ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

PRODUCTION OF SPECIAL RESINS FOR USE IN POLYURETHANE

M.Sc. THESIS

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Department of Polymer Science and Technology

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JANUARY 2022

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

POLİÜRETANDA KULLANILMAK İÇİN ÖZEL REÇİNELER ÜRETİMİ

YÜKSEK LİSANS TEZİ

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OCAK 2022

Tibet HÜTEN, a M.Sc. student of İTU Graduate School student ID 515191015, successfully defended the thesis/dissertation entitled "PRODUCTION OF SPECIAL RESINS FOR USE IN POLYURETHANE", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my dear family,

FOREWORD

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ABBREVIATIONS

NCO	: Isocyanate group
MDI	: Diphenylmethane diisocyanate
OP50	: 50% - 50 % mixture of 4,4’- and 2,4’- MDI
TMP	: Trimetylol propane
TPG	: Tripropylene glycol
HDI	: 1,6-hexane diisocyanate
IPDI	: Isophorone diisocyanate
HMDI	: Dicyclohexane diisocyanate
TMXDI	: Meta-tetramethylxylene diisocyanate
TDI	: Toluene diisocyanate
TDI-80/20	: Blends of 2,4- and 2,6- isomers of TDI in 80/20 ratio
TDI-65/35	: Blends of 2,4- and 2,6- isomers of TDI in 65/35 ratio
TDI-100	: Pure TDI
TDA	: Toluene diamine
MDA	: Diphenylmethane dianiline
PTMEG	: Polytetramethylene glycol
PPG	: Polypropylene glycol
PCL	: Polycaprolactone
DBA	: Dibutylamine
CASE	: Coatings, adhesives, sealents and elastomers
DSC	: Differential scanning calorimetry
FTIR	: Fourier transform infrared
OH	: Hydroxyl group amount
PU	: Polyurethane

SYMBOLS

Da	: Dalton
CPa	: Santipoise
T_m	: Melting Temperature
T_c	: Crystallization Temperature
T_g	: Glass Transition Temperature
MPa	: Megapascal
N	: Newton

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PRODUCTION OF SPECIAL RESINS FOR USE IN POLYURETHANE

SUMMARY

Polyurethane prepolymers, generally reaction products of diols and diisocyanates, are considered an important part of polyurethane chemistry due to their direct contribution to final properties. Isocyanate and polyol react and form a strong, reinforcing urethane bond. Prepolymers are generally prepared with a 2/1 ratio of isocyanates to polyols to ensure an NCO (isocyanate) terminated structure. NCO terminated structure later reacts with chain extenders and crosslinkers to produce polyurethane structure with larger molecular weight.

In prepolymer chemistry, isocyanate is considered a reactive component of the reaction medium. Apart from their role as a reactive component, they also arrange the mechanical properties of polyurethane. Therefore, a proper type of isocyanate should be considered for its application.

In microcellular elastomeric shoe sole polyurethane chemistry, diphenylmethane diisocyanate (MDI) has high consumption. Crude 4,4'- MDI has been chosen as the core of formulation for its highly reactive para-positioned NCO groups to form more reinforcing urethane bonds. However, a phenomenon called dimerization creates a dilemma on its high consumption in prepolymers. The reactivity of isocyanate is proportional to its rate of dimerization. Since crude MDI is a highly reactive material it has more tendency for dimerization.

Dimerization is a phenomenon occupying a reaction between two isocyanates. The formation of dimers in the reaction medium reduces the free isocyanate components to react with polyols, creating a different reaction profile. Remaining free isocyanates in the reaction medium will react with a polyol to form a polyurethane structure with less frequent reinforcing urethane bonds. Therefore, fewer urethane bonds result in weaker mechanical properties. Changes in mechanical properties and reaction profiles are known symptoms of dimerization.

Apart from these symptoms, dimers are known for their high melting and freezing points. According to this phenomenon, optimal operation and storage temperature of prepolymer will be in a more narrow spectrum. Prepolymer with a higher melting point will take a longer time to melt. Therefore, a more complicated pathway of processing should be considered.

Storage conditions of prepolymers are also affected by dimerization. Dimerization rate is faster in 5 to 40 °C and above 50 °C . Therefore, prepolymers should be stored under 0 °C to evade dimerization. When the freezing point of a prepolymer is high and closer to the dimerization area, its stability during storage will dropdown. Freezing temperature is a key element to observing the storage stability of prepolymers.

Isomers of crude MDI (2,4'- MDI and 2,2'- MDI) can be mixed with crude MDI to lower its melting and freezing temperatures for better operation and storage temperatures. Today, two forms of isocyanates named OP50 (50% - 50% mixture of 2,4'- and 4,4'- MDI) and carbodiimide modified MDI used for storage stabilization

and improvement on melting of the prepolymer. Isomers of crude MDI have orto positioned NCO groups with low reactivity due to steric hindrance and show less tendency to dimerization.

In literature, there is no concise study on the effect of OP50 and carbodiimide modified MDI in both melting and freezing points of prepolymers. Our study aims to investigate the effects of change in isocyanate and polyol components on freezing and melting points of prepolymers while preventing a dramatic change in mechanical properties.

Prepolymers with carbodiimide modified MDI in 7-12 % show the lowest freezing temperature, the starting point of freezing, melting temperature, the starting point of melting. Its projections on mechanical properties in polyurethane (PU2) show improvement on elongation at break, tensile strength. Modulus shows a decrease due to loss of crystallinity. Besides from the best formulation, the mechanical properties of polyurethanes made from the other two best prepolymers are also investigated. PU3 which was made from PREP5 did not show a significant loss in mechanical properties same as the PU2.

However, PU4 where PREP6 was used, show losses in compression set and tear resistance due to a lower amount of hydrogen and urethane bonding. It has the highest elongation at break value for its low level of crystalline hydrogen bonds.

From shelf life observations in jars at 21 °C, found formula withstand freezing for 38 days while reference formula withstands for 19 days. Freezing showed a faster propagation in PREP1 than PREP4. At the end of 150 days, PREP1 completely frozen while PREP4 stayed in liquid form. For this reason, the formulation was found successful to be used in standard polyurethane applications and increasing the shelf life of prepolymers.

POLİÜRETANDA KULLANILMAK İÇİN ÖZEL REÇİNELER ÜRETİMİ

ÖZET

Poliüretan prepolimerleri, genellikle diollerin ve diizosiyanatların reaksiyonu sonucu elde edilen ve son özellik setlerine direk etki etmelerinden dolayı poliüretan kimyasında önemli bir yere sahiptirler. İzosiyanat ve poliol reaksiyona girerek güçlü, destekleyici üretan bağları oluştururlar. Prepolimerler genellikle NCO (izosiyanat grubu) uç grubunu sağlamak için 2/1 izosiyanat/poliol oranında hazırlanırlar. NCO uçlu yapı sonrasında zincir uzatıcılar ve çağraz bağlayıcılarla reaksiyona girerek daha yüksek molekül ağırlığına sahip poliüretanı oluştururlar.

Prepolimer kimyasında, izosiyanatlar reaksiyon ortamının reaktif bileşenleri olarak kabul edilirler. Reaktif bileşen olmalarının yanında, poliüretanın mekanik özelliklerini de etkilemektedirler. Bu nedenle, uygulama alanına göre izosiyanat seçimi yapılmalıdır.

Mikrohücresel elastomerik ayakkabı tabanı poliüretan kimyasında, difenilmetan diizosiyanat (MDI) en çok tüketilen izosiyanat türüdür. Saf 4,4’- MDI yüksek reaktif yapısı ve para pozisyonunda bulundurduğu NCO grupları nedeniyle daha çok destekleyici üretan bağları yaparak yapının dayanımını arttırır. Ancak, dimerizasyon denen fenomen, prepolimerlerde yüksek hacimde kullanımı ile ilgili bir ikilem yaratmaktadır. İzosiyantların reaktifliği dimerleşme hızlarıyla doğru orantılı olarak kabul edilir. Saf MDI yüksek derecede reaktif olduğundan dimerizasyona daha da yatkın halde olmaktadır.

