiary amines do not give amide functionanlity and form acylammonium intermediate. This intermediate is hydrolyzed by water and carboxylic acid is produced where tertiary amine is released back again to react with another carbonyl group. In short, tertiary amines act as catalysts in ester hydrolysis [31, 32]. Therefore, tertiary amines cause more damage than primary and secondary amines do. Nucleophilic attack of amines is carried out by lone pair electrons on the nitrogen. In order to deactivate catalytic effect of tertiary amines, lone pair electrons shoud be blocked. Quaternization can be a reasonable solution to this problem which is addressed in the present dissertation.

Quaternary ammonium cations are permanent cations with formula NR_4^+.Unlike ammonium ion of primary, secondary and tertiary amines, quaternary formation does not depend on pH of the medium. Alkylation of amines produce quaternary ammonium cations [33]. Alkyl-iodides, sulfuric-, sulfurous- and *p*-toluenesulfonic acid esters are common alkylating agents for amines. Triester and alkyl phosphates were used in the preparations of dialkylphosphate ionic liquids by reacting with tertiary amines [34, 35].

2. AIM OF THE STUDY

In a broad picture, the aim of the study is inhibition of tertiary amine catalyzed hydrolytic degradation of polyethylene terephthalate in tire cords during vulcanization. Therefore, quaternization is selected as a coherent method. Especially, methylation seems to be a good candidate of quaternization. The methylation, due to the absence of beta hydrogen should prevent a potential Hofmann Elimination reaction which may release back the tertiary amine. Methylating ability and chemical suitability of TMP will be investigated. Additionally, catalytic activity of 2-vinyl pyridine unit in VP-latex is screened with melt degradation studies in melt polymerization set-up and extruder system because polyethylene terephthalate fibers are coated with it prior to place in tire. Subsequently, reactivity of VP-latex towards methylation will be investigated.

3. EXPERIMENTAL

3.1. Methylation of Tertiary Amines

The methylation reactions were performed with respect to literature [35].

3.1.1. 3.1.1. Synthesis of N,N-diethyl-N-methylethanaminium and its counterion

TMP (0.1 mL, 8.57x10^{-4} mole) and triethylamine (0.143 mL, 1,03x10^{-3} mole) are added in a tube. The molar ratio is 1.2:1.0 between triethylamine and TMP. The tube was sealed and mounted in silicon oil bath. Temperature of the reaction was kept at 110^{o}C for 12 hrs. After the reaction is completed, excess triethylamine is evaporated with rotary evaporater. The product is light-yellow viscous liquid. ^{1}H-NMR (DMSO-d_6, 400 Mhz, in ppm): 3.77(s,9H), 3.34(d,6H), 3.25(q,6H), 2.88(s,3H), 1.19(t,9H).

3.1.2. 3.1.2. Synthesis of 1-methylpyridin-1-ium and its counterion

TMP (0.1 mL, 8.57x10^{-4} mole) and pyridine (0.83 mL, 1,03x10^{-3} mole) are added in a tube. The molar ratio is 1.2:1.0 between pyridine and TMP. The tube was sealed and mounted in silicon oil bath. Temperature of the reaction was kept at 110^{o}C for 12 hrs. After the reaction is completed, excess pyridine is evaporated with rotary evaporater. The product is dark-blue viscous liquid. ^{1}H-NMR (DMSO-d_6, 400 Mhz, in ppm): 9.04(d,2H), 8.58(t,2H), 8.14(t,2H), 4.37(s,3H), 3.61(s,9H), 3.29(d,6H).

3.1.3. 3.1.3. Methylation of 2-vinyl pyridine unit in VP-latex

VP-latex (50 mg, 7,14x10^{-5} mole 2-vinyl pyridine) was placed in a tube with 5 mL toluene. After addition of TMP (0,02 mL, 1,71x10^{-4}) , the tube was sealed and mounted in silicon oil bath. Temperature of the reaction was kept at 100^{o}C for 8h. At the end of the reaction, the mixture is precipitated into ethanol.

3.2. Degradation Experimentation of PET

Degradation experiments can be categorized into two groups. Experimentations were performed either in melt polymerization set-up or co-rotating twin screw extruder.

3.2.1. Degradation of PET in Melt Polymerization Set-up

Degradation experiments were carried out in glass melt reactors . ESM- 4450 48 x 48 1/16 DIN Universal Input PID Process Controller with Smart I/O Module System and silicon oil was used to heat the reactors. Only amorphous type of PET was used. Generally, reactors are mounted in silicon oil at 280^{o}C. However, one of the experiments was performed at 190^{o}C in order to observe temperature effect on degradation. Reaction time was set to 30 minutes once the polymer started melting. Heidolph overhead stirrer was used. The rate of the stirrer was 50 rpm. The additives are mixed with grinded amorphous PET prior to experimentation. For each experiment 15g of PET is used. The weight percent amounts and types of additives are summarized in Table 3.1

Table 3.1. The Weight Percent Amounts of Additives.

