ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**PREPERATION OF OIL-BASED POLYURETHANES
FOR BIOMEDICAL APPLICATIONS IN THE
ABSENCE OF SOLVENT AND CATALYST**

**M.Sc. Thesis by, B.Sc.
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Department: Polymer Science and Technology

Programme: Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YAĞ BAZLI POLİÜRETANLARIN BİYOMEDİKAL UYGULAMALAR İÇİN ÇÖZÜCÜ VE KATALİZÖR OLMADAN HAZIRLANMASI

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ABBREVIATIONS

HMDI	**:**	Hexamethylene diisocyanate
TDI	**:**	Toluene diisocyanate
MDI	**:**	Diphenyl methane diisocyanate
GPC	**:**	Gel Permeation Chromatography
^{1}H-NMR	**:**	Hydrogen Nuclear Magnetic Resonance
DSC	**:**	Differential Scanning Calorimeter
TGA	**:**	Thermal Gravimetric Analysis
FTIR	**:**	Fourier Transform Infra Red
PU	**:**	Polyurethane
TDA	**:**	Toluylene diamine
MDA	**:**	Diaminodiphenylmethane
DABCO	**:**	Tri-ethylene diamine1,4 diazo(2,2,2)bicyclooctane
HPLC	**:**	High Performance Liquid Chromatography
NMR	**:**	Nuclear Magnetic Resonance
DBTDL	**:**	Dibutyltin dilaurate
HTPB	**:**	Hydroxyl-terminated polybutadiene
IPTS	**:**	Isocyanato propyl triethoxy silane
IPDI	**:**	Isophorene diisocyannate
PG	**:**	Partial glyceride
HV	**:**	Hydroxyl value
AV	**:**	Acid value
THF	**:**	Tetrahydrofuran
PDI	**:**	Polydispersity index
KOH	**:**	Sodium hydroxide
HCl	**:**	Hydrochloric acid

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T_g	**:** Glass transition temperature
M_w	**:** Weight average molecular weight
M_n	**:** Number average molecular weight
k	**:** Rate constant
C	**:** Concentration

PREPERATION OF OIL-BASED POLYURETHANES FOR BIOMEDICAL APPLICATIONS IN THE ABSENCE OF SOLVENT AND CATALYST

SUMMARY

Polyurethanes have great importance as biomaterials because they are biocompatible and have very good mechanical properties. They can be used as catheters, heart-assist pumps, short term implants, hospital bedding, surgical drapes and wound dressing [1].

Polyurethanes are generally produced from petroleum based polyols and isocyanates in the presence of catalyst using the solvent method. Catalyst and solvent affect the purity of polymer and they are not preferred in polyurethane synthesis for biomedical applications. The aim of this thesis is the synthesis of oil-based polyurethanes in the absence of catalyst and solvent in order to obtain polymer in medical purity. Polyurethanes were prepared in two steps; 1) synthesis of hydroxyl containing material from linseed oil and glycerol and, 2) reactions of hydroxyl containing material with diisocyanates. Toluene-2.4-diisocyanate and hexamethylene diisocyanate were used as isocyanate component. Reactions were achieved under nitrogen atmosphere with or without catalyst.

Hydrogen Nuclear Magnetic Resonance (^{1}H-NMR) and Fourier Transform Infra Red (FTIR) were used for structural characterization of polymers. Gel Permeation Chromotography (GPC) was used for determination of molecular weight. Thermal Gravimetric Analysis (TGA) and Differantial Scanning Calorimeter (DSC) were used for investigation of thermal properties.

Free isocyanate content of the reaction mixture was determined by wet and FTIR methods during polymerization reaction. Obtained data were evaluated in the view of reaction kinetics.

YAĞ BAZLI POLİÜRETANLARIN BİYOMEDİKAL UYGULAMALAR İÇİN ÇÖZÜCÜ VE KATALİZÖR OLMADAN HAZIRLANMASI

ÖZET

Poliüretanlar biyomateryaller olarak oldukça öneme sahiptirler. Çünki, poliüretanlar biyouyumludurlar ve çok iyi mekanik özelliklere sahiptirler. Kateter, kalp pompası, kısa dönem implant, hastane yatağı, cerrahi kumaş ve yara örtüsü olarak kullanılabilirler [1].

Poliüretanlar, genellikle petrolyum bazlı polioller ve izosiyanatlardan katalizör ve çözücü kullanılarak üretilirler. Katalizör ve solvent kullanımı polimerin saflığını etkilediği için biyomedikal amaçlarla üretilecek poliüretan sentezlerinde kullanımı tercih edilmemektedir. Bu nedenle, bu çalışmada medikal amaçlarla kullanılacak yağ bazlı poliüretanların kütle polimerizasyonu yöntemi ile katalizörsüz sentezlenmesi amaçlanmıştır. Poliüretanlar iki aşamada hazırlanmışlardır; 1) Keten yağı ve gliserinden elde edilen hidroksil içerikli materialın sentezi, 2) hidroksil içerikli materyalin diizosiyanatlarla reaksiyonları. İzosiyanat bileşeni olarak ise toluene diizosiyanat ve hegzametilen diisosiyanat kullanılmıştır. Reaksiyonlar azot ortamında katalizörlü ve katalizörsüz olarak gerçekleşirilmiştir.

Polimerlerin yapıları Hidrojen Nükleer Manyetik Rezonans (H-NMR) ve Fourier Transform Infra Red (FTIR) spektroskopi ile aydınlatılmıştır. Son ürünlerin molekül ağırlıklarının belirlenmesinde Jel Geçirgenlik Kromatografisi (GPC), termal özelliklerin belirlenmesinde Termal Gravimetrik Analiz (TGA) ve Diferansiyel Taramalı Kalorimetre (DSC) kullanılmıştır.

Reaksiyon karışımlarının serbest izosiyanat miktarları yaş yöntem ve FTIR yöntem ile belirlenmiştir. Elde edilen veriler reaksiyon kinetiği yönünden değerlendirilmiştir.

1. INTRODUCTION

Polyurethane products have diverse applications including many consumer items, such as furniture, mattresses, bedding, carpet padding and appliances [1]. Since 1940s, polyurethane (PU) has been used in the manufacture of everything from baby toys to airplane wings, and continues to be adapted for up-to-date technology [2].

Segmented thermoplastic polyurethanes can exhibit properties as very soft thermoplastic elastomers and strong, rigid thermoplastics depending on their chemical composition, backbone structures and resultant microphase morphologies and they find applications in many different fields, such as; textile fibers, adhesives, protective coatings, membranes and biomaterials. Synthesis, characterization and investigation of structure-property relations of thermoplastic polyurethane have found much interest both for academic and industrial researchers for almost 50 years. The potential impact of polyurethanes will be very strong in many emerging fields, such as biomaterials and tissue engineering [3] due to their excellent blood compatibility and good physical properties [4].

The kinetics of urethane formation has been frequently studied in the solvent media. However, the studies on the kinetics in the bulk polymerization mode will be of more relevance to the propellant processing, and hence, more desired. It may be considered that the kinetics in the bulk will be quite different from that in solution [5].

Natural sourced polymers show better biocompatibility and require less time for biodegradability, which result in increase of the interest in the production of renewable natural sourced polymers as an alternative to the petroleum-based polymers [4, 6].

In this study, polyurethane was synthesized from renewable sources in the absence of solvent and catalyst to be used as a wound dressing. The reactions were monitored by FTIR. The produced polyurethane was characterized by Gel Permeation Chromatography (GPC), Hydrogen Nuclear Magnetic Resonance (^{1}H-NMR), Differential Scanning Calorimeter (DSC) and Thermal Gravimetric Analysis (TGA).

2. THEORETICAL PART

2.1 Polyurethanes

Polyurethanes (PU's) are formed in the reaction of isocyanates with polyols as shown in Equation 2.1. Where, "n" is the number of repeating units, R represents hydrocarbon group that includes hydroxyl group and R' represents the hydrocarbon group that is included in the structure from isocyanate group.

$$HO-R-OH + OCN-R'-NCO \longrightarrow [-R-O-C(=O)-NH-R'-NH-C(=O)-O-]_n \quad (2.1)$$
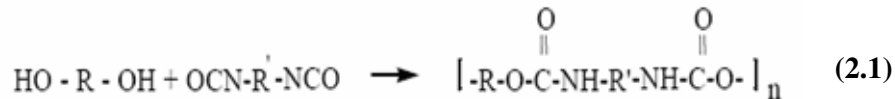
It is assumed that urethane reaction begins with the attack of alcoxide ion onto the carbon atom of isocyanate group (Equation 2.2).

$$R_1-N\overset{(-)}{=}C\overset{(+)}{=}\overset{(-)}{O} + \overset{(+)}{H}\cdots\overset{(-)}{O}R_2 \longleftrightarrow R_1-N-C=O \longrightarrow R_1NHC\,OOR_2 \quad (2.2)$$
$$H\cdots O-R_2$$
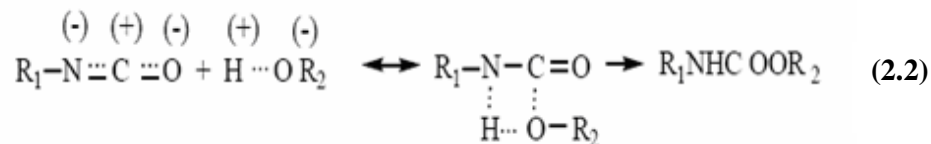
The increase of positive charging on the carbon atom results in increase of the will be resulted with an increase in reaction rate. This also explains the distinctly higher reactivity of aromatic isocyanates over aliphatic isocyanates [7, 8].

The amount of isocyanate required is calculated from the hydroxyl content of the polyol. Typically the isocyanate is slowly added to the polyol with continuous stirring at ambient temperature and then heated to 65-125 $^{\circ}$C. An exotherm is evident, and the viscosity slowly builds as the reaction proceeds [10]. It is known that polyurethane formation reactions generally obey second order rate law [7, 8].

Polyurethanes are an important subclass of the family of thermoplastic elastomers. Polyurethanes can be assumed as block copolymers that include soft and hard segments (Figure 2.1). The soft segment is typically a low glass transition temperature (Tg) polyether, polyester or polyalkyldiol, generally molecular weight of 400-5000 g/mol. The hard segment is usually a high glass transition temperature,

possibly semicrystalline aromatic diisocyanate, linked with a low molecular weight chain extender. As a general rule the isocyanates are hard segments that impart rigidity to the polymer and are effective in crosslinking. The polyol is called soft segment. Soft segments give elastomeric properties to the polyurethanes. The physical and mechanical properties of polyurethanes mainly depend on the distribution of soft and hard segments in the material. The mechanical and physical modifications can be obtained in the material by changing the phase distribution between soft and hard segments [7, 8, 9].
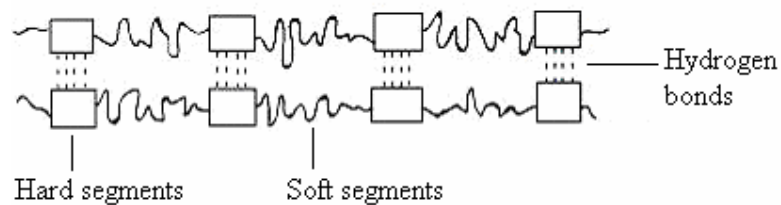
Figure 2.1: Segmented Polyurethane Structure

The other important parameter that influences the structural and mechanical properties of polyurethanes is the amount of crosslinking. While the amount of the crosslinking in the structure increases, the resistance that is formed against the applied force increases and the amount of the extension in the material decreases. For that reason, the ratio of the hard and soft segment and the amount of the crosslinking should be modified properly to attain the ideal properties of the end product [11].

Unlike polyurethanes excellent mechanical properties, the heat resistance properties are quite poor. They can protect the mechanical properties to 80-90°C. Thermal degradation begins above 250 °C. The heat resistance of the material is directly proportional to the crosslinking of the material. In addition to that, it is possible to add heterosiclic groups such as imide to the main chain to improve their heat resistance. [12, 13].

The raw materials used in the production of polyurethanes can be classified in three groups as isocyanates, polyols and chain extenders. Moreover, water, blowing agents, catalysts, structure regulators and solvents can also be used as supplementary materials in the production of some special products such as elastomers, foams, coverings. Wide range of materials can be obtained by changing any raw material,

formulation and process. Therefore, the diversity of the end product can be provided [14, 15].

The density and hardness of the polyurethane vary with the type of monomer(s) and adding other substances. Furthermore, different additives can be improved the fire performance, stability in difficult chemical environments and other properties of the polyurethanes [16].

2.2 Raw Materials

2.2.1 Isocyanates

Isocyanate is the first essential component of a polyurethane polymer. Isocyanates, the esters of isocyanate acid, were first synthesized by Wurtz in 1848. Prominent nineteenth century scientists, such as Hofmann and Curtius, studied the chemistry of isocyanates, but it took almost a century to be recognized that diisocyanates are ideally suited to undergo addition polymerization reaction with polyester or polyether diols to form polyurethanes [17].

Polymeric diphenylmethane diisocyanate, which is a blend of molecules with two-, three-, and four- or more isocyanate groups is an example of a polymeric isocyanate and has an average functionality of 2.7. When isocyanates are partially reacted with a polyol, they form a prepolymer. The important characteristics of isocyanates are NCO % content, their molecular backbone, functionality, and viscosity.

Although the properties of the polyurethane are determined mainly by the choice of polyol, the diisocyanate presents some influence, and must be suited to the application. The functional group reactivity and the number of functional isocyanate groups influence the cure rate. Functionality and the molecular shape influence the mechanical properties. Diisocyanate choice also affects the stability of the polyurethane upon exposure to light. Polyurethanes that are made with aromatic diisocyanates yellow with exposure to light, whereas those made with aliphatic diisocyanates are stable [16].

Isocyanates of the general structure shown in Equation 2.3, react vigorously with amines, alcohols, and carboxylic acids.

The main chemical feature of isocyanates is their high reactivity toward nucleophiles such as alcohols, phenols, and amines. However, in certain situations this high reactivity can pose problems, particularly toward moisture [18].

$$R-\ddot{N}-C=\ddot{O} \longleftrightarrow R-\ddot{N}=C=\ddot{O} \qquad\qquad (2.3)$$

$$\updownarrow$$

$$R-\ddot{N}=C-\ddot{O}$$
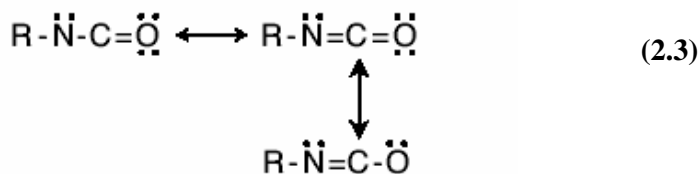
Isocyanates are divided into two groups; mono- and di-isocyanates. The monoisocyanates are subdivided into alkyl and aryl isocyanates; unsaturated isocyanates; halogenated alkyl and aryl isocyanates; carbonyl, thiocarbonyl and imidoyl isocyanates; sulfur isocyanates; phosphorus isocyanates; and inorganic isocyanates. The diisocyanates are also classified as aliphatic diisocyanates and aromatic diisocyanates [19].