Dimerizasyon iki izosiyanat grubu arasındaki reaksiyon sonucu gerçekleşen bir fenomendir. Reaksiyon ortamında dimer oluşumu poliolle reaksiyona giren serbest izosiyanat bileşenlerinin sayısını azaltarak farklı bir reaksiyon profili oluşturacaktır. Bu da ortamda az miktarda kalan serbest izosiyanatların reaksiyon ortamında polyolle reaksiyona girmesiyle daha az sık üretan bağ oluşumu anlamına gelmektedir. Bu sebeple, üretan bağlarının az oluşu daha kötü mekanik özelliklere sebep olacaktır. Mekanik özelliklerde kötüleme ve reaksiyon profili dimerizasyonun bilinen semptomlarıdır.

Bu semptomlar dışında, dimerler yüksek erime ve donma noktalarıyla bilinmektedirler. Bu fenomene göre, prepolimerin operasyon ve depolama sıcaklıkları daha dar bir aralıkta olmaktadır. Yüksek erime noktalı prepolimerin erimesi için daha uzun zaman gerekmekteedir. Bu nedenle, işlenmesinin daha karmaşık bir yolla gerçekleceşeceği aşikardır.

Bunların dışında, prepolimerlerin depolama koşulları dimerizasyondan etkilenmektedir. Dimerizasyon hızı 5-40 °C aralığında ve 50 °C yukarısında yüksektir. Bu sebeple, prepolimerler 0 °C altında dimerizasyondan kaçınmak için depolanmalıdırlar. Donma noktası burada prepolimerlerin depolama dayanımını gözlemlemek adına anahtar bir kavramdır.

Saf MDI'ın izomerleri (2,4'- MDI ve 2,2'- MDI) saf MDI ile karıştırlarak daha düşük erime ve donma sıcaklıklarına ve dolayısıyla daha iyi operasyon ve depolama sıcaklıklarına ulaşılabilmektedir. Bu günlerde OP50 (%50 - %50 2,4'- ve 4,4'- MDI karışımı) ve karbodiimide modifiyeli MDI depolama dayanımı ve erime sıcaklığını iyileştirmek adına kullanılabilmektedir. Saf MDI'ın izomerleri orto pozisyonlu NCO gruplarına, sterik engellemeden dolayı düşük reaktiviteye ve bundan dolayı da düşük dimerleşme eğilimine sahiplerdir.

Literatürde OP50 ve karbodiimid modifiyeli MDI'ın prepolimerlerde erime ve donma noktası üzerindeki etkisi üzerinde yoğunlaşan bir çalışma bulunmamaktadır. Çalışmamız, izosiyanat ve poliol üzerinde yapılan değişikliklerle prepolimerlerde erime ve donma noktasındaki değişimleri gözlemlemektir. Bu sırada mekanik özelliklerde fazla bir düşüş olmamasına dikkat edilmelidir.

7-12 % oranında karbodiimid modifiye MDI içeren prepolimer en düşük donma sıcaklığını, donma başlangıç sıcaklığını,erime sıcaklığın, erime başlangıç sıcaklığını göstermiştir. Poliüretanın mekanik özelliklerindeki yansıması (PU2) ise kopmada uzama yüzdesi, kopmadaki basınç, kalıcı deformasyon yüzdesindeki iyileşmelerde gözükmüştür. Modulus kristallik düştüğü için azalım göstermiştir.

Bunun dışında, en iyi prepolimer formülasyonu hariç diğer en iyi iki prepolimerden de poliüretan sentezlenmiş ve mekanik özellikleri incelenmiştir. PU3 PREP5 numaralı prepolimerden yapılmış olup PU2 gibi mekanik özeliklerde herhangi önemli bir kayıp göstermemiştir. Ancak PREP6'dan hazırlanan PU4'te yırtılma ve basma seti değerlerinde daha düşük miktarlarda oluşan hidrojen bağları ve üretan bağlarından ötürü önemli düşüşler gözlenmiştir. En yüksek kopma anında yırtılma değerine daha düşük miktarda kristal hidrojen bağına sahip olması sebebiyle sahiptir.

Kavanozlarda raf ömrü gözlemlerinden ise, bulunan formülün 38 gün donmadan kaldığı bunun haricinde referans olarak alınan formülün 19 gün donmadan kaldığı tespit edilmiştir. Donma PREP1'de PREP4'e göre daha hızlı bir ilerleme seyretmiştir. 150 gün sonra, PREP1'in tamamen donduğu ve PREP4'ün ise halen sıvı halde kaldığı görülmüştür. Buna göre, PREP4 formülasyonu standart poliüretan uygulamalarında başarılı görülmüş ve prepolimerlerin raf ömrünü uzatmada başarılı olmuştur.

1. INTRODUCTION

Diphenylmethane diisocyanate (MDI) is the most used isocyanate component in many microcellular polyurethane applications. Reactivity of MDI shows a difference in three forms of its isomers according to the movement capability of benzene rings around methylene bridge. In 4,4'- MDI, benzene rings cannot move easily on methylene bridge and form a one plane formation with isocyanate groups on both ends. Due to one plane formation of isocyanate groups, they have the most distance between them and in the para position. With the distance, the possibility of weaker reactions like Van der Waals become very unlikely. Due to the lack of weaker interactions, isocyanate end groups tend to make reactions with polyols which can create reinforcing urethane bonds or with other isocyanate groups to form a dimer. Dimerization is a cycloaddition reaction between two isocyanates. In dimerization, free isocyanate groups in prepolymer medium react with each other to form dimer. In polyurethane chemistry, prepolymer should have enough isocyanate groups to form an estimated polyurethane structure for any application. However with dimerization since some of the free isocyanate groups are used in cycloaddition reaction, isocyanate groups occupied with urethane bond formation will be less than expected. Less urethane bond formation will show a different reaction profile as creating a different polyurethane structure than estimated. Deterioration in mechanical properties due to less frequent urethane bonds and change in reaction profile are the most known symptoms of dimerization. Dimerization decreases the storage stability of the prepolymer. Dimers have high melting and crystallization temperatures which create difficulty during storage and processing. 4,4'- MDI kept in high amounts in prepolymer formulations due to its contribution to mechanical properties. However, dimerization increases the melting and crystallization temperatures of the prepolymer. The freezing or crystallization of prepolymer starts at the intersection point of crystallization temperature of prepolymer and storage temperature. However with the dimerization, since both of the temperatures will increase, the intersection occurs in higher temperatures which is a possible temperature zone for a high dimerization rate. If intersection occurs in a high dimerization rate temperature zone, prepolymer freezes and since solid particles are closely packed they can easily interact with each other. Therefore, they can dimerize very fast which will result in a prepolymer with a higher temperature of freezing and melting. Prepolymer will be become harder to process since it melts in high temperatures and also it will be frozen most of the time and will dimerize better since the molecules are more packed in the most period of time resulting in a highly tolerant material during storage.

1.1 Purpose of Thesis

The aim of this work is to improve the storage stability of an industrial prepolymer by shifting the intersection temperature between the crystallization temperature of the prepolymer with storage conditions to lower levels. If intersection occurs in lower temperature zones, the freezing will happen in the low rate of dimerization zone and can further improve the storage stability. PREP1 is the industrial prepolymer formulation which needs improvement.

1.2 Literature Review

1.2.1 Literature survey of stable and liquid prepolymer formulations

In literature, studies are mostly related to the adhesive industry. Formulations in the adhesive industry generally consist of polyether polyols which are polymerization products of ethylene oxide, propylene oxide, and/or butylene oxide. Especially in the polyol part, polyether polyol was used to obtain a liquid prepolymer. However, there haven’t been a study on the effect of polyester polyol on the crystallization and melting temperature of prepolymers. As isocyanates, 50% - 50% mixture of 4,4’- and 2,4’-MDI, known as OP50, and carbodiimide modified MDI is used in industry to control melting and crystallization temperature of prepolymers. However, most of the studies were made in higher concentrations of OP50 and carbodiimide-modified MDIs. Therefore, due to the lack of reactivity in isocyanate, shorter chains are formed and mechanical properties show depression. Crystallinity also can be lowered by adding polymeric MDI however obtained mechanical properties by polymeric MDI were found to be lesser than carbodiimide modified or OP50 MDI. For this reason, these two forms of MDI are preferred over polymeric MDI [1].

Boros et al [2] investigated the relative stability of three different isomer forms at room temperature with thermodynamical geometric models.