	Additive	**Weight % Ratio)**
KM1	No Additive	
KM2	No Additive	
KM3	VP-latex	3.33
KM4	SBR	3.33
KM9	VP-latex	6.66

3.2.2. Degradation of PET in Extruder System

Contiuous blending of PET and VP was performed with a Gülnar co-rotating twin screw extruder. The screw diameter of extruder is 18mm and L/D (length/diameter) ratio is 40:1. The extruder system consists of 13 zones. One of them is melt pump

section which helps to stabilize output pressure. The average temperature of chambers in the extruder system was 280^{o}C. The medium was under nitrogen during experiment. The screw rate was 30 rpm and feeding rate was 850 g/h. The extruder was fed with mixture of additives and amorphous or SSP PET chips. The mixture was prepared prior to experimentation. The weight percent amounts of additives with the type of PET are summarized in Table 3.2

Table 3.2. Types of PET and The Weight Percent Amounts of Additives.

	PET Type	**Weight % Ratio of VP-latex)**
KE1	Amorph	0.1
KE2	SSP	0.1
KE4	SSP	No Addition
KE6	SSP	0.3
KE7	SSP	1
KE8	SSP	3

3.3. Gel Permeation Chromatography (GPC) Analysis

The samples were dissolved in hexafluoroisopropanol (HFIP) before GPC analysis.

3.4. Intrinsic Viscosity (IV) Analysis

The test method is confidential data.

3.5. Carboxylic End Group (CEG) Analysis

The test method is confidental data

4. RESULTS AND DISCUSSION

In this study, the main goal is to prevent tertiary amine catalyzed degradation of PET fibers during the green tire vulcanization. Quaternarization was the method preferred to block the catalytic activity of the tertiary amines released from the accelerators. In order to produce quaternary ammonium cation, among other alkylating agents, TMP was chosen. However, the quaternary alkyl substituent can undergo Hofmann Elimination (Figure 4.1) in the presence of beta hydrogen at elevated temperatures (>100^{o}C). The quaternization was aimed by methylation of the amines to prevent the release of tertiary amines back again.

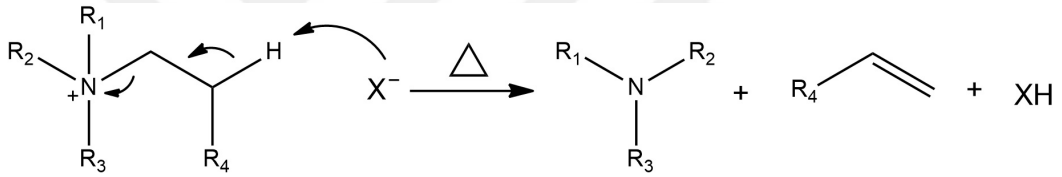


Figure 4.1. Mechanism of Hofmann Elimination.

4.1. Methylation Studies Using TMP

Although present in the literature, TMP is not a commonly used, at least to the best of our knowledge, agent for methylation of amines. Therefore to check the efficiency of TMP in methylating amines, triethylamine and pyridine were used as model compounds for tertiary alkyl and aromatic amines repectively. The experiments were carried out without solvent in a sealed reaction vessel with TMP and the amine in question.

NMR results (Figure 4.3 and 4.5) show that triethylamine (Figure 4.2) and pyridine (Figure 4.4) were methylated succesfully indicating that both alkyl and aromatic amines can be quaternized by TMP. In the case of triethylamine the methyl peaks move from 2.5 to 3.25 indicating the formation of the tetramethyl ammonium species. In the pyridine case the hydrogen chemical shift at the position 2 moves from 7.1 to

