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FLEXIBLE POLYURETHANE REBOND FOAM PREPOLYMER SYTHESIS WITH LOW POLYMERIC DIISOCYONATE CONTENT

CİHAN EFE KILIÇ
A THESIS SUBMITTED FOR THE DEGREE OF
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GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

DÜŞÜK DİİZOSİYONAT YOĞUNLUKLU ESNEK POLİÜRETAN PREPOLİMER BAĞLAYICI SENTEZİ

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YÜKSEK LİSANS TEZİ
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TEKNİK ÜNİVERSİTESİ

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SUMMARY

Desirable chemical and physical properties of Polyurethanes (PUs) such as mechanical flexibility associated with their chemical structure make these polymers attractive for adhesive applications. In this work, three types of isocyanate functional prepolymers were synthesized with low isocyanate (NCO) content to observe their chemical, physical and mechanical properties. Initially, isocyanate terminated prepolymer were synthesized through single step with petroleum passed polyol. In order to compare the durability, viscosity and tackiness of prepolymer, bio-based polyols used to synthesize isocyanate functional prepolymers with different NCO/OH content. The effect of MDI and pMDI as a cross-linker on the degree of H-bonding was examined by Fourier Transform Infrared-Attenuated Total Reflectance Spectroscopy (FTIR-ATR) and H1 Nuclear Magnetic Resonance Spectroscopy (H1 NMR). Also the effect of alternative polyols on mechanical, chemical, and physical properties on the polyurethane were analyzed with differential scanning calorimeter (DSC), Termal gravimetric Analysis (TGA) and X-ray diffraction (XRD). Atomic force microscopy (AFM) was used to determine PUs morphology and roughness. Brookfield rotational viscometer were used to differentiate the polyols effect on the PUs.

Key Words: Polyurethane, Biopolyol, Isocyanate, Rebonded Foam Adhesive, Polyurethane Adhesive.

ÖZET

Poliüretanlar (PUs) mekaniksel esneklik gibi beklenen birçok fiziksel ve kimyasal özellik gösterebilmelerinden dolayı yapıştırıcı alanında sıklıkla tercih edilmektedir. Bu çalışmada, düşük NCO oranı içeren üç farklı prepolimer sentezlenerek, bu prepolimerin kimyasal, fiziksel ve mekaniksel özelliklerinin incelenmesi gerçekleştirilmiştir. İlk olarak, petrol bazlı poliol kullanılarak izosiyanat uçlu prepolimer sentezlenmiştir. Prepolimerin mukavemet, viskozite, yapışkanlık değerlerinin karşılaştırılabilmesi için biyo bazlı poliol kullanılarak farklı NCO/OH oranında, izosiyanat uçlu prepolimer sentezlenmiştir. Fourier Transform Infrared-Attenuated Total Reflectance Spectroscopy (FTIR-ATR) ve H1 Nuclear Magnetic Resonance Spectroscopy (H1 NMR) tekniği kullanılarak çapraz bağlayıcı olarak MDI ve pMDI'nın hidrojen bağı ile bağlanma derecesine etkisi gözlemlenmiştir. Farklı poliol guruplarının poliüretanin mekanik, kimyasal ve fizikler özelliklere etkisi Diferansiyel taramalı kalorimetre (DSC), termal Gravimetric Analysis (TGA) ve X-Ray kırınım (XRD) ile incelenmiştir. PUs lerin yüzey mormolojisi Atomik Kuvvet Mikrsokobu (AFM) ile incelenmiştir. Brokfield rotasyonal viskometre kullanılarak farklı poliollerin PUs ler üzerindeki etkisi incelenmiştir.

Anahtar Kelimeler: Poliüretan, Biopolyol, İzosiyonat, Rebonded Köpük Yapıştırıcı, Poliüretan Yapıştırıcı.

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LIST of ABBREVIATIONS and ACRONYMS

Abbreviations and Acronyms		**Explanations**
AFM	:	Atomic force microscopy
DSC	:	Differential scanning calorimeter
FTIR-ATR	:	Fourier transform infrared-attenuated total reflectance spectroscopy
HDI	:	Hexamethylene diisocyanate
IPDI	:	Isoprene diisocyanate
MDI	:	Methyl diisocyanate
NCO	:	Isocyanate
PPG 2000	:	Polypropylene glycol 2000
PU	:	Polyurethane
TDI	:	Toluene disiocyanate
Tg	:	Glass transition temperature
Tm	:	Melting point
VOC	:	Volatile organic compound
XRD	:	X-ray diffraction
^{1}H-NMR	:	Hydrohen Nuclear Magnetic Resonance

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1. INTRODUCTION

In 1937, polyurethanes (PUs) were discovered by Otto Bayer, since than it has become a success story, which is now billion-dollar business [1]. PUs are class of polymers that are used in coatings or as elastomeric items, foams and adhesives [2]. The general form of PUs, flexible polyurethane foam, is the prior material for furniture, bedding, packing, and transporting due to its easiness of manufacturing process. There has been a considerable amount of research about PUs binders and adhesives in literature [3-6]. PU adhesives were known with the reputation for reliability and high performance [7]. There are many types of PU adhesive which are unique and fit the applications [8]. Contrary to other consumer plastics, there has been a huge effort to re-use PUs waste in the industry. There have been years of research focusing on PUs recycling, which can be economical and environmentally friendly. [9]

There are four major methods for PUs recycling and each one results in energy saving and material recovery. [10] Both chemical and physical recycling are as old as history of PUs. [11] In chemical recycling process of PUs, alcoholysis, hydrolysis, glycolysis and fractionation are the main focused ways to follow up. [12] Thus, physical recycling methods of PUs are performed today to process either flexible or rigid foam [13].

Mechanical recycling, on the other hand, done by utilizing flexible foams into small pieces and angulate one another with a binder adhesive. During the mechanical recycling, flexible foam pieces are made by padding with binder adhesive under certain pressure, heat, and steam, and it is cured to make recycled flexible foam [14].

Adhesives for such processes have attracted great attention due to their production advantages. Many research groups reported their work on PUs adhesives for such applications [15-18]. Adhesive properties and thermal stability are important for the PUs recycle process, and these factors have directly depended on mechanical, chemical, and physical properties of the polymeric adhesive such as high wettability and cohesive force which is governed by internal hydrogen bonding [19-20].

General idea behind the PU synthesis is the reaction of isocyanate with hydroxyl group and chain extender [21-25]. Despite methyl diisocyanate (MDI), polymeric MDI and toluene disiocyanate (TDI) are the mainly used ones for PU and PU adhesive synthesis [26-27]. There are certain standards like ASTM D5155 for PU based adhesives for recycling process which specify the NCO content, viscosity and mechanical properties.

1.1. PU Chemistry

There are many different types of PUs in high demand due to the versatility of PU chemistry [28,29]. PUs have a broad spectrum from flexible to rigid structure and solid or liquid phases that can be altered by the additives, too. Rigid foams are generally preferred for insulation purposes since flexibles are used as protection applications for transportation of bedding and furniture, whereas elastomers exist in as either thermosets or thermoplastics [30].

- Current Drawback and PU

PU is a polymeric material consisting of isocyanate and alcohol unit and its market has been expanding greatly since 1937, and its market grow to around $55.5 billion USD by 2016 [31].

When compared with natural materials like wood, PUs have special characteristic properties that are attractive like low density, low thermal conductivity, permeability, and high dimensional stability [32].

Except certain applications, toluene diisocyanate (TDI), dipheniylmethene diisocyanate (MDI), and custom formulated special isocyanates are used, and PU can be produced by adjusting the formulation, reaction conditions, and additives [33].

Polycondensation reaction is the general method (Figure 1.1) for synthesizing PUs [34-36].

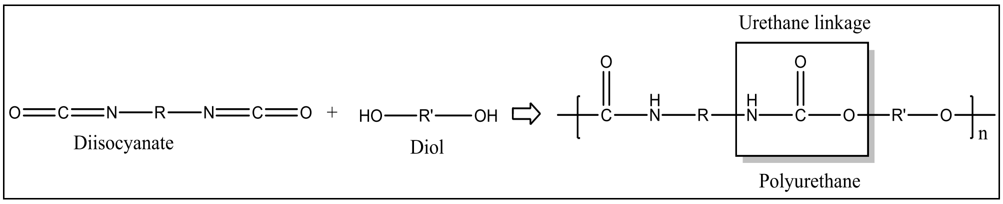


Figure 1.1: Conventional synthesis of polyurethane.

Diisocyonates contain two reactive isocyanate units and they can be aromatic such as MDI or TDI. They also can be aliphatic such as hexamethylene diisocyanate

(HDI) or isoprene diisocyanate (IPDI), which are quite toxic to use even in the reaction medium [37].

- Reaction of Isocyanates

Isocyanates are very reactive with active hydrogen atoms and also with themselves. Under normal conditions, it provides carbon nitrogen with a double bond, and this strong reactive unit is even stronger in the aromatic isocyanates than aliphatic ones [38]. It has been represented in the isocyanate reactions in the Figure 1.2 to better observe the PU chemistry.

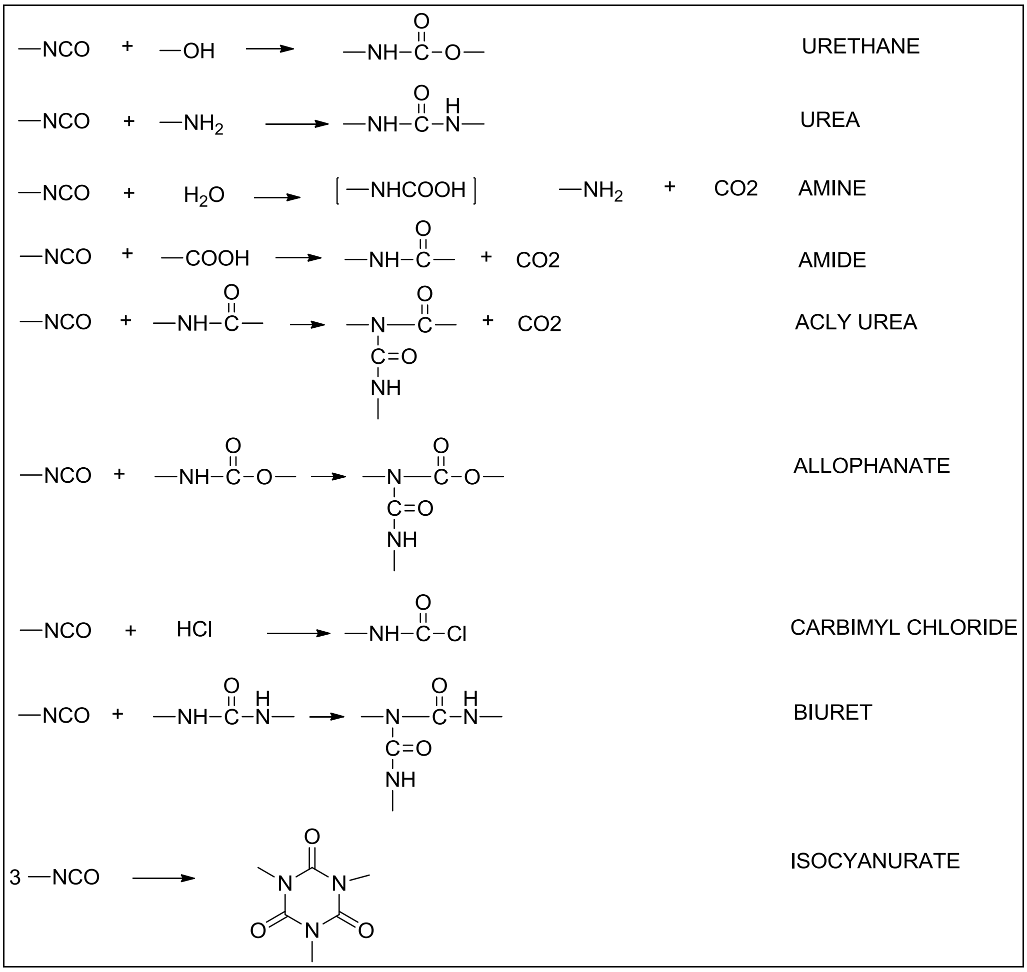


Figure 1.2: Reaction of isocyanate with active hydrogen compound.

- Polyols

During the polycondensation reaction, predominant partner for isocyanate is the polyhydroxyl compound which is called as polyols. The OH number (in mg KOH) determines these compounds, and there are certainly two types of polyols exists on the market; Polyether polyols and Polyester polyols [39].

- Polyether Polyols

Polyether polyols are the most commonly used polyols for PU production. They can be synthesized by alkali-catalyzed polymerization in short or long chain with two or eight hydroxyl unit per molecule. The structure of the PU can be controlled by selecting the length, composition of the polyether chain and functionality.

Table 1.1: Initiators for polyether polyols.

Functionality 2	**Functionality 2**	**Functionality 2**
Propylene glycol Ethylene glycol Water Methyldiethanolamine	Glycerol Trimethylolpropane 1,2,6-hexanediol Triethanolamine Phosphoric acid	Pentaerithritol Methyl glycoside Ethylenediamine Toluenediamine
Functionality 2	**Functionality 2**	**Functionality 2**
Diethylene triamine	Sorbitol	Sucrose

Polyols for the flexible applications are preferred with low functionality such as dipropylene glycol or glycerin.

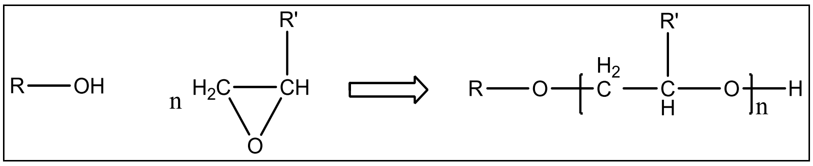


Figure 1.3: Synthesis of polyether polyols.

Polyols can be extending with propylene oxide to terminate with secondary amine unit and in order to modify the rheological property, compatibility and reactivity, co-reactant can be used to synthesize the polyether polyols [40].

- Polyester Polyols

Polyester polyols are used less than polyether polyols in PU applications. Although it is more complex and expensive to synthesize polyester polyols than polyether ones, there are aliphatic and aromatic ones in the market.

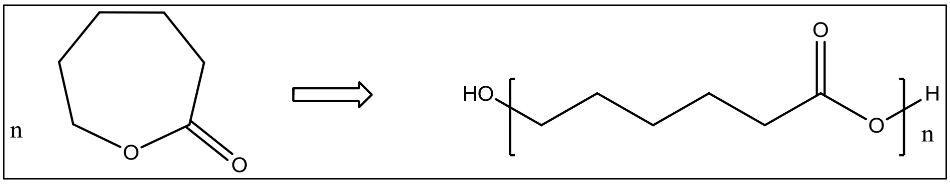


Figure 1.4: Polyester polyol synthesis.

PUs which are synthesized by using polyester polyols have good mechanical properties and they are relatively resistive to oxidation. Polyester polyols are alternatively functional from 2 to 8, and PUs that are synthesized by using them have lower viscosity than polyether used ones [41].

- Bio Polyols

Natural oil or vegetable oil is the predominant alternative for the petroleum base polyols in PU synthesis, and researchers have successfully synthesized it by using them [42-43]. They perform in the PU foam applications as good as petroleum based polyols, even better in both thermal stability and oxidation resistance [44].

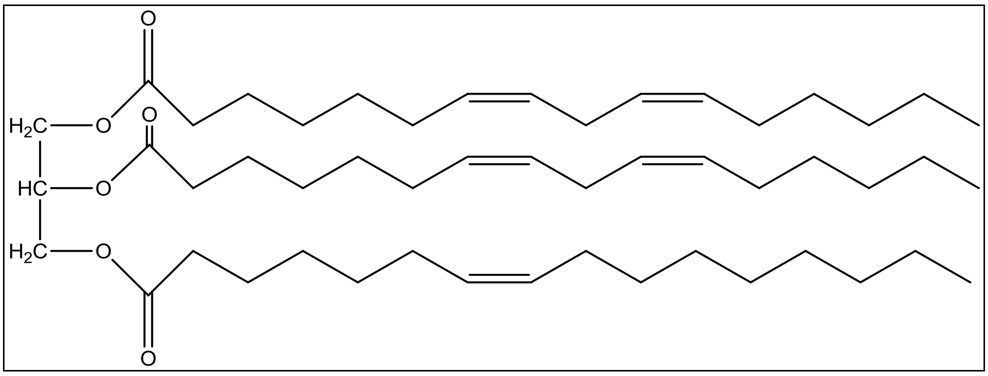


Figure 1.5: Typical structure of triglyceride.

In the industrial applications, PUs, which are produced by vegetable oils and diamines, have wide range of mechanical properties which are useful for many applications [45]. To illustrate, rigid polyurethane foam has been synthesized by replacing polypropylene-based polyol with soybean oil based one, and Suqin Tan et. all got comparable results such as surface morphology and mechanical strength [46]. Studies reported that the adhesion strength of PUs were ten times higher than commercial PU adhesives which petroleum based polyols used to synthesize [47-49].

- Preparation of PU

PUs are available to be synthesized by alternative systems according to its application. One shut method and prepolymer method are the two common mechanisms to synthesize flexible systems.

- One-Shut Method

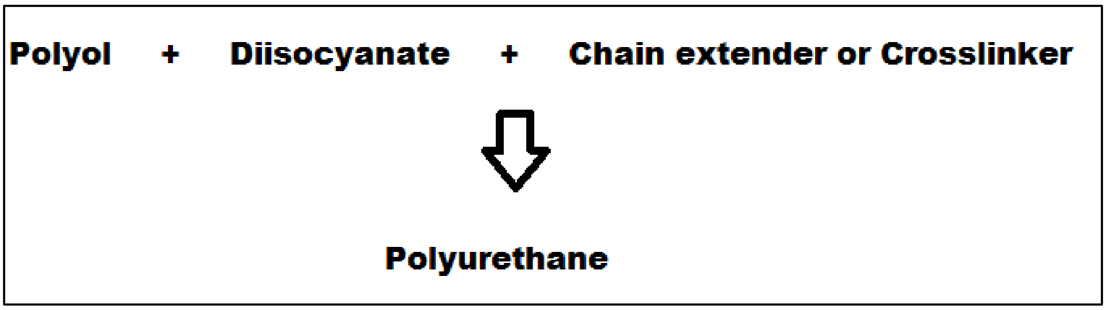


Figure 1.6: One-shut method PU synthesis.

In the one-shut mechanisms, the entire raw materials are mixed via certain conditions as represented in the Figure 1.6 [50]. According to the type of application, additives like cross linker or chain extender determine the conditions and mechanical properties of the PU.