Both aromatic and aliphatic isocyanates are commercially available. Depending on their chemical structure, the aromatic isocyanates are faster reacting by a factor of between 2-10. The most important commercial aromatic isocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), while the important aliphatic isocyanates are hexamethylene diisocyanate (HMDI) and isophorene diisocyanate (IPDI) [8, 20]. Some of examples of the diisocyanates are shown in Figure 2.2.
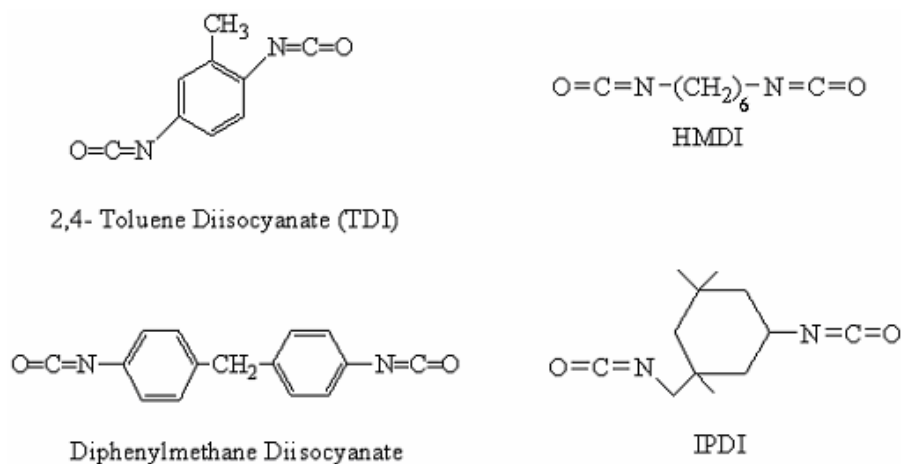
Figure 2.2: Diisocyanate Structures

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2.2.2 Polyols

The second essential component for the polyurethane polymer is the polyol. The first commercially available polyether polyol was poly(tetramethylene glycol) introduced in 1956 by DuPont. In the following years, BASF and Dow Chemical improved less expensive polyether polyols. These polyether polyols exerted technical and commercial advantages such as low cost, ease of handling, and better hydrolytic stability; and quickly supplanted polyester polyols in the manufacture of polyurethane goods. Polyols are the compounds with hydroxyl end groups. While, lower molecular weight compounds act as chain extenders or as crosslinkers, higher molecular weight polyols are the actual basis for the formation of the polyurethanes. These higher molecular weight polyols are obtained mainly from two classes of products: the polyethers and the polyesters.

The polyols used in polyurethane synthesis are polyether based and polyester based polyols and they have molecular weight between 400-5000 [8, 16].

The choice of initiator, extender, and molecular weight of the polyol greatly influence its physical state, and the physical properties of the polyurethane polymer. Important characteristics of polyols are their molecular backbone, molecular weight, primary hydroxyl groups content, initiator, functionality, and viscosity.

When linear difunctional polyethylene glycol segments, commonly called polyether polyols, are used to create the urethane links, softer, elastic, and more flexible polyurethanes result. This strategy is used to make elastomeric fibers and soft rubber parts, and also foam rubber. When polyfunctional polyols are used, more rigid products result and as these create a three-dimensional cross-linked structure, which, again, can be in the form of low-density, foam [16].

The polyethers are more easily designed when the polarity of the backbone is important. For instance, one can use polyethers to construct polyurethanes that are hydrophilic or hydrophobic or react to water at all levels between these extremes. Polyether polyols have higher hydrolytic stability than the polyester polyols, but they are more sensitive to different kinds of irradiation and oxidation at elevated temperatures. Polyethers permit the development of biocompatible and hemocompatible devices [7, 8, 10]. Poly (tetramethylene ether) glycol as an example

for a polyether and polyethylene adipate as an example for polyester are shown in Figure 2.3.

$$OH-\left[(CH_2)_4O\right]_n H$$

poly(tetramethylene ether) glycol

$$HO(CH_2)_2-\left[OCO(CH_2)_4COO(CH_2)_2\right]_n OH$$

polyethylene adipate
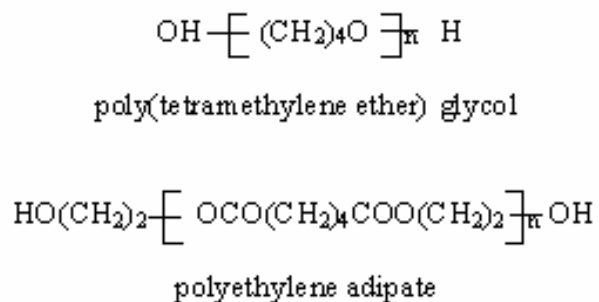
Figure 2.3 Polyol Structures

Modified soy-based plant oil polyols, an economical and environmentally friendly alternative to petroleum for biodegradable polymer synthesis [21], are also successfully incorporated as a replacement for conventional polyols to produce polyurethane [22].

2.2.3 Diamines and Diols

Besides the polyols, di- and polyamines has an important role for the formation of polyurethanes. They are used in two ways: as starters for polyols and as chain extenders. Ethylene diamine as an example for aliphatic amines, toluylene diamine (TDA) and diaminodiphenylmethane (MDA) as examples for aromatic amines are used as starting molecules for the manufacture of polyethers [8].

Low molecular weight di-functional compounds such as hydroxyl amines, glycols or diamines are used as chain extenders. The use of a chain extender is to increase the molecular weight of the hard segment enables the phase separation in the final material. They are used to influence the end properties of the PU. The selection of a diamine or diol sets whether urea groups or urethane groups are formed. This influences the degree of phase separation that occurs, which then influences the mechanical properties of the products. Generally, the usage of aliphatic chain extenders supplies more soft materials with respect to usage of aromatic chain extenders. They increase the molecular weight and the consistency of hydrogen bond. Some of the commercially used chain extenders are; 1, 4 butandiol, ethylene diamine and ethylene glycol [8, 20].

2.2.4 Additives

Catalysts, stabilizers, crosslinkers, surfactants, blowing agents, flame-retardants, fillers, pigments and solvents are examples of the additives.

Catalysts are required to facilitate polyurethane formation. Because, even though isocyanates react directly with linear polyols, the rate of reaction decreases rapidly as the size of the substituents on the higher alcohols increases. Catalysts for the isocyanate and alcohol reaction are mild and strong bases, such as sodium hydroxide, sodium acetate and triamines, and metals especially tin compounds. Commonly used catalysts include tertiary amines, such as tri-ethylene diamine 1,4 diazo(2,2,2)bicyclooctane (DABCO) [7].

2.3 Applications of Polyurethanes

Polyurethanes are used in many different areas in the modern life. They have widespread applications from automobile industry to medicine. They are used in the production of furniture, coatings, adhesives, foams, fibers, dye, elastomers, artificial organ and various medical equipments [23].

Their structure makes them suitable to be used in such various applications. Polyurethanes can be obtained with different mechanical and physical properties by varying the type on the raw material used in the synthesis.

Polyurethanes can be found in many of the products that we use in our daily lives. They have diverse and widespread applications, including many consumer items, such as furniture, mattresses, bedding, carpet padding and appliances [24].

Polyurethane is also used in furniture manufacture for casting soft edges around tabletops and panel that are stylish, very durable and prevent injury. These are used in school tables, hospital and bank furniture as well as shop counters and displays.

Polyurethane materials are largely formulated as paints and varnishes for finishing coats to protect or seal wood. "Oil-modified" polyurethanes, whether water-borne or solvent-borne, are presently the most widely used wood floor finishes.

While exterior use of polyurethane varnish may be problematic due to its susceptibility to deterioration through ultra-violet light exposure, polyurethanes are

typically the most resistant to water exposure, high humidity, temperature extremes, and fungus or mildew, which also adversely affect varnish and paint performance.

Moreover polyurethane is used on the bottom of some mouse pads in making solid tires. Some surfboards are made with a solid polyurethane core. Skateboarding and modern roller blading became economical with the introduction of tough, abrasion-resistant polyurethane parts [16].

Today's polyurethanes are formulated to provide good biocompatibility, flexural endurance, high strength, high abrasion resistance and processing versatility over a wide range of applications. Therefore, they are used in a number of medical device applications. These attributes are important in supporting new applications continually being found by medical device manufacturers including cardiovascular devices, dialysis devices, non-allergenic gloves, medical garments, hospital bedding, and surgical drapes as well as in a variety of injection molded devices. Their most common use in medical devices is in short-term implants. They are appropriate for a variety of uses where advantages such as cost effectiveness, longevity, toughness and high stress/strain properties are desired [25].

Polyurethanes outperform many other materials in flexibility, abrasion resistance and tear resistance. This is because many devices that are used in these areas can rub against other materials and bend continually. Without polyurethanes, the continued rubbing and bending would make the device weakening or may cause failure in extreme cases [26].

Due to their comfort, patients prefer to use polyurethane medical devices than the other materials. They are also used in many soft elastomeric medical applications such as indwelling catheters and vascular access. Since soft polyurethanes are stronger than other soft materials, they are unique materials for elastomeric medical applications [25].

Due to appreciable physical and mechanical properties and good tissue and blood compatibility in comparison to the other elastomers, polyurethanes have been widely used for various biomedical applications such as vascular prostheses, artificial hearts, in catheter and general purpose tubing, feeding tubes, endotracheal tubes, surgical drains, intra-aortic balloon pumps and wound dressings [25, 26].

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Thermoplastic polyurethanes, also known as polyurethane elastomers, have similar molecular structures with human proteins. Protein absorption, the beginning of the blood coagulation cascade, was found to be slower and/or less than other materials which makes them ideal candidates for a diversity of medical applications requiring adhesive strength and unique biomimetic and antithrombotic properties. Being used as a sealant to bind bundles of hollow fibers in artificial dialysis cylinders is a good example for that purpose.

Biomedical polyurethanes can lead the way to eliminate some acute and chronic health challenges by the appearance of new surgical implants. Polyurethanes are popular in cardiovascular and other biomedical fields due to their good biocompatibility as well as their mechanical properties. Many of those polyurethanes have elastomeric properties that are accompanied by toughness, tear resistance and abrasion resistance. They have been generally used in applications such as the artificial heart and pacemaker lead insulation.

Polyurethanes have really important role in the medical industry. Moreover, by superior of their range of properties, they will continue to play an important role in the future of science and medicine [26].

A wound dressing is an adjunct used for application to wound in order to promote healing and/or prevent further harm.

Historically, a dressing was usually a piece of material, sometimes cloth, but the use of cobwebs, dung, leaves and honey has also been described. However, modern dressings include gauzes (which may be impregnated with an agent designed to help sterility or to speed healing), films, gels, foams, hydrocolloids, alginates, hydro gels and polysaccharide pastes, granules and beads. Dressings can be impregnated with antiseptic chemicals, as in boracic lint or where medicinal castor oil was used in the first surgical dressings [27].

A wound dressing is designed to be in direct contact with the wound, which makes it different from a bandage, which is primarily used to hold a dressing in place. Dressings are frequently used in first aid and nursing [16]. There are mainly three types of wound dressing materials; foam, gel and film types. Film type is one of the well known applications in this field since vapor permeability, which is required for recovering of the pain. Not only it protects the pain from external effects, but also it

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can absorb the inflammation that is produced onto the pain. One of the best properties of film product is easy to be applied by the patients [7].

Different parameters are broached to evaluate the biocompatibility of polymers. These are; skin irritation, blood compatibility, cell toxicity, and carcinogenicity. The failure of one of these parameters might cause the body regret the material. If the material is successful on these biocompatibility tests, the antibacterial behaviors of the material are monitored. Since hydrophilic materials sprinkle proteins instead of adsorbing them, which will cause adsorption of water, they should be chosen as wound dressing material [28].

Wounds kept moist are healed faster than those that were left exposed to the air or covered with traditional dressings. Ideal dressings should control the moisture content, so that the wound stays moist; protect the wound from infection, remove slough and maintain the optimum pH and temperature to encourage healing.

An "ideal" wound dressing must be sterile, breathable, and encourage a moist healing environment. Then this will reduce the risk of infection, help the wound heal more quickly, and reduce scarring [27].

2.4 Triglyceride Oil-Based Polyurethanes

The usage of polyols derived from domestic vegetable oils products for production of polyurethane began garnishing attention around 2004, not only the rising costs of petrochemical feed stocks but also an enhanced public desire for environmentally friendly products [29].

Natural oil triglycerides have been employed for a long time as a feedstock for paints, coatings, lubricants, etc. In recent years, the synthesis of structural polymeric materials from these natural oils has been improved significantly.

Natural oils (plant oils and marine fish oils) possess a triglyceride structure with highly unsaturated fatty acid side chains. The multiple C-C bonds make those biological oils ideal monomers of natural origin for the preparation of biopolymers.

Plant oils, which are triglycerides of fatty acids, have a number of excellent properties like the utilization for production polymeric materials such as

polyurethanes. The biobased polyurethanes are prepared by the condensation polymerization of plant oil polyols and diisocyanates.

Most of the urethane polymers are lightly cross-linked materials with low thermo-mechanical and physical properties. Rigid polyurethanes with higher compressive strength and oxidative and thermal stability are prepared from hydroxylated soybean oil, glycerol and isocyanates. In the literature, there are some examples of polyurethanes prepared from castor oil and various aliphatic and aromatic diisocyanates [30].

Urethane modified polyetheramide resins can be used as an anticorrosive coatings material [31]. Linseed oil based urethane alkyd resins have good solvent resistance, hydrolysis resistance and superior abrasion performance. Uralkyds are adapted to waterborne application and new polyurethane dispersions with drying oil modification [32, 33]. In the form of foamed polyurethane rubber, polymerized castor oil is utilized in seat cushions [14].

Furthermore, polyurethanes from soybean oil have good thermal, oxidative and weather stability, and can be used as a matrix in composite materials [34].

Shape memory polymers, such as heat-shrinkable tubing and films, have been widely used in cable and wire as well as the medical and packaging industries. Due to their low cost, easy processibility, and large variations in starting materials, shape memory polymers also possess great potential as materials for civil engineering, machinery manufacturing, electronics and communications, household materials, etc. Shape memory soy oil plastics are a new class of shape memory materials. More importantly, these materials are the first shape memory polymers prepared from renewable natural resources. Thus, the new soy oil plastics have certain advantages over petroleum-based shape memory polymers, and have definitely broadened the variety and applications of these functional materials [30].

2.5 Kinetics of Polyurethane Reactions

Different characterization methods have been used to monitor the polymerization reactions kinetics. The methods can be classified into two groups: indirect methods, which measure a physical property that can be functionally related to the extent of

reaction, and direct methods, which measure the concentration of reactant or product species. Some of the examples to those methods;

- Di-n-butylamine titration method (wet method)

- FTIR spectroscopy method

- UV spectroscopy method

- HPLC, High performance liquid chromatography method

- Viscosity measurement method

- Torsional braid method

- NMR spectroscopy method [35].

2.5.1 Wet Method

Wet method is a general method which determines the isocyanate concentration in polyurethane synthesis [36]. It is studied with reference to the standard test method of ASTM D 2572-97. It is described in section 3.5.1 with in detail.

Wet method is an alternative choice when solid particles exist in the media. However, it requires a lot of study to provide the repeatability of the results.

2.5.2 FTIR Spectroscopy Method

FTIR spectroscopy method is performed by monitoring the reaction by following the consumption of isocyanate. It is not appropriate when solid particles exist in the media.

Functional groups and absorption bands positions in urethane reactions;

- ✓ The absorption band of hydroxyl (-OH) group that enter into reaction is monitored at 3590-3650 cm^{-1}. The intensity decreases during the reaction.

- ✓ The tension band of isocyanate radical (-NCO) that enter into reaction is monitored at 2255-2270 cm^{-1}. The intensity decreases during the reaction.

- ✓ The produced urethane (-NH-COO-) band in the reaction is monitored at 1698-1725 cm^{-1}. The intensity increases during the reaction. It is also known as absorption band belongs to tension titration of amid and C=O [37].

2.5.3 Determination of Reaction Order

It is obligatory to obtain experimental data in order to be able to determine the reaction order. The rate constant can be varied with changing the temperature of the reaction, adding a catalyst, or changing the catalyst. A catalyst will provide a route for the reaction with lower activation energy. In the presence of a catalyst, the activation energy decreases, and moreover, there are a massive increase in the fraction of the molecules, which are able to react. There will be more molecules, which can react in the presence of the catalyst compared to having no catalyst.

The methods for determination of the rate order are different applications of differential and integral method. These methods are; reaction rate constant method, graphical method, half life method, van't Hoff method etc.

A practical approach for determination of the rate order is to make characteristic kinetics plots. For each integrated rate law, there is a characteristic plot which will produce a straight line. These characteristic plots are presented in the Table 2.1. The species A is a reactant in the chemical reaction.

In our study, the characteristic kinetics plots method is used; the straight line is determined and the reaction order is equal to the order of the correlation that is used [38].