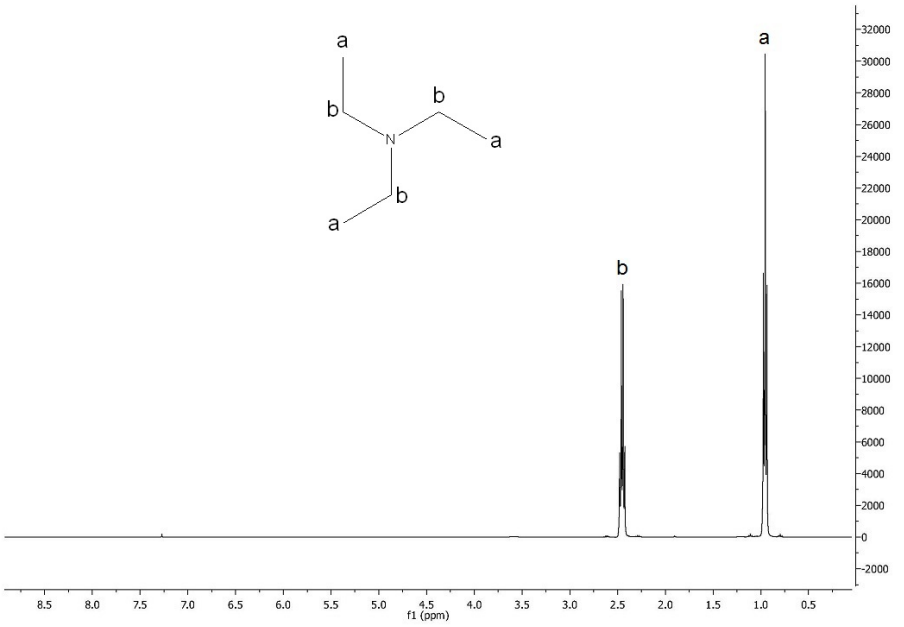


Figure 4.2. ^{1}H-NMR Spectrum of Triethylamine ($CDCl_3$).

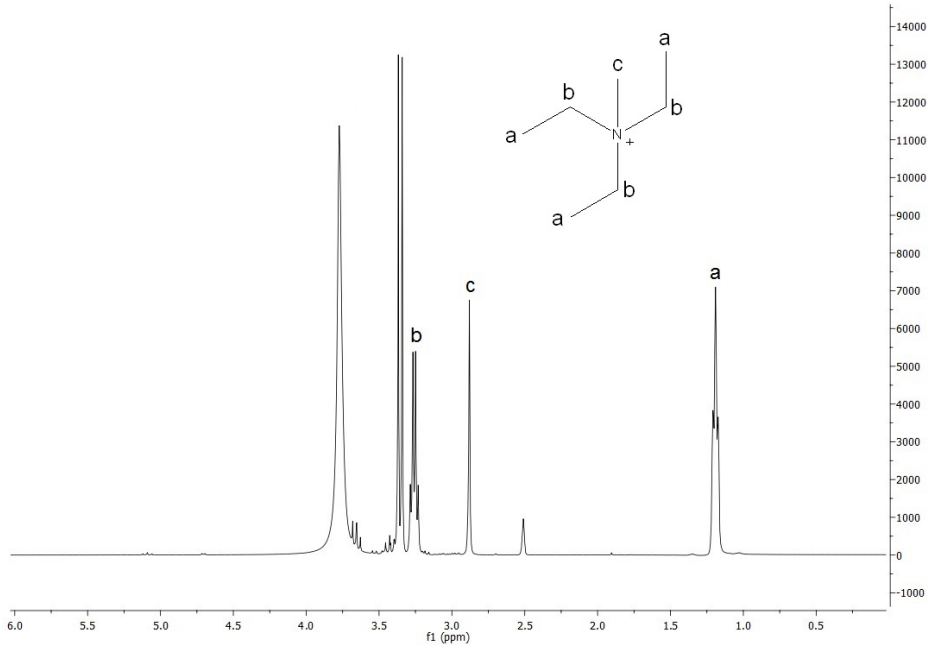


Figure 4.3. ^{1}H-NMR Spectrum of N,N-Diethyl-N-Methylethanaminium and a Counterion (DMSO-d_6).