The relative stability of isocyanates are calculated by thermodynamic geometrical models. According to G3MP2B3 [3] and M06-2X [4] models, o,o-MDI has the lowest enthalpy, gibbs free energy, total electric energy and entropy than other isomers. Enthalpy value found zero in both models which indicate there have been no phase transitions in o,o-MDI. Gibbs free energy and total electric energy found zero in both models which indicates o,o- MDI is the most stable isomer. The most unstable isomer is found as p,p- MDI isomer. As for their dimers, according to the B3LYP/6- 31G model [5], p,p-MDI is the most stable dimer than other isomers. The most unstable dimer was found as o,o-MDI dimer.

There are patents about storage stable and liquid prepolymer formulations however no academic study has been found on crystallization and melting temperatures of prepolymers.

In 1978, in U.S. Pat. Nos. 4,115,429 and 4,118,411 [6], a prepolymer was achieved which is both liquid and stable at -5 °C for at least 48 hours. The experiment consisted of five steps which simulate the effects of difference in glycols, 4,4'/2,4' isomer distributions, NCO/OH ratio, reaction temperature. In the first step, different types of glycols reacted with isocyanates with 35 % by weight of the 4,4'-isomer and 65 % by weight of the 2,4'-isomer distribution. Chemical structures of applied glycols are shown in Figure 1.1.

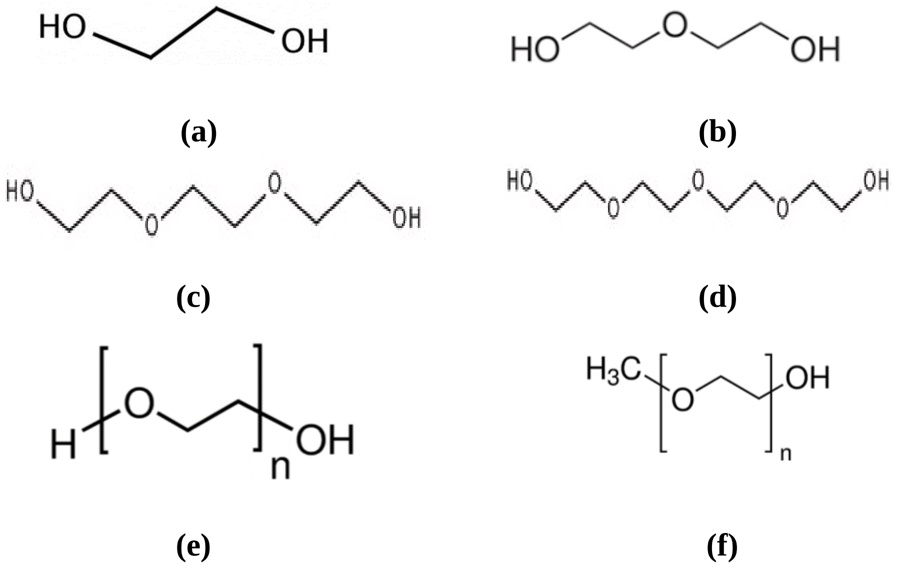


Figure 1. 1 Structures of (a) ethylene glycol (b) diethylene glycol (c) triethylene glycol (d) tetraethylene glycol (e) polyethylene glycol (f) polyoxyethylene glycol.

Their conditions at -5 °C (for 48 hours) shown in Table 1.1 below.

Table 1. 1 Glycol Type - conditions of prepolymers at -5°C for 48 hours [6].

Glycol Type	Condition of prepolymer at -5°C for 48 hours
Ethylene Glycol	Solid
Diethylene Glycol	Gel
Triethylene Glycol	Liquid
Tetraethylene Glycol	Liquid
Polyethylene Glycol	Liquid

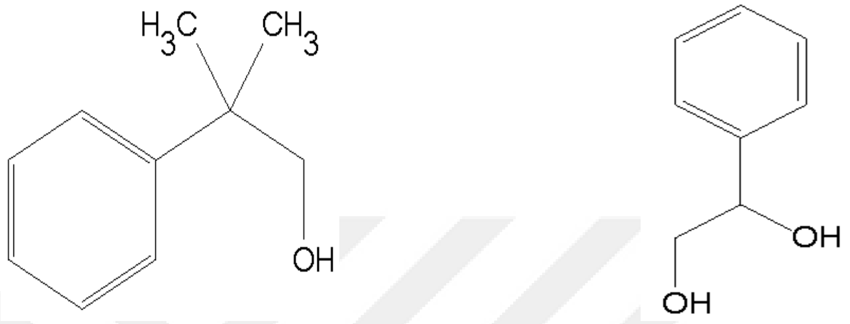
Prepolymers made with triethylene glycol, tetraethylene glycol and polyethylene glycol found liquid in -5 °C for 48 hours. In the second step, the prepolymer is composed of diisocyanate components with different 4,4’/2,4’ isomer distributions. Their conditions at -5 °C (for 48 hours) are shown in Table 1.2.

Table 1. 2 Isomer distribution- conditions of prepolymers at -5°C for 48 hours [6].

Isomer Distribution (4,4’/2,4’ MDI ratio)	Condition of prepolymer at -5°C for 48 hours
100/0	Solid
80/20	Solid
60/40	Liquid
35/65	Liquid

Prepolymers with diisocyanate components which have a 4,4’/2,4’ isomer ratio of 60/40, 57/43, and 35/65 found liquid at -5 °C for 48 hours. In third step, the effect of the difference in NCO/OH ratio (10, 8, 4.9, 3.0) and NCO content (24, 22.2, 17.2, 11.7) was observed on the storage stability of prepolymer in 48 hours at -5 °C . In all different NCO/OH ratios liquid prepolymers were obtained. In the final step, all samples stored in a deep-freezer for 100 hours at -22 °C and checked for stability against freezing and/or crystallization. Prepolymers made with diethylene glycol were found in a gel-like form at the end of 100 hours. Triethylene glycol, tetraethylene glycol, polyethylene glycol, all prepolymers with different isomer distributions except 100/0 and 80/20, prepolymers made with different reaction temperatures stayed liquid at the end of 100 hours. Prepolymers made with polyethylene glycol were found completely solid. However, at ambient temperature, they can easily melt without heating, shaking, or stirring. Prepolymers made in 100/0 and 80/20 isomer distributions found white, crystalline, completely solid and do not melt at ambient temperature.

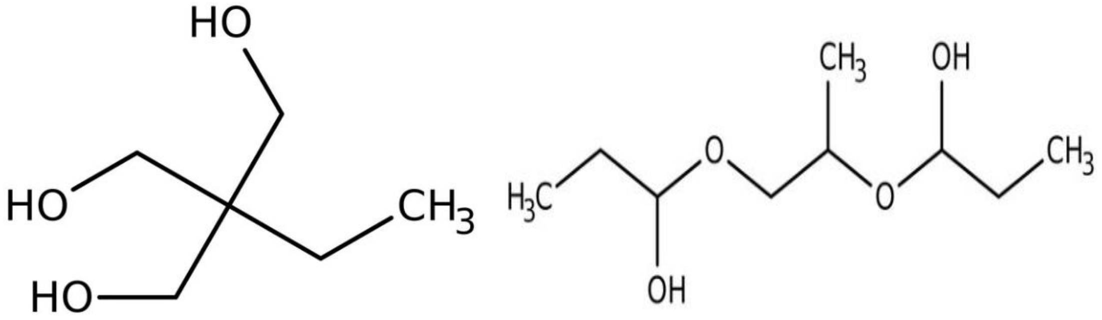
In 1984, in U.S. Pat. No. 4,490,300 [7] created a liquid stable prepolymer formulation. Aliphatic diols with aromatic pendant groups (2-methyl-2-phenyl-1,3- propanediol, phenyl-1,2-ethanediol) reacted with different 4,4’/2,4’ isomer ratio distributed isocyanates (98/2, 35/64 and 100/0) resulted in a stable, liquid prepolymer. Structures of added aliphatic diols with pendant groups are shown in Figure 1.2.



(a) **(b)**

Figure 1. 2 Structures of 2-methyl-2-phenyl-1,3- propanediol (a), phenyl-1,2-ethanediol (b).

In 1984 in U.S. Patent 4,490,302 [8] a liquid diphenylmethane diisocyanate composition with functionality higher than 2.0 and having a free NCO content of 20-30 by weight obtained. Trimethylolpropane (TMP) was dissolved, over a one-to-one-and-one-half-hour period, in tripropylene glycol (TPG) and a monohydroxy alcohol at 70 °C . And the mixture was later added to a flask filled with 4,4’- MDI. Structures of TMP and TPG are shown in Figure 1.3.