- Prepolymer Method

In this method, two main components diisocyanete and polyol are mixed in certain conditions. Afterwards, chain extender or catalysts are treated in the second stage to prepare prepolymer for the usage [51-52]. Additional group's functionality determines the repeating unit of the chain as shown in Figure 1.7.

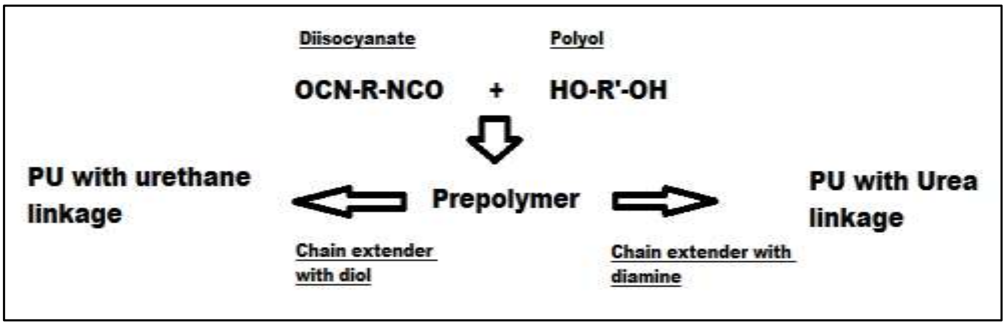


Figure 1.7: Preparation of prepolymer method.

1.2. Applications of Polyurethanes

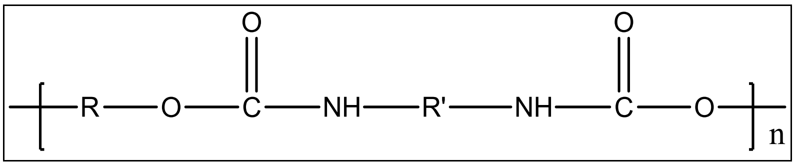
Almost a century ago, polycondensation and polymerizations were the main two topics to gain plastics in the industry. In 1937 German scientist Otto Bayer and his coworkers proceeded a complete polyaddition reaction [53]. Since then, by the selection of reactant and additives, PUs have been used in many industries as a rigid crystalline plastic, flexible elastomer, and viscoelastic gel. The wide range of modifications and properties make PUs an indispensable component for construction, automotive and home furniture industries [54-56].

- Flexible Foam

The polyol group used in the PU reaction determines the final structure of the PU. Polyols which have long chain such as polyesterpolyols or polyetherpolyols are used to produce flexible foams. Ethylene or propyleneoxide based polyetherpolyols are used to generate viscoelastic foams for bedding purpose or integral foams for outer surfaces [57].

By optimization of propylenoxide to ethyleneoxide in polyetheroxide and hydroxyl functionality like tree narrows the molecular weight distribution of the PU which discriminates the cell skeleton of the PU [58]. Since PU flexible foams for furniture application is a highly considerable choice for economic reasons, foams are tested specifically according to ASTM D3453 and D5672 [59].

- PU Adhesive



$$\left[-R-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O- \right]_n$$

Figure 1.8: General form of PU.

Adhesion is a process which transfers a load surface from adhered to the adhesive side, and it could happen with chemical or physical force to the applied surface [60]. In other words, adhesive-bonded result mainly from the intermolecular forces between the adhesive and the substrate. Substrate wetting by adhesive is crucial for high strength for intermolecular force which results the good adhesion to the substrate [61-62]. In the general structure of linear PU was derived from hydroxyl containing polyol and isocyanate contained group reaction. PU adhesives are complex polymers which interact intimately and thus curing proceeds. During the process, viscose adhesive material becomes rigid solid between applied surfaces and cohesively cross-linked to the adherents [63-64].

Although, traditionally PU adhesives produced by reaction of petroleum based polyol with diisocyanate, there have been deep research about instruction of biobased renewable materials to integrate the PU based systems [65-66]. Because of the limited choice of isocyanates, researchers focused on the development of the alternative natural polyol components such as lignocellulosic biomass, carbohydrates like starch which were commonly used for the production of biobased polyols [67-69]. The development of adhesives has led to many industrial areas, especially the discovery of the flexible PU adhesives [70].

In addition to urethane linkage, PU adhesive contains aromatic or aliphatic hydrocarbons, ethers, amides and ether groups. The reaction between isocyanate and hydroxyl group creates urethane repeating bond on the polymer chain. During that reaction, urea and carbon dioxide may occur as by-products by the reaction of water and isocyanate.

Although PU adhesives have poor thermal oxidative and moisture resistance than acrylic adhesives, there are certain advantages to use them, such as, PU adhesives wet almost all the substrates and small particle sizes may allow them to penetrate the applied surface, they are ready to combine the surface with hydrogen bond and covalent bond [71]. Although initial strength is relatively easy for the adhesives, the reliability of adhesion technology obtains good durability of adhesives in environmental conditions [72].

- Types of PU adhesives

There are many unique types of PU based adhesives, and each of them differentiates the applications.

The first one is the water borne PU based adhesives which have quite high molecular weight and dispersed in water (PUD). PUD characteristics are certain, and they are more different than solvent based ones especially in the film formation capability. The composition of the polymer characteristics and backbone depend on the formulation details of PUD. There are free isocyanate residues existing on PUD and quite a small amount of volatile organic compound (VOC) [73].

The second is solvent based PU adhesives which are obtained by higher molecular weighted polyols reaction with diisocyanate than dissolution for this polymer in a proper solvent system. Solvent evaporation derives this kind of PU adhesives from may industrial applications such as wood, plastic, textile, leather and rubber [74].

1.3. The Aim of This Study

In this study, three types of new prepolymers have been synthesized for the recycling of flexible PU foam. In the first one, polyether polyol was used and in the following reactions, special bio-based polyols were integrated to system with different ratios. Later, the resultant prepolymers were characterized.

2. EXPERIMENTAL

2.1. Materials

The reagents for PU adhesive were obtained from suppliers. Ongronat 3800 is a carbodiimide-modified 4-4’methylene diphenyl diisocyanate (Borsod Chem), PM-200 is a diisocyanato-diphenylmethane(MDI)-based isocyanate (Yantai Wanhua Polyurethanes Co., Ltd.), Polypropylene glycol 2000 (PPG 2000) (Fred Holmberg&CO, Cas: 9082-00-2), Polyol NJ-360N polyether based polyol 3 functional and 28 hydroxy value (Jurong Ningwu New Material Development Company, Cas: 9082-00-2), Bipolyol RD Vegetable Oil Based (estimated bio carbon content ~ 83 %) 2.1 functional and 350-390 hydroxy value (PolyLabs SIA) di-(2-ethylhexyl)phthalate (LG Chem, Cas:117-81-7), TEGOSTAB B 8110 is a silicone surfactant (Evonik Industries AG) were used trough this study.

Table 2.1: Formulation details of PU1, PU2 and PU3.

	PU1(%weight)	**PU2(%weight)**	**PU3(%weight)**
NJ360-N(polyol 1)	32,94	27,20	11,78
Bipolyol RD (polyol 2)	-	3,05	12,03
PPG2000 (polyol 3)	0,35	0,32	0,26
4-4'MDI	40,63	46,57	53,69
pMDI	14	10,83	12,78
TEGOSTAB 8110	0,58	0,54	0,43
DOP	11,48	11,48	9,03

2.2. Prepolymer PU1 Synthesis

Theoretical NCO% contents of the prepolymer PU1 has been calculated according to ASTM D2572-97 and amounts of isocyanates and polyols are added to the reaction medium accordingly as showed below.

$$polyol\ 2\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{28} = 2003{,}57\ g/eq \tag{2.1}$$

$$polyol\ 2\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{658{,}89}{2003{,}57} = 0{,}33\ (fn)\ g/mol \tag{2.2}$$

$$polyol\ 3\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{56} = 1001{,}79 g\ /eq \tag{2.3}$$

$$polyol\ 3\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{7}{1001{,}79} = 0{,}01 \frac{g}{mol} \tag{2.4}$$

$$total\ equavalent\ OH = 0{,}33 + 0{,}01 = 0{,}34\ g/mol \tag{2.5}$$

$$Isocayanate\ 1\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{28} = 150{,}07\ g/eq \tag{2.6}$$

$$eq.\%NCO\ \ of\ Isocyanate\ 1\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{812{,}7}{150{,}07} \tag{2.7}$$

$$= 5{,}42\ eq$$

$$Isocayanate\ 2\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{31{,}10} = 135{,}05\ g/eq \tag{2.8}$$

$$eq.NCO\ \ of\ Isocyanate2\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{280{,}08}{135{,}05} \tag{2.9}$$

$$= 2{,}07\ eq$$

$$total\ eq.NCO = 5{,}42 + 2{,}07 = 7{,}49\ eq \tag{2.10}$$

$$Theoretical\ \%NCO$$

$$= \frac{(Total\ eq.NCO - Total\ eq.OH) * 42 * 100}{(eq.NCO\ Iso1 + eq.NCO\ Iso2 + poly3\ eq.wt. + poly2\ eq.wt.)} \tag{2.11}$$

$$= \frac{(7{,}49 - 0{,}34) * 42 * 100}{(280{,}08 + 812{,}70 + 7{,}0 + 658{,}89)} = 17{,}0899$$

PU1 (%0 biobased polyol content) synthesis by using only petroleum based polyol. One-pot prepolymer preparation of PU1 is represented as shown in Figure 2.1 below.

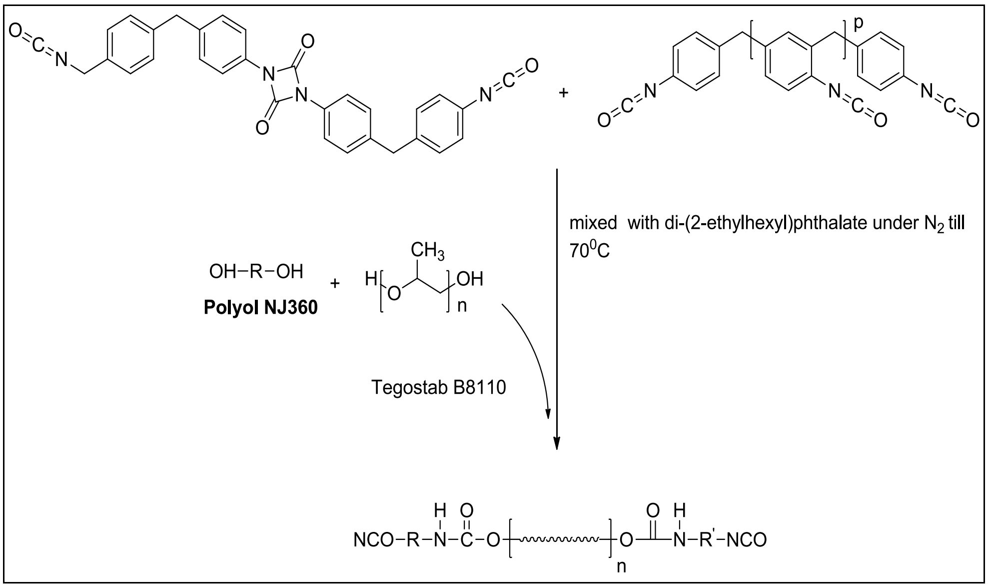


Figure 2.1: Chemical route for PU1 prepolymer synthesis.

Ongronat 3800, PM-200 and di-(2-ethylhexyl) phthalate are added to two-litter round bottom flask under nitrogen. When the temperature of the reaction reaches 70ºC, PPG 2000, Polyol NJ-360N, and TEGOSTAB B 8110 blend added to reaction between 30 and 40 minutes. After the addition, %NCO content is observed and the reaction cooled down to the 40ºC for characterizations.

2.3. Prepolymer PU2 Synthesis

Theoretical NCO% contents of the prepolymer PU2 have been calculated according to ASTM D2572-97 and amounts of isocyanates and polyols are added to the reaction medium accordingly as showed below.

$$polyol\ 1\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{370} = 151{,}62\ g/eq \tag{2.12}$$

$$polyol\ 1\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{61{,}09}{151{,}62} = 0{,}40\ (fn)\ g/mol \tag{2.13}$$

$$polyol\ 2\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{28} = 2003{,}57\ g/eq \tag{2.14}$$

$$polyol\ 2\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{543{,}92}{2003{,}57} = 0{,}27\ (fn)\ g/mol \tag{2.15}$$

$$polyol\ 3\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{56} = 1001{,}79g\ /eq \tag{2.16}$$

$$polyol\ 3\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{6{,}50}{1001{,}79} = 0{,}01\ g/mol \tag{2.17}$$

$$total\ equavalent\ OH = 0{,}40 + 0{,}27 + 0{,}01 = 0{,}68\ g/mol \tag{2.18}$$

$$Isocayanate\ 1\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{28} = 150{,}07\ g/eq \tag{2.19}$$

$$eq.\%NCO\ \ of\ Isocyanate1\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{931{,}44}{150{,}07} = 6{,}21\ eq \tag{2.20}$$

$$Isocayanate\ 2\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{31{,}10} = 135{,}05\ g/eq \tag{2.21}$$

$$eq.NCO\ \ of\ Isocyanate2\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{216{,}61}{135{,}05} = 1{,}60\ eq \tag{2.22}$$

$$total\ eq.NCO = 6{,}21 + 1{,}60 = 7{,}81\ eq \tag{2.23}$$

$$Theoretical\ \%NCO$$

$$= \frac{(Total\ eq.NCO - Total\ eq.OH) * 42 * 100}{(eq.NCO1 + eq.NCO2 + poly3eq.wt. + poly2eq.wt. + pol1eq.wt.)} \qquad (2.24)$$

$$= \frac{(7{,}81 - 0{,}68) * 42 * 100}{(216{,}61 + 931{,}44 + 61{,}09 + 543{,}92 + 6{,}50)} = 17{,}0256$$

PU2 (%10 bio-based polyol content) has been synthesized by using petroleum based polyol and Biopolyol RD. One-pot prepolymer preparation of PU2 is represented as shown in Figure 2.2 below.

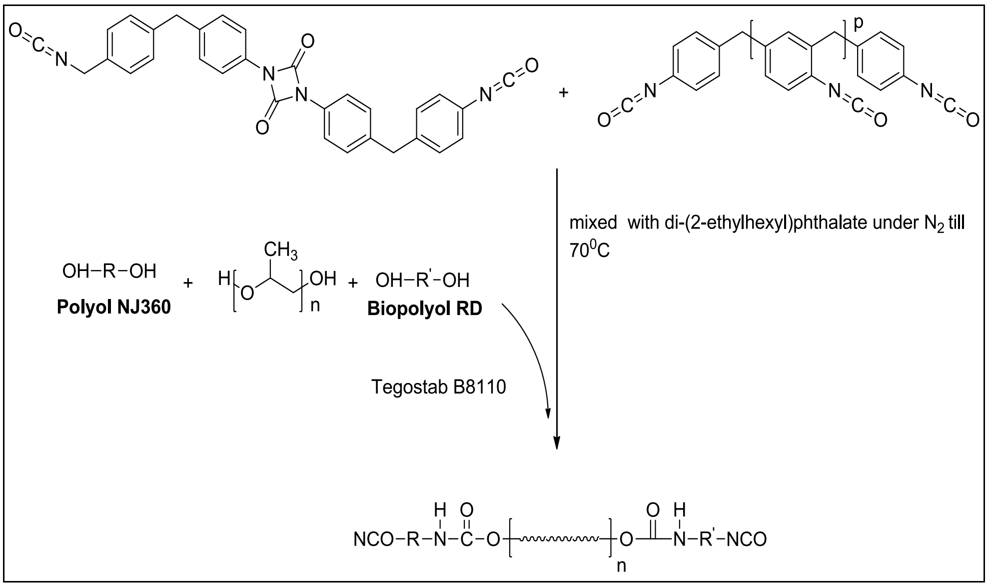


Figure 2.2: Chemical route for PU2 prepolymer synthesis.

PU2 (10% bio based polyol weight/total weight of polyol) has been synthesized by using only petroleum based polyol. Ongronat 3800, PM-200 and di-(2-ethylhexyl) phthalate added to two litter round bottom flask under nitrogen. When the temperature of the reaction reaches 70ºC, PPG 2000, Polyol NJ-360N, Bipolyol RD and TEGOSTAB B 8110 blend added to reaction between 30 and 40 minutes. After the addition, %NCO content observed and reaction cooled down to the 40ºC for characterizations.

2.4. Prepolymer PU3 Synthesis

Theoretical NCO% contents of the prepolymer PU3 have been calculated according to ASTM D2572-97, and the amounts of isocyanates and polyols are added to the reaction medium accordingly as showed below.

$$polyol\ 1\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{370} = 151{,}62\ g/eq \tag{2.25}$$

$$polyol\ 1\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{240{,}67}{151{,}62} = 1{,}59\ (fn)\ g/mol \tag{2.26}$$

$$polyol\ 2\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{28} = 2003{,}57\ g/eq \tag{2.27}$$

$$polyol\ 2\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{235{,}55}{2003{,}57} = 0{,}12\ (fn)\ g/mol \tag{2.28}$$

$$polyol\ 3\ eq.wt. = \frac{56100}{OH\ value} = \frac{56100}{56} = 1001{,}79g\ /eq \tag{2.29}$$

$$polyol\ 3\ mol.wt. = \frac{weight\ of\ polyol}{eq.wt.of\ OH} = \frac{5{,}11}{1001{,}79} = 0{,}01\ g/mol \tag{2.30}$$

$$total\ equavalent\ OH = 0{,}59 + 0{,}12 + 0{,}01 = 1{,}71\ g/mol \tag{2.31}$$

$$Isocayanate\ 1\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{28} = 150{,}07\ g/eq \tag{2.32}$$

$$eq.\%NCO\ \ of\ Isocyanate1\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{1073{,}80}{150{,}07} \\ = 7{,}16\ eq \tag{2.33}$$

$$Isocayanate\ 2\ eq.wt. = \frac{4202}{NCO} = \frac{4202}{31{,}10} = 135{,}05\ g/eq \tag{2.34}$$

$$eq.NCO\ \ of\ Isocyanate2\ = \frac{weight\ of\ isocayanate}{eq.wt.} = \frac{255{,}67}{135{,}05} \tag{2.35}$$
$$= 1{,}89\ eq$$

$$total\ eq.NCO = 7{,}16 + 1{,}89 = 9{,}05\ eq \tag{2.36}$$

$$Theoretical\ \%NCO$$
$$= \frac{(Total\ eq.NCO - Total\ eq.OH) * 42 * 100}{(eq.NCO\ 1 + eq.NCO2 + poly3eq.wt. + poly2eq.wt. + pol1\ eq.wt.)} \tag{2.37}$$
$$= \frac{(9{,}05 - 1{,}71) * 42 * 100}{(255{,}67 + 1073{,}80 + 240{,}67 + 235{,}55 + 5{,}11)} = 17{,}0289$$

PU3 (%50 bio based polyol content) has been synthesized by using petroleum based polyol and Biopolyol RD. One-pot prepolymer preparation of PU3 represented as showed Figure 2.3 below.