Table 2.1: The Characteristic Kinetic Plots Depending on Reaction Orders

Reaction Order	Differential Rate Law	Integrated Rate Law	Characteristic Kinetic Plot	Units of Rate Constant
Zero	$-\dfrac{d[A]}{dt} = k$	$[A] = [A]_0 - kt$	$[A]$ vs t	mole L^{-1} sec^{-1}
First	$-\dfrac{d[A]}{dt} = k[A]$	$[A] = [A]_0\, e^{-kt}$	$\ln [A]$ vs t	sec^{-1}
Second	$-\dfrac{d[A]}{dt} = k[A]^2$	$[A] = \dfrac{[A]_0}{1 + kt[A]_0}$	$1/[A]$ vs t	L $mole^{-1}$ sec^{-1}

2.5.4 Examples for the Kinetics Studies of Polyurethane in Literature

In a study of Schapman et al., polyurethane was synthesized with dibutyltin dilaurate (DBTDL) catalyst. Hydroxyterminated polybutadiene (HTPB), a commercial polymer synthesized by radical polymerization was used as polymer and IPTS;

isocyanato propyl triethoxy silane was used as a croosslinking agent. The reaction was monitored by two methods that are FTIR and volumetric titration. Resonance of CH of 1,4 double band at $960cm^{-1}$ was taken as reference in FTIR. The disappearance of isocyanate band at $2270cm^{-1}$ was monitored. In the study, both catalyzed and uncatalyzed reactions were performed at $30-60^{o}C$. At the end of the kinetic evaluations the second order kinetics was observed [39].

Kincal et al. carried out the kinetic study of the reaction between HTPB and isophoron diisocyanates (IPDI) in bulk state by using FTIR spectroscopy. He recorded the intensity differences on the tension resonance band of IPDI on NCO group. He cited that the reaction obeys second order kinetics. Tension band of C=C at 1640 cm^{-1} was taken as the reference band, and the tension band at 2255 cm^{-1} for NCO was taken. Estimating these two intensives, reaction was monitored. Furthermore, a calibration curve was formed and all the absorption values were converted to NCO concentration by using this calibration curve. The urethane formation band occurred in 1725 cm^{-1}. The urethane reactions were performed at $40-60^{o}C$ in that study [40].

3. EXPERIMENTAL PART

3.1 Chemicals

Linseed oil was used to obtain partial glyceride (PG) which is the hydroxyl source for the polyurethane synthesis. Some properties of the linseed oil are given in Table 3.1.

Table 3.1: Some Properties of Linseed Oil

Refractive index, n_D^{20}	1.4812
Acid value (mgKOH/g sample)	1.1
Saponification value (g NaOH/g oil)	197
Iodine value (g iodine/100g oil)	166.8
Fatty acid composition (%)	
$C_{16:0}$	11%
$C_{16:1}$	3.2%
$C_{18:0}$	11.6%
$C_{18:1}$	31.6%
$C_{18:2}$	21.4%
$C_{18:3}$	20%
Other	1.2%

Glycerine, anhydrous (Merck) was used in PG synthesis. It has a molecular weight of 92.1 g/mol and a density of 1.26g/ml.

Toluene 2.4 diisocyanate (TDI) (Merck), 80:20 blends of the 2.4 and 2.6 isomers with a molecular weight of 174.16 g/mol and a density of 1.22 g/ml, was used in polyurethane synthesis as isocyanate component.

Hexamethylene diisocyanate (HMDI) (Merck), has a molecular weight of 168.2 g/mol and a density of 1.05 g/ml, was used in polyurethane synthesis as isocyanate component.

Sodium sulfate (Na_2SO_4) (Merck) was used as dryer.

Calcium hydroxide ($Ca(OH)_2$) and 24 wt.% solution of lead naphthenate in white spirit were used as catalysts.

Diethyl ether (technical grade), sulfuric acid, 96% (Carlo Erba) were used for preparation of PG.

Potassium hydroxide (KOH) (Riedel-de Haen), acetic anhydride (Merck), pyridine (Merck), di-n-butylamine (Merck), hydrochloric acid (HCl), 37% (Merck), isopropyl alcohol (Reidel-de Haen), toluene anhydrous (Reidel-de Haen) were used for the chemical analysis of semiproducts and products.

Phenol ftalein, tymol blue and bromphenol blue (Merck) were used as indicators during titrations.

Tetrahydrofuran (THF) (Sigma Aldrich) was used in determination of molecular weight without any further purification.

3.2 Polymer Preparation

Polymer preparation was achieved in two steps. The first step was the preparation of PG mixture from linseed oil and glycerine. The second step was the synthesis of polyurethane (PU) from PG mixture and diisocyanates.

3.2.1 Preparation of Partial Glyceride Mixture

The reaction between linseed oil and glycerine is shown in Equation 3.1. The reaction was carried out in 250 ml three-necked flask equipped with a stirrer, a thermometer, and nitrogen inlet tube (Figure 3.1).

Linseed oil and glycerine (8.5 wt.% of the oil) were put into the reaction flask. The mixture was stirred and heated till the temperature reached up to 218 °C. At this temperature, calcium hydroxide (0.1 wt.% of the oil) was added as catalyst. Then the temperature was adjusted to 232 °C. The reaction was performed at this temperature for 45 minutes under the nitrogen atmosphere.
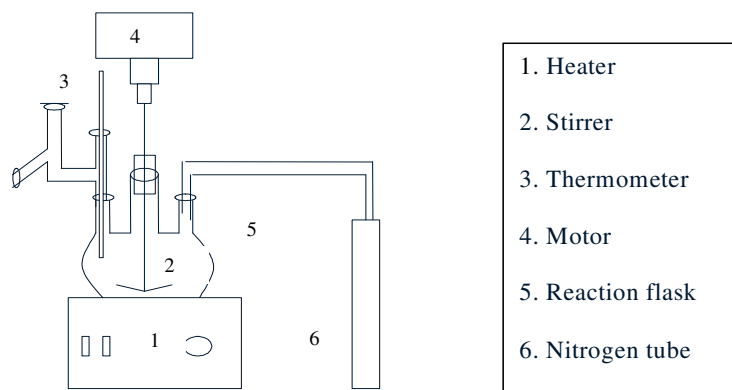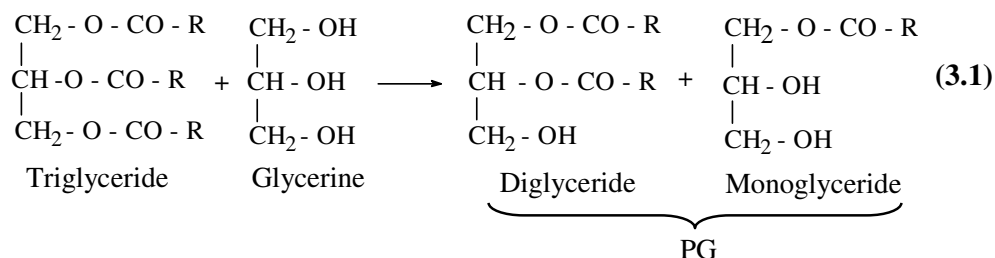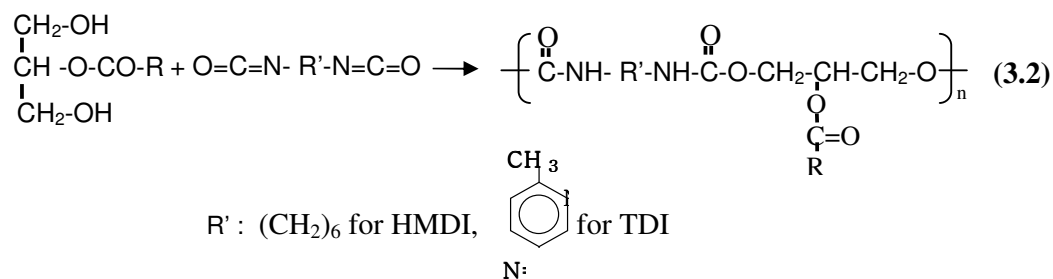
Figure 3.1: Experimental Set-up for Preparation of PG

After cooling the reaction mixture, it was solved with diethyl ether and washed first with dilute hydrochloric acid and then with distilled water to remove the catalyst and unreacted glycerol. The ethereal solution was then dried over sodium sulfate for one night. The solution was filtered through a filter paper placed onto a funnel. Then the solvent was removed by using rotary evaporator and hydroxyl and acid values of PG were determined [41]. The reaction product is the mixture of diglyceride, monoglyceride and unreacted tryglyceride (Equation 3.1).

$$
\begin{array}{c}
\underset{\text{Triglyceride}}{
\begin{array}{l}
CH_2 - O - CO - R \\
| \\
CH - O - CO - R \\
| \\
CH_2 - O - CO - R
\end{array}}
\; + \;
\underset{\text{Glycerine}}{
\begin{array}{l}
CH_2 - OH \\
| \\
CH - OH \\
| \\
CH_2 - OH
\end{array}}
\longrightarrow
\underset{\text{Diglyceride}}{
\begin{array}{l}
CH_2 - O - CO - R \\
| \\
CH - O - CO - R \\
| \\
CH_2 - OH
\end{array}}
\; + \;
\underset{\text{Monoglyceride}}{
\begin{array}{l}
CH_2 - O - CO - R \\
| \\
CH - OH \\
| \\
CH_2 - OH
\end{array}}
\end{array}
\qquad (3.1)
$$

PG

3.2.2 Preparation of Polyurethane Sample

PG mixture was taken into reaction flask and heated to 45°C, and an equivalent amount of isocyanate component was slowly added over a 5 min period. The temperature was set to 90-95 °C. The reaction was achieved under the nitrogen atmosphere with or without catalyst [42]. The reaction between monoglyceride portion of PG mixture and diisocyanate is shown in Equation 3.2.

$$CH_2\text{-OH}$$
$$CH\text{-O-CO-R} + O=C=N\text{-}R'\text{-N=C=O} \longrightarrow \left[\begin{array}{c} O \quad\quad\quad O \\ \| \quad\quad\quad \| \\ C\text{-NH-}R'\text{-NH-C-O-CH}_2\text{-CH-CH}_2\text{-O} \\ \quad\quad\quad\quad O \\ \quad\quad\quad\quad C=O \\ \quad\quad\quad\quad R \end{array} \right]_n \quad \textbf{(3.2)}$$
$$CH_2\text{-OH}$$

R' : $(CH_2)_6$ for HMDI, [CH$_3$ ring structure] for TDI

In catalyzed reactions, lead naphthenate solution was added in the amount of 0.02 wt.% of the oil portion. The codes of produced polyurethanes are given in Table 3.2.

Table 3.2: The Codes of PU Samples

Type of diisocyanate	Catalyst content (wt.%)	Code
TDI	0,02422	PU-TDI-C (1)
TDI	0,01218	PU-TDI-C (2)
TDI	-	PU-TDI-UC (1)
TDI	-	PU-TDI-UC (2)
TDI	-	PU-TDI-UC (3)
HMDI	0,1607	PU-HMDI-C (1)
HMDI	0,1589	PU-HMDI-C (2)
HMDI	-	PU-HMDI-UC (1)
HMDI	-	PU-HMDI-UC (2)
HMDI	-	PU-HMDI-UC (3)

3.3 Characterization of Intermediate Products

Hydroxyl value of partial glyceride mixture and the free isocyanate content of reaction mixtures in the polyurethane synthesis were determined.

3.3.1 Determination of Hydroxyl Value

Wet method was used for determination of hydroxyl value of PG [43]. Hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount

of acetic acid capable of combining by acetylating with 1g of sample and it is obtained by the Equation 3.3.

$$\text{Hydroxyl Value} = \left(\frac{56.1 \times N \times (V_2 - V_1)}{W} \right) + \text{Acid Value} \qquad \textbf{(3.3)}$$

where;

W = Weight of sample (g.)

V_1 = Amount of KOH used in test (ml.)

V_2 = Amount of KOH used in blank (ml.)

N = Normality of KOH

In order to calculate the hydroxyl value, acid value must be known. Acid value is the number of mg potassium hydroxide required to neutralize 1g of sample. In the experiment approximately 1g of sample was dissolved by 30 ml toluene- alcohol solution and titrated by KOH dissolved in alcohol. Equation 3.4 was used as calculation of acid value.

$$\text{Acid Value} = \frac{56.1 \times N \times V}{W} \qquad \textbf{(3.4)}$$

where;

N: Normality of potassium solution

V: Volume of potassium hydroxide solution used (in ml)

W: Weight of PG sample (in g).

3.3.2 Determination of Free Isocyanate Content

Wet and FTIR spectroscopy methods were used for determination of the free isocyanate content of the sample in the polyurethane synthesis.

Wet Method

Free isocyanate content of the samples was determined according to the ASTM standard [44]. According to this method, 0.1g of sample containing approximately 1.1 milliequivalents of free isocyanate was dissolved in 25ml of dry toluene, and then

25 ml of 0.1N di-n-butylamine solutions was added and continued swirling for 15 min with stopper in place. 100ml of isopropyl alcohol and 4 to 6 drops of bromphenol blue indicator solution were added and the solution was titrated with 0.1N hydrochloric acid to a yellow end point. The free isocyanate content was calculated by using the Equation 3.5.

$$\text{Free isocyanate}, \% = \frac{[(B - V) \times N \times 0.0420]}{W} \times 100 \qquad (3.5)$$

where;

B   = volume of HCl for titration of blank, ml,

V   = volume of HCl for titration of the specimen, ml,

N   = normality of HCl, N,

0.0420   = milliequivalent weight of the NCO group,

W   = grams of specimen weight, g.

FTIR Method

The height of the isocyanate (NCO) stretching band at 2263 cm^{-1} was measured for the reaction mixture. The height of the corresponding peak was decreased during the reaction as shown in Figure 3.2.
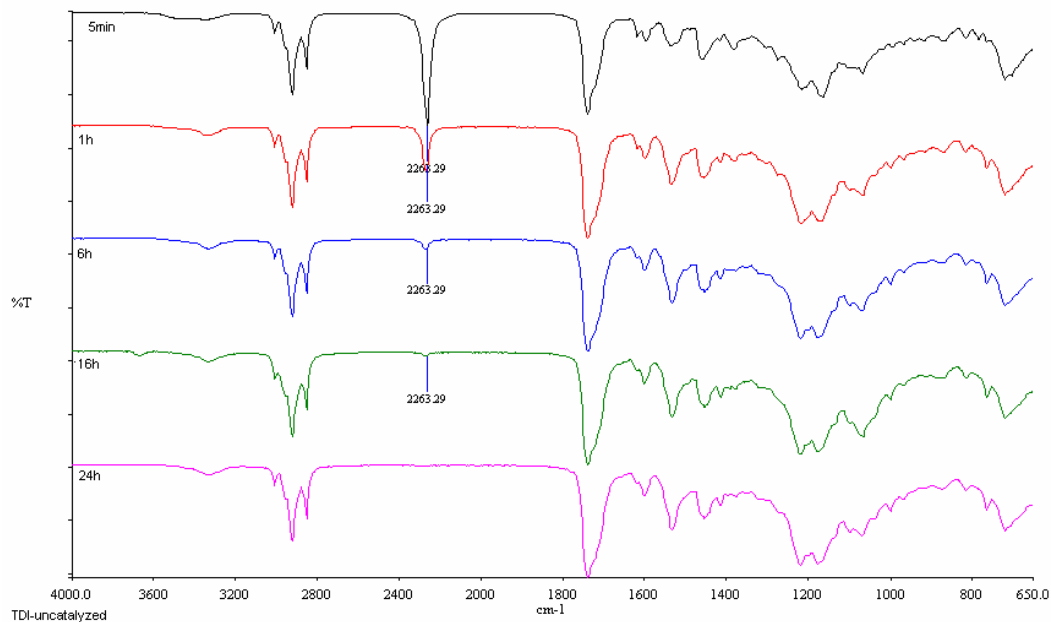
Figure 3.2: FTIR Spectra of Reaction Mixture

3.4 Characterization of Polymers

Infrared spectra of the polymers were recorded in a Perkin Elmer Spectrum One Model Fourier Transform Infrared (FTIR) spectrometer. ATR mode was used.

The polymers were characterized by ^{1}H Nuclear Magnetic Resonance (^{1}H-NMR) with Bruker 250 MHz spectrometer using deuterium chloroform as a solvent and tetra methyl silane as an internal standard.

Gel Permeation Chromatography (GPC) was used for determination of molecular weight for polymers. Chromatograms were obtained by using an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) at a flow rate 0.3ml/min. Calibration of GPC was performed by using polystyrene standards. Thermal behavior of the polymers was determined by Differential Scanning Calorimeter (DSC). Perkin Elmer Diamond DSC instrument was used under nitrogen atmosphere with a heating rate of 20ºC/min. Temperature and enthalpy calibration of DSC was obtained by using indium, lead and tin standards.