(a) **(b)**

Figure 1. 3 Structures of trimethylol propane (a), tripropylene glycol (b).

Different isocyanate components were obtained in different MDI: a mixture of TMP and TPG: mono alcohol ratios. Appearances, conditions of obtained isocyanates observed and summarized in Table 1.3 below.

Table 1. 3 MDI: Apperance and conditions of isocyanates with different MDI: Mixture of TMP and TPG:Mono alcohol mixture ratios [8].

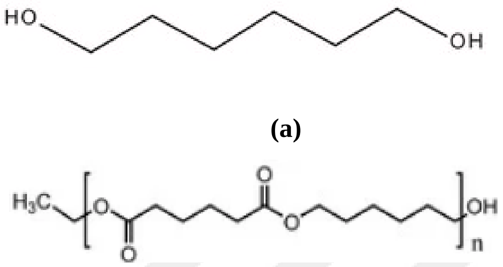
MDI: Mixture of TMP and TPG:Mono alcohol mixture ratio in isocyanate component	Appearance	Condition
5:6:1	Clear	Liquid
6:4:1	Clear	Liquid
7:1:1	Clear	Liquid
7:4:1	Clear	Liquid
7:7:1	Clear	Liquid
7:8:1	Clear	Liquid
8:3:1	Hazy	Liquid
9:5:1	Hazy	Liquid

Isocyanates show haziness in higher amounts of 4,4'-MDI due to a high freezing point of 4,4'-MDI. Besides their appearance, their freezing points were observed. The freezing point of all clear diphenylmethane diisocyanates was found at 14 °C .

In 2004 in EP 1 122 270 B1 [9] three different isocyanate compositions, isocyanate blend 1 an isocyanate blend consists of 98 % 4,4'- MDI and less than 2 % 2,4'- MDI by weight, isocyanate blend 2, prepolymer obtained by reaction of isocyanate blend 1 with tripropylene glycol, isocyanate blend 3, prepolymer obtained by reaction of isocyanate blend 2 with 2,methyl-1-propanol, zinc acetylacetonate and benzoyl chloride and three different polyol compositions with polyol 1, a polyether glycol obtained with propylene oxide as an initiator, polyol 2, a polyether glycol obtained with propylene oxide/ethylene oxide (80:20) as an initiator, polyol 3. 1,4-butanediol used to observe freezing points of isocyanate blends and both of their effects on prepolymer's mechanical properties (All three of polyols mixed and used in the study). As isocyanate blend 3 increased in formulation, obtained prepolymers were observed to have the lowest freezing point with 5 °C when compared to prepolymers with isocyanate blend 2 which has 15 °C. Mechanical properties of prepolymers obtained with the mixture of isocyanate blend 2 and 3 were found similar to prepolymers obtained by just isocyanate blend 2.

1.2.2 Literature survey of liquid polyester polyol formulations

Improvements on freezing and melting points of prepolymer by polyester polyol component have not been found on literature survey. However, combinations on obtaining less crystalline and liquid polyester polyols have been found in the literature.In general, crystalline structure origins from raw materials with linear chains in a regular and simple form. The linear chain and symmetry of raw materials directly affect the crystallinity of polyester polyols. For example, hexanediol adipate which is a linear polyester polyol contributes to the crystal backbone in polyurethane. Both hexanediol and adipic acid are linear symmetrical raw materials. Polyesters of this type are solids at room temperature [10]. Their structures are shown in Figure 1.4.

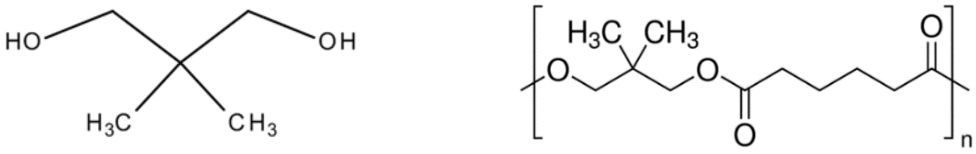


(a)

(b)

Figure 1. 4 Structures of 1,6 hexanediol (a), poly (hexanediol adipate) (b).

The crystallinity of polyester polyol decreases with the addition of raw materials with side groups. An example can be shown as neopentyl glycol. Neopentyl glycol adipate is a liquid [10]. Their structures shown in Figure 1.5.



(a) **(b)**

Figure 1. 5 Structures of neopentyl glycol (a), poly (neopentyl glycol adipate) (b).

Another way of decreasing crystallinity was found to blend crystalline and amorphous polyols to obtain an intermediate level of crystallinity. The same can be applied to glycols with different levels of crystallinity [10]. In literature, the level of side groups, branching and special configurations of aromatic groups was found useful to decrease crystallinity. Branched polyesters obtained from adipic acid, diethylene glycol with trimethyol propane or adipic acid, diethylene glycol with glycerol are known to be liquid at room temperature. Polyesters consisting just linear monomers without side groups are adipic acid with 1,4-butanediol, adipic acid with 1,6-hexanediol behave semi-crystalline while polyesters with methyl or ethyl side groups as adipic acid with a mixture of 2-methyl-1,5-pentanediol, 2-ethylbutanediol and 1,6-hexanediol, 2-methyl glutaric acid with 1,4-butanediol, 2-methyl glutaric acid with 1,6-hexanediol, 2-methyl glutaric acid with a mixture of 2-methyl-1,5-pentanediol, 2-ethylbutanediol and 1,6-hexanediol behaving perfectly amorphous.[11] In orto-phthalic based polyester diols, orto positioned aromatic rings in the structure known to disrupt crystallinity [12]. The general structure is shown in Figure 1.6.

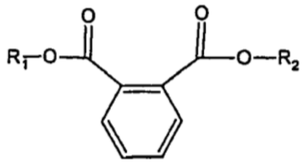


Figure 1. 6 Structure of an ortho-pthalate based polyol [12].

In literature, polyester polyols prepared with adipic acid + ethylene glycol + 1,4-butanediol and adipic acid+hexamethylene glycol + neopentyl glycol have lower solidification points than adipic acid + ethylene glycol and adipic acid + 1,4 butanediol. The general comparison is shown in Table 1.4 [11]. Polyesters synthesized from adipic acid with ethylene glycol, adipic acid with 1,6-hexanediol and adipic acid with neopentyl glycol are known to be solid in room temperatures.

Table 1. 4 Comparison of Solidification Points and Viscosities at 75 °C of Different Polyester Polyol Compositions [11].

Structure	Solidification Point (°C)	Viscosity at 75°C (mPa.s)
Adipic acid+ ethylene glycol	52	540
Adipic acid + ethylene glycol + 1,4-butanediol	17	625
Adipic acid + 1,4 butanediol	56	670
Adipic acid+hexamethylene glycol + neopentyl glycol	27	640

Raw material - form of polyester polyol relationship shown in Figure 1.7.

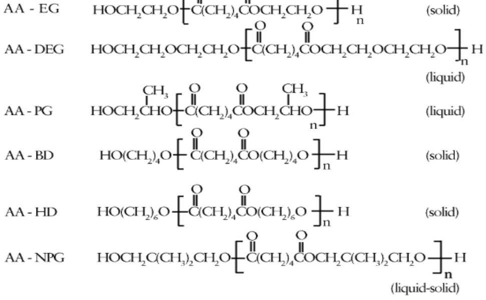


Figure 1. 7 The structure of some representative polyester polyols used in polyurethane applications [12].

2. THEORETICAL PART

2.1 Isocyanates

In 1848, Würtz made the first synthesis of isocyanate by alkalizing the calcium cyanate with sulfuric acid esters. In 1884, Hentschel further improved this method with amine phosgenation. Until 1937, when Otto Bayer discovered polyol – isocyanate addition reaction, isocyanates were just a curiosity. Even with the discovery of several other methods to produce isocyanate, in the industrial aspect, amine phosgenation is the most preferred method. All isocyanates have at least two NCO groups to react with water, polyols, chain extenders and crosslinkers. The general synthesis reaction is shown below in Figure 2.1 [13].

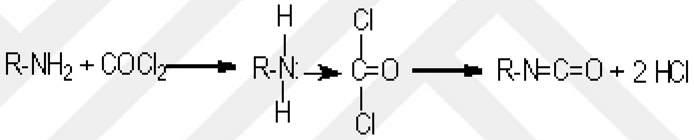


Figure 2. 1 Isocyanate synthesis [13**].**

To eliminate the excess of phosgene, the reaction is generally carried out in a chlorinated aromatic solvent. The process is, in general, complicated and has some side reactions as seen in Figure 2.2 [13].