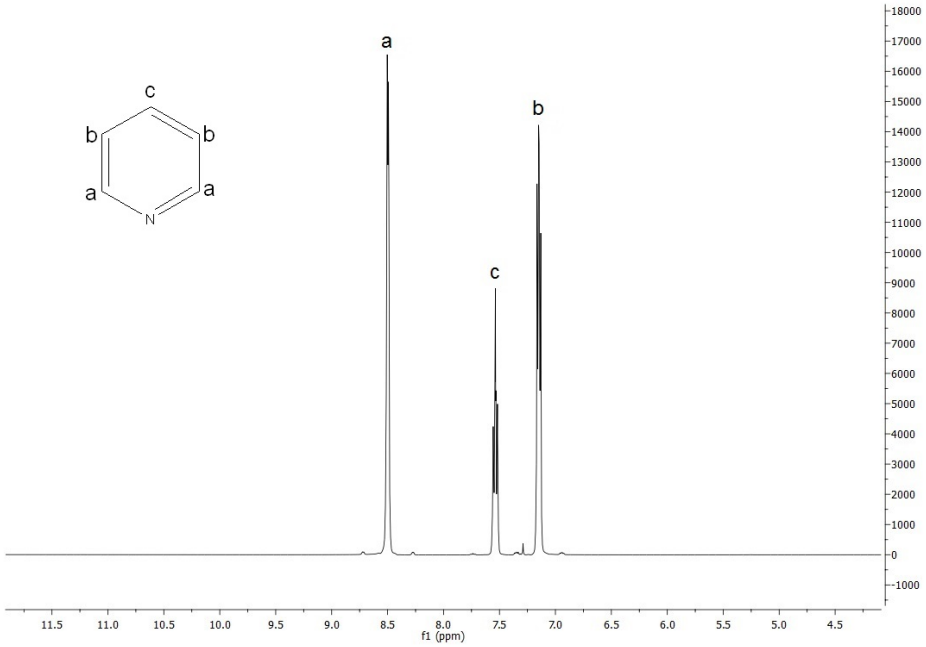


Figure 4.4. ^{1}H-NMR Spectrum of Pyridine ($CDCl_3$).

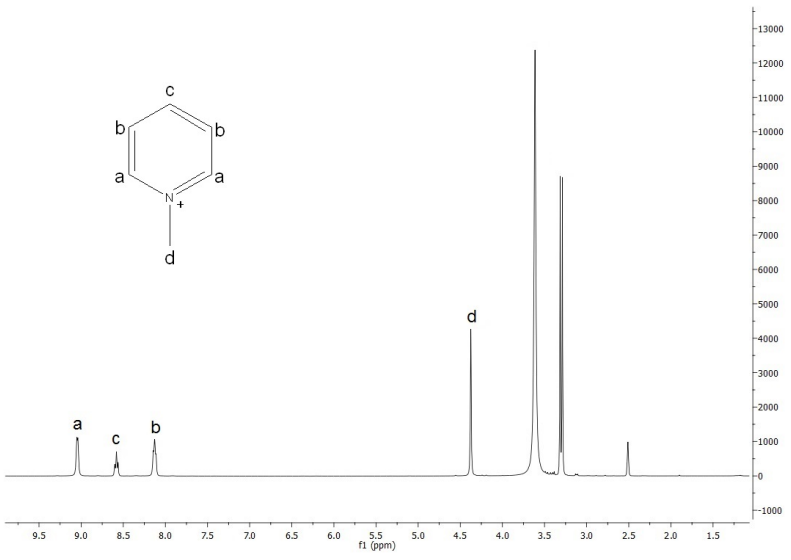


Figure 4.5. ^{1}H-NMR Spectrum of Synthesis of 1-Methyl Pyridin-1-ium and a Counterion (DMSO-d_6).

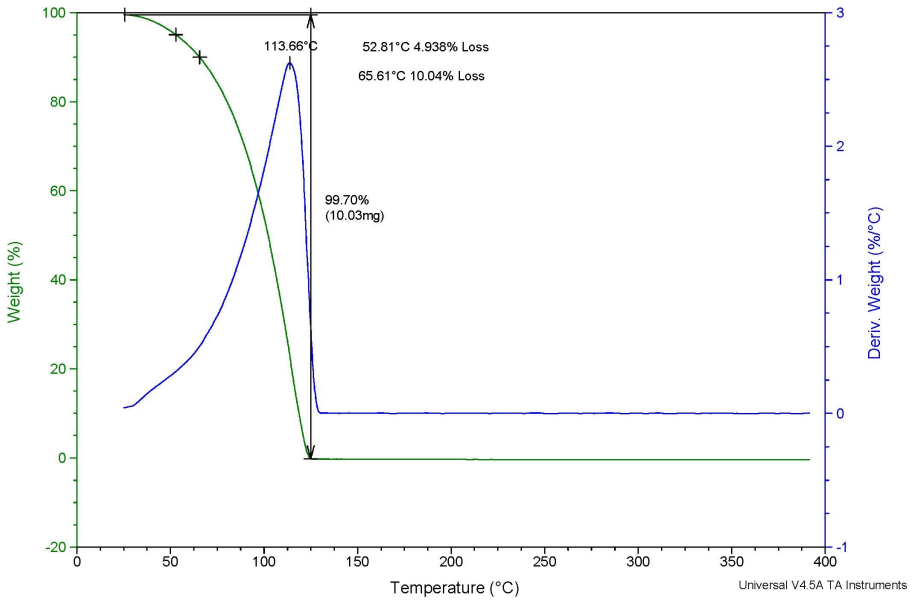


Figure 4.6. TGA Spectrum of TMP.