Thermogravimetric Analysis (TGA) was used for determination of thermal behavior of the polyurethanes. TA TGA Q 50 analyzer was used from 25 to 600 ºC under the nitrogen atmosphere at a heating rate of 20ºC/min.

3.5 Kinetic Study

The rate equation can be considered as seen in Equations 3.6 where C stands for concentration, t for the reaction time, k for the rate constant and n for the reaction order.

$$\frac{d[C]}{dt} = -k[C]^n \tag{3.6}$$

Integral method was used for evaluation of kinetic data. The rate equation was integrated to retrieve the concentration-time relationship for first, second and third order reactions. For each integrated rate law, there was a characteristic plot, which produced straight line. The straight lines for each reaction were chosen by looking at the regression coefficients of the lines, and the slope of the straight line gave the rate constant.

4. RESULTS AND DISCUSSION

4.1 Characterization of Polymers

Partial glyceride (PG) mixture was synthesized as the hydroxyl containing material for polyurethane synthesis. The hydroxyl and acid values of PG mixture was found 121.3 mg KOH/g sample and 4.2 mg KOH/g sample, respectively.

The structure of polyurethanes synthesized in the absence of catalyst and solvent (PU-TDI-UC (1) and PU-HMDI-UC (1)) were characterized by ^{1}H-NMR, GPC, TGA and DSC.

4.1.1 Characterization of Polymers by ^{1}H-NMR

The NMR spectrums of PU-TDI-UC (1) and PU-HMDI-UC (1) are shown in Figures 4.1 and 4.2, respectively. In the case of PU-TDI-UC, it is expected that the urethane N-H proton show peak around 8.0-9.0 ppm. The absence of this peak can be explained by the existence of hydrogen bonding between C=O and N-H groups in polymer chain, which prevents to appear corresponding peak. While aromatic benzene protons of urethane group give resonance signal on 7.04 ppm, CH protons addicted to ester group give signal on 5.33 ppm, metanoxy groups addicted to –CONH give signal between 4.29 and 4.08 ppm and methylene group addicted to aromatic benzene give signal on 2.18 ppm.
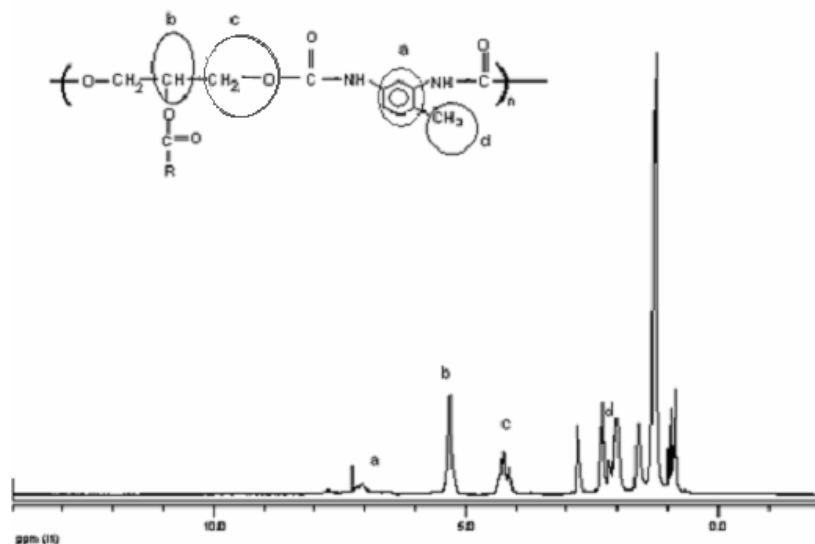
Figure 4.1: ^{1}H-NMR Spectra of PU-TDI-UC (1)

In Figure 4.2, the resonance signals between 5.37 and 5.25 ppm belong to –CH=CH– protons. It is not able to be seen the resonance signal of NH protons which normally shows peak around at 8.0 and 9.0 because of the formation of hydrogen bonding in polymer structure. When –CH protons addicted to ester groups give resonance signals between 4.29 and 4.07 ppm, metanoxy groups addicted to –CONH give signal on 3.11 ppm. Methylene groups addicted to –NH group and other methylene groups give resonance signals on 2.34-2.25 and on 1.57-0.81, respectively.
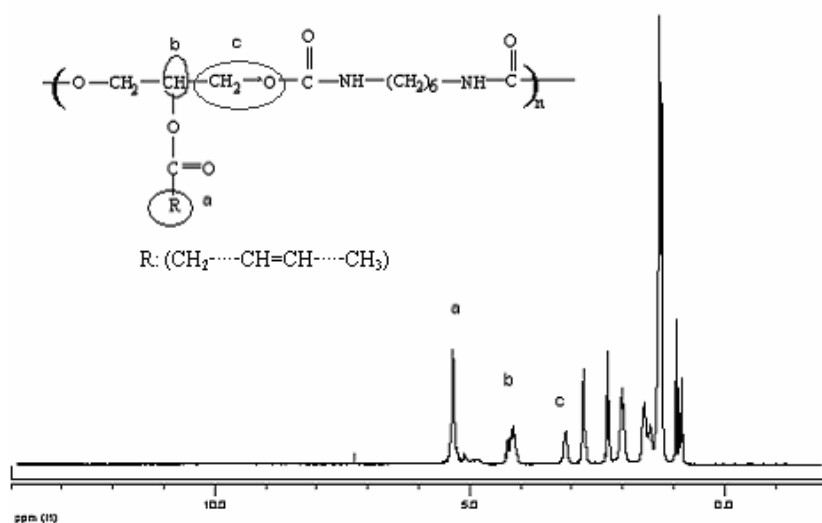
Figure 4.2: ^{1}H-NMR Spectra of PU-HMDI-UC (1)

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4.1.2 Determination of Molecular Weight

The weight average molecular weight (Mw) and polydispersity index (PDI) of the polymers obtained are given in Table 4.1. It was found that TDI-based PU's has higher molecular weight than HMDI-based PU's. This result can be explained by aromatic structure of TDI. It is known that aromatic isocyanates are much more reactive than aliphatic isocyanates. On the other hand, it was observed that polydispersity index (PDI) of PU's were increased with increasing of molecular weights.

PDI is a measure of the distribution of molecular weight in a given polymer sample. When molecular weight increased, the chain length of the polymer chains depart from uniform. Typical PDI's vary based on the mechanism of polymerization and it can be affected by a diversity of reaction conditions. For typical step-growth polymerization, values of the PDI can range around 2 [45]. Because polyurethane formation is step-growth polymerization, it is possible to see monomer, trimer, and oligomer at anytime in the reaction mixture. The PG mixture is a mixture of monoglyceride, diglyceride and unreacted triglyceride. The presence of the diglyceride and triglyceride portions in the reaction mixture cause high PDI's because of the one and none hydroxyl groups in their structure, respectively.

Table 4.1: Molecular Weight Data of Polymers

Polymer	Mw	PDI
PU-TDI-UC (1)	10220	3.70
PU-TDI-C (1)	4136	2.14
PU-HMDI-UC (1)	4560	2.14
PU-HMDI-C (1)	1677	1.74

4.1.3 Thermal Analysis of Polymers

The glass transition temperature (Tg) of polyurethanes obtained by DSC are given in Table 4.2. TDI-based polyurethanes have higher Tg than HMDI-based polyurethanes. The aromatic structure causes the rigidity in polymer chains and therefore the Tg of the polymer increases [46].

Table 4.2: Thermal Analysis Results of Polymers

Polymer	Tg (^{o}C)	Temperature at weight loss (^{o}C)			Weight loss at 800°C (%)
		20%	40%	60%	
PU-TDI-UC (1)	-15.3	300	350	395	98.33
PU-TDI-C (1)	-23.4	295	375	407	98.57
PU-HMDI-UC (1)	-19.6	345	375	405	99.45
PU-HMDI-C (1)	-42.5	330	390	437	98.07

The TGA results are given in Table 4.2. 20% weight losses of PU's were obtained at lower temperatures for catalyzed reactions with compared to uncatalyzed reaction products. On the other hand, the same trend was not observed for 40% and 60% weight loss of PU's. This result can be explained with the catalyst effect of metal added into the reaction medium as catalyst during PU synthesis. The metal ion increases the degredation rate at low temperatures, as explained in the literature [9].

HMDI-based PU's gave higher degradation temperatures than TDI-based PU's at the same weight loss. The aromatic rings, with 2.4- and 2.6-isocyanate groups formed more rigid chains but also more asymmetrical, which makes the interactions between the hard segments difficult, and thus reduced their thermal resistance [47].

4.2 Determination of Free Isocyanate Content by Wet and FTIR Methods

Synthetic mixtures were prepared from TDI or HMDI and PG mixtures. Since the composition was known, free isocyanate content of each mixture could be easily calculated. Free NCO content of each sample was also determined by wet and FTIR methods and two different graphs were drawn from these data (Figures 4.3 and 4.4). The first graph was obtained from the results of wet analysis and calculated data for synthetic mixtures. The free isocyanate content of the samples could be successfully determined by wet method, because the curve is a straight line, the slope is to be almost 1, and the regression coefficient (R^2) is very close to 1.
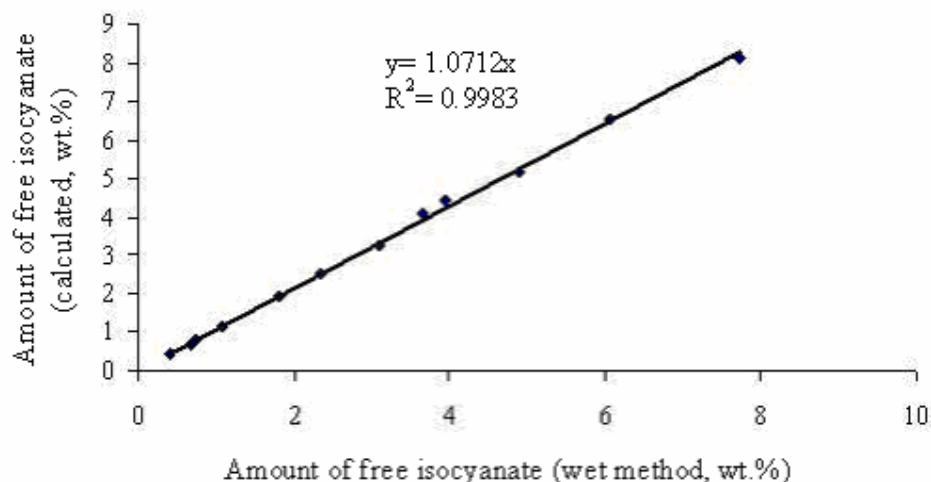
Figure 4.3: Calibration Curve for Wet Method

Another calibration curve was obtained from the intensity of absorption band at 2263cm^{-1} for NCO stretching and calculated free isocyanate of synthetic mixture in FTIR method.
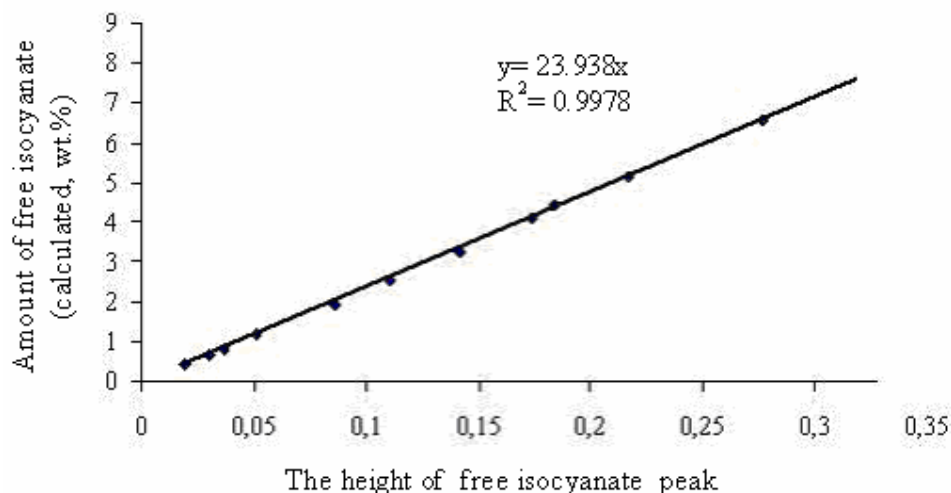
Figure 4.4: Calibration Curve for FTIR Method

In the second part of the study, both wet and FTIR methods were used for the determination of free NCO content of the reaction mixture in the polyurethane synthesis. The calibration curves were used for determination of free NCO content of the samples. The obtained results are given in Figure 4.5 for synthesis PU-TDI-C (1).
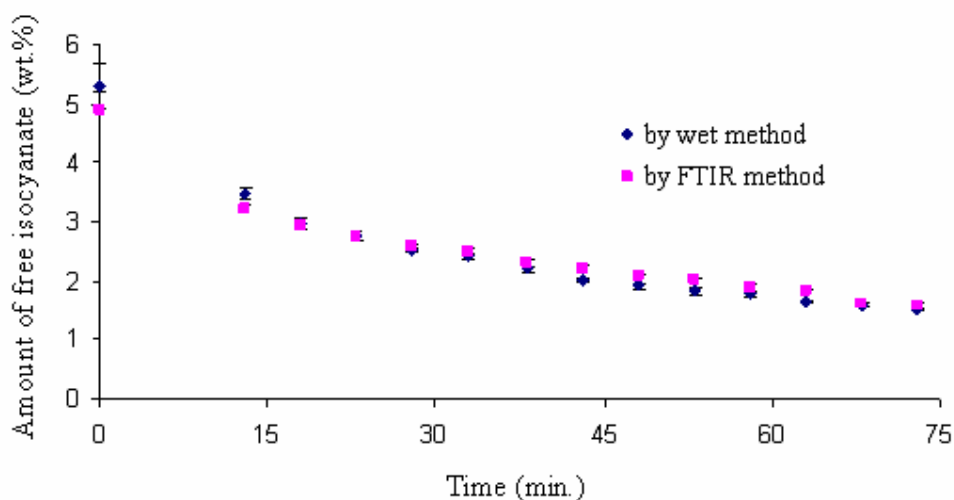
Figure 4.5: Free NCO Content of the Reaction Mixture Determined by Wet and FTIR Methods

The data for wet and FTIR methods are very close to each other and the error bars overlapped. Figure 4.6 shows the experimental mean values of the free isocyanate groups in the reaction mixture, which were determined by both wet, and FTIR methods. All of the data are distributed uniformly around the diagonal. It is suggested from these results that FTIR method can be successfully used for determination of free NCO content as an alternative of the wet method.
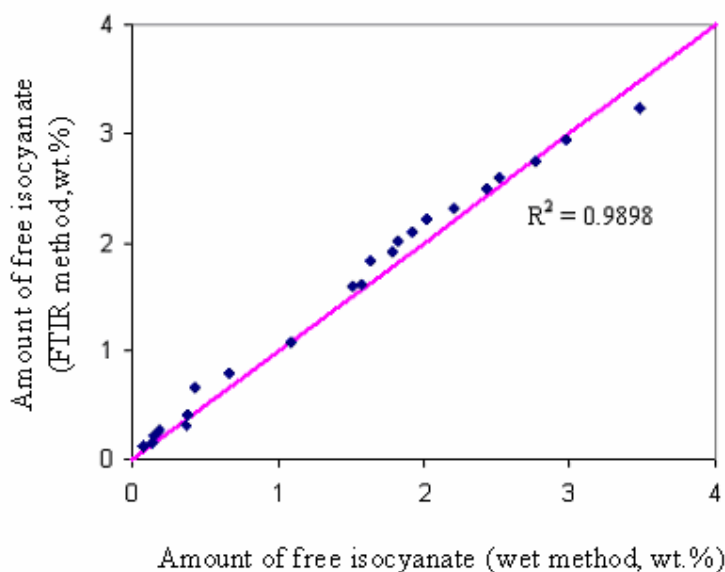
Figure 4.6: The Results of FTIR Method versus Wet Method

4.3 Evaluation of the Data on the Base of Reaction Kinetic

The amounts of free isocyanate (NCO) of the reaction mixtures of PU-TDI-C (1), PU-TDI-UC (1), PU-HMDI-C (1) and PU-HMDI-UC (1) as a function of time are given in Figure 4.7.
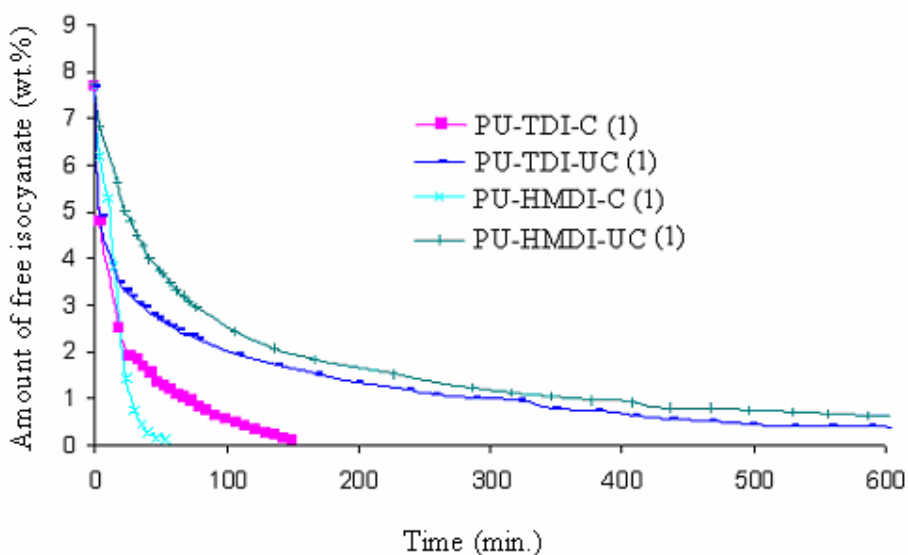
Figure 4.7: Amount of Free Isocyanate of the Reaction Mixtures (wt.%) as a Function of Time

The all reactions investigated in this study were followed by FTIR method, and the results were evaluated in the view of reaction kinetics. The drawn graphs to obtain reaction orders and rate constants for TDI and HMDI-based PU's were given in Appendix A. In these graphs, C represents the free isocyanate (NCO) content (wt.%) of the sample. The obtained reaction orders and rate constants from the graphs are presented in Table 4.3. It was taken the average results for the repeated reactions.