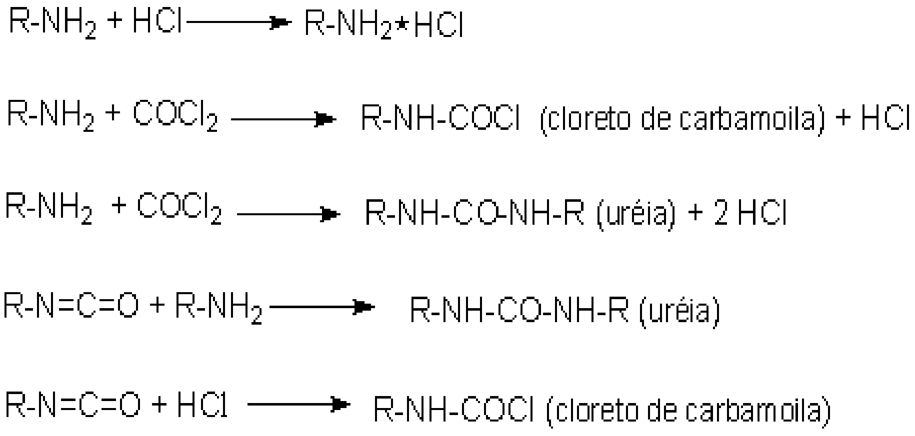


Figure 2. 2 Side reactions in isocyanate synthesis [13].

Urea, which is a side product, converted to carbodiimide. In the following reactions, carbodiimide reacts with phosgene to produce a material with chloride. Later on, chloride will be joined in the product [13].

$$R\text{-}NH_2 + HCl \longrightarrow R\text{-}NH_2{\star}HCl$$

$$R\text{-}NH_2 + COCl_2 \longrightarrow R\text{-}NH\text{-}COCl \text{ (cloreto de carbamoila) } + HCl$$

$$R\text{-}NH_2 + COCl_2 \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R \text{ (uréia) } + 2\,HCl$$

$$R\text{-}N{=}C{=}O + R\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R \text{ (uréia)}$$

$$R\text{-}N{=}C{=}O + HCl \longrightarrow R\text{-}NH\text{-}COCl \text{ (cloreto de carbamoila)}$$

Figure 2. 3 Side reactions in isocyanate synthesis [13].

2.1.1 Aliphatic isocyanates

The biggest problem in aromatic diisocyanate-based polyurethanes is known as yellowing. For this reason, aliphatic isocyanates are used in applications like coating to sustain color stability.

Most used aliphatic diisocyanates are 1,6-hexane diisocyanate (HDI), isophorone diisocyanate (IPDI), dicyclohexane diisocyanate (HMDI) and meta-tetramethyl xylene diisocyanate (TMXDI) [13].

Most known aliphatic isocyanates are shown in Figure 2.3 [13].

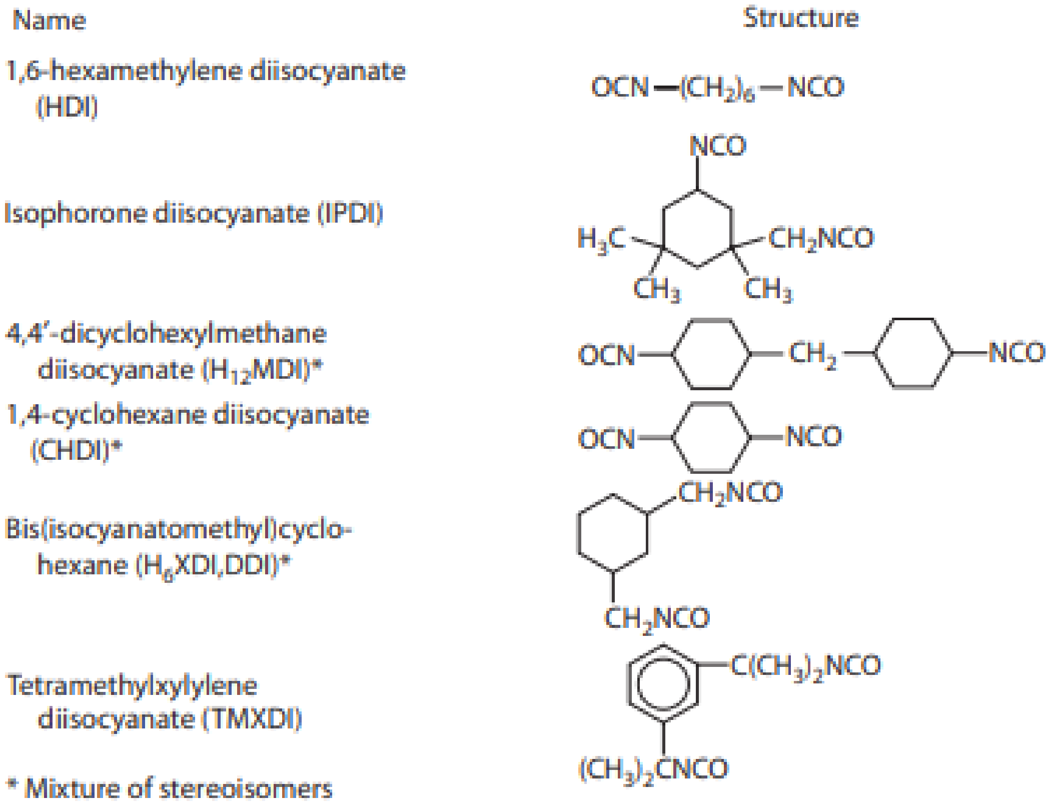


Figure 2. 4 Mostly used aliphatic isocyanates [14].

Aliphatics show less reactivity than aromatics. Bulky groups close to the reaction zone decrease the general reactivity. In IPDI, NCO groups bonded to primary or secondary carbon will have different reactivities. In TMXDI, reaction with water is slow due to the steric hindrance effect of tertiary isocyanate. Therefore, it can disperse in water [13].

2.1.2 Aromatic isocyanates

Most used aromatic diisocyanates shown in Figure 2.4.

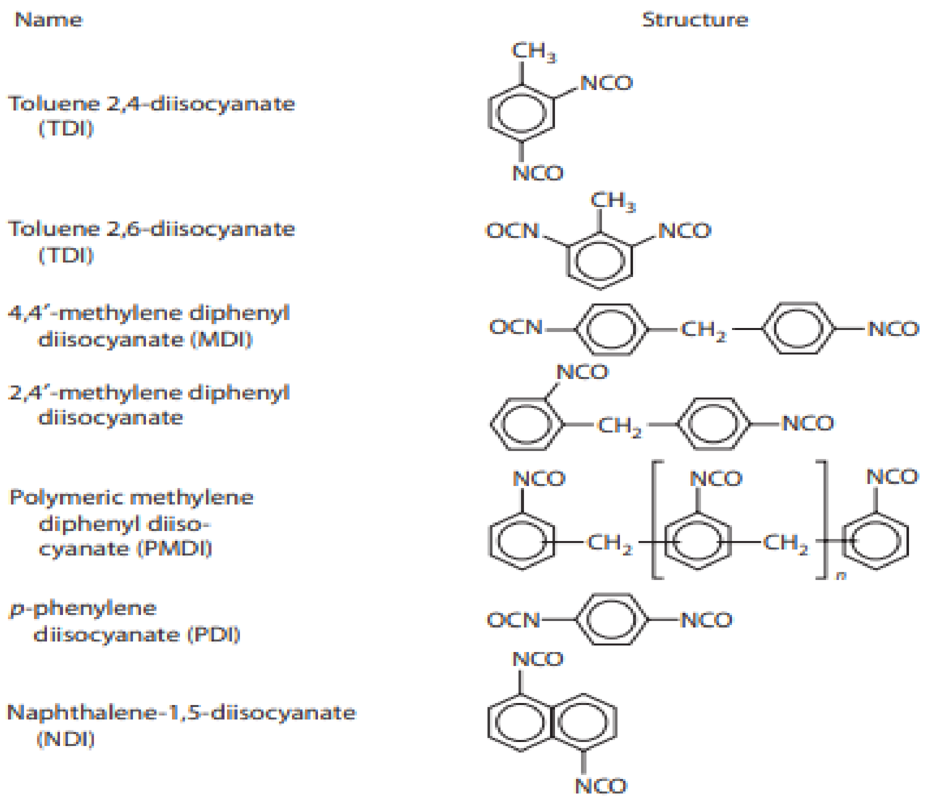


Figure 2. 5 Mostly used aromatic isocyanates [14].