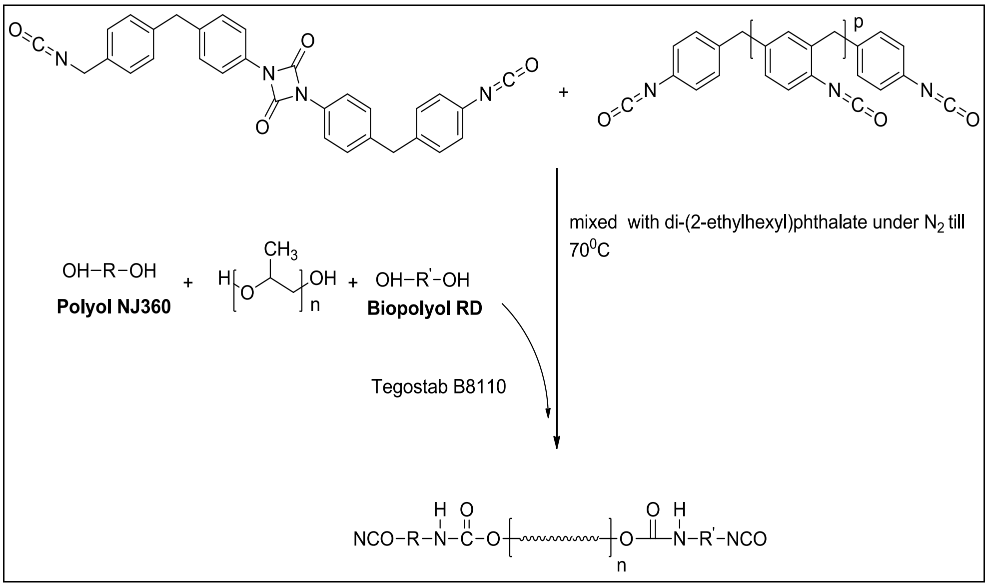


Figure 2.3: Chemical route for PU3 prepolymer synthesis.

Ongronat 3800, PM-200 and di-(2-ethylhexyl) phthalate has been added to two-litter round bottom flask under nitrogen. When temperature of the reaction reaches

70ºC, PPG 2000, Polyol NJ-360N, Bipolyol RD and TEGOSTAB B 8110 blend have been added to reaction between 30 and 40 minutes. After the addition, %NCO content is observed and reaction cooled down to the 40ºC for characterizations.

2.5. Characterization Methods

In this study three types of PU based prepolymer synthesized and they were characterized by using FTIR-ATR, 1H-NMR, DSC, TGA, XRD, and AFM. Theoretical %NCO values of prepolymers tested by using Karl Fischer titration.

2.5.1 Karl Fischer Titration

PU prepolymer formulations are derived according to theoretical %NCO values. Therefore, resultant prepolymer's %NCO values are characterized byTitroline Karl Fisher automatic titration by ASTM D2572-97. Toluene (sigma aldrich, Cas: 108-88-3), methanol (sigma aldrich, Cas:67-56-1), 0.1N HCl (sigma aldrich, Cas:7647-01-0) and n-dibutylamine (sigma aldrich, Cas:111-92-2) have been used in the titration system.

2.5.2 FTIR-ATR Spectroscopy

PU polymers has been characterized in cured versions by using Bruker FTIR-ATR Alphus model. Each sample was scanned by ART unit, which has ZnSe crystal, with a resolution 4 cm^{-1} between 4000-400 cm^{-1} for 32 times. The spectral analysis of FTIR data was observed in Origin 9 software.

2.5.3 1H Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR analysis WAS measured on Varian 500 Mhz instrument using CDCl3 or DMSO as solvents, depending on the solubility of the propolymers. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

2.5.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a general choice to determine the molecular orientation dependence of melting point (Tm) and glass transition temperature (Tg) of the polymeric materials. DSC thermograms were recorded by using standard aluminum plates to analyze thermal behavior of the prepolymers. TA instrument DSC AQ20 was used with heating rate 10ºC.min^{-1} in the range of -90ºC and 250ºC.

2.5.5 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a Q50 thermogravimeter (TA instruments) by heating PU samples from 20°C to 700°C at a rate of 10°C/min under Nitrogen atmosphere.

2.5.6 X-Ray Diffraction Measurements

X-Ray Diffraction measurement (XRD) was observed to determine the crystallinity of the prepolimeric materials. Rigaku Ultima-IV X-Ray Diffractometer (Japan) with a copper target ($\lambda = 1.54$ Å), 40 kV 30 mA, and equipped with a graphite monochromator was used to performed the analysis. Samples were observed in the range 2θ=5-80° with a step of 0.02° at the rate of 2°min-1.

2.5.7 Atomic Forced Microscopy

AFM was observed with Ambient AFM/MFM (Nano magnetics Instruments) in Middle East Technical University, Chemistry Department, Instrumental laboratory. PU1, PU2 and PU3 polymers dried under N2 gas to observe morphological structures. Silicone cantilever (rectangular with 225 µm long) was used in tapping mode with force constant 48 N/ma from 1 micro m/s to 8 micro m/s.

3. RESULTS AND DISCUSSIONS

3.1. Karl Fischer Titration

Theoretical calculations of the prepolymers determined the formulations of PU1, PU2 and PU3 synthesis according to ASTM D5155. After the reaction of each step, %NCO content analysis was made according to following equations;

$$\%NCO = \frac{(B-EQ1)T*M*F1}{W*F2} \tag{3.1}$$

3.1.1 PU1 %NCO Analysis

PU1 prepolymer’s experimental %NCO analysis was done in the Titroline 7750 automatic titration according to ASTM D2572-97.

Table 3.1: PU1 %NCO titration values.

B (ml)	Blank	24,5930
EQ1 (ml)	Peak value	20,358
T (m)	Factor of solvent	1
F1	Factor	4,2020
F2	Factor	1
M (mol)	Mole	1
W (g)	weight	1,25450

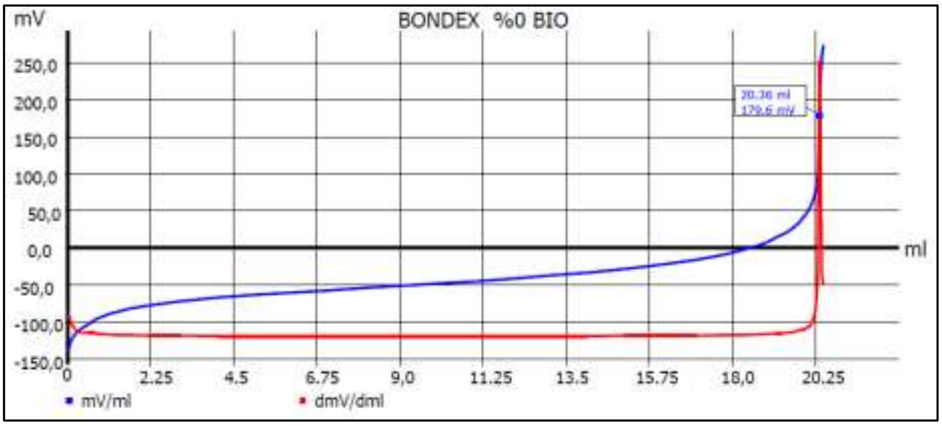


Figure 3.1: Titration curve for PU1 prepolymer.

According to that titration curve;

$$\%NCO = \frac{(B-EQ1)T*M*F1}{W*F2} = \frac{(24{,}5930-20{,}358)1*1*4{,}2020}{1{,}25450*1} = 14{,}185 \qquad (3.2)$$

Although theoretical value is 17,0899, experimental results have shown 14,185. That is still acceptable in the ASTM D5155 range.

3.1.2 PU2 %NCO Analysis

PU2 prepolymer’s experimental %NCO analysis was done in the Titroline 7750 automatic titration.

Table 3.2: PU2 %NCO titration values.

B (ml)	Blank	24,5930
EQ1 (ml)	Peak value	20,398
T (m)	Factor of solvent	1
F1	Factor	4,2020
F2	Factor	1
M (mol)	Mole	1
W (g)	weight	1,24830

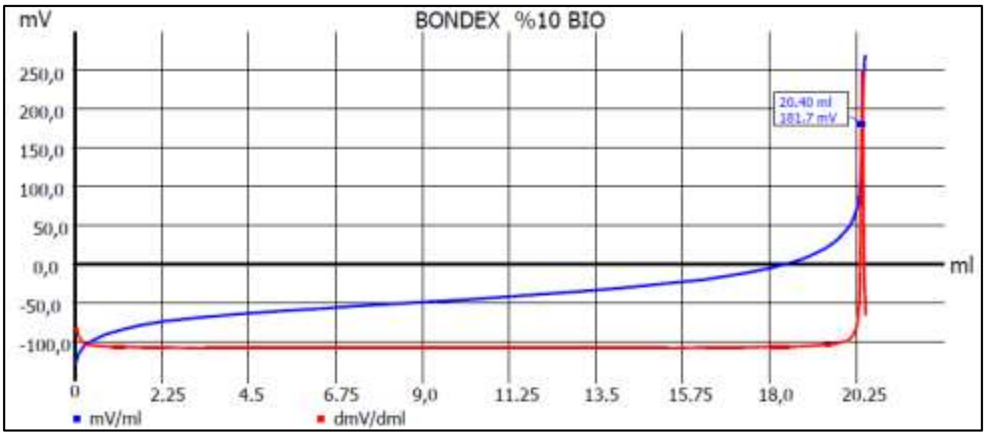


Figure 3.2: Titration curve for PU2 prepolymer.

According to that titration curve;

$$\%NCO = \frac{(B-EQ1)T*M*F1}{W*F2} = \frac{(24{,}5930-20{,}398)1*1*4{,}2020}{1{,}24830*1} = 14{,}121 \qquad (3.3)$$

Although theoretical value is 17,0256, experimental results has shown 14,121. That is still acceptable in the ASTM D5155 range.

3.1.3 PU3 %NCO Analysis

PU3 prepolymer’s experimental %NCO analysis was done in the Titroline 7750 automatic titration.

Table 3.3: PU3 %NCO titration values.

B (ml)	Blank	24,5930
EQ1 (ml)	Peak value	21,490
T (m)	Factor of solvent	1
F1	Factor	4,2020
F2	Factor	1
M (mol)	Mole	1
W (g)	weight	0,92995

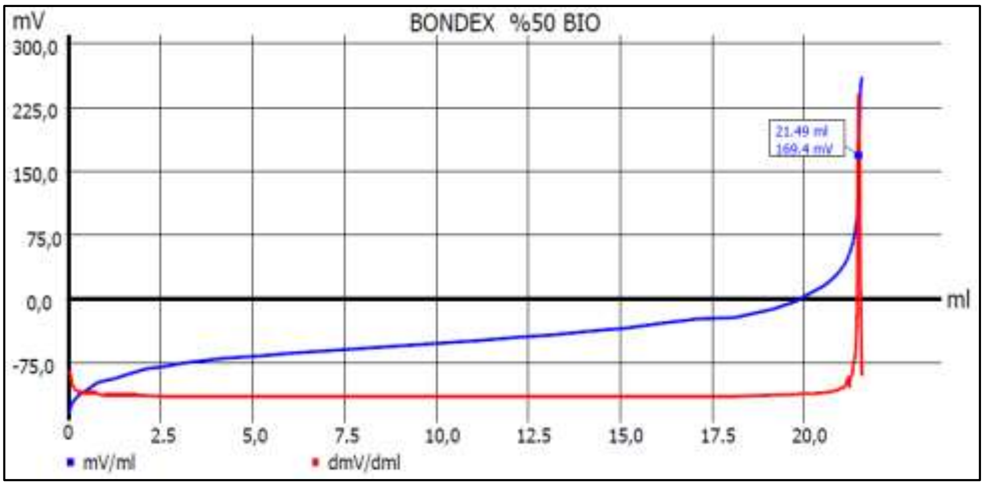


Figure 3.3: Titration curve for PU3 prepolymer.

According to that titration curve;

$$\%NCO = \frac{(B-EQ1)T*M*F1}{W*F2} = \frac{(24{,}5930-21{,}490)1*1*4{,}2020}{0{,}92995*1} = 14{,}0209 \tag{3.4}$$

Although theoretical value is 17,0256, experimental results has shown10,370. That is still acceptable in the ASTM D5155 range.

It has been observed that theoretical values and experimental data of the PU1, PU2 and PU3 are slightly different from each other. However, ASTM D1555 determines the standard test methods for polyurethane raw materials which is between 14%-19% NCO content. That proves the acceptance of the synthesized PUs in the field. The difference between theoretical and experimental value depends on two main reasons as human error and factor value change of the chemicals used in those procedures.

3.2. FTIR-ATR

Each bond of the molecule has vibrational and rotational energy and in infrared region that energy depends on the energy levels of that bonds [75]. It is known that the energy of the bond depends on the elements and nature of the bond and total energy of the bond directly is affected by the molecules translational, vibrational, rotational end electronic energy. Peak area and intensity of a specific bond could change according to environment of that particular vibrational bond [76-77].

Table 3.4: Principle vibrational frequencies of amide bonds.

Wavenumber (cm^{-1})	**Assignment**
3000-3600 cm^{-1}	arises from a Fermi resonance between N–H stretching and overtone
1600-1800 cm^{-1}	involves C=O stretching vibrations
1520-1570 cm^{-1}	corresponds to coupling between N–H bending and C–N stretching vibrations
1220-1330 cm^{-1}	contains a large percentage of N–H n bending and C–N stretching
<800 cm^{-1}	corresponds to out-of-plane vibrations of CO–NH group

The synthesis of the polymeric materials was controlled by using FTIR-ATR analysis. The result of polyol and isocyanate was observed by detailing the characteristic functional units of prepolymers as shown in Figure 3.4

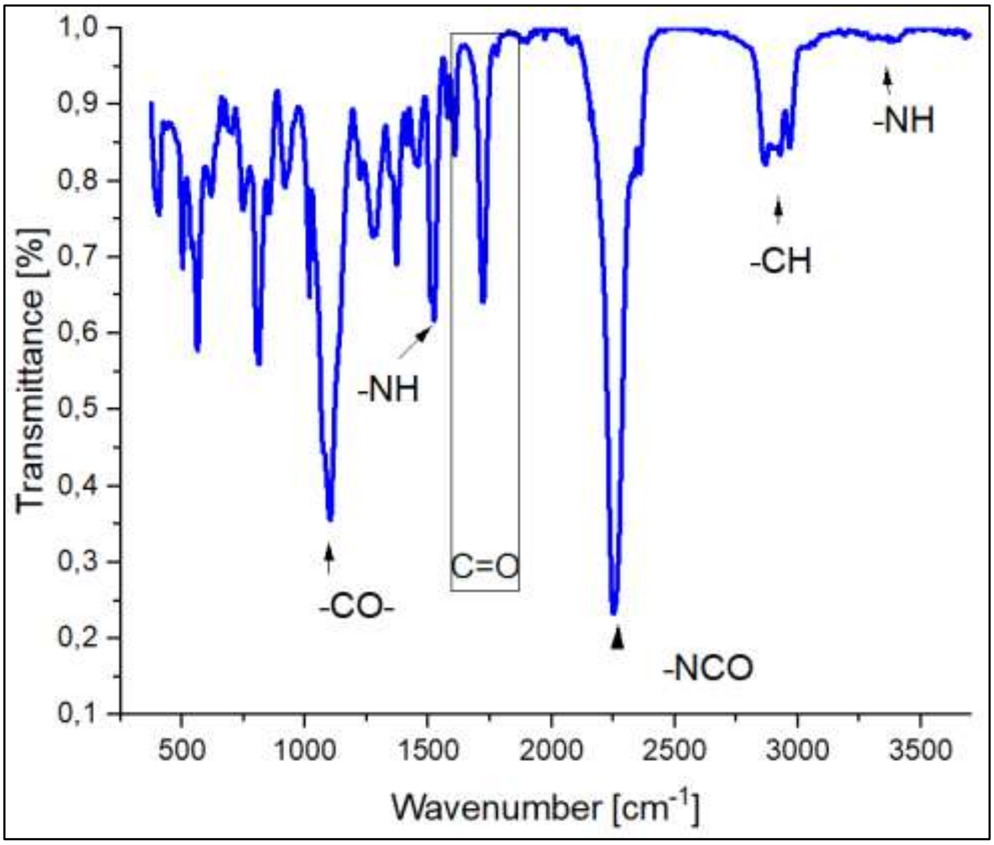


Figure 3.4: PU1 FTIR-ATR analysis.

Reaction medium was checked with analysis of free isocyanate peak in 2225 cm^{-1}. C=O stretching vibration of urethane bond was observed between 1600-1800 cm^{-1}. N-H bending depends on amide bond observed around 1500-1570 cm^{-1}. Furthermore, around 3000 cm^{-1}, C-H stretching was analyzed. C-O-C stretching of ester function was also determined around 1100-1200cm^{-1}. Synthesized prepolymer was also derived by comparing used isocyanate to derivate the intensity of NCO concentration. As shown in Figure 3.5, NCO characteristic peak at 2225 cm^{-1} less was derived in the PU1 analysis. It still shows NCO stretching peak in the prepolymer since it has double isocyanate termination in the head and end.