As it can be seen in Figure 4.8 and Table 4.3, the presence of the catalyst has a great effect on the reaction rate. The reaction rate increases dramatically when catalyst was used. As it is seen in Table 4.3, PU-TDI-UC has a higher rate constant than PU-HMDI-UC because of the aromatic structure of TDI.

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Table 4.3: Reaction Orders and Rate Constants Obtained From the Reactions

Reaction	Catalyst Content (wt.%)	Reaction Order	Rate constant [k, (%NCO)$^{-1}$ (sec)$^{-1}$]	Regression coefficient (R^2)
PU-TDI-C (1)	0.02422	2	0.0125	0.9941
PU-TDI-C (2)	0.01218	2	0.0067	0.9446
PU-TDI-UC (1)	-	2	0.0030	0.9701
PU-TDI-UC (2)	-	2	0,0039	0.9654
PU-TDI-UC (3)	-	2	0,0034	0.9816
PU-HMDI-C (1)	0,1607	1	0.0752*	0.9626
PU-HMDI-C (2)	0,1589	1	0.0782*	0.9813
PU-HMDI-UC (1)	-	2	0.0029	0.9876
PU-HMDI-UC (2)	-	2	0.0020	0.9968
PU-HMDI-UC (3)	-		0.0024	0.9988

*sec^{-1}

The TDI-based polyurethane synthesis (PU-TDI-UC and PU-TDI-C) obey second order rate law. The HMDI-based polyurethane syntheses in the absence of catalyst also obey second order rate law; however catalyzed reactions for preparation of HMDI-based polyurethane obey first order rate law.

Reaction mechanism between hydrocarbon polyols and aromatic or aliphatic diisocyanates commonly follow second order kinetics [48]. On the other hand, there are some studies, which show that the reaction order can be changed in the presence of catalyst. The apparent orders of the catalyzed esterification reactions between castor oil and oleic acid, for example, change with changing the catalyst type [49]. Senatalar et al. investigated the effects of two Lewis acid catalysts, tin chloride and cobalt chloride, on the kinetics of the esterification reaction between castor oil and oleic acid. The reaction carried out without catalyst was second order. On the other hand, reaction order was to be one and zero for the reaction with tin chloride catalyst and cobalt chloride catalyst, respectively [50].

5. CONCLUSION

The aim of this study is to synthesize polyurethanes from oil-based sources without solvent and catalyst and developing a method for monitoring the reaction by FTIR. The produced partial glyceride (PG) for preparation of polyurethane was reacted with two different isocyanates, TDI and HMDI with and without catalyst in bulk polymerization system. Then the prepared polyurethanes were characterized by using FTIR, GPC, NMR, DSC and TGA.

Polyurethanes from oil-based PG mixture and TDI or HMDI were successfully synthesized in the absence of catalyst by bulk polymerization and as a result of the study, it is suggested that FTIR spectroscopy can be successfully used to follow the reaction in the bulk state. The kinetic data can be obtained from the analysis of reaction mixture by FTIR spectrum.

The polyurethane formation between PG of linseed oil and TDI obeys second order rate law. The kinetic study of the polyurethane formation also shows that the reaction is enormously speeded up in the presence of catalyst. The influence of catalyst is account with varying the amount of catalyst in the reaction.

The polyurethane syntheses without catalyst from PG of linseed oil and HMDI obey second order rate law, while the catalyzed reactions obey first order rate law.

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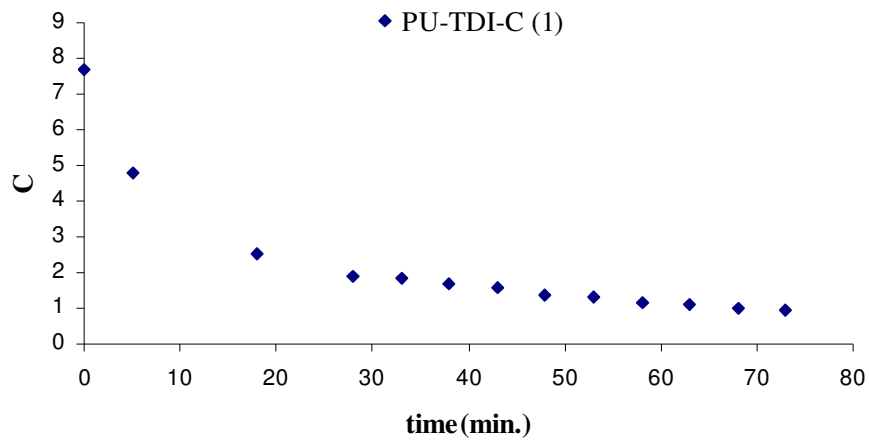
Figure A.1: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-TDI-C (1) as a Function of Time