9.0 showing again the quaternization together with the appearance of the methyl peak at 4.4 ppm. However, both experiments in TGA (Figure 4.6) and volatility test using balance showed that TMP was evaporating even at room temperature. This was noted as a potential drawback that needs to be addressed before any large scale industrial application. Thus at this point TMP seemed to be reasonable candidate at least in lab scale for the quaternization of tertiary amines.

While preparing for the actual experiments where the TMP would be used as the quaternizating agent in green tire vulcanization, It was noticed that the tire cords were coated with Resorcinol/Formaldehye/Latex (RFL).This coating is a common coating used to promote a high adhesion between rubber and the PET tire cords. RFL consists of resin solution of resorcinol/formaldehyde (RF) and dispersed latex particles. The latex part contains a special VP-latex which is a terpolymer of styrene, butadiene and 2-vinyl pyridine (VP) (Figure 4.7).

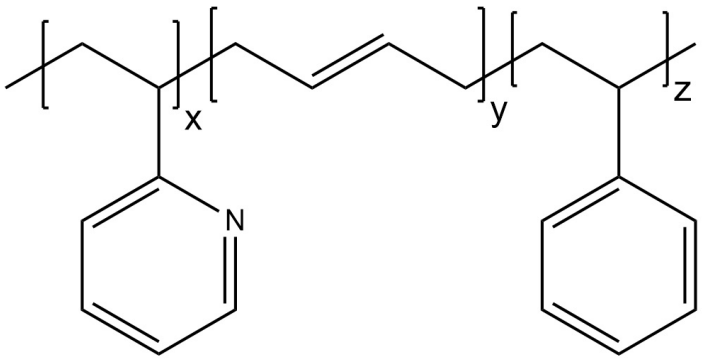


Figure 4.7. Repeating Unit of VP-Latex.

At this point, we realized that the presence of VP content could interfere with the quaternarization process. Although the VP is present as 2-VP isomer, thus the amine component might be sterically hindered by the polymeric chain for the methylation process, the fact that pyridine could be quaternized by TMP could be a potential problem. This would not only consume the TMP added but also alter the polarity of the VP-latex which acts as an interface. A second but even more important point also came into our attention, the effect of VP-latex on PET degradation was not studied or published in the literature. VP-latex together with other amines released during the vulcanization process could be involved in tertiary amine catalyzed hydrolysis of PET fibers. Thus, both concerns, quaternization of the 2-VP component, a potential catalytic activity of the 2-VP in hydrolysis then became two main research subjects.

4.2. The Potential Effect of 2-VP Latex on PET Degradation

First potential catayltic activity of 2-VP repeat units on hydrolytic degradation of PET was investigated. Experiments can be divided into two groups, ones that were done in melt polymerization set-up and second ones carried out in co-rotating twin screw extruder (Figure 4.8)

Sample names with KM are indication of degradation in melt polymerization set-up and KE is used for the samples in the extruder system. GPC, IV, CEG tests were conducted in order to analyze the effect of VP-latex on PET.In both studies,

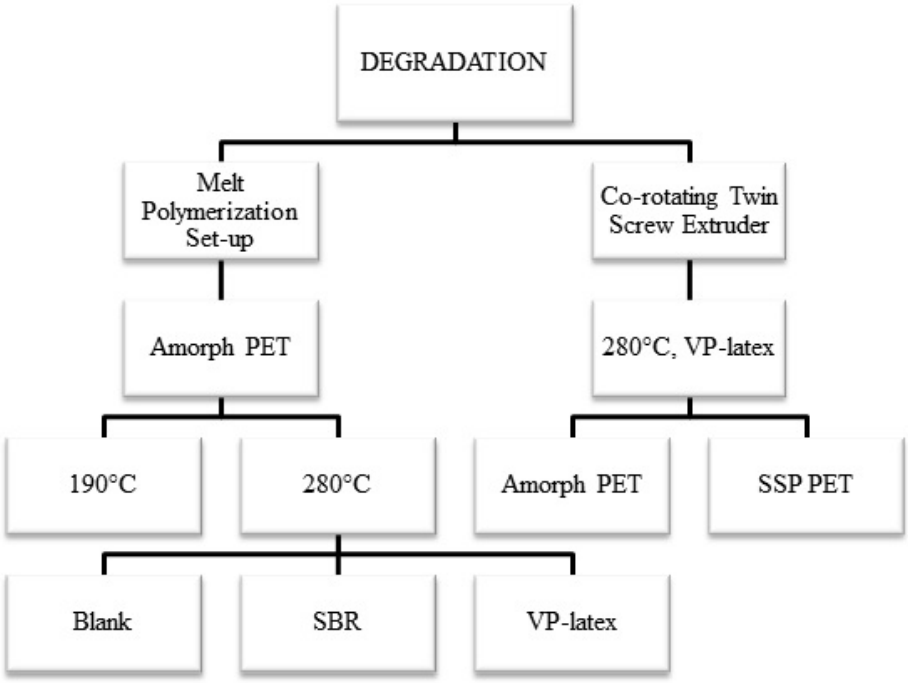


Figure 4.8. Schematic Representation of Degradation Study.

blank experiments or in other words background experiments were carried out to investigate the melt behaviour/self-degradation of the amorphous and SSP PET with the experimental set-ups used in the absence of VP-latex.