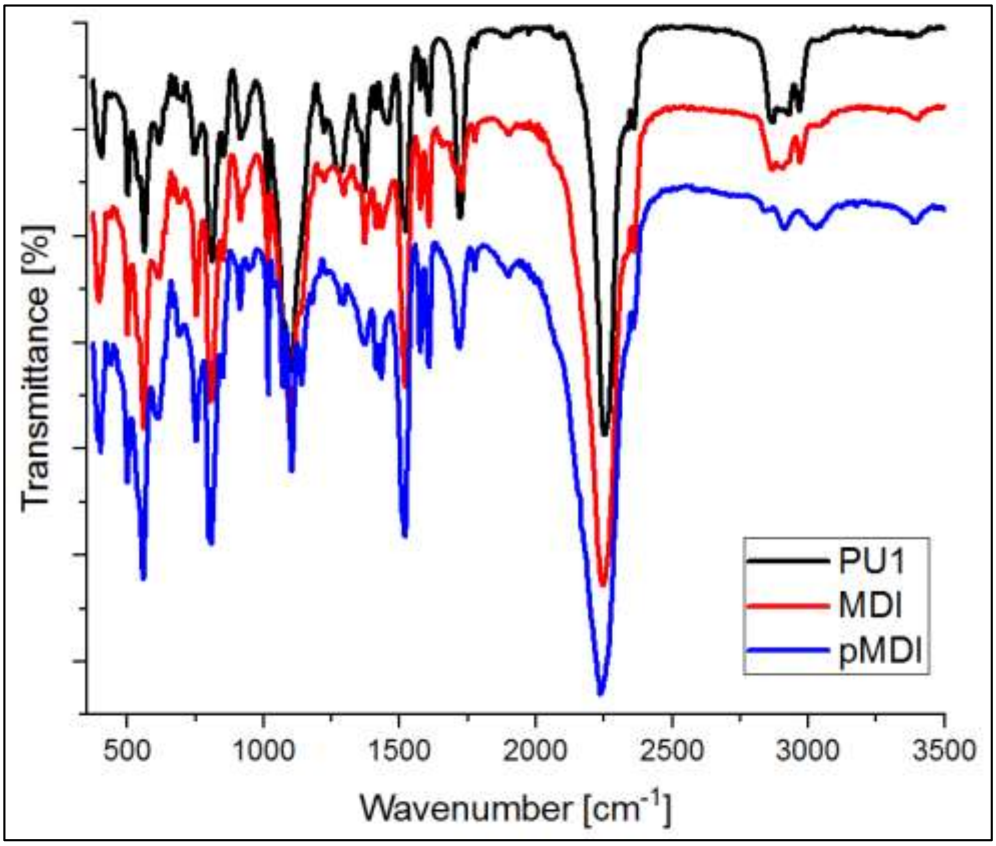


Figure 3.5: FTIR-ATR comparative analysis of a) PU1, b) MDI, c) pMDI.

Less than 800 cm^{-1}, out of plane vibration of CO-NH (amide) bond of PU1 prepolymer was characterized.

Additionally, biopolyol to petroleum based polyol and isocyanate reaction was observed by detailing the characteristic functional units of prepolymer PU2 as shown in Figure 3.6.

Polymerizations steps of the reaction was followed by time dependent FTIR analysis too. When the reaction is started at 70ºC samples are collected at 0 min, 30 min, 60 min 90 min and 120 min than observed the functional group changings.

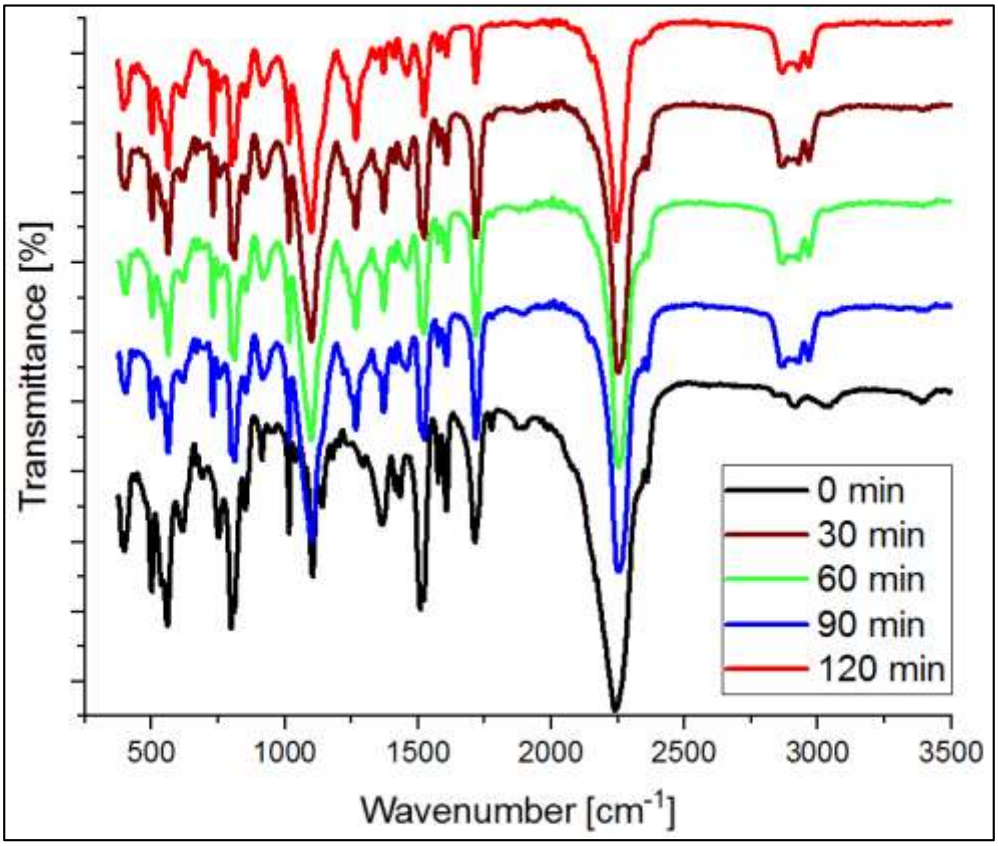


Figure 3.6: Gradual FTIR-ATR analysis of PU1 prepolymer.

Figure 3.6 showed that initial characteristic functional groups of isocyanates around 2225 cm^{-1} gets weaker while reaction time flows. Derivation of the peak intensities are changing during the reaction. COC urethane characteristic bond were intense at the end of the reaction which supported polymeric structure occurrence.

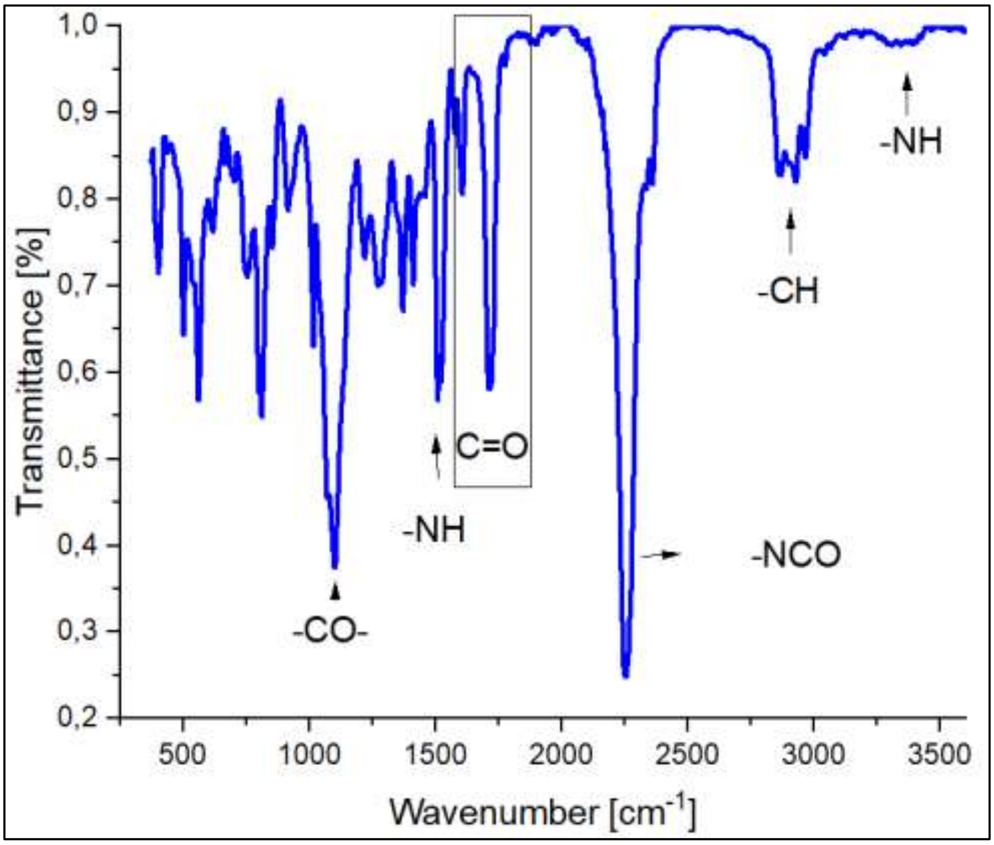


Figure 3.7: PU2 FTIR-ATR analysis.

More similar to the PU1 prepolymer, functional group observation was made on FTIR-ATR spectrum as represented in Figure 7. C=O stretching vibration of urethane bond was observed between 1600-1800 cm^{-1}. N-H bending depends on amide bond observed around 1500-1570 cm^{-1}. Furthermore, around 3000 cm^{-1}, C-H stretching analyzed. C-O-C stretching of ester function was also determined around 1100-1200cm^{-1}.

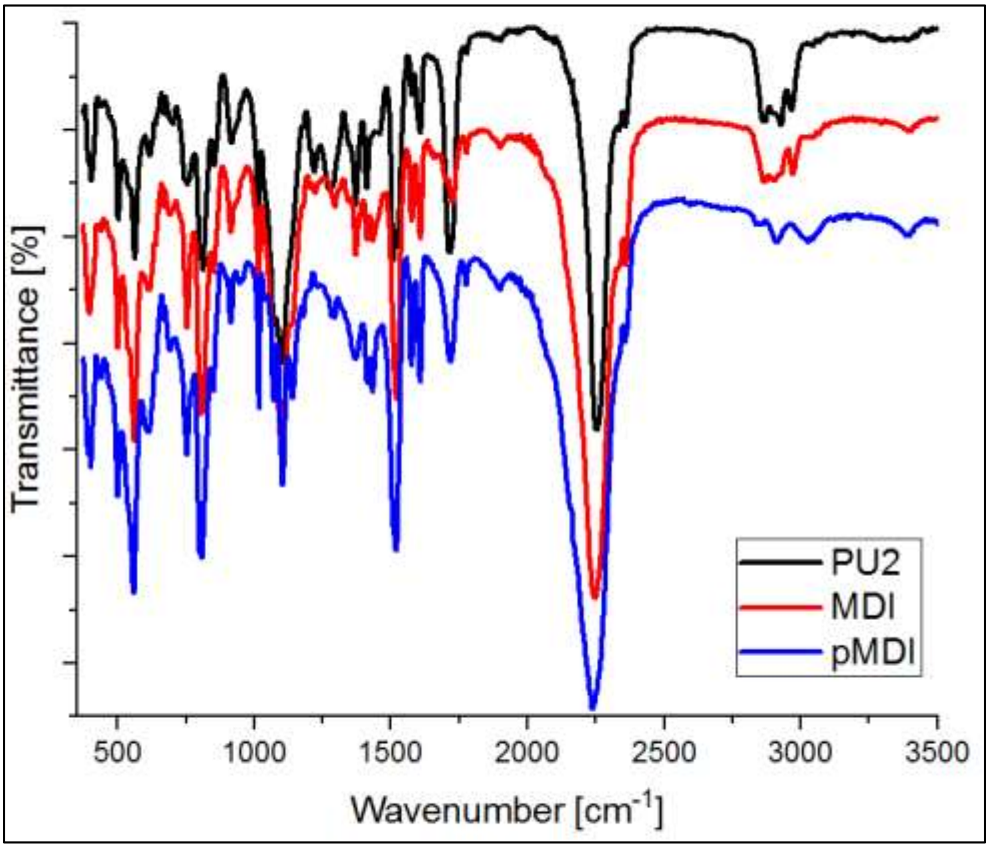


Figure 3.8: FTIR-ATR comparative analysis of a) PU2, b) MDI, c) pMDI.

Synthesized prepolymer was also derived by comparing used isocyanate to derivate the intensity of NCO concentration. As shown in Figure 3.8, pMDI and MDI content of NCO characteristic peak at 2225 cm^{-1} less was derived in the PU2 analysis which proves the reaction of polyols and isocyanates. It still shows NCO stretching peak in the prepolymer since it has double isocyanate termination in the head and end.

Gradual reaction medium also analyzed by observing samples at 0 min, 30 min, 60 min, 60 min, 90 min and 120 min.

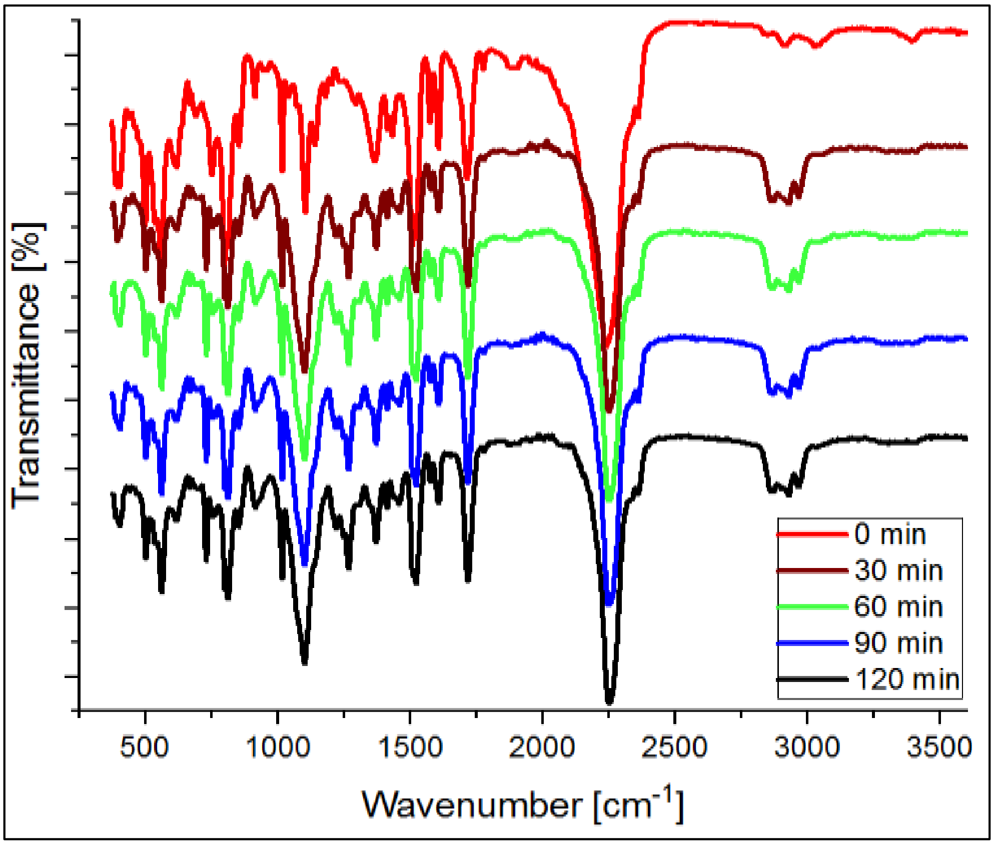


Figure 3.9: Gradual FTIR-ATR analysis of PU2 prepolymer.

In reaction medium at 0 min, isocyanate characteristic functional unit was the most intense one. However, after 120 min COC urethane linkage around 1150 cm^{-1} was observed and NCO characteristic peak at 2225 cm^{-1} were comparingly less derived after the 120 min.

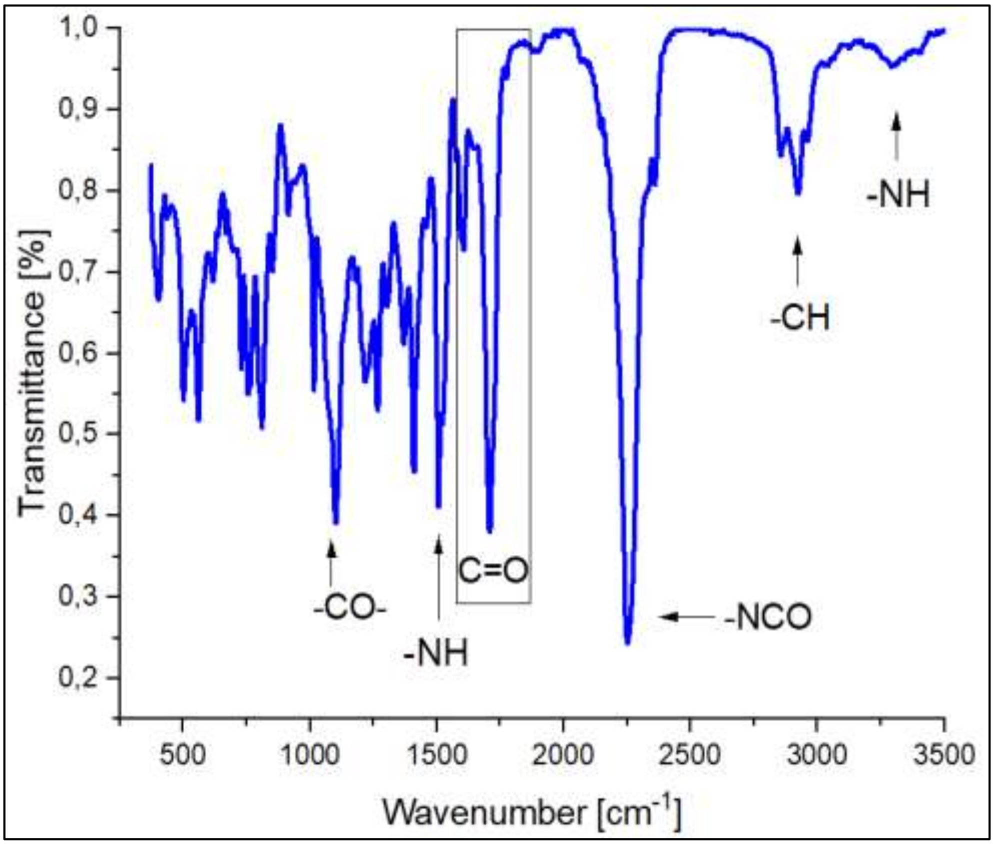


Figure 3.10: PU3 FTIR-ATR analysis.

PU3 prepolymer, functional group observation was made on FTIR-ATR spectrum as represented in Figure 3.10. C=O stretching vibration of urethane bond observed between 1600-1800 cm^{-1}. N-H bending depends on amide bond observed around 1500-1570 cm^{-1}. Furthermore, around 3000 cm^{-1}, N-H stretching was analyzed. Since biopolyol content is 50% of total polyol used, C-O-C stretching of ester function is stronger when compared with PU1 and PU2 around 1100-1200cm^{-1}.