$$y = -0,0334x + 2,0367$$
$$R^2 = 0,7841$$
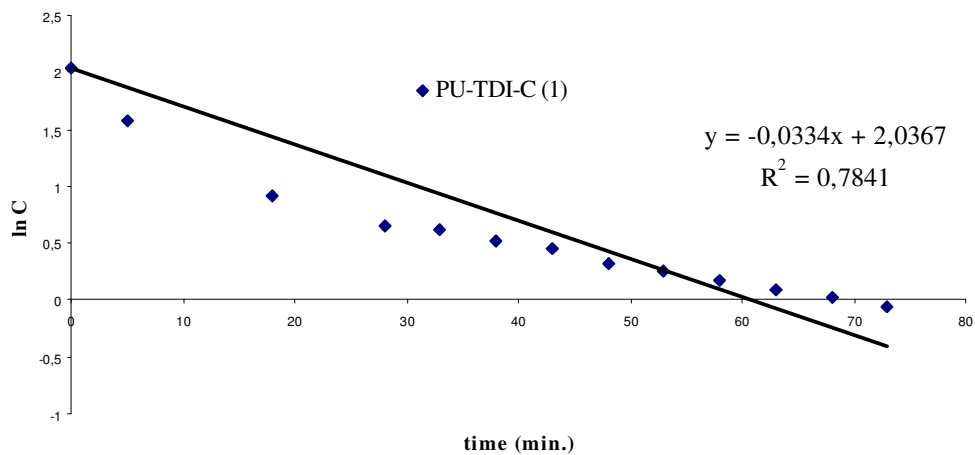
Figure A.2: ln[free NCO(wt.%)] versus time graph of PU-TDI-C (1)
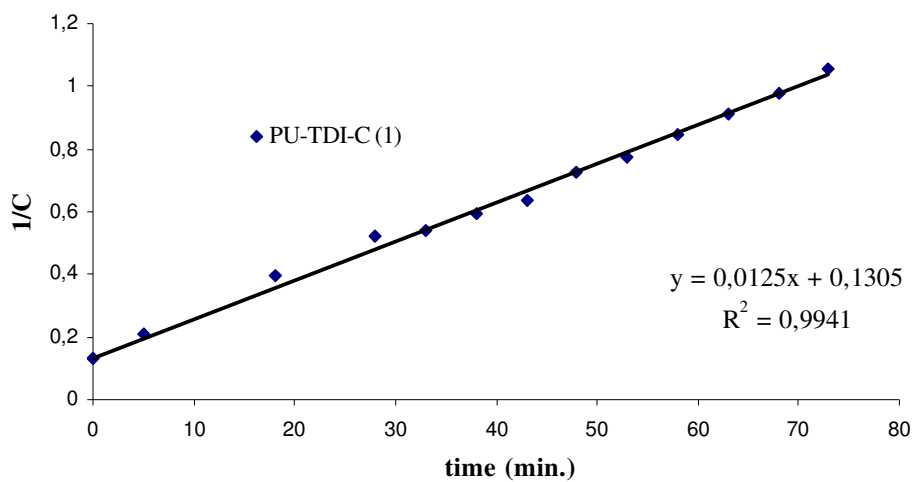
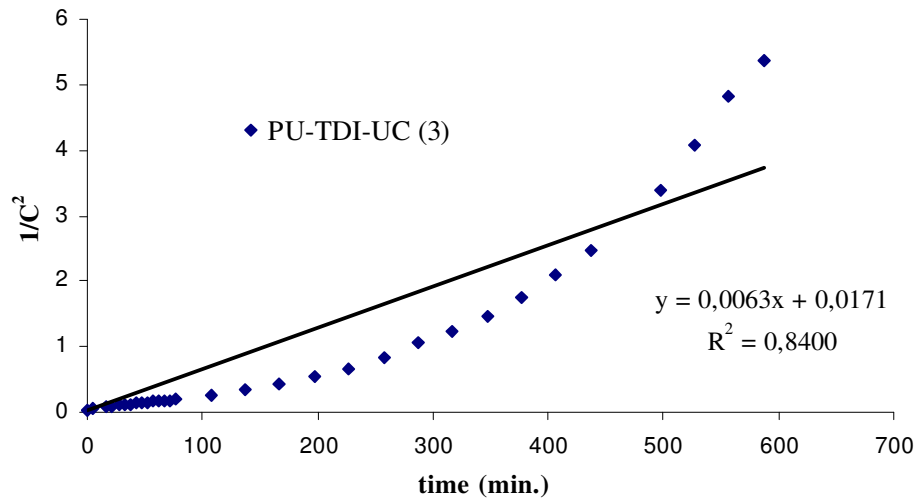**Figure A.3:** 1/[free NCO(wt.%)] versus time graph of PU-TDI-C (1)
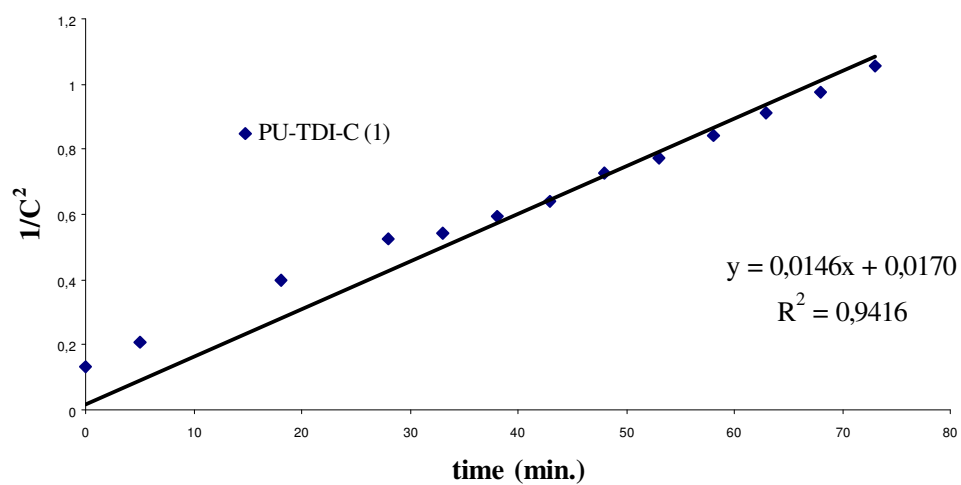
Figure A.4: 1/[free NCO(wt.%)]^2 versus time graph of PU-TDI-C (1)
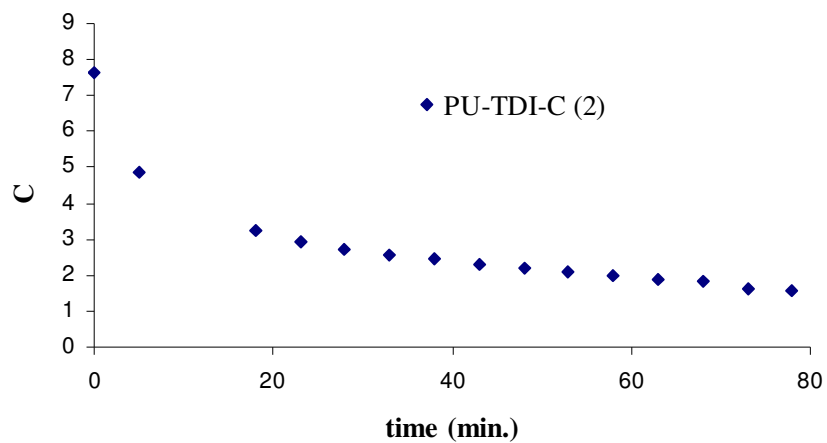
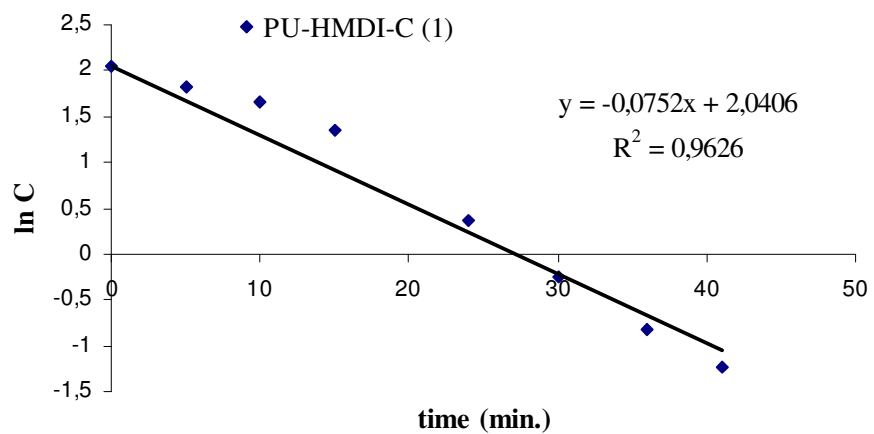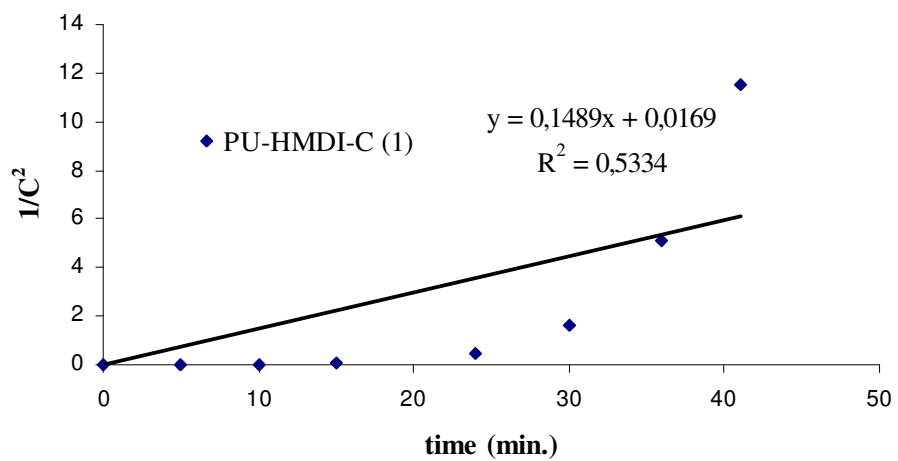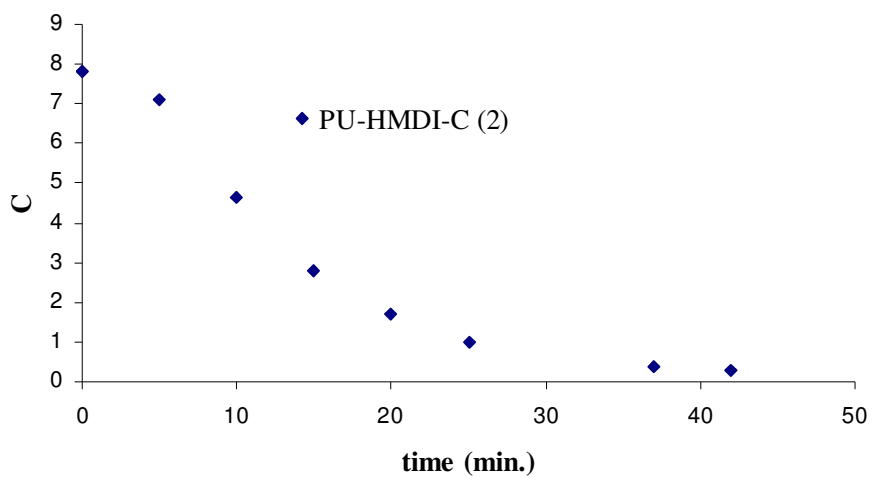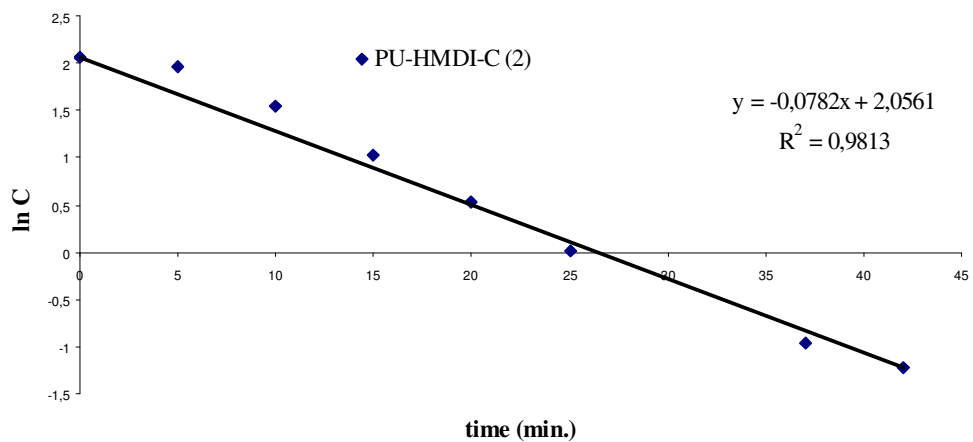**Figure A.5:** Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-TDI-C (2) as a Function of Time
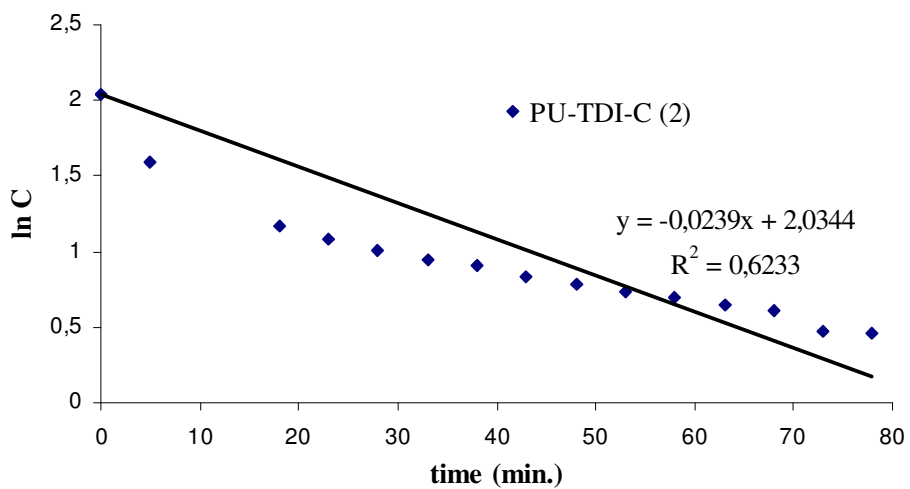
Figure A.6: ln[free NCO(wt.%)] versus time graph of PU-TDI-C (2)
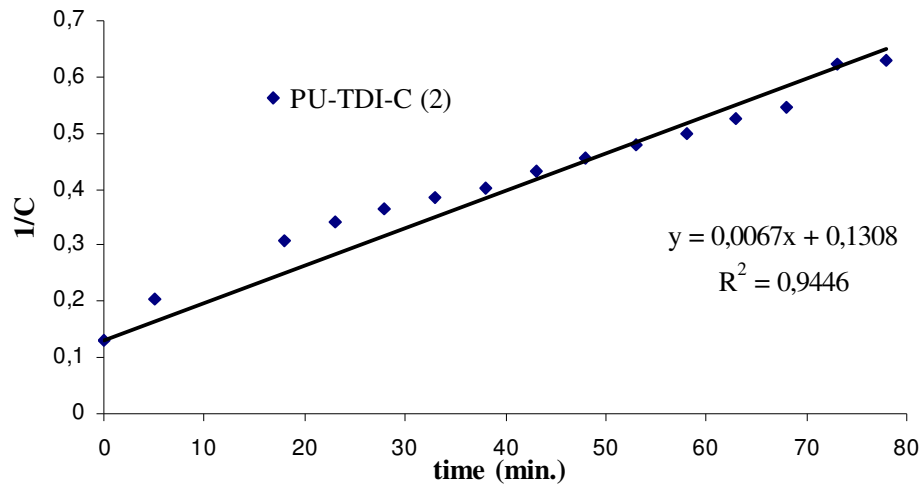
Figure A.7: 1/[free NCO(wt.%)] versus time graph of PU-TDI-C (2)
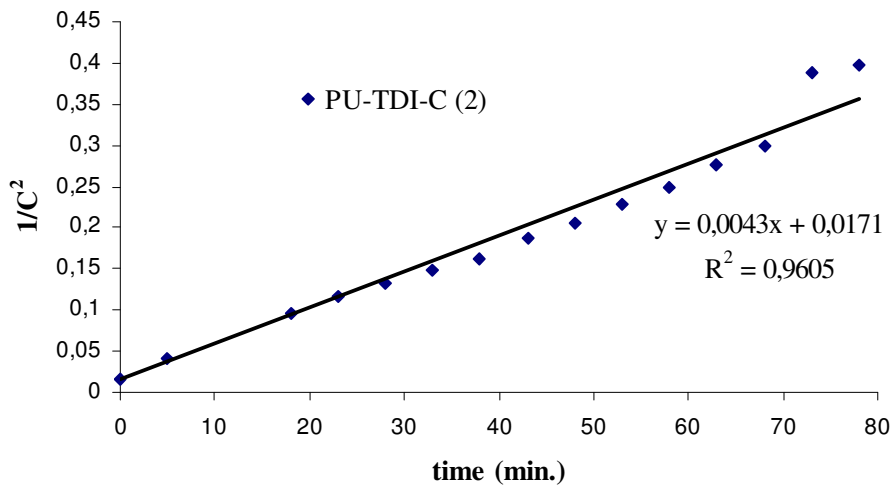
Figure A.8: 1/[free NCO(wt.%)]^2 versus time graph of PU-TDI-C (2)
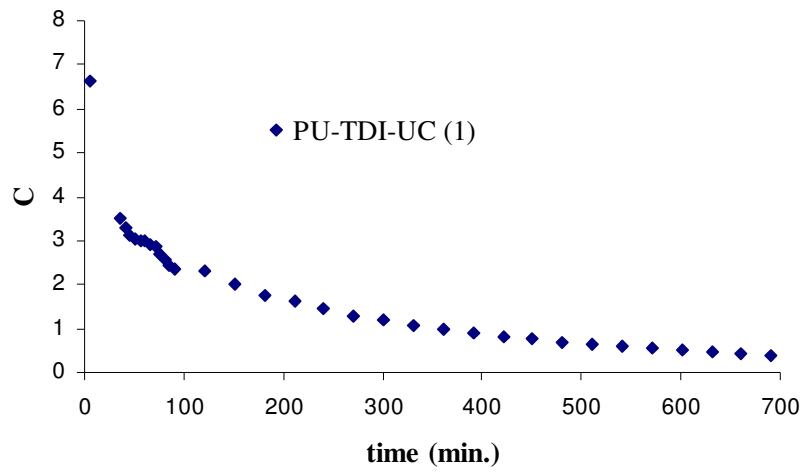
Figure A.9: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-TDI-UC (1) as a Function of Time
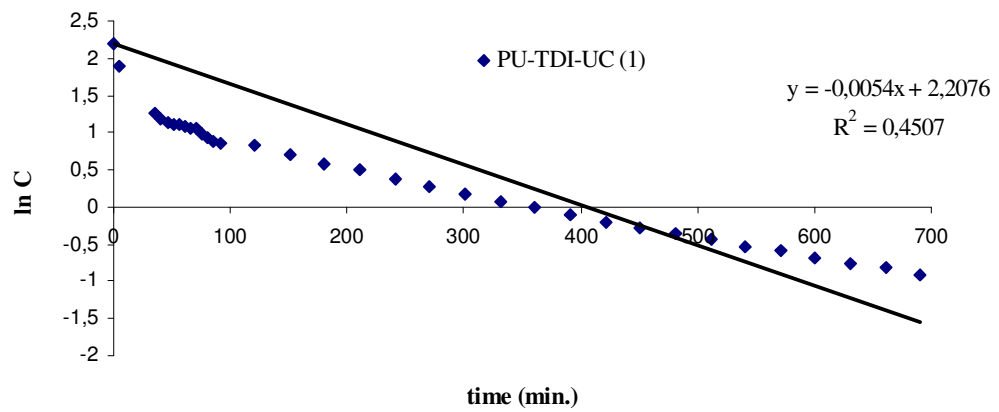
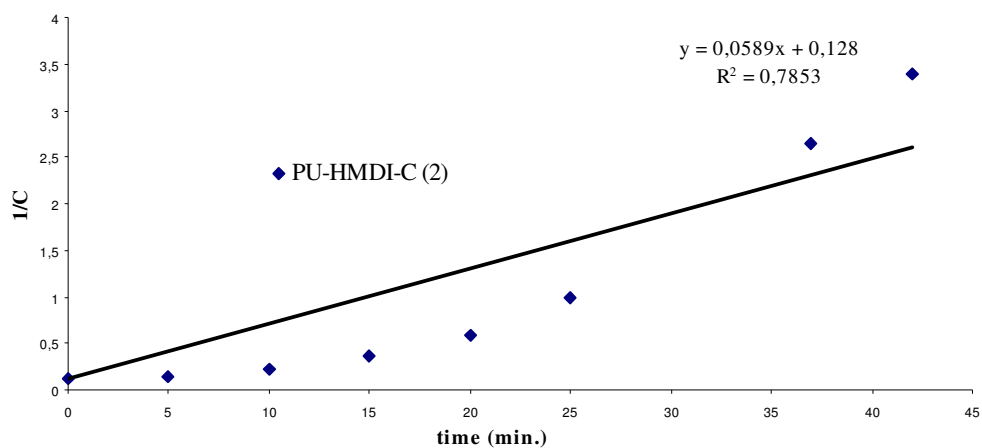**Figure A.10:** ln[free NCO(wt.%)] versus time graph of PU-TDI-UC (1)
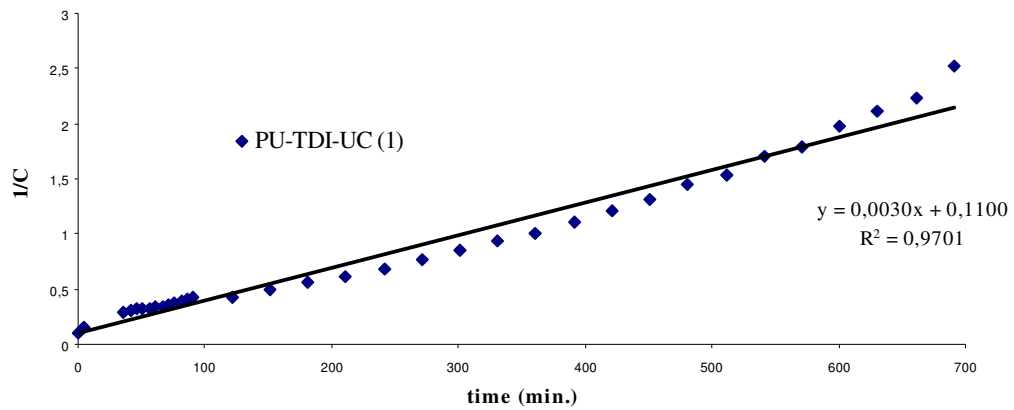
Figure A.11: 1/[free NCO(wt.%)] versus time graph of PU-TDI-UC (1)
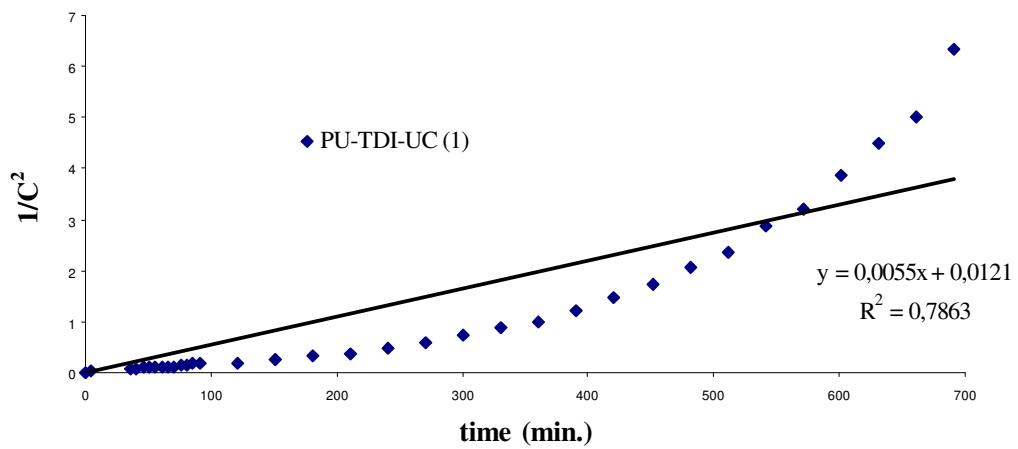
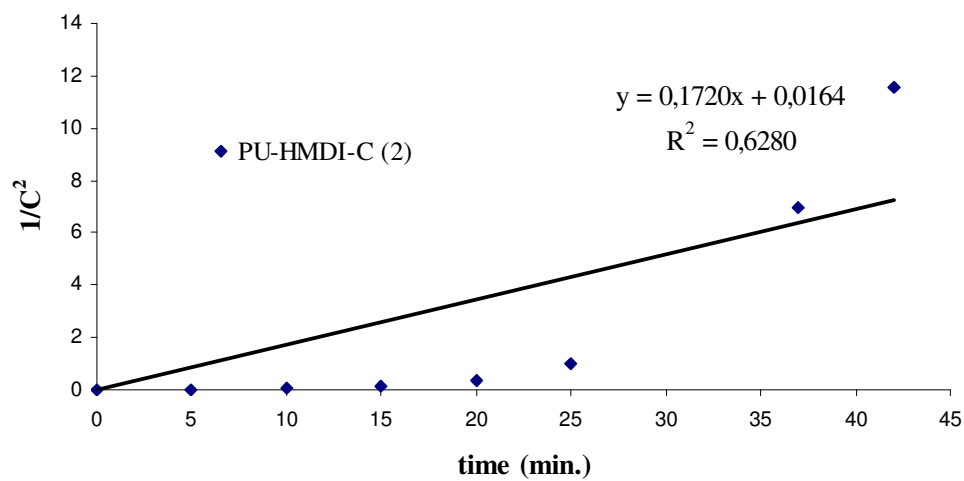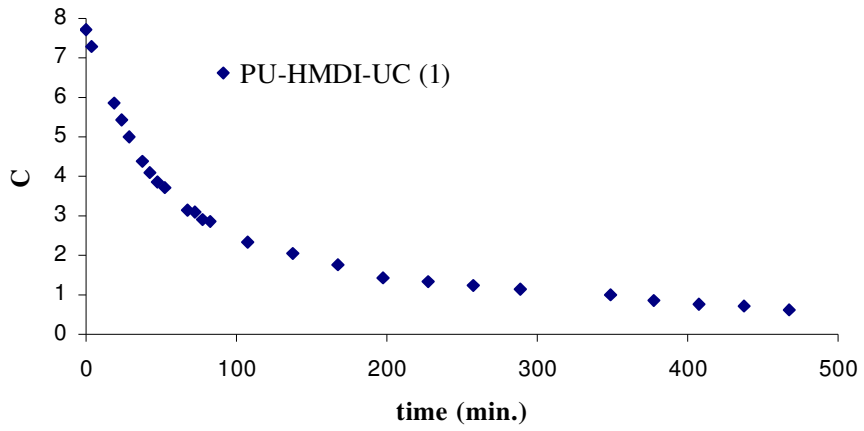**Figure A.12:** 1/[free NCO(wt.%)]^2 versus time graph of PU-TDI-UC (1)
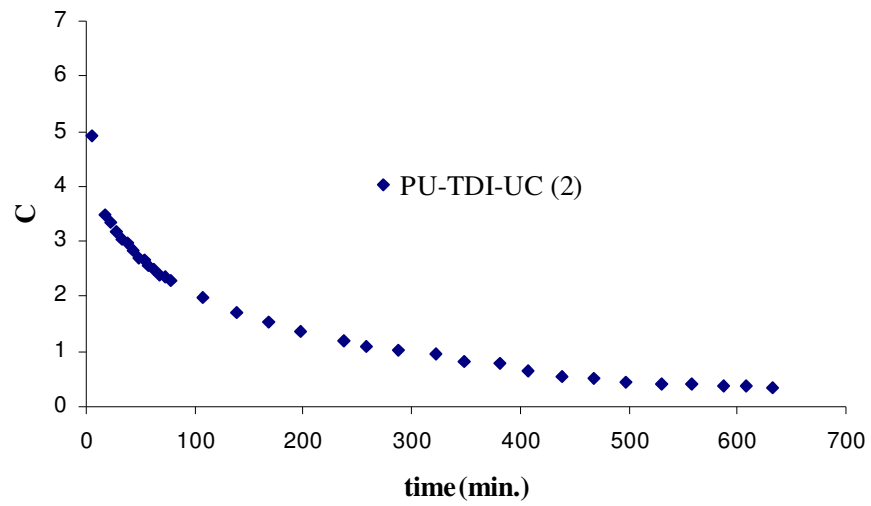
Figure A.13: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-TDI-UC (2) as a Function of Time