Experiments are carried out in melt-polymerization set-up: In melt degradation experiments, only amorphous PET was used since it is very difficult to melt SSP PET in such a set-up without any decomposition. Melt degradations were carried out at 280^{o}C which is above the melting point of amorphous PET, except one experiment which was carried out at 190^{o}C (KM2). Amorphous PET is tested solely or mixed with VP-latex. The VP-latex with changing weight-percent ratios were added.

Blank experiments were carried out at 190^{o}C and 280^{o}C with amorphous PET in the melt polymerization set-up (Table 4.1). KM1 which was run at high temperature showed every indication of thermal and hydrolytic degradation with a decrease in IV and M_w and increase in CEG. However, at lower temperature, 190^{o}C, IV, M_w and CEG values in other words all numbers increased. This most probably indicates chain

Table 4.1. Temperature Effect on CEG, IV and M_w.

	Temp.(C)	**CEG (mmol/kg)**	**IV (dL/g)**	**M_w (g/mol)**
Commercial		27.6	0.6	24380
KM1	280	33.97	0.373	16340
KM2	190	34,63	0,637	32500

extension/polycondensation of hydroxyl and carboxylic acid chain ends together with some degradation of PET chains producing low molecular weight chains which are responsible for the higher CEG values.

The results show that PET undergoes significant changes at both temperatures in the melt polymerization set-up. The final dropped values then served as reference background values for the studies carried out with the 2-VP latex.

Then the effect of different weight percent ratio of VP-latex on PET degradation was examined (Table 4.2). The results showed that there was an increase in CEG values and decrease in M_w's as a result of VP-latex addition. Thus VP-latex seemed to affect the PET degradation. However, interestingly there was no significant change in the measured values when the percent ratio of VP-latex was doubled (Table 4.2).

Table 4.2. Effect of Different Weight-Percent Ratio of VP-latex on CEG,IV and M_w.

	Weight%Ratio of VP-latex	**CEG (mmol/kg)**	**M_w (g/mol)**
KM1	0	33.97	16340
KM3	3.33	66.71	16000
KM9	6.66	66.99	13620

**Amorphous PET, 280°C*

This could be interpreted as VP-latex not having a catalytic effect on hydrolytic degradation. Its action could be purely physical, where the soft VP-latex could increase

the mobility of the PET chains where individual PET chains can now experiment higher actual shear force causing chain scission as a result of mechanical energy. To check that the action of VP-latex was physical rather than chemical, another experiment with SBR-latex (KM4), with no VP repeat unit, was designed. Indeed, the results obtained (Table 4.3) were similar to the ones obtained with the VP-latex.

Table 4.3. Effect of Different Types of Additives on IV and M_w.

	Additive Type	**IV (dL/g)**	**M_w (g/mol)**
KM3	VP-latex	0.447	16000
KM4	SBR	0.402	14930

**Amorphous PET, 280°C*

Thus, it was concluded that the action of the VP-latex was rather physical than chemical.

Experiments are carried out in extruder system: In extruder system, both amorphous and SSP PET were used. Temperature was set to 260°C on the extruder system. However, the chamber temperature was 280°C and at this temperature PET melts with the help of mechanical energy or shear force coming from screws. Similar to melt degradation experiments, amorphous and SSP PET were added alone or with different weight-percent ratios of VP-latex.

Table 4.4. Effect of Different Weight-Percent Ratio of VP-latex on IV of SSP PET.

	Weight%Ratio of VP-latex	**IV (dL/g)**
KE2	0.1	0.480
KE6	0.3	0.460
KE7	1	0.452
KE8	3	0.444

**SSP PET, 280°C*

The effect of VP-latex addition in different weight-percent ratio on SSP PET in extruder system was screened(Table 4.4). There is a slight decrease in IV values corresponding increase in percent ratio of VP-latex addition. However, the rate of decrease is not parallel to the amount of addition. The trend among these results is analogous to the experiments in melt polymerization set-up.