4,4'- diphenylmethane diisocyanate (MDI), 1,5-naphthalene diisocyanate (NDI) and 2,4- toluene diisocyanate (TDI) (as 80:20 mixture) are the most used isocyanates [15, 16, 17].

However, TDI and MDI have more frequent usage in the industry.

2.1.2.1 Toluene diisocyanate (TDI)

TDI is generally used as blends of 2,4- and 2,6- isomers in 80/20 (TDI-80/20) and 65/35 (TDI-65/35) ratios. Besides, they can be used in their pure form (TDI-100) [16, 17, 18].

TDI synthesis

General production scheme of TDI shown in Figure 2.5. TDI production is applied in three steps. First toluene nitrated with the sulphonitric mixture. Therefore, ortho, meta and para nitrotoluene mixture was obtained. In the following step, isomer separation carries out with a fractional distillation procedure.

In the second part of the nitration;

- when p-nitrotoluene is nitrated, the product will be 2,4- dinitrotoluene (TDI-100).
- when o-nitrotoluene is nitrated, the product will be 65 % 2,4- and 35 % 2,6- dinitrotoluene mixture (TDI-65/35).
- when the original mixture is nitrated directly or after the separation of p-nitrotoluene, the product will be 80 % 2,4- and 20 % 2,6- dinitrotoluene mixture (TDI-80/20).

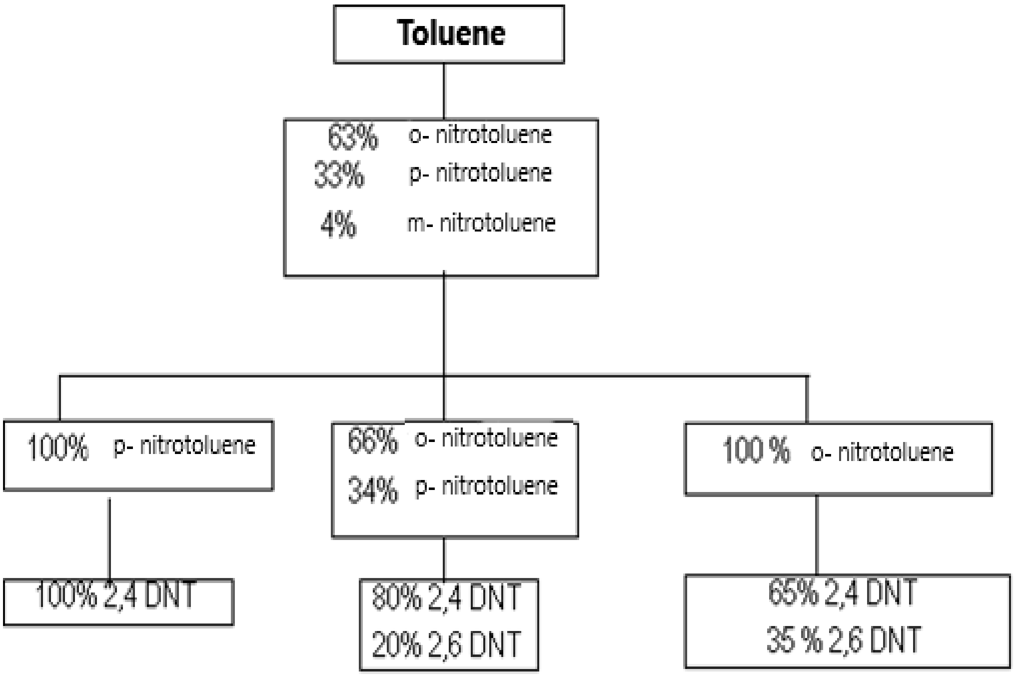


Figure 2. 6 TDI production process [13].

Formed dinitrotoluenes (DNT) hydrogenated to toluene diamines (TDA) with hydrogen in synthesis gas from steam hydrocarbon reform. Furthermore, formed carbon monoxide reacts with chlorine to form phosgene ($COCl_2$). Later, phosgene reacts with TDA to produce TDI. The reaction mechanism is shown in Figure 2.6 [13]. TDI-80/20 form of TDI is used for normal applications while the TDI-100 form of TDI is preferred for high-performance applications [19]. Physical properties of TDI-100, TDI-80/20, TDI-65/35 are shown in Table 2.1. respectively.

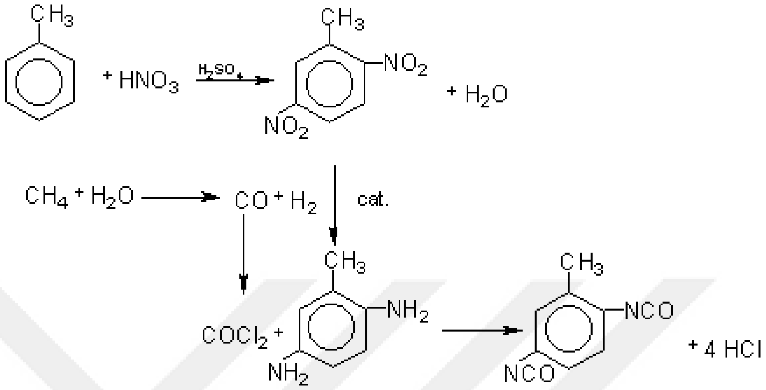


Figure 2. 7 Reactions of TDI production [13].

Table 2. 1 Physical properties of different TDI isomers [20].

TDI Isomers	Physical form	Molecular weight	Equivalent weight	Boliling point (°C) at 760 mmHg	Freezing point (°C)
100/0 (2,4/2,6 ratio)	Liquid	174.16	87.08	251	21.4
80/20 (2,4/2,6 ratio)	Liquid	174.16	87.08	251	14.0
65/35 (2,4/2,6 ratio)	Liquid	174.16	87.08	251	8.5

2.1.2.2 Diphenylmethane diisocyanate (MDI)

MDI is considered as the most reactive isocyanate and generally reacts with polyols, chain extenders (diols) or crosslinking agents (triols). If 4,4’- MDI and its prepolymer chains extended with diols as 1,4- butanediol linearity and symmetry of hard block segment gives elastomers a perfect phase segregation and superior dynamic properties. Therefore, MDI-based polyurethanes will gain excellent mechanical and dynamic properties [21].

MDI synthesis

MDI can be produced in three steps:

1. Condensation of aniline and liquid formaldehyde
2. Phosgenization of polymeric MDA in solvent
3. Isolation of pure MDI

The general steps of MDI synthesis are shown in Figure 2.7.

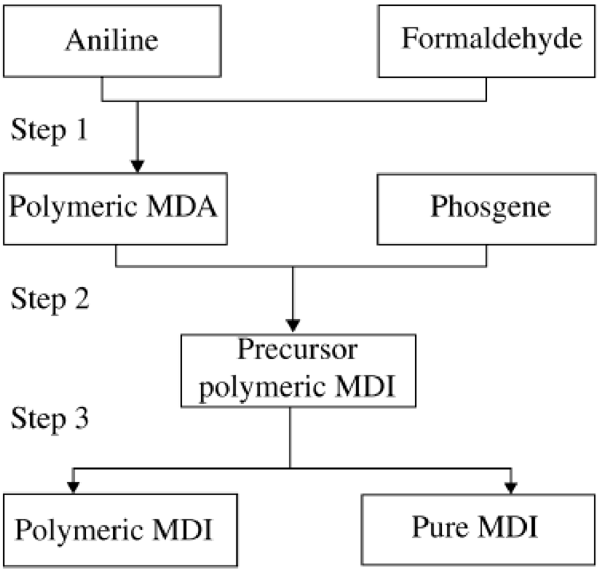


Figure 2. 8 Production steps of MDI [16, 17, 18].

Condensation of aniline and liquid formaldehyde

First step involves the catalytic reaction of aniline with formaldehyde accompanied by hydrochloric acid catalyst. In this step isomeric mixtures of diphenylmethane dianiline (MDA) form. MDA is a compound with aromatic amino groups.