$y = -0,0059x + 2,0383$

$R^2 = 0,5542$
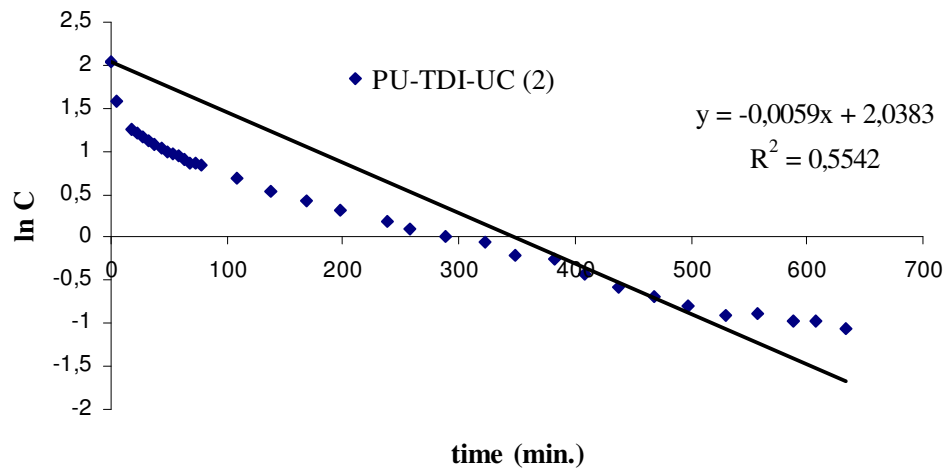
Figure A.14: ln[free NCO(wt.%)] versus time graph of PU-TDI-UC (2)
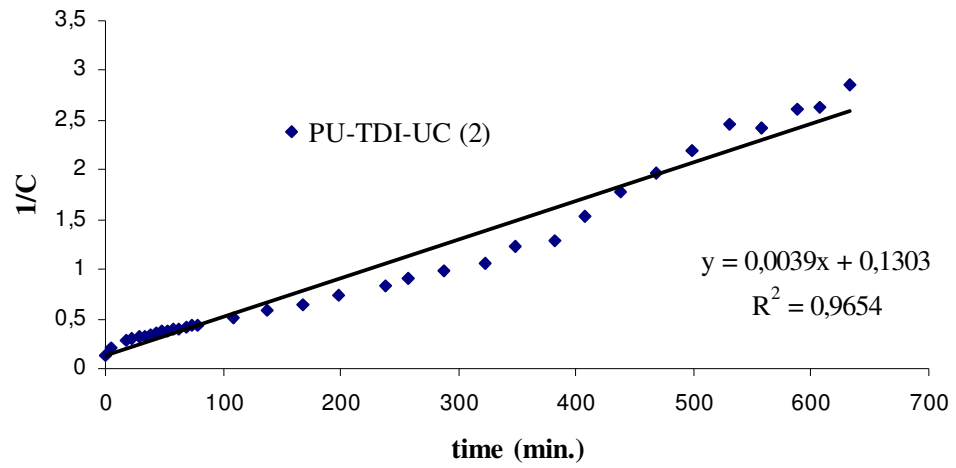
Figure A.15: 1/[free NCO(wt.%)] versus time graph of PU-TDI-UC (2)
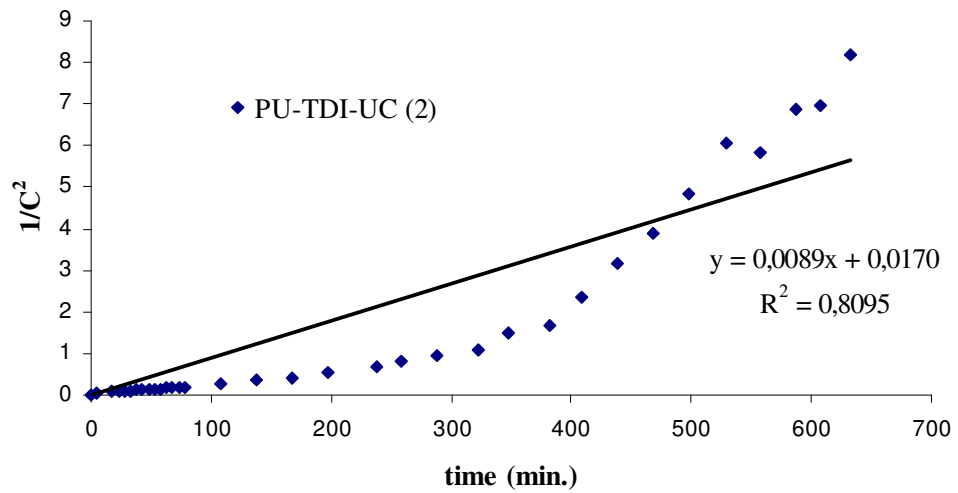
Figure A.16: 1/[free NCO(wt.%)]^2 versus time graph of PU-TDI-UC (2)
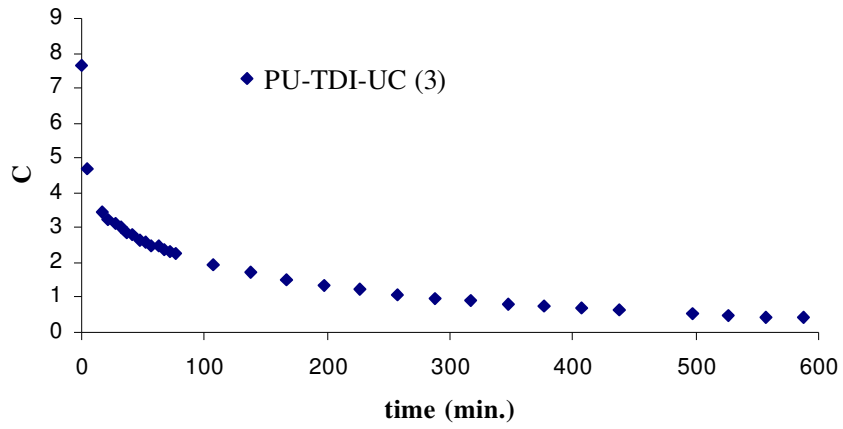
Figure A.17: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-TDI-UC (3) as a Function of Time


$y = -0,0061x + 2,0345$

$R^2 = 0,3561$
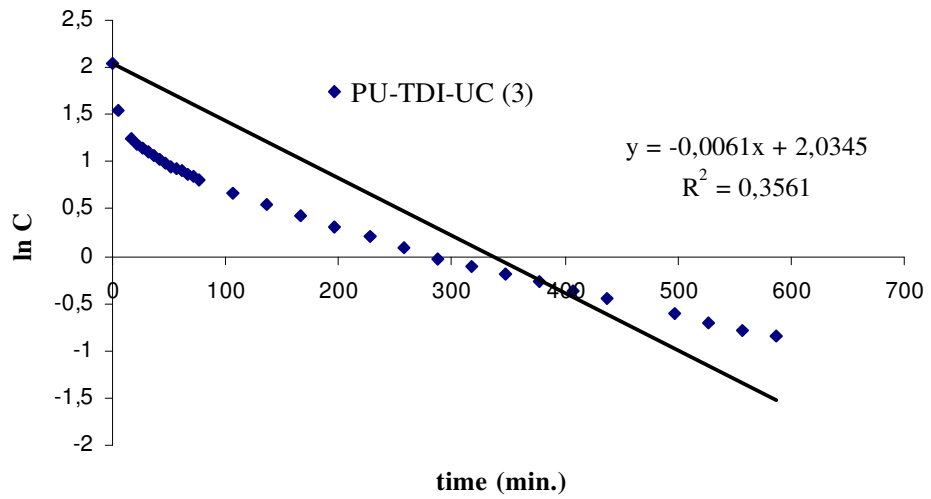
Figure A.18: ln[free NCO(wt.%)] versus time graph of PU-TDI-UC (3)
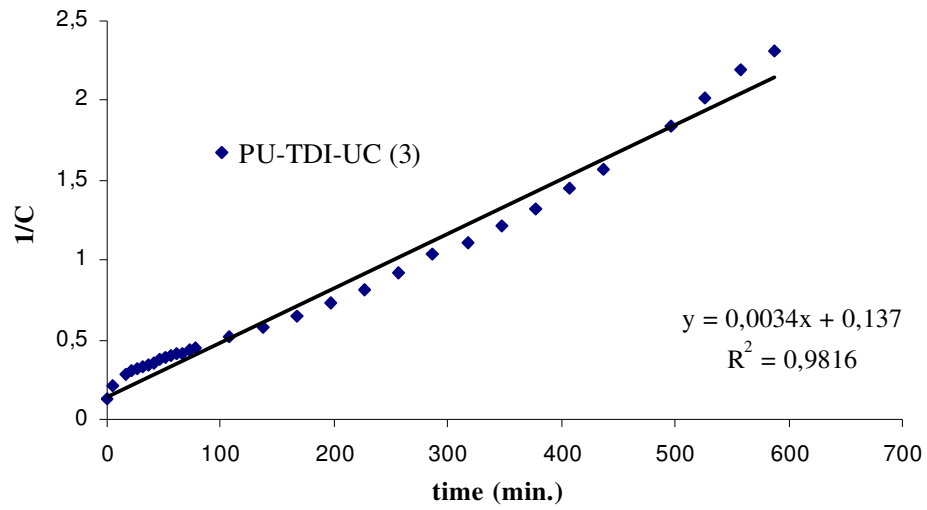
Figure A.19: 1/[free NCO(wt.%)] versus time graph of PU-TDI-UC (3)

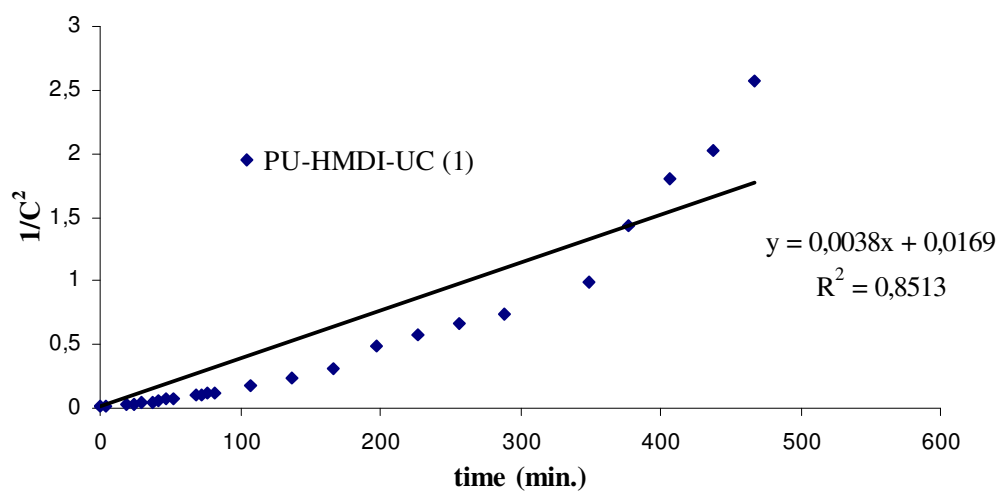**Figure A.20:**1/[free NCO(wt.%)]^2 versus time graph of PU-TDI-UC (3)
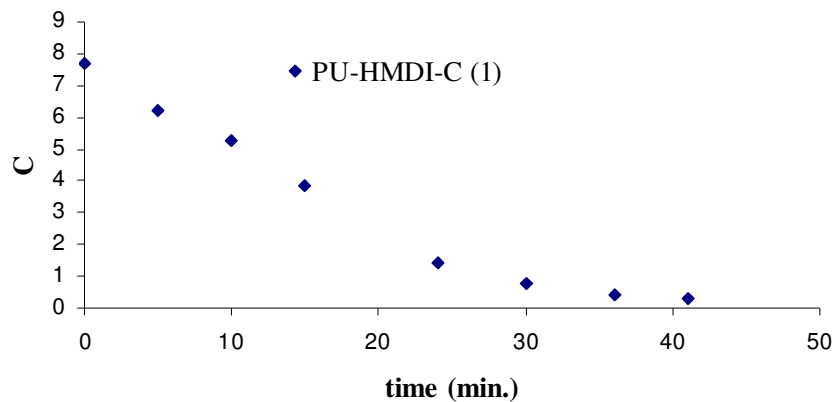
Figure A.21: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-HMDI-C (1) as a Function of Time

$y = -0,0752x + 2,0406$
$R^2 = 0,9626$

Figure A.22: ln[free NCO(wt.%)] versus time graph of PU-HMDI-C (1)
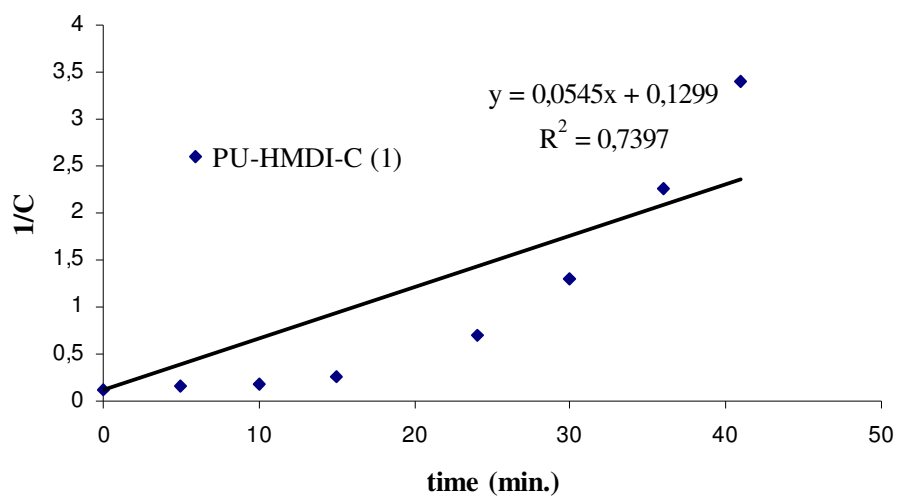
Figure A.23: 1/[free NCO(wt.%)] versus time graph of PU-HMDI-C (1)