Table 4.5. Effect of Shear Force in the Set-up on IV

	Weight%Ratio of VP-latex	**IV (dL/g)**
KM3	3.33	0.447
KM9	6.66	0.391
KE1	0.1	0.385

**280° C*

Experimentations in melt polymerization set-up resulted in higher IV value although they were carried out with higher weight ratio of VP-latex (Figure 4.5). It can be concluded that in the presence of VP-latex, the mechanical energy is delivered throughout the mixture well. As the shear force or mechanical energy is increased, the degree of mechanical deterioration is amplified. This trend also supports our previous assumption.

It is understood that VP-latex as polymeric tertiary amine does not cause any hydrolytic degradation of PET because the pyridine functionality may be hindered by the the polymer backbone.

4.3. Methylation Studies of 2-VP Latex with TMP

Although the results suggested that the aromatic amine of the 2-VP unit was most probably hindered enough to prevent the nucleophilic attach to PET chains, a small molecule like TMP could approach and potentially methylate the pyridine of the 2-VP latex.

Lastly, methylation of VP-latex was studied to determine its reactivity towards alkylation. In NMR graph (Figure 4.9), the important peak is around 8.5 ppm. It is the peak of hydrogen in the position of 5 in 2-vinyl pyridine. Furthermore, while the reaction mixture was precipitated in ethanol, the total solution was expected as transparent. However, significant turbidity was developed. Thus, NMR spectrums (Figure 4.10 and 4.11)of both precipitate and solution were obtained. The hydrogen peak at 8.5 ppm in NMR results of precipitate and solution was remained. As a result, continuation of the hydrogen peak presence at 8.5 ppm and absence of a peak around 9.0 ppm as a sign of methyl attachment to the pyridine group in NMR results, it may be concluded as VP-latex was not methylated with TMP.

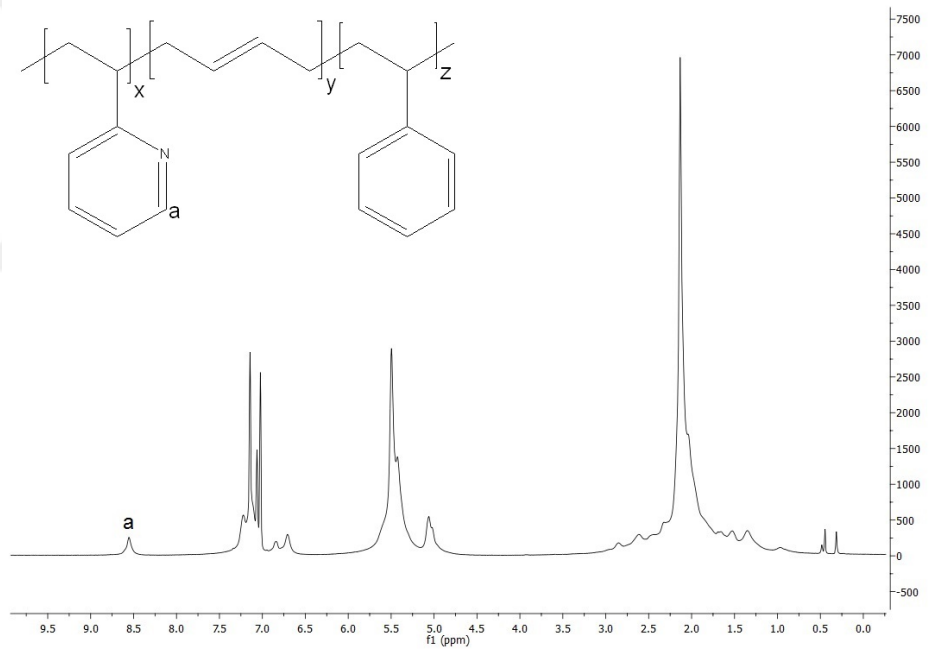


Figure 4.9. ^{1}H-NMR Spectrum of VP-latex (Toluene-d_8).