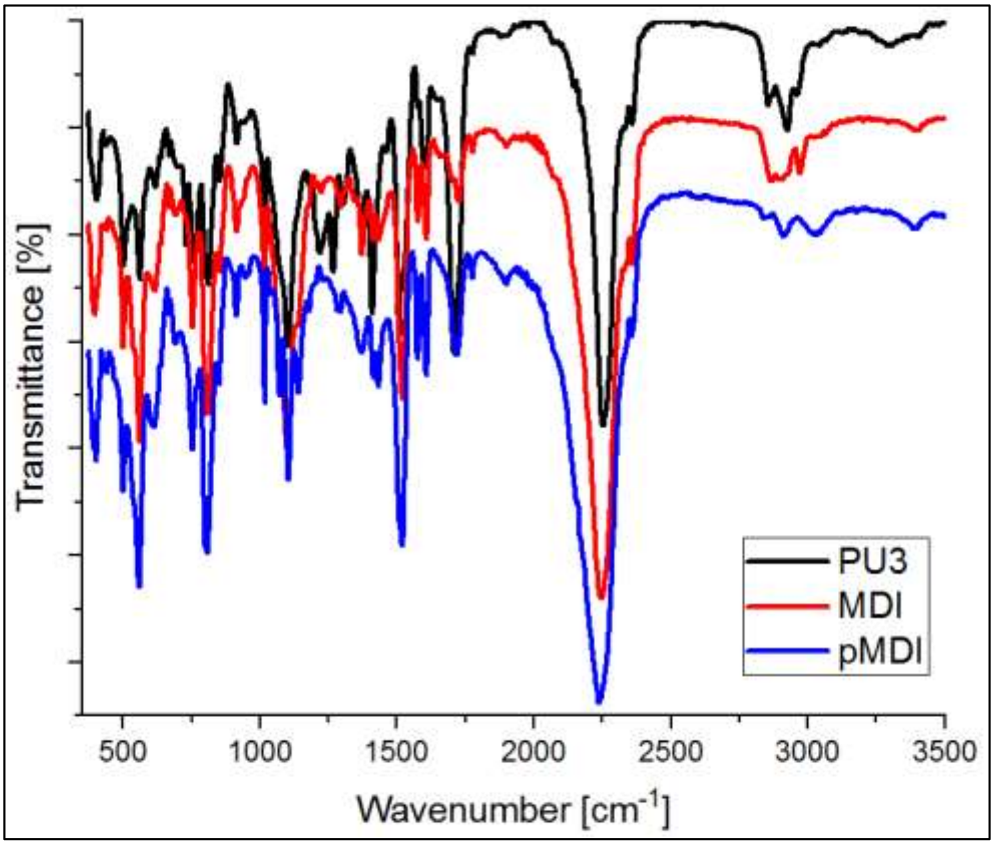


Figure 3.11: FTIR-ATR comparative analysis of a) PU3, b) MDI, c) pMDI.

PU3 comparative analysis was observed with pMDI and MDI too. NCO characteristic peak intensity is less than pure isocyanates here which was as expected.

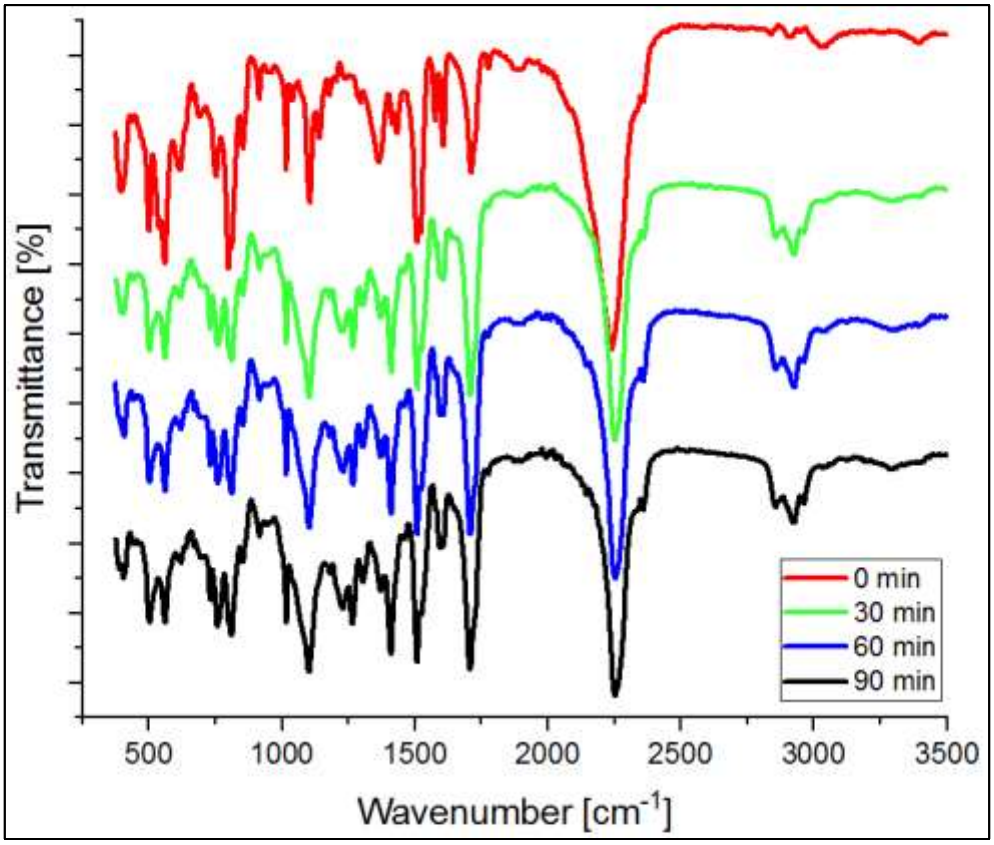


Figure 3.12: Gradual FTIR-ATR analysis of PU3 prepolymer.

Gradual FTIR-ATR analysis shown in Figure 3.12 illustrates that NCO characteristic peak around 2225 cm^{-1} decreased during the addition of polyol into the reaction medium. When compared with PU1 and PU2 C=O, double bond stretching intensity also increased around 1600-1800 cm^{-1}. The effect of the addition of biopolyol also integrated the characteristic peaks for rest of the FTIR spectrum.

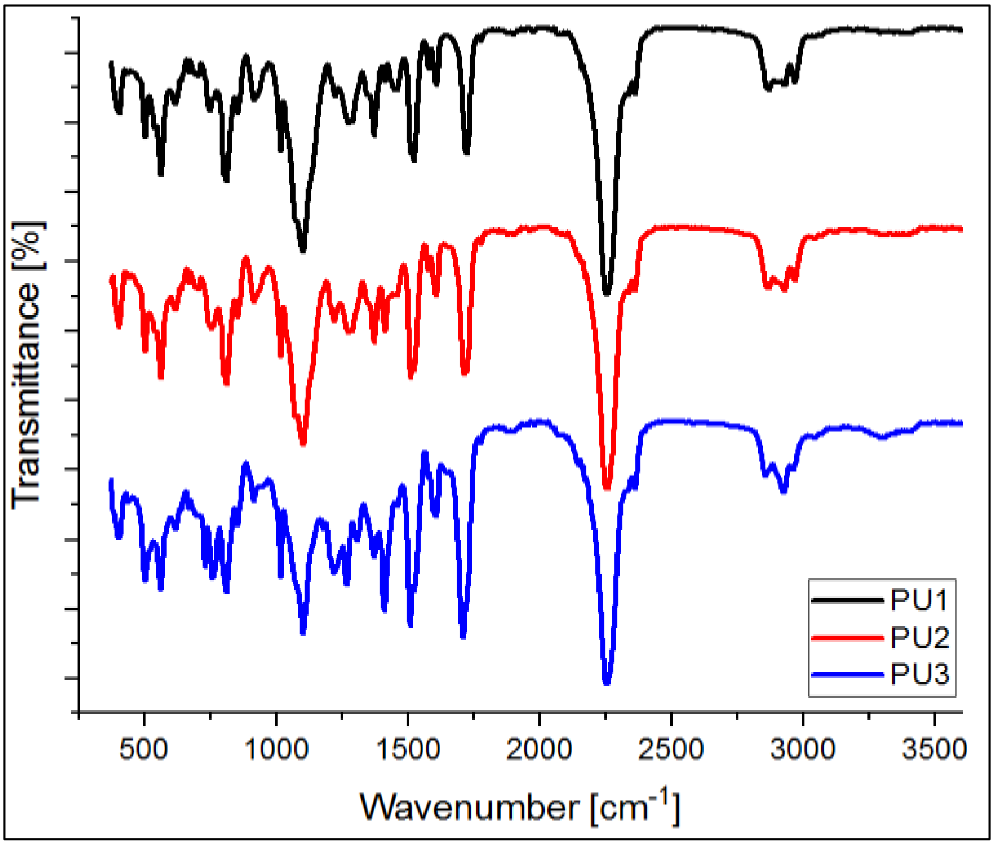


Figure 3.13: Comparative Analysis of PU1, PU2 and PU3.

FTIR-ATR analysis of PU1, PU2 and PU3 was compared successfully amongst each other in Figure 3.13. Each synthesized propolymer was differentiated in the polyol characteristic regions where CO-NH is out of plane vibration below 800 cm^{-1} as shown in Figure 13.

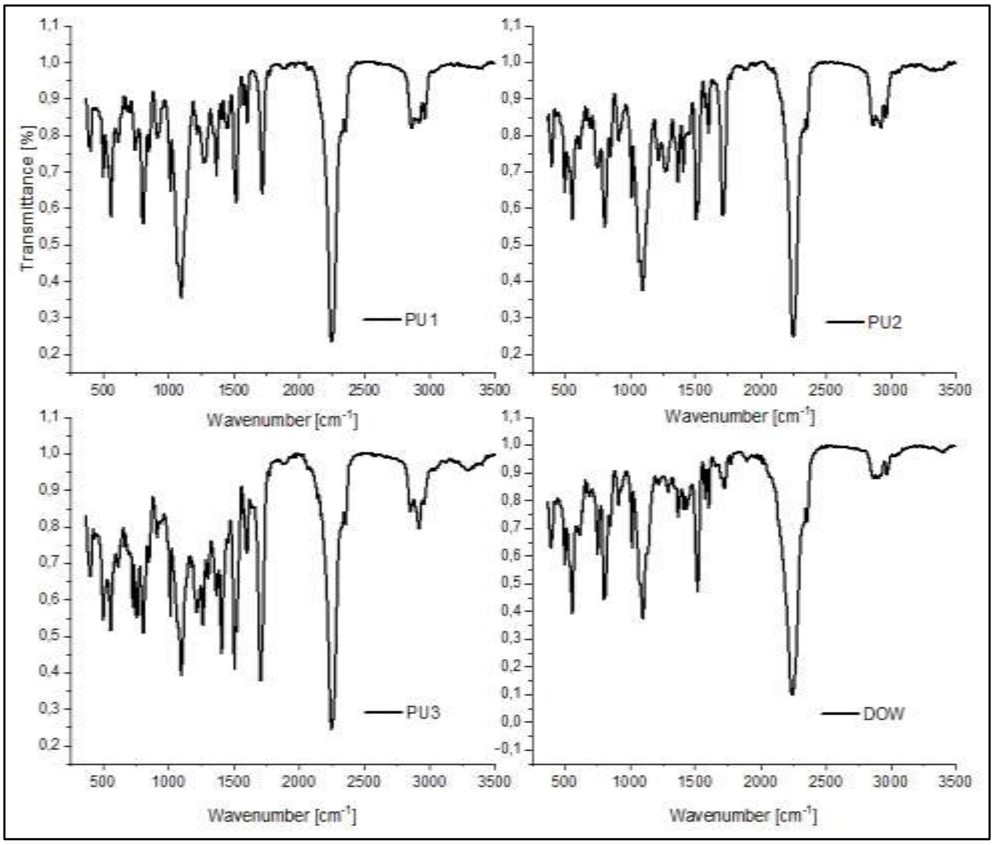


Figure 3.14: FTIR results of PU1, PU2, PU3 and Dow VARAMER MF 1513.

PU1, PU2 and PU3 has been characterized and compared with the literature example Dow Varamer MF 1513. Although there are intensity differences, especially below 800 cm^{-1}, FTIR analysis has clearly confirmed that structural identification of four prepolymers are almost identical.

3.3. ^{1}H Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR analysis has been done to determine the polymerization reaction for the bipolyol terminated prepolymers. Reaction samples have collected at 0 min, 60 mins and 120 mins for PU2 and PU3 prepolymers.

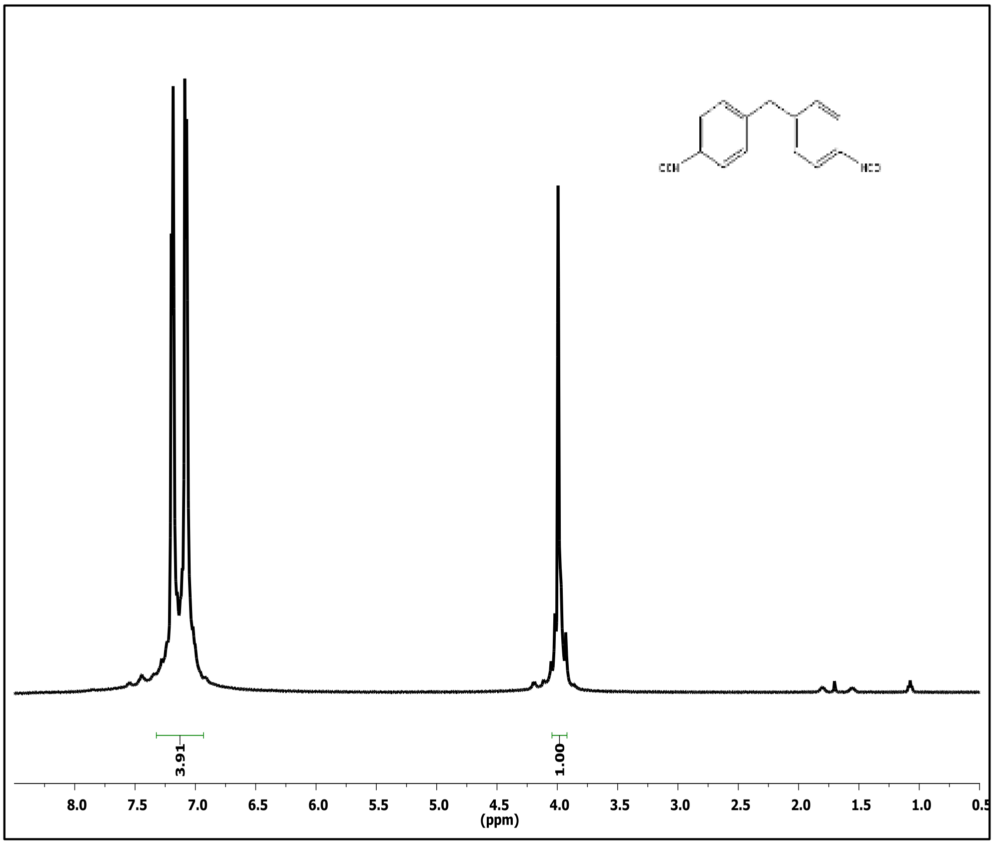


Figure 3.15: ^{1}H NMR analysis of PU2 at 0 min.

Figure 3.15 shows the initial medium of the reaction. It is obvious that aromatic hydrogens coming from the MDI has been determined between 7.0 and 7.3 ppm as A-B system. Around 4.0 ppm, aliphatic CH2 peak was determined. Integration of peaks revealed symmetric structure as well.

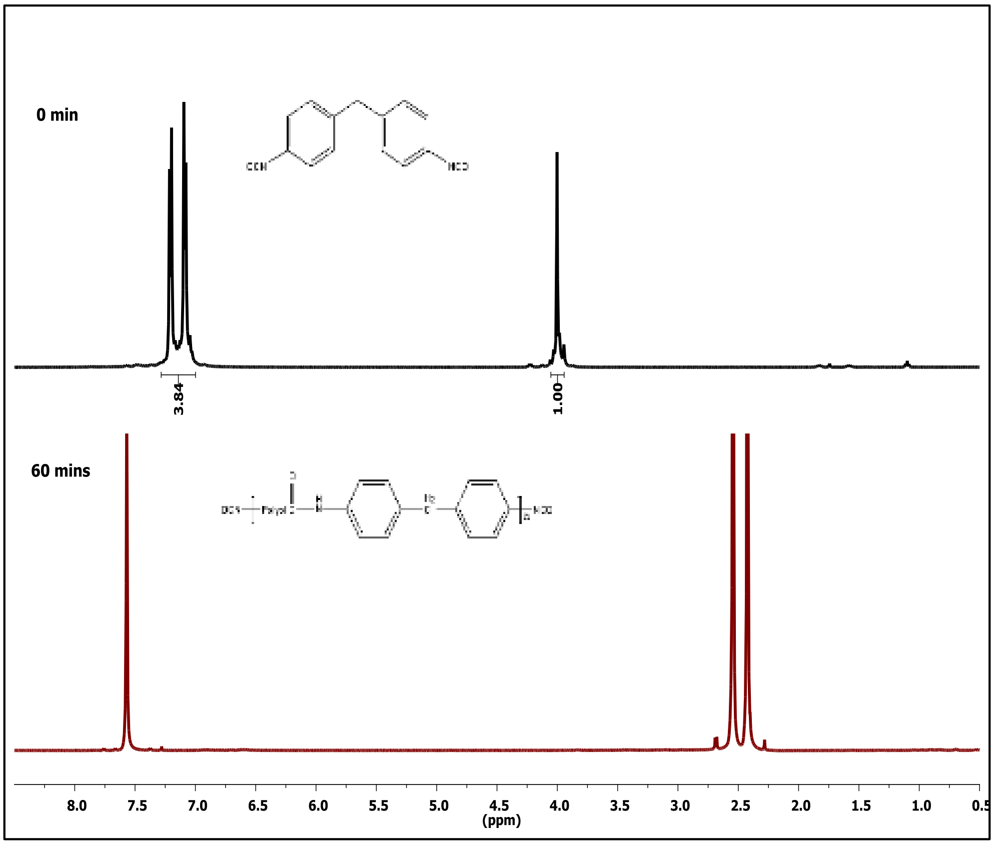


Figure 3.16: ^{1}H NMR analysis of PU3 at 0 min and 60 mins.

Since polymerization mechanism is one-pot condensation, we have the same peak ^{1}H-NMR analysis for PU2 & PU3 prepolymer at 0 min. On the other hand, after the addition of polyol mixture, PU3 prepolymers was not able to observe since they were too crosslinked and not able to dissolve any common solvent. It may be assumed that same reaction occurrence as PU2 having is valid for PU3 prepolymer.