The chemical structure of MDA is shown in Figure 2.8 [13].

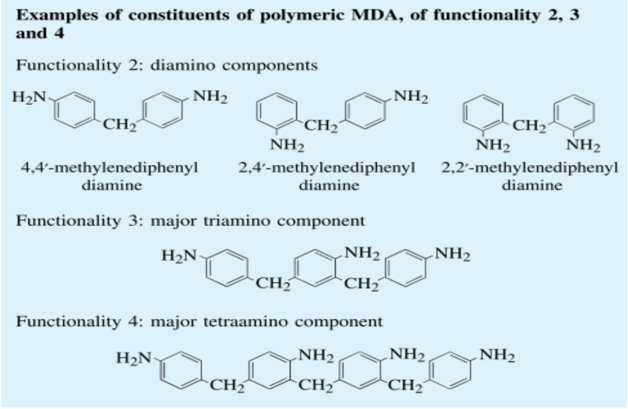


Figure 2. 9 Chemical structure of MDA [18].

Phosgenization of polymeric MDA in solvent

The second step consists of the conversion of aromatic amino groups in polymeric MDA to isocyanate groups. The reaction is a phosgenization reaction accompanied by solvents as monochlorobenzene [18]. A typical phosgenization reaction is shown in Figure 2.9.

$$\mathrm{R{-}NH_2 + COCl_2 \longrightarrow R{-}NCO + 2HCl}$$

Figure 2. 10 General phosgenization reaction [18].

Further on, hydrogen chloride and solvent are taken away from the reaction medium with distillation. The remaining product is named polymeric MDI [18].

Polymeric MDI can be thought of as a mixture of chemical mixtures of homologs. Its structure and content are shown in Figure 2.10 and Figure 2.11 respectively [18].

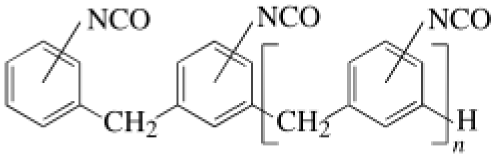
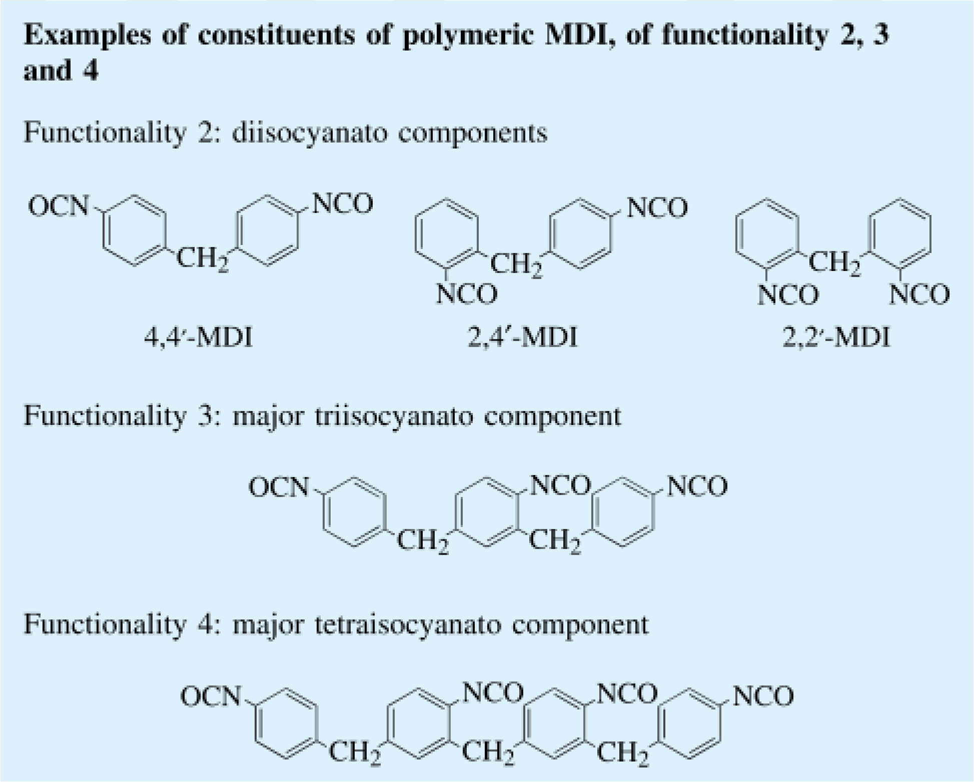


Figure 2. 11 Chemical structure of polymeric MDI [18].



Examples of constituents of polymeric MDI, of functionality 2, 3 and 4

Functionality 2: diisocyanato components

Functionality 3: major triisocyanato component

Functionality 4: major tetraisocyanato component

Figure 2. 12 Chemical structure of polymeric MDI and isomers [18].

Isolation of pure MDI

In the last step, pure MDI is obtained with distillation or crystallization of polymeric MDI. This procedure is named isolation. Commerical pure MDI generally has 95 % 4,4’- MDI and low content of 2,4’- MDI. The general system is shown in Figure 2.12 [18].

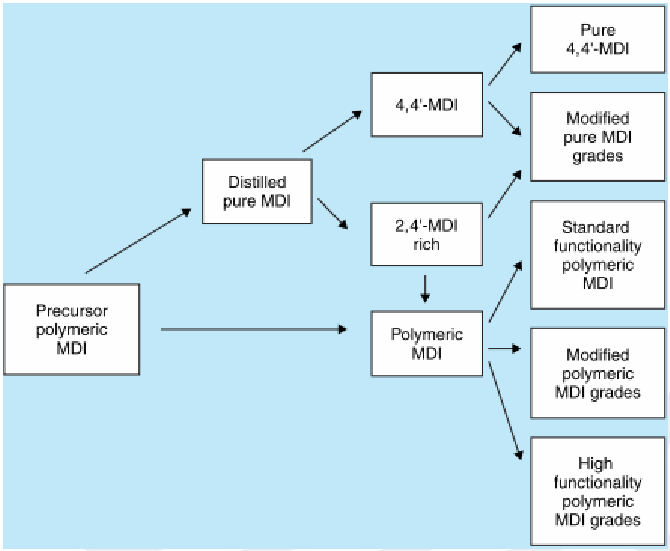


Figure 2. 13 Some routes to grades of pure MDI and polymeric MDI [18].

Classes of MDI

MDI’s have four classes in the industry [21];

1. Pure monomeric MDI, 4,4’- MDI
2. Isomeric mixture of 4,4’- and 2,4’- MDI
3. Polymeric MDI
4. Modified MDI

The most known kinds of MDI are shown in Figure 2.13.

Isomeric positions of isocyanates affect their reactivity. In 4,4’- MDI two isocyanate groups have the same reactivity while in 2,4’- MDI, two isocyanate groups have significant differences in reactivity. The 4-positioned (para) isocyanate group will be three or five times more reactive than 2-positioned (orto) isocyanate group with steric hindrance [21].

Pure monomeric MDI has a melting point of 38,5 °C . Its high reactivity and linear structure are useful in hard segment formation in polyurethane chains. Monomeric MDI can be used in CASE applications, shoe sole microcellular elastomers and fibers.

General product standards and general properties of monomeric MDI are shown in Table 2.2 and Table 2.3 respectively [21].

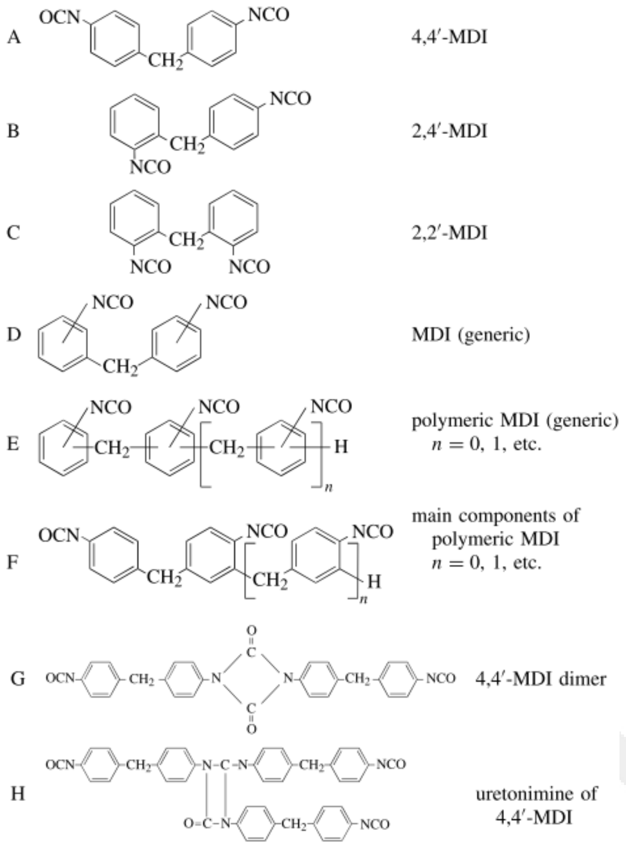


Figure 2. 14 Forms of MDI [18].