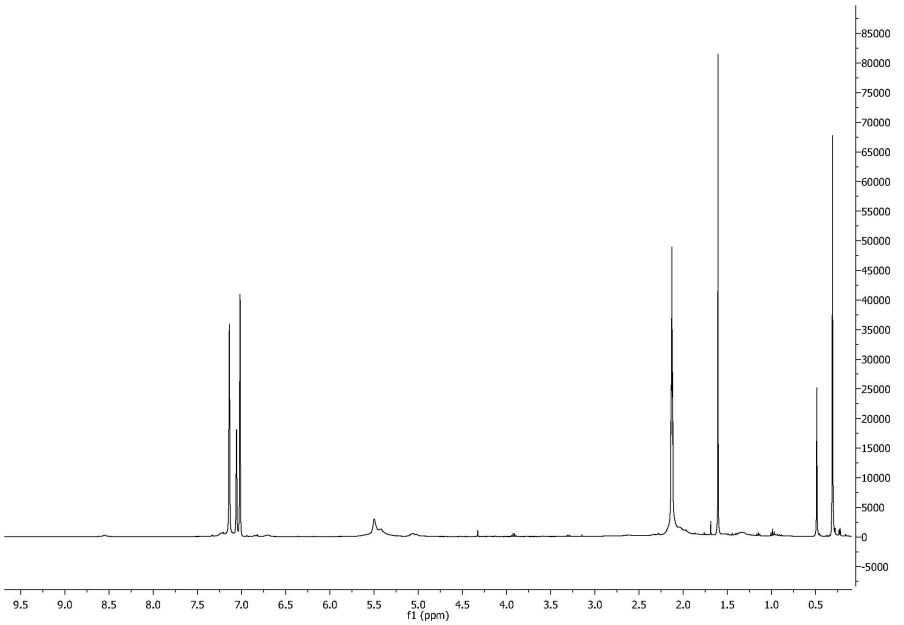


Figure 4.10. ^{1}H-NMR Spectrum of Precipitate (Toluene-d_8).

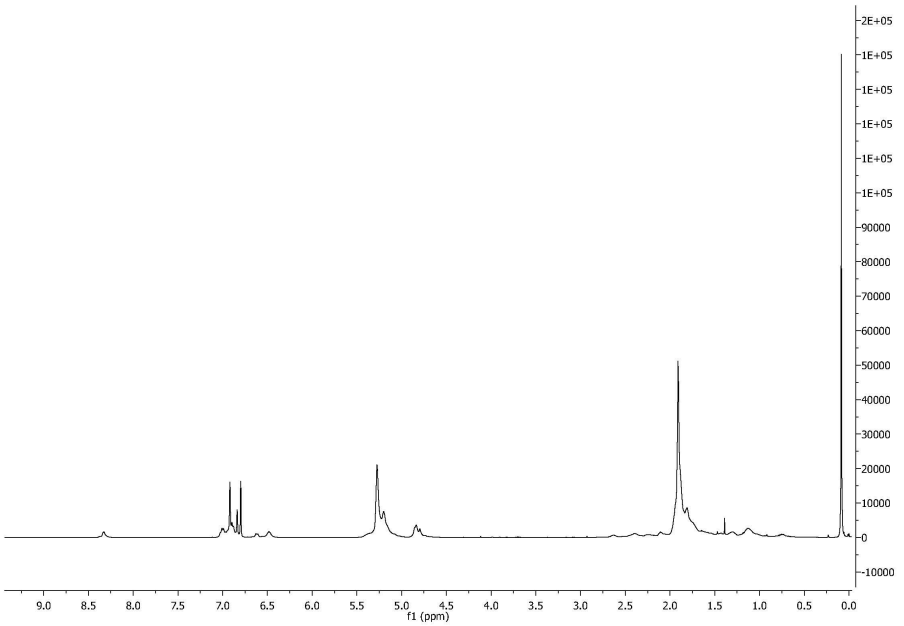


Figure 4.11. ^{1}H-NMR Spectrum of Solution (Toluene-d_8).

5. CONCLUSION

In this study, hydrolytic degradation of PET in tire which is catalyzed by liberated tertiary amines from accelerators during vulcanization was the targeted problem. Quaternization was adopted as a reasonable method to disable nucleophilicity of the amines. Methylation rather than any alkylation was chosen to overcome Hofmann Elimination.

TMP exhibited efficient capability to methylate alkyl and aromatic amines. However, it was discovered that TMP is a volatile compound.

It was realized then that VP-latex containing dip is used to coat tire cords, the concentration of the study is shifted from the amines to VP-latex which has 2-vinyl pyridine units. Thus, the study continued with investigation of catalytic capacity of VP-latex on hydrolytic degradation in tire. The experiment results showed that VP-latex does not have any chemical effect on hydrolytic degradation of PET but its action can be described as physical.

Finally, methylation of VP-latex was tested because it was suspected that VP-latex may cause quaternization of the amines and consume the reagent. It was understood that VP-latex is inert to TMP. The fact that VP-latex does not degrade PET and it cannot be methylated with the TMP is promising for the work. Otherwise any reaction with TMP would consume the methylating reagent and also modify the polarity of the VP-latex which is responsible PET-latex binding.

6. FUTURE WORK

The only drawback of TMP seems to be its volatility. As a future work, non-volatile thermally and hydrolytically stable methylation agent will be synthesized.

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