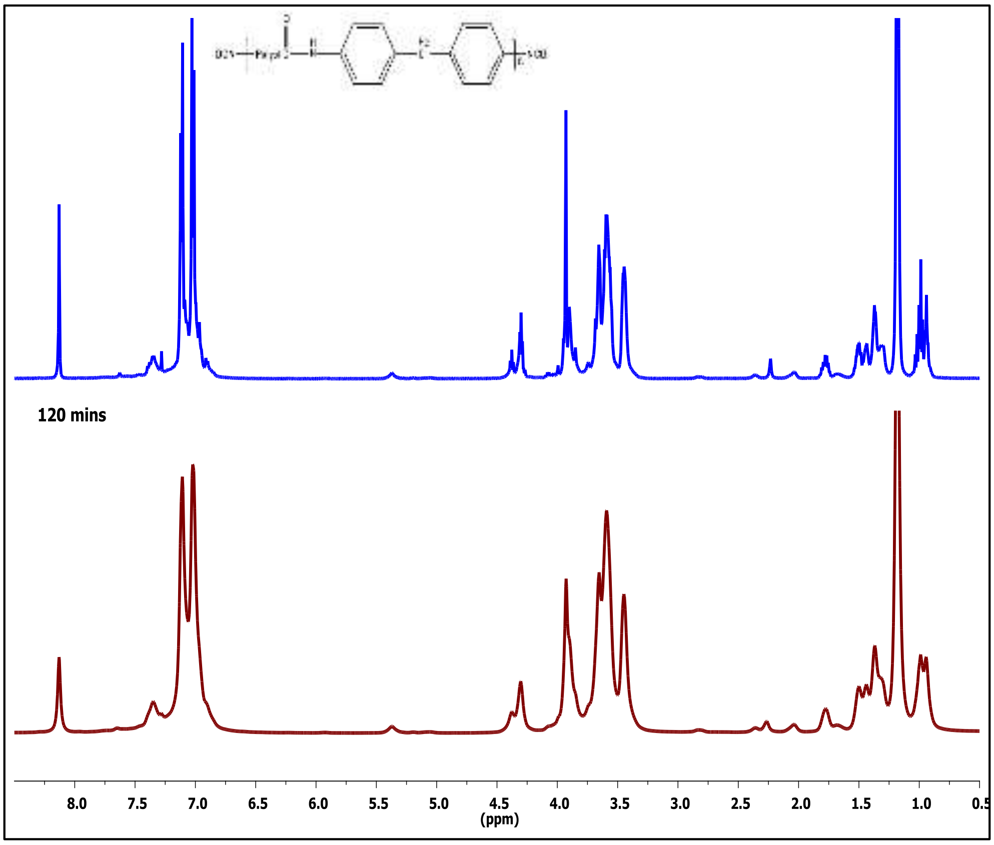


Figure 3.17: ^{1}H NMR analysis of PU2 at 60 and 120 mins.

After the additions of polyol mixture and other reagents, at 60 mins, sample analysis clearly shows the polymerization reaction. At 8.13 ppm, the amide NH hydrogen occurs and between 4.5 and 3.25 ppm, and the peaks coming from the polyol component can be determined. We have also aliphatic CH_2 and CH peaks between 1.7 and 1.0 ppm coming from the polyol part, too. It is understood from the comparative analysis that polymer peaks are quite broad when compared with the starting point which indicates the polymerization reaction occurred.

PU3 gradual ^{1}H NMR detection could not be processed because of the solubility problems. Although DMSO added to the prepolymer, it was not good enough to take MNR analysis.

3.4. Differential Scanning Calorimetry

Thermal characterization of the polymers is the main differentiation which derives the usage of the polymeric material. In order to observe glass transition temperature of the polymers, PU1, PU2 and PU3 adhesive films were prepared with 100µm applicator and dried it under N_2 in 24 hours.

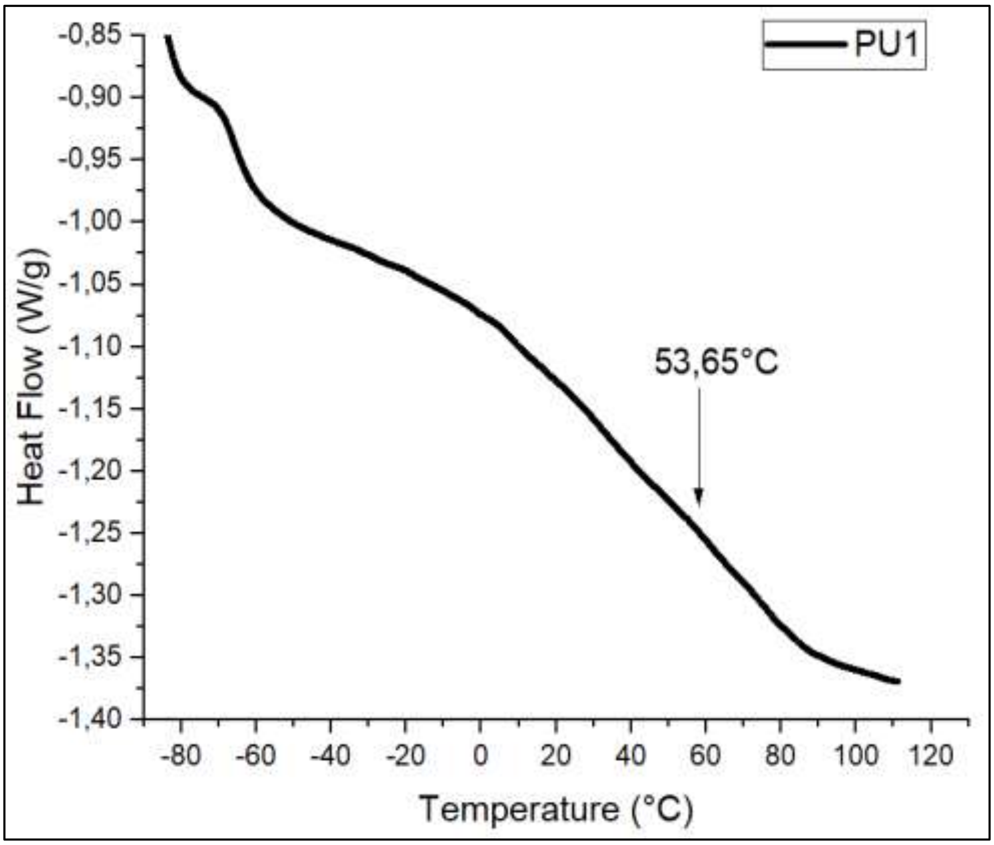


Figure 3.18: DSC thermogram of PU1.

When PU is pure and Tg remains unchanged, there should be 40°/50°C first Tg data [78-79]. Between -90°C to 130°C, we have reported for the PU1 prepolymer and its resultant is 53.65°C Tg, which is expected as the dried film pure solid in room temperature.

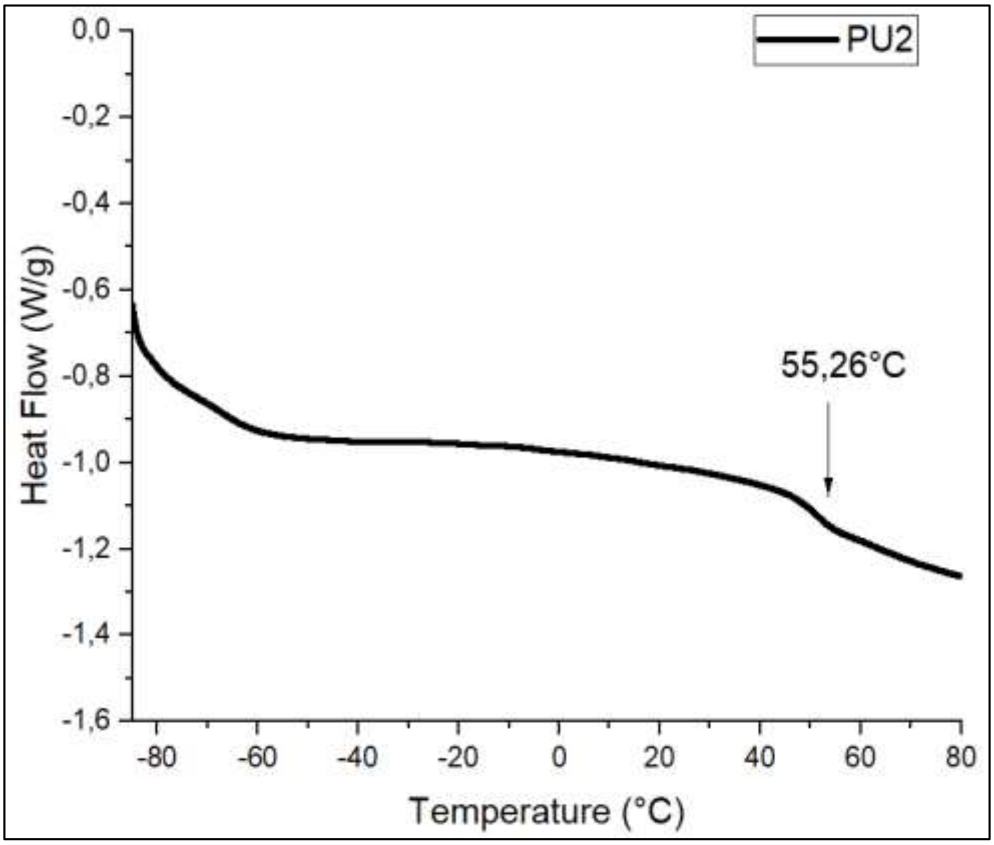


Figure 3.19: DSC thermogram of PU2.

Between -85°C to 80°C, we have reported for the PU2 prepolymer and its resultant is 55.26°C Tg, which is expected as the dried film pure solid in room temperature.

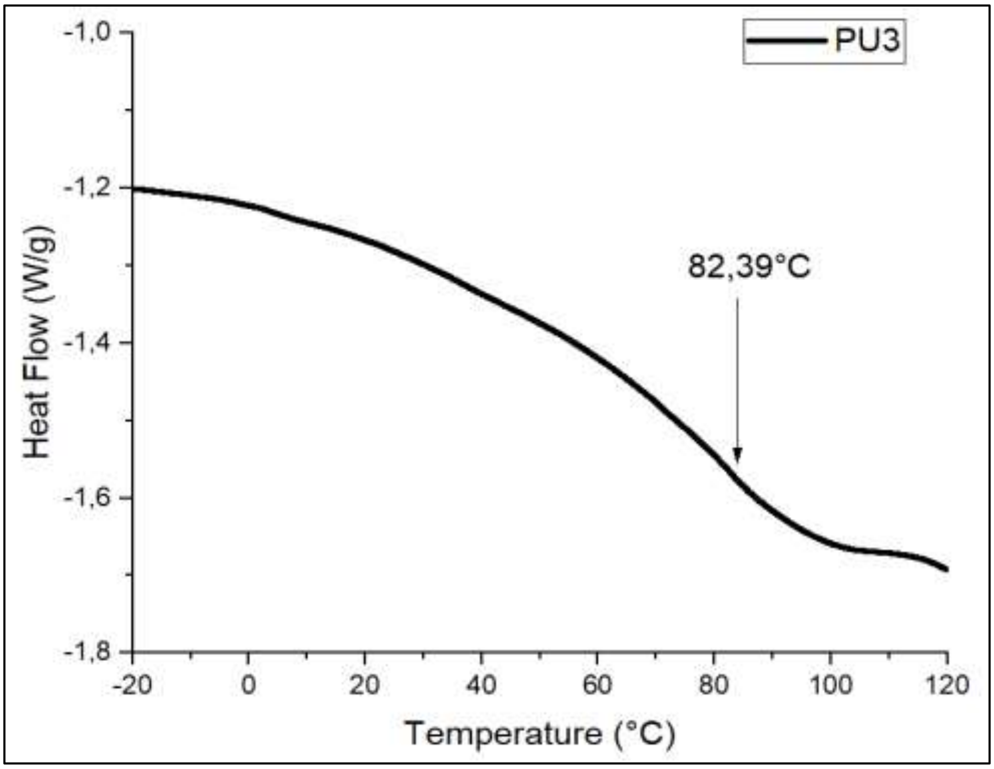


Figure 3.20: DSC thermogram of PU3.

Between -20°C to 120°C, we have reported for the PU3 prepolymer and it resultant 82.39°C Tg which is expected as the dried film pure solid in room temperature.

Although %NCO contents of the prepolymers are almost identical, viscosities are much more different. In Brookfield DV2T viscomerty at 25°C, we observed the crosslink effect of the biopolyol addition on the system which is PU1 1490 cPs., PU2 2665 cPs, PU3 300,000 cPs. This characteristic behavior also affected the the Tg results. The biopolyol increases the Tg values since it causes more crosslinking.

3.5. Thermal Gravimetric Analysis

It was reported in the literature that urethane stability affected by the content of urethane repeating unit, cross-linking density and hydroxyl formed urethane. [80-81] Temperature of thermal decomposition of polyurethane has been reported as three steps [82-84]; first hard segment and urethane linkage and then second and third decomposition come from soft segments.

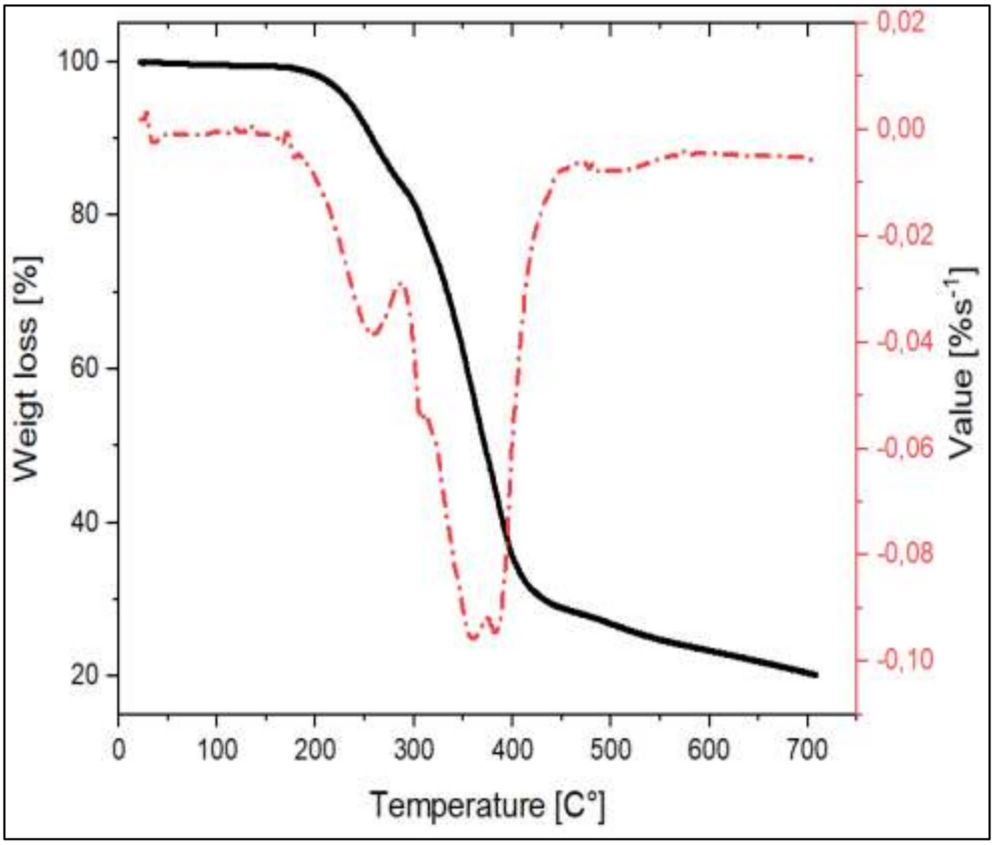


Figure 3.21: TGA-DTGA Thermogram of PU1 prepolymer.

In the TG analysis, there were two degradations expected as Wang et.al [84] suggested. In the thermal decomposition process first degradation occurred on the rigid segment %20 weight loss between 250ºC-300ºC, and soft and semi-rigid segment degradation occurred with 45% weight loss between 350ºC-400ºC for PU1 as shown Figure 3.21.

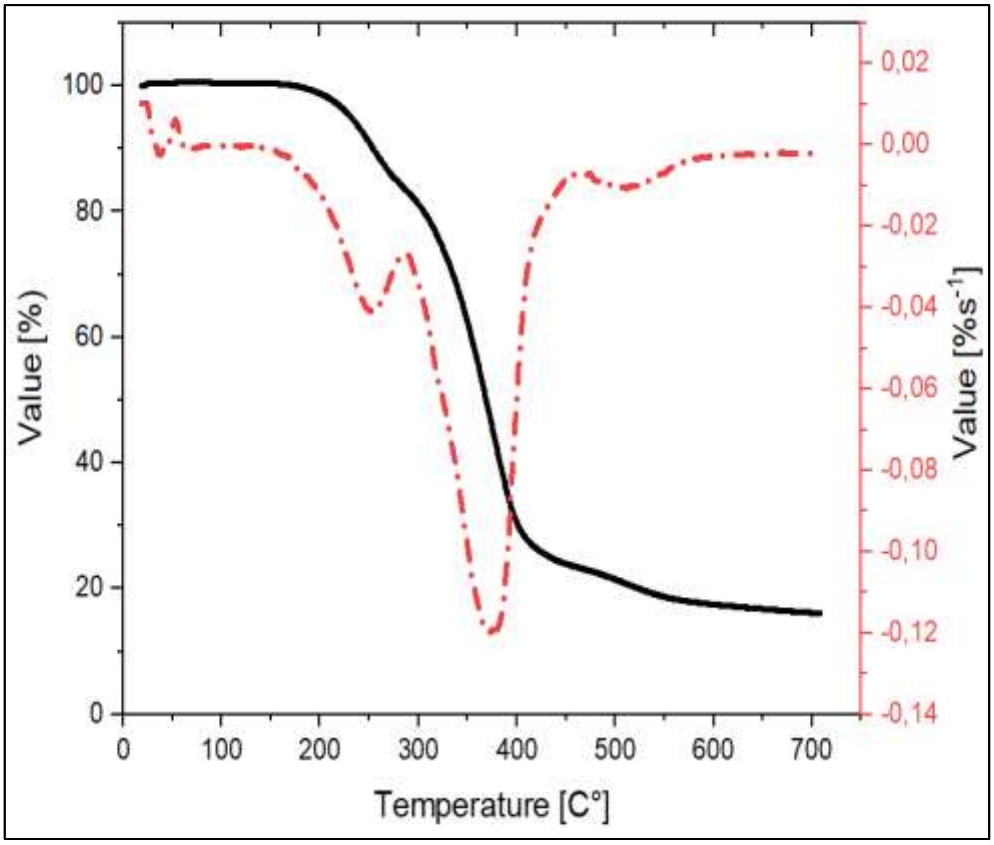


Figure 3.22: TGA-DTGA Thermogram of PU2 prepolymer.