Figure A.24: 1/[free NCO(wt.%)]^2 versus time graph of PU-HMDI-C (1)
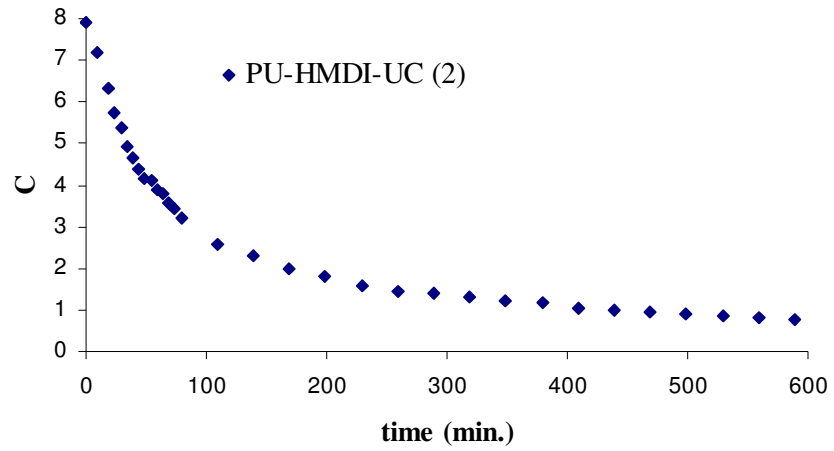
Figure A.25: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-HMDI-C (2) as a Function of Time
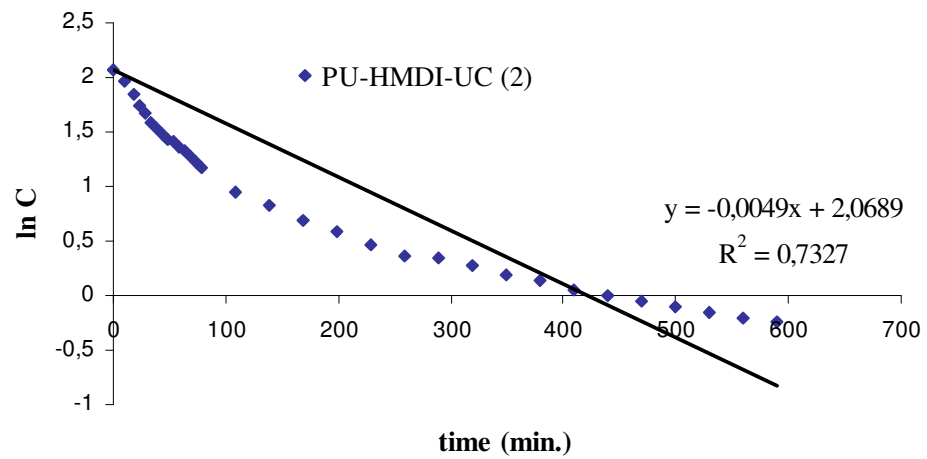

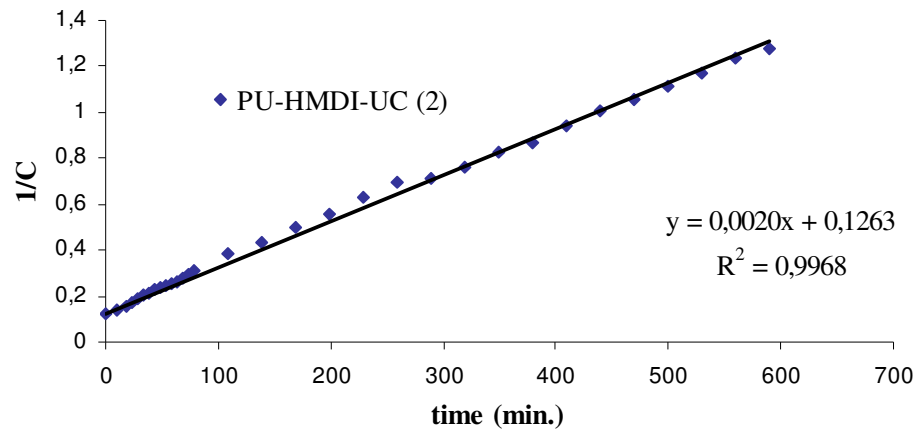**Figure A.26:** ln[free NCO(wt.%)] versus time graph of PU-HMDI-C (2)

Figure A.27: 1/[free NCO(wt.%)] versus time graph of PU-HMDI-C (2)

Figure A.28:1/[free NCO(wt.%)]^2 versus time graph of PU-HMDI-C (2)

Figure A.29: Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-HMDI-UC (1) as a Function of Time

$y = -0,0064x + 2,041$
$R^2 = 0,7887$
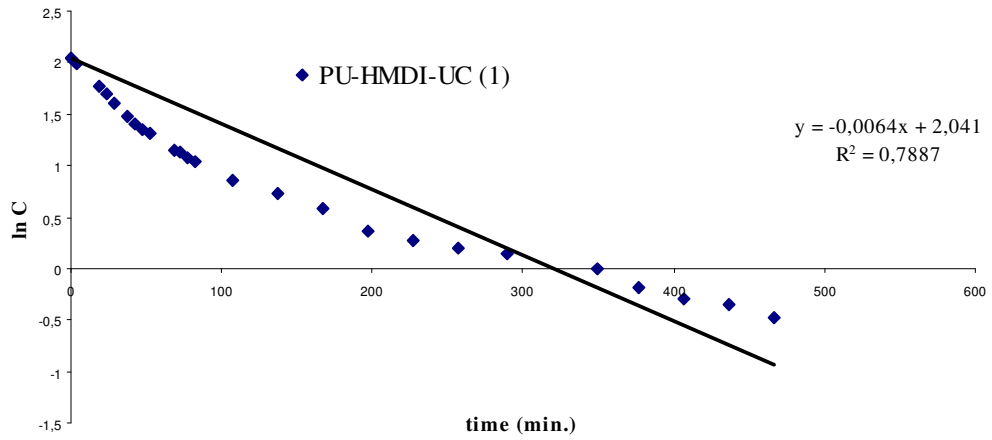
Figure A.30: ln[free NCO(wt.%)] versus time graph of PU-HMDI-UC (1)
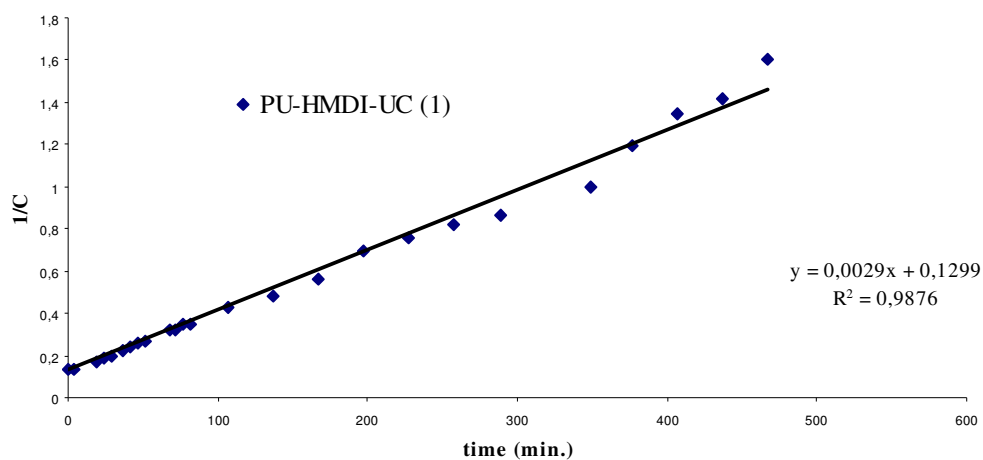
Figure A.31: 1/[free NCO(wt.%)] versus time graph of PU-HMDI-UC (1)

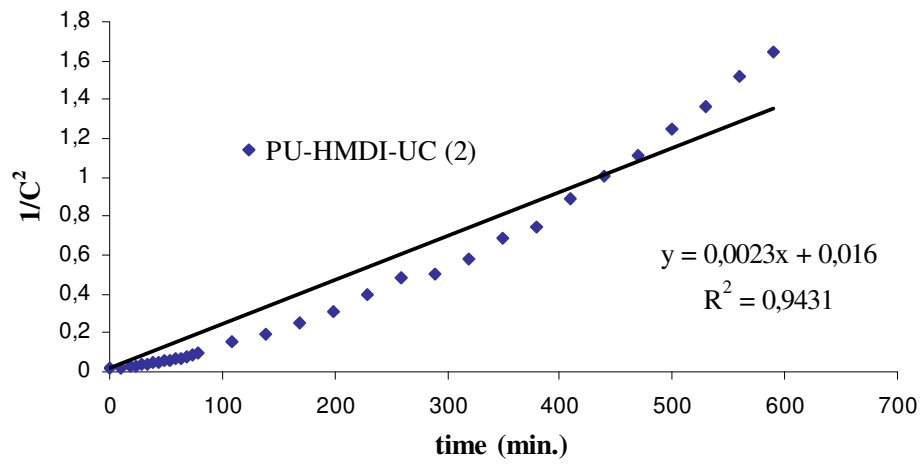**Figure A.32:** 1/[free NCO(wt.%)]^2 versus time graph of PU-HMDI-UC (1)

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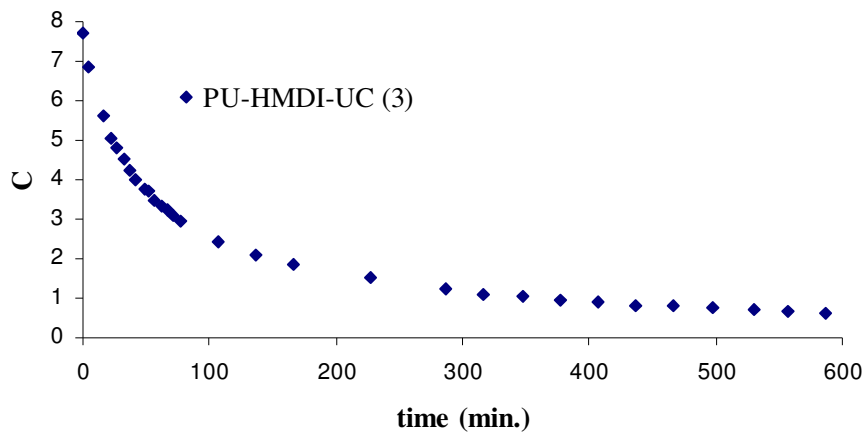**Figure A.33:** Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-HMDI-UC (2) as a Function of Time

$y = -0{,}0049x + 2{,}0689$

$R^2 = 0{,}7327$

Figure A.34: ln[free NCO(wt.%)] versus time graph of PU-HMDI-UC (2)

Figure A.35: 1/[free NCO(wt.%)] versus time graph of PU-HMDI-UC (2)

Figure A.36: 1/[free NCO(wt.%)]^2 versus time graph of PU-HMDI-UC (2)

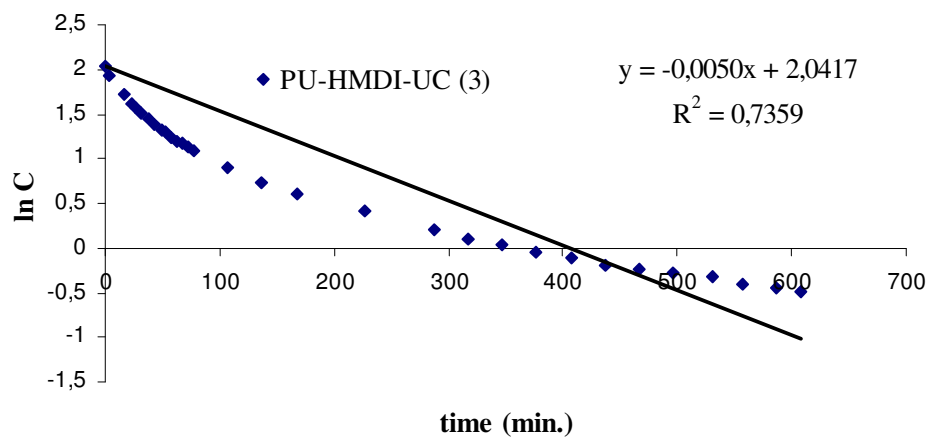**Figure A.37:** Amount of Free Isocyanate of the Reaction Mixture (wt.%) of PU-HMDI-UC (3) as a Function of Time

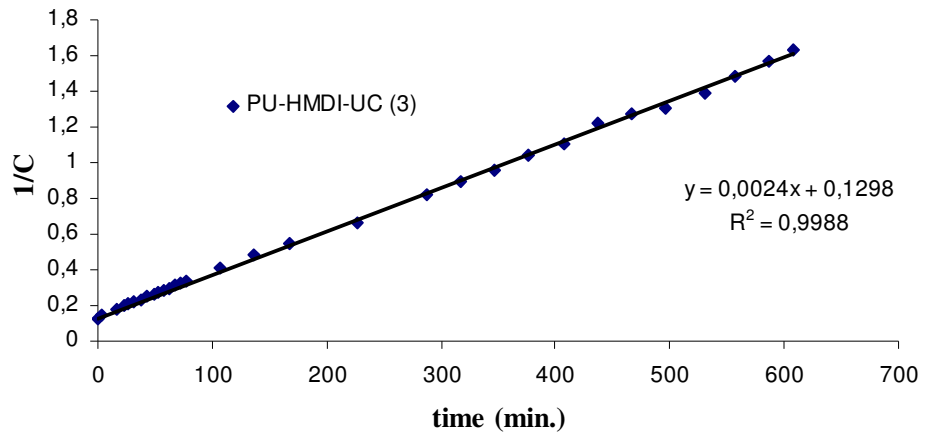**Figure A.38:** ln[free NCO(wt.%)] versus time graph of PU-HMDI-UC (3)

Figure A.39: 1/[free NCO(wt.%)] versus time graph of PU-HMDI-UC (3)

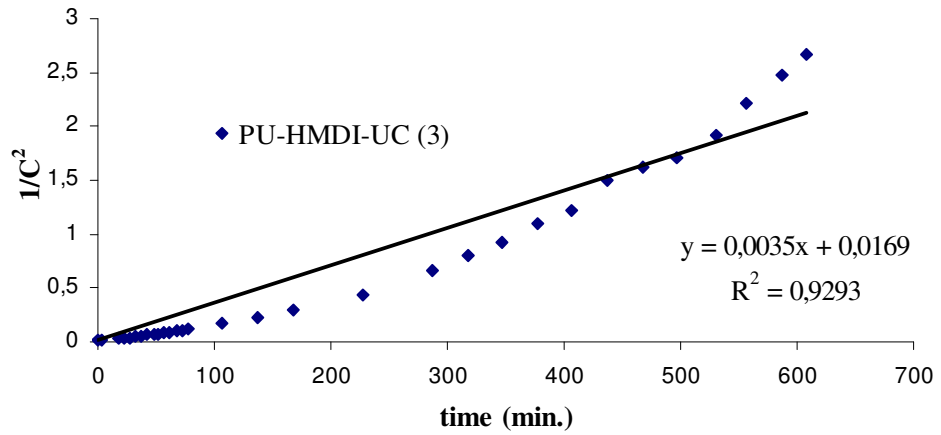**Figure A.40:** 1/[free NCO(wt.%)]^2 versus time graph of PU-HMDI-UC (3)

BIOGRAPHY

Hande MADRA was born in Adapazarı in 1979. She was graduated from Sakarya Anatolion High School in 1996. She graduated from Istanbul Technical University, Department of Chemical Engineering, as a Chemical Engineer in 2002. In 2003 she was accepted to "Polymer Science and Technology", master degree program in Istanbul Technical University and she is still continuing her studies in the same department.