In Figure 3.22 we observed that there are two thermal decompositions for PU2 prepolymer too. First and second decompositions are observed as if PU1 analysis. However, weight losses are quite different than each other. Addition of biopolyol to the prepolymeric system narrowed the first weight loss percentage and extended the semirigid degradation. Derivative TG analysis also confirms the change of the prepolymers thermal comparison.

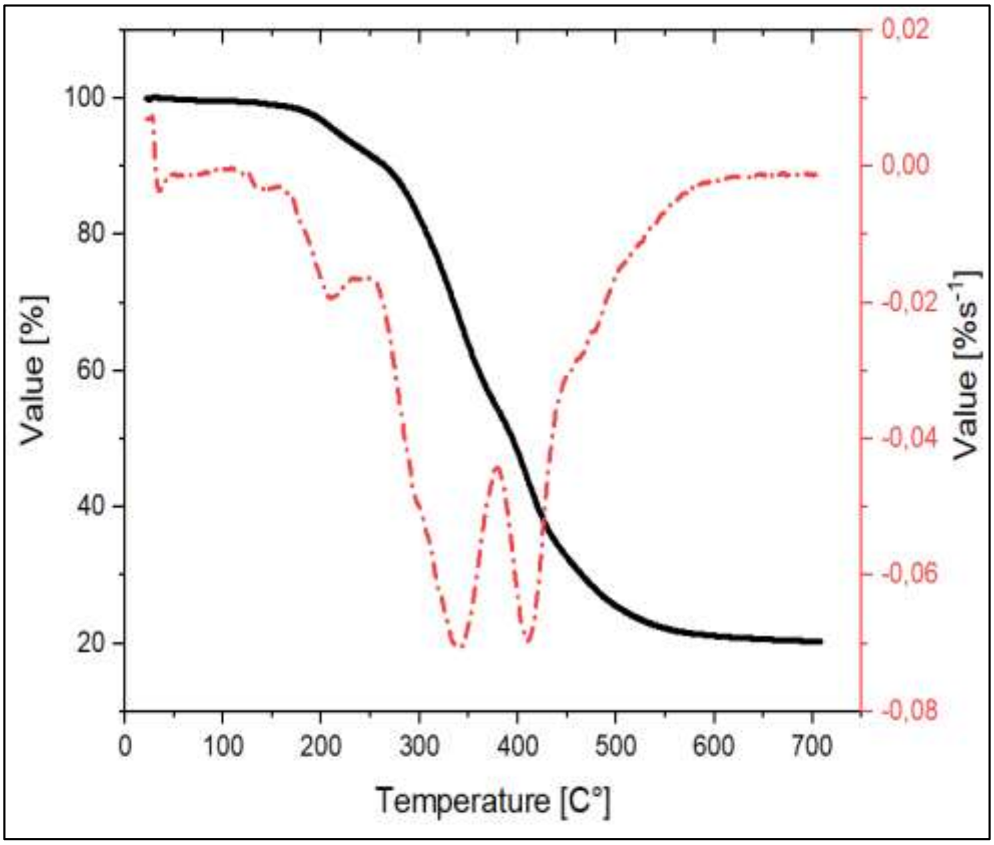


Figure 3.23: TGA-DTGA Thermogram of PU3 prepolymer.

Although PU1 and PU2 have also two thermal degradation segments, PU3 has three decomposition regions. The rigid segment of prepolymer decomposed between 200ºC and 250ºC, second and semirigid one determined between 300º-350ºC and last one was between 380ºC-450ºC. Furthermore, first decomposition, we have very narrow weight loss different than first two prepolymers. That could be the effect of biopolymer content to the prepolymer.

3.6. X-Ray Diffraction Measurements

In order to examine the crystalline property and morphological structure of the synthesis prepolymers, XRD diffraction analysis was carried out.

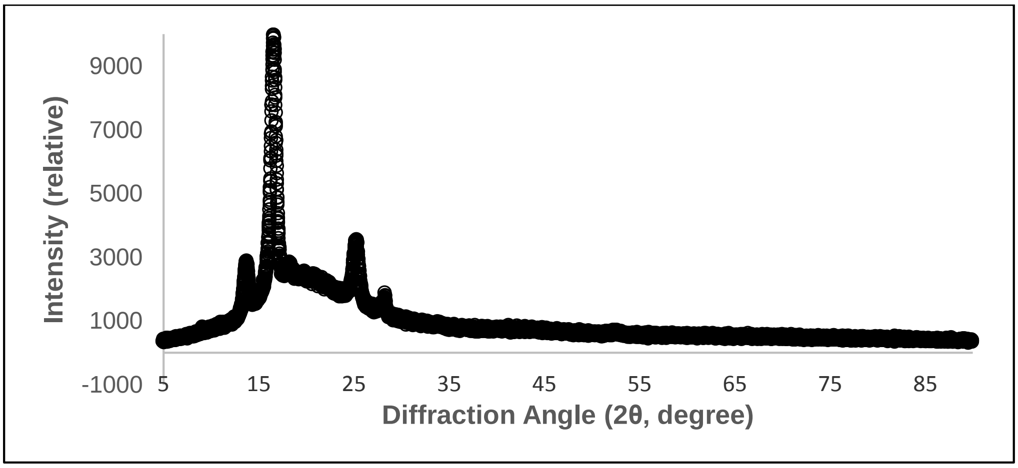


Figure 3.24: XRD curve of PU1 in the range 5° to 90°.

The XRD diffractogram of PU1 exhibits three sharp peak at 2Ө angles around 13.79°, 16.65° and 25.27°. We may see that specific degrees contain some crystallinity.

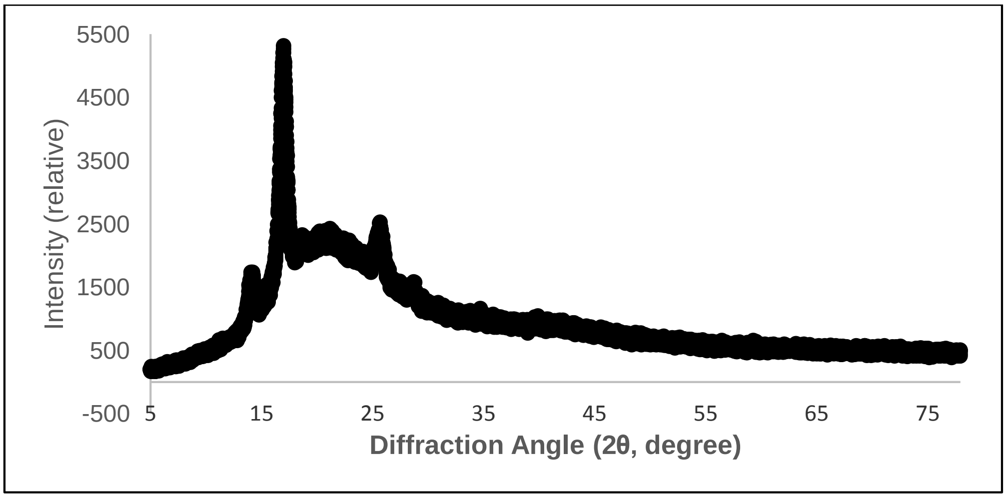


Figure 3.25: XRD curve of PU2 in the range 5° to 80°.

The XRD diffractogram of PU2 exhibits three sharp peaks at 2Ө angles around 14.16°, 17.01° and 25.73°. Around 20° we see broad distribution which a diffraction is not also. We may see that specific degrees contain some crystallinity and that property is differentiated from PU1.

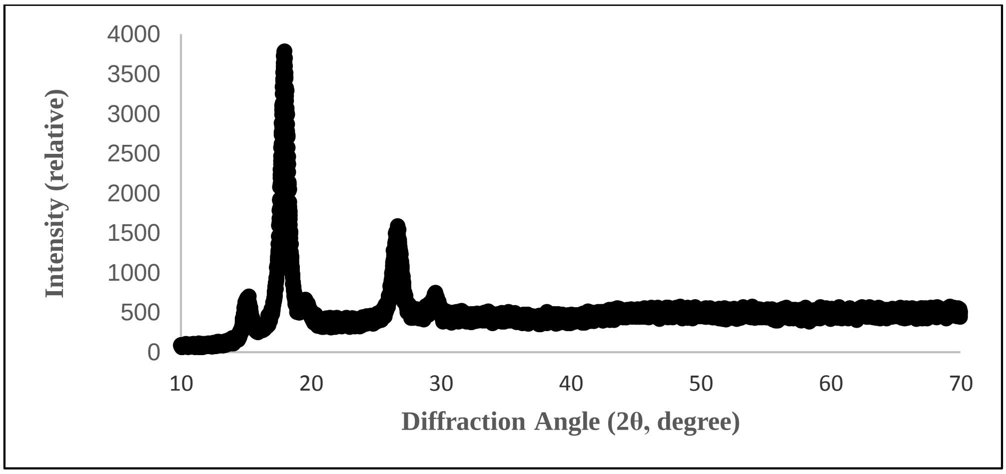


Figure 3.26: XRD curve of PU3 in the range 10° to 70°.

The XRD diffractogram of PU3 exhibits three sharp peaks at 2Ө angles around 15.09°, 17.96° and 26.63°. We may see that specific degrees contain some crystallinity and that property is differentiated from PU1.

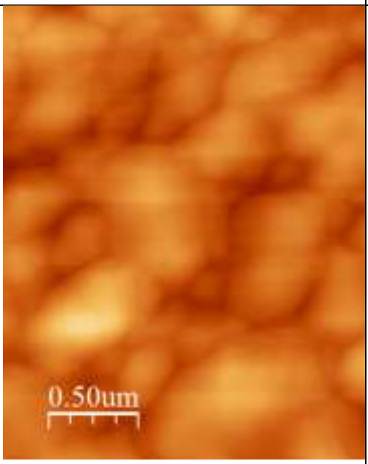
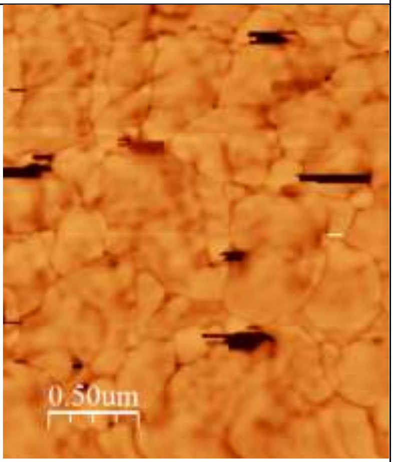
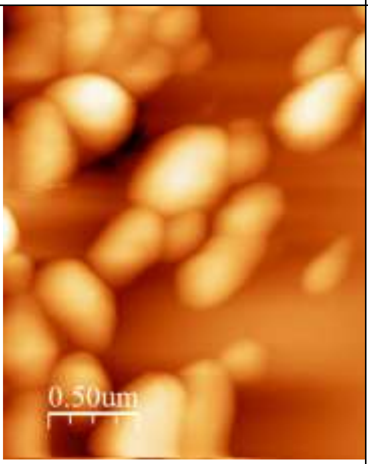
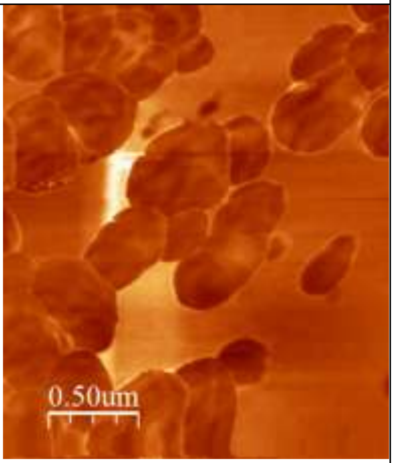
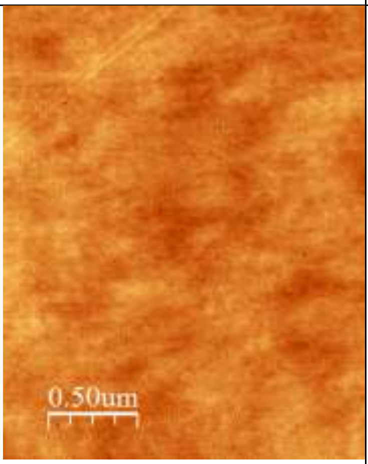
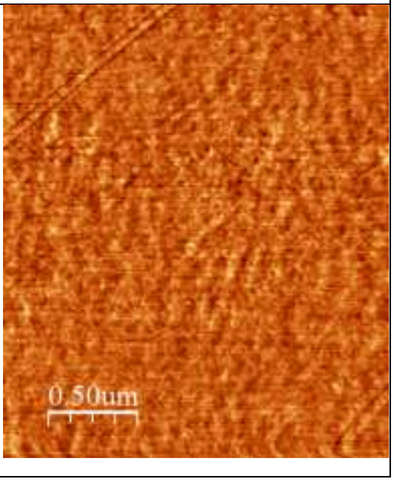
It has been analyzed in the literature the crystalline properties of PUs by Trovati et al. [85]. PU crystallinity can be explained by degree of crosslinking which is directly proportional of the hydrogen bonding in the polymer chain [86], That specific bon is correlated with the polyol and degree of hydrolysis. It has been observed in the XRD results that bio based polyols can easily crosslink than petroleum based ones. Although PU1, PU2 and PU3 showed sharp peaks on the diffractogram, they do not match in the reported results on that specific degrees in the literature.

3.7. Atomic Force Microscopy

AFM measurement were obtained with dried film of PU1, PU2 and PU3 which were formed with 50μm applicator un the glass surface and dried under N2 in 48 hours.

During the curing process, the effect of functional units, chemical linkages with interface and unreacted isocyanate group effect has been investigated by Gutman L. et al., Brown H. R. et al. Scott-s J. et al. [87-90]. According to that analysis, increasing roughness can cause the chemical bonding with applied surface which indicates more adhesion in that adhesive. In this analysis, roughness of the prepolymers has been observed in topography and phase images.

Table 3.5: AFM images of PU1, PU2, PU3.

	Topography	Phase
PU1		
PU2		
PU3		

In the AFM images of PU1 and PU2 indicates bubbles in the topology. That is provided by the phase images too and RMS of PU1 is 18 nm whereas RMS of PU2 is 18nm as well. However, in the PU3 we can easily estimate that dries film surface is quite different from the original petroleum based prepolymer which is PU1. This can be interpreted as the excess amount of bio-based polyol affected the rheological properties of the polymer film since RMS of PU3 is 0,24nm which is a quiet smooth surface. Dillingham et al. [91] have studied the isocyanate containing adhesives in different surfaces, and the effect of the roughness of the adhesion. It can be understood that high RMS data indicates more roughness on the polymeric material which can derive the better adhesion on the applied surface.

3.8. Mechanical Analysis

Mechanical analysis of the PU adhesives was made by a simple application. First wetting ability of the prepolymers were tested with the same conditions. 5ml PU1 and PU2 were applied to the commercial PU 25 cm2 foam surface and their fusion ability are check in 24 hours.

Table 3.6: Curing and wetting test of PU1 and PU2.

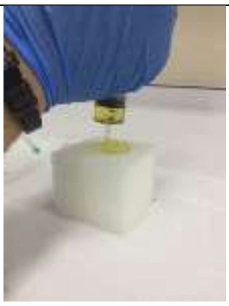
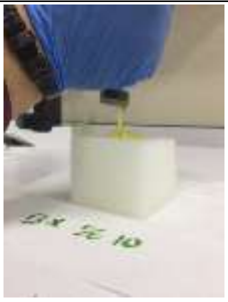
	PU1	PU2
25 cm2 foam surface		
Aplication		

Table 3.6: Continues.

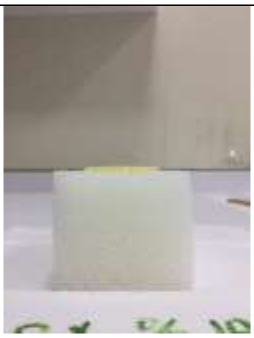
3 minutes		
55 minutes	-	
180 minutes	-	
24 hours		
Wetting in to foam		

Table 3.6: Continues.

Elongation		
Break		

PU1 has the lower viscosity compared with the PU2. As the results reported on the Table 3.6, PU1 wet the applied surface earlier than PU2. That wetting was also obtained after 24-hour curing in open air. Since %NCO contents of the propolymers are the same, PU2 showed more crosslinking ability, which makes it more difficult to wet the applied surface. PU3 analysis was not made since it had more than 300,000 cPs. (Brookfield Vicometry, S7, 25°C).

5 ml adhesives applied to the 3,0 cm x 5,2 cm commercial three identical PU foam surface. After 24 hour of curing time, their bonding abilities are tested by using DEVOTRANS GP 14975 CKS according to ASTM D412 ISO 6259 – 1 standard.

PU1 applied foam cured open air 24 hours and max force observations was made as shown in Table 3.6.

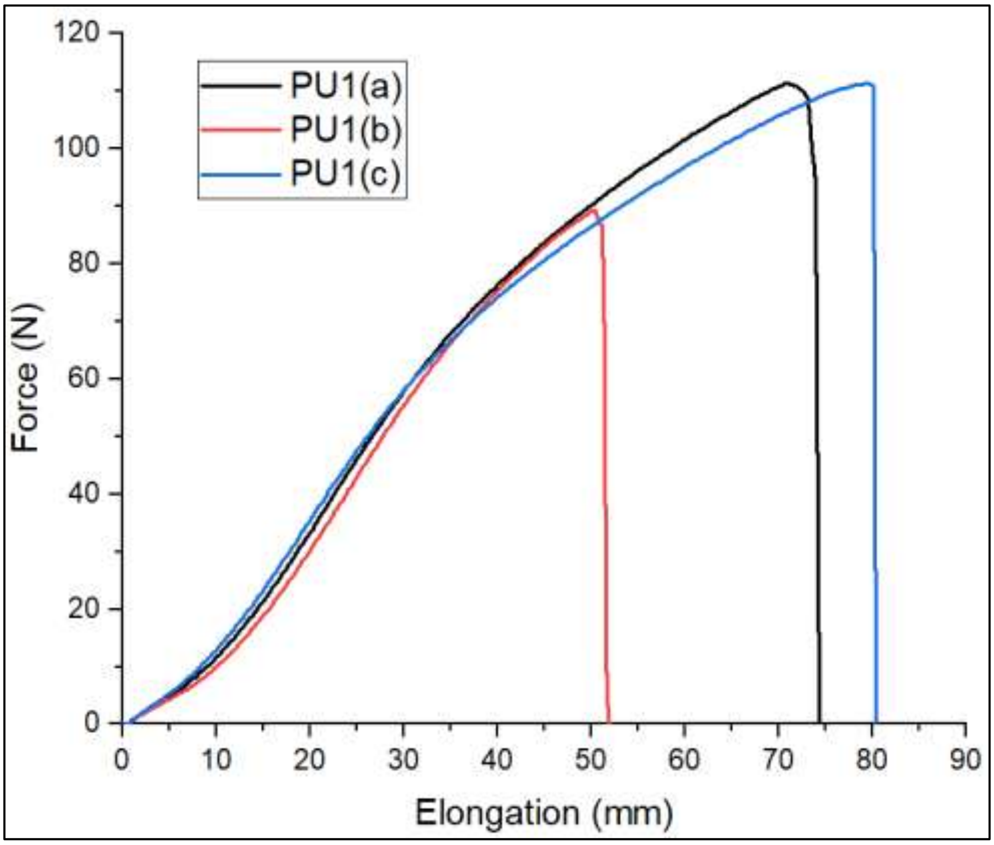


Figure 3.27: Mechanical analysis of PU1 applied PU foam.

Table 3.7: Mechanical analysis data of PU1 applied PU foam.

Sample No	Max. Force (Fmax) (N)	Elongation (Δlmax) (mm)	Fmax (εmax) %	Break (kmax) (N)/(mm)	Break elong. (Δlκ) (mm)	Break elong. (εκ) %
1	111.322	70.946	77.1152	2.1408	74.33	80.7935
2	89.313	50.387	54.7685	1.7176	63.088	68.5739
3	111.273	79.495	86.4076	2.1399	80.463	87.4598
Avr.(x)	103.97	66.94	72.76	2	72.63	78.94

PU1 tested three identical samples and according to test results, used foam pieces deform at 103.97 N max force.

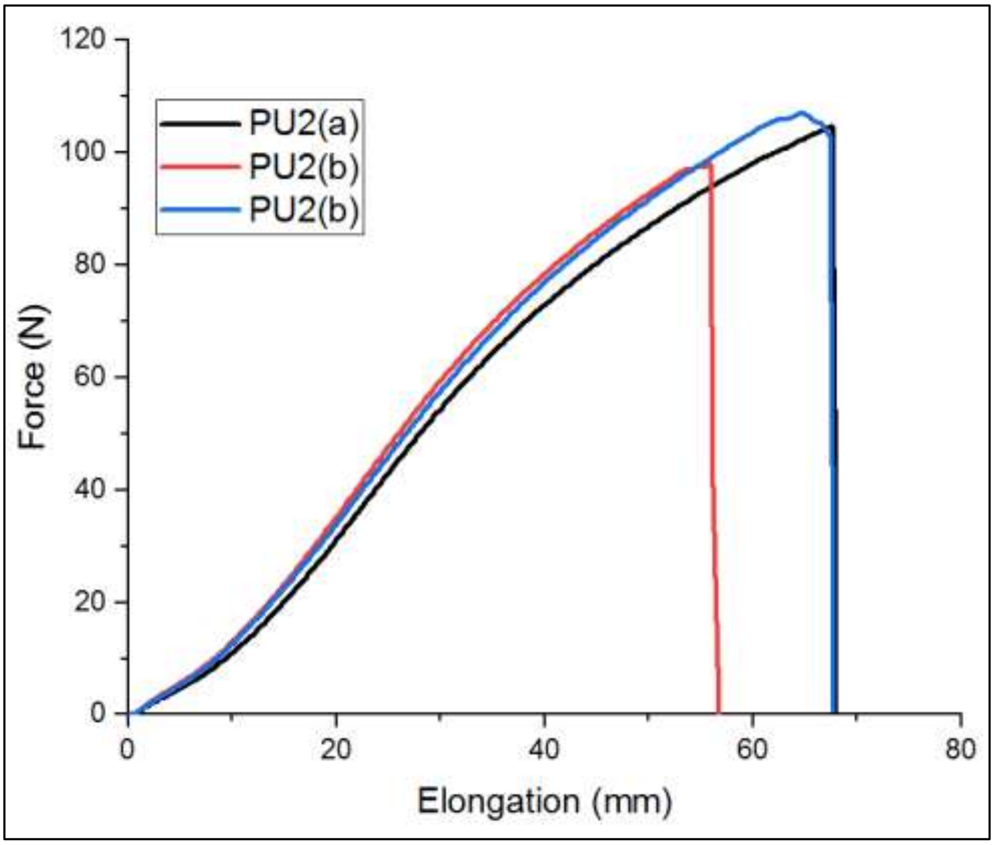


Figure 3.28: Mechanical analysis of PU2 applied PU foam.

Table 3.8: Mechanical analysis data of PU2 applied PU foam.

Sample No	Max. Force (Fmax) (N)	Elongation (Δlmax) (mm)	Fmax (εmax) %	Break (kmax) (N)/(mm)	Break elong. (Δlκ) (mm)	Break elong. (εκ) %
1	104.606	67.627	73.5076	2.0117	67.968	73.8783
2	118.685	98.84	107.4348	2.2824	109.473	118.9924
3	106.938	64.89	70.5326	2.0565	67.735	73.625
Avr.(x)	110.08	77.12	83.82	2.12	81.73	88.83

Furthermore, PU2 applied foams tested also three identical foam pieces and max force resulted in 110.08 N. As a result, as analyzed from the figures, PU1 and PU2 have almost the same bonding force.

On the other hand, each experiment revealed that synthesized binders are mechanically stronger compared with the applied PU foam surface. That was also observed by comparing the film performance of the synthesized binders and literature example.

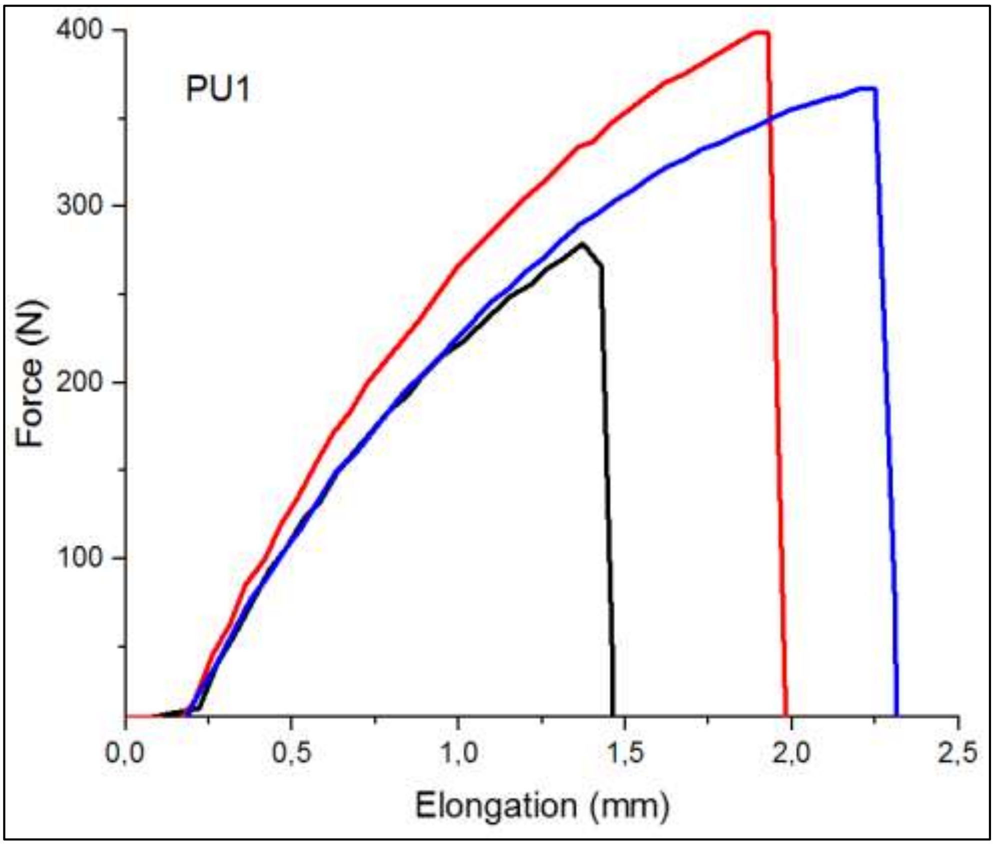


Figure 3.29: Mechanical analysis of PU1 film.

The binder itself cured 72 hours under N2 than test samples observed according to ASTM D412 ISO 6259 – 1. As Figure 3.29 showed, three identical samples of PU1 prepared and they performed 348.13 N average max force before they broke down. Comparing with the applied surface test results, binder itself is 3.5 times more powerful than Pu foam.

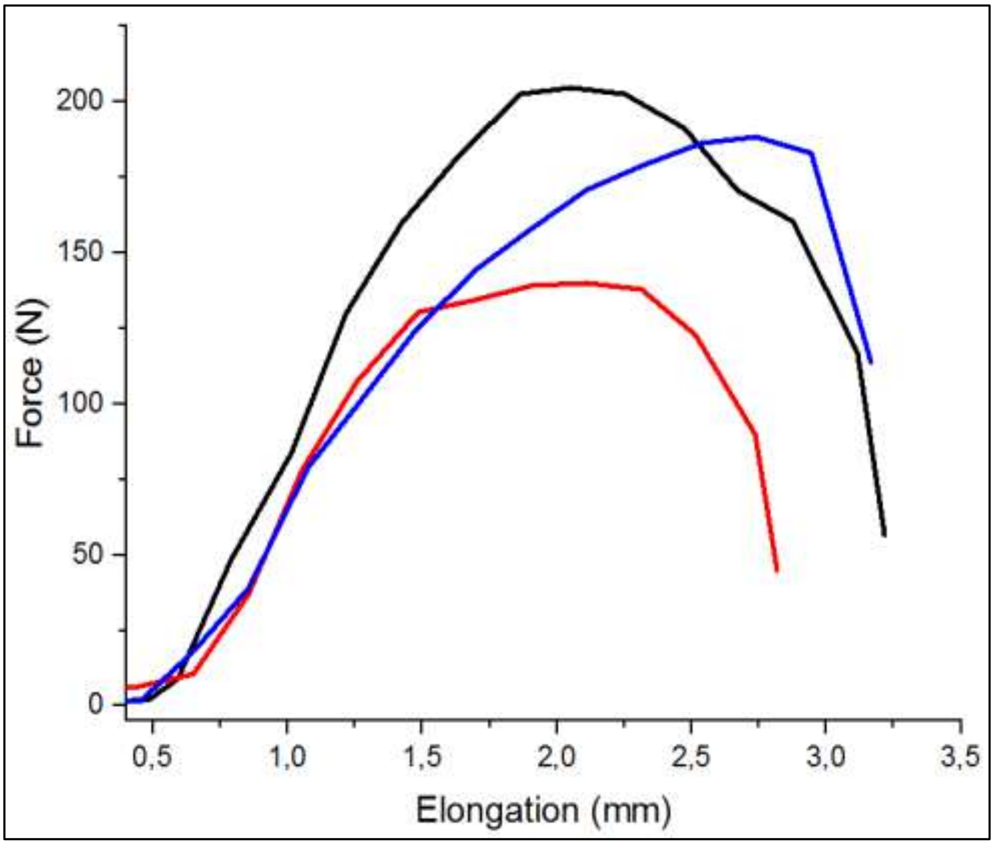


Figure 3.30: Mechanical analysis of Dow RF 1015 film.

Since PU1 was synthesized by using only petroleum based polyols, the literature example of that also tested by same procedure. The data indicates the literature example of that binder system has 177.59 N average max force before they broke down. According to that analysis, PU1 performed twice higher mechanical performance.

It was also expected that addition of biopolyol will increase the film mechanical analysis since there will be more hydrogen bonding between polymeric chains.

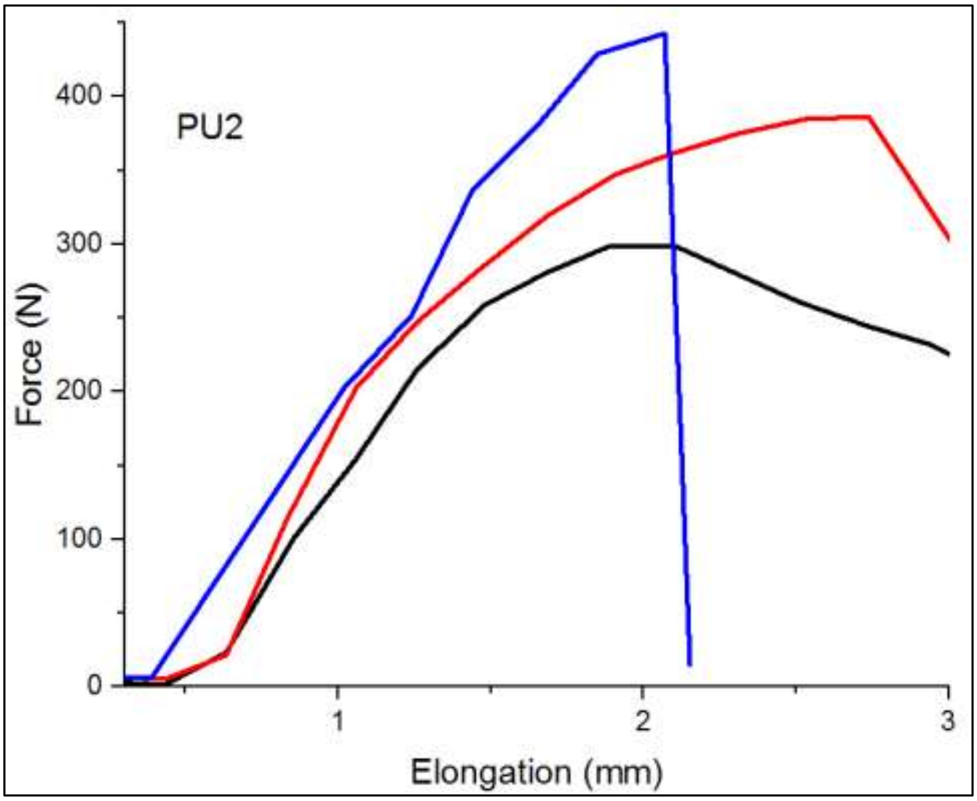


Figure 3.31: Mechanical analysis of PU1 film.

Mechanical analysis of PU2 films supported the idea of performance incensement by the addition of biopolyol. Figure 3.31 shows that PU2 film has 375.79 N average max force before they break down, and that is almost 10% more than PU1 performance.

4. CONCLUSION

Despite simplicity of polyurethane chemistry, isocyanate and polyol choice can generate diverse morphological and mechanical differences. There is certain effect of polyol selection on the mechanical performance of the PUs.

This study aimed to synthesize NCO terminated PU based flexible adhesive for PU foam recycle. To do so, petroleum based polyether polyol was used to synthesize prepolymer in one-pot reaction mechanism. One pot mechanism is an advantage in prepolymer synthesis. This enabled to optimize the reaction conditions such that the reaction time was reduced to 2 hours instead of 8 hours. Synthesized prepolymer PU1 has been characterized by Karl Fischer titration, AFM, DSC, and XRD. The results are compared with the literature and the industrial example Dow RF1015. According to FTIR analysis PU1 has almost the same functional units as the examples. In addition, the glass transition temperature of 54ºC is very similar to the industrial example (52ºC) Even though the reaction time is significantly reduced, there is no significant differences between the synthesized PU1 and the industrial version.

1H-NMR analysis was also done to determine the polymerization process, and PU2 prepolymer successfully showed the formation of the prepolymer in time in CDCl3 solvent. Polymeric peaks are clearly observed at 60 mins sample analysis, and the characteristic regions on the field showed the aliphatic carbon hydrogen bonds. Unfortunately, the addition of biopolyol caused crosslinking that showed itself as a problem at the stage of sample preparation for NMR. Although DMSO successfully dissolved PU3 prepolymer, it was not enough to observe the NMR data. It is assumed that the addition of polyol initiated a fast polymerization reaction with isocyanate, and that resulted in the cross-linked prepolymer.

It has been correlated that urethane polymer’s stability is affected by the concentration of the urethane repeating unit, cross-linking unit density, and either primary or secondary hydroxyl functionality of the urethane. To investigate that, this research was alternated by using biobased polyols in two different ratios. Increasing biobased polyols were expected to integrate crystallinity, increase Tg and change mechanical properties of the propolymers. To understand that effect, biopolyol integrated prepolymers were characterized by using Karl Fischer, AFM, DSC and XRD. Since estimated calculations of all prepolymer are closed to each other and experimental data also revealed almost the same NCO numbers for PU1 and PU2, PU3 in Karl Fischer titration analysis.

Addition of biobased polyol to the reaction was expected to change the rheological properties. PU1 and PU2 has relatively the same roughness estimated by AFM analysis. This indicates a similar adhesion behavior. It was also noticed that increasing the amount of biobased polyol results in very smoot and homogenous surface.

On the other hand, it has been observed that the addition of biobased polyol increased the viscosity of the prepolymer. PU3 had such a high viscosity compared to PU1 and PU2 such that it was very difficult to operate Brookfield viscometer.

Biobased polyols addition resulted in more crosslinks than other such that thermal activities of prepolymers were also affected by biobased polyol addition. Increasing piopolyol concentration was expected to increase the Tg values of the prepolymers. DSC analysis revealed that PU1 had the lowest Tg and PU3 had the highest one. Thermal activities of the prepolymers were also analyzed by TGA. Literature degradation points for PU based polymers as hard and soft segments were determined for all of the three prepolymers. Therefore, the addition of biopolyol to the system alternated the weight loss of the prepolymers.

Adhesion of the PU1 and PU2 was tested for mechanical properties. Film procedure was applied for both prepolymers to the PU foam. Lap share results also supported the AFM results in adhesion ability of the prepolymers. In the mechanical analysis, synthesized prepolymers showed successful increase in maximum force value compared to the literature examples. Unfortunately, PU3 could not be studied because of the viscosity problem. The prepolymers were also analyzed for their film performance. Film strength of the prepolymers was also correlated with the lap sheer results.

As future work of this study, biopolyol content of the formulation can be done. 50% content resulted in a very high viscosity. In order to achieve fully biobased system, different kinds of biopolyls can be studied by considering the functionality and OH values.

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