Table 2. 2 General product standards of monomeric MDI [21].

Item	Evaluation Method	Unit	Spec
Degree of purity	ASTM D 1638	wt%	Min 99.8
Solidfying point	ASTM D 1638	°C	Min 38.5
APHA color	ASTM D 1638	-	Max 20
Hydrolyzable chlorine	ASTM D 1638	wt%	Max 0.002
Cyclohexane insoluble	-	wt%	Max 0.2

Table 2. 3 General properties of monomeric MDI [21].

Appearance	Boiling Point	Freezing point	Ignition point	Molecular weight
White solid	314	38.7	196	250

MDI with a high 2,4’-isomer ratio is named as orto rich MDI. Since it has lower reactivity than 4,4’- MDI, chain extension will be less than expected. Lack of chain results in a weaker polyurethane backbone. They are generally used as an alternative to TDI [21].

MDI with a high 2,4’-isomer ratio will have;

- lower melting point
- longer reaction time (curing time)
- increased compatibility with polyol
- better compression set

General product standards and general properties of orto rich MDI are shown in Table 2.4 and Table 2.5 respectively [21].

Table 2. 4 General product standards of orto rich MDI [21].

Item	Evaluation Method	Unit	Spec
Degree of purity	ASTM D 1638	wt%	Min 99.5
NCO content	ASTM D 1638	wt%	33.6
Solidfying point	ASTM D 1638	°C	Min 38.5
APHA color	ASTM D 1638	-	Max 20
Degree of purity	ASTM D 1638	wt%	Min 99.5

Table 2. 5 General properties of orto rich MDI [21].

Appearance	Boiling Point	Freezing point	Molecular weight
Light yellow, transparent liquid	208	20	250

Polymeric MDI has 2.2 to 2.9 average functionality. It contains MDI isomers with oligo-isocyanate products. Polymeric MDI has good storage stability at room temperature and can stay in liquid form until 0 °C . In elastomers, they contribute to branching and crosslinking [21].

General product standards and general properties of polymeric MDI are shown in Table 2.6 and Table 2.7 respectively [21].

Table 2. 6 General product standards of polymeric MDI [21].

Item	Evaluation Method	Unit	Spec
NCO content	ASTM D 1638	wt%	30.0 - 32.0
Viscosity (25 °C)	ASTM D 1638	cps	150- 250
Specific gravity (25°C)	ASTM D 1638	-	1.230- 1.250

Table 2. 7 General properties of polymeric MDI [21].

Appearance	Boiling Point	Freezing point
Light yellow, transparent liquid	200- 208	Below -20

Dimerization in monomeric MDI

Monomeric MDI is known for its high degree of crystallinity. In industry, disruption in crystallinity is achieved with the carbodimidization technique. In this method, monomeric MDI is put into a catalyzed condensation reaction to obtain carbodiimide and cyclic uretonimine structures. The reaction mechanism is shown in Figure 2.14

[21]. The functionality of carbodiimide modified MDI is higher than 2.0 due to its reversible uretonimine groups. Their freezing point is below 10 °C [21].

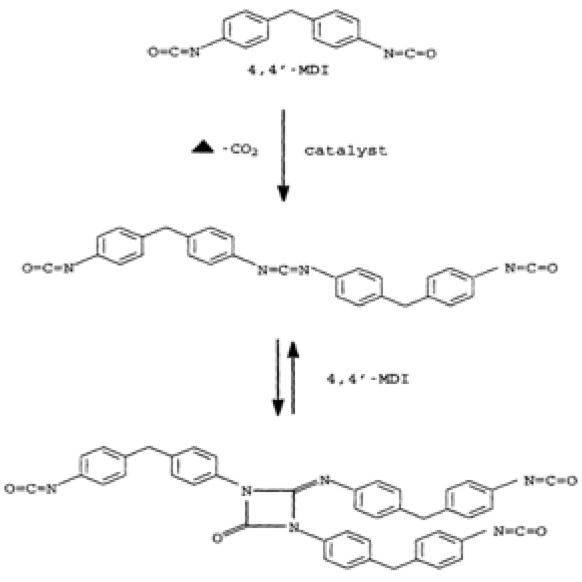


Figure 2. 15 Formation of carbodimide and uretonimine structure respectively [21].

General product standards and general properties of modified MDI are shown in Table 2.8 and Table 2.9 respectively [21].

Table 2. 8 General product standards of modified MDI [21].

Item	Evaluation Method	Unit	Spec
NCO content	ASTM D 1638	wt%	28.5-29.5
Viscosity (25 °C)	ASTM D 1638	cps	20-60
Specific gravity (25 °C)	ASTM D 1638	-	1.195- 1.25

Table 2. 9 General properties of modified MDI [21].

Appearance	Boiling Point	Freezing point	Vapor pressure (25 °C)	Ignition point
Clear, light yellow liquid	208	Below 10	0.0003	210

The abovementioned MDI forms are summarized in Table 2.10.

Table 2. 10 Summary of MDI forms and applications [21].

Functionality	Products	Applications
2,0	Pure MDI	Prepolymers, flexible adhesives, elastomeric fibers, thermoplastic polyurethanes (TPU's), shoe soles, high performance elastomers, leather coatings, sealants, etc
2,0 – 2,1	Modified pure MDI, High o,p containing MDI, Prepolymers form pure MDI	Cast elastomers, RIM elastomers, flexible coatings and adhesives, micro cellular foams
2,1 – 2,5	Liquid low functionality polyisocyanates; isomer blends with p-MDI blends	Flexible foams, semi rigid foams in automotive parts energy absorbing, sport floorings, cast elastomers, electrical encapsulation
2,7 – 2,8	Low viscosity polymeric MDI	Flexible foams, semi rigid foams in automotive parts energy absorbing, sport floorings, cast elastomers, electrical encapsulation
> 2,9	High viscosity polymeric MDI	Rigid polyurethane and isocyanurate foams, fire resistant construction foams

Another occasion in MDI is the dimerization phenomenon. This phenomenon involves the cycloaddition reaction of two aromatic diisocyanates to form a dimer or uretidione structure. Dimerization is an exothermic reaction and is generally catalyzed with pyridines or phosphines. The reaction mechanism is shown in Figure 2.16 [18, 22]. Pure MDI slowly dimerizes at room temperature. Dimer formation decreases the free NCO groups in isocyanate resulting in a lower amount of isocyanate groups to contribute to the urethane bond.

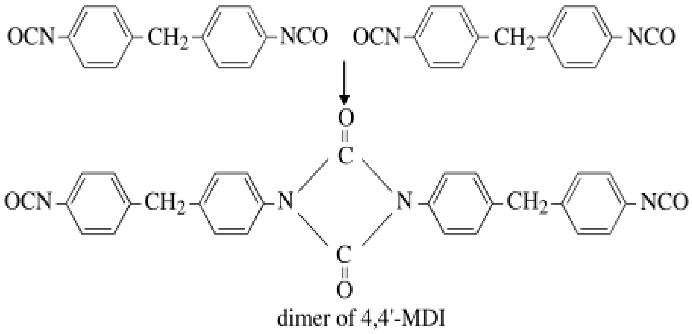


Figure 2. 16 Dimerization reaction [18].

Since isocyanate groups help in the formation of hard reinforcing segments, the physical properties of polyurethane will show deterioration.

To minimize dimerization, pure MDI must be stored below 0 °C as solid or in 40-45 °C intervals in liquid form. For this reason, as long as MDI is in liquid form, its molecules have more distance than its solid form. Therefore, their interactions will be more limited to produce dimer (except temperatures above 55 °C).[18, 22]

The relation of the rate of dimerization with temperature is summarized in Figure 2.17 [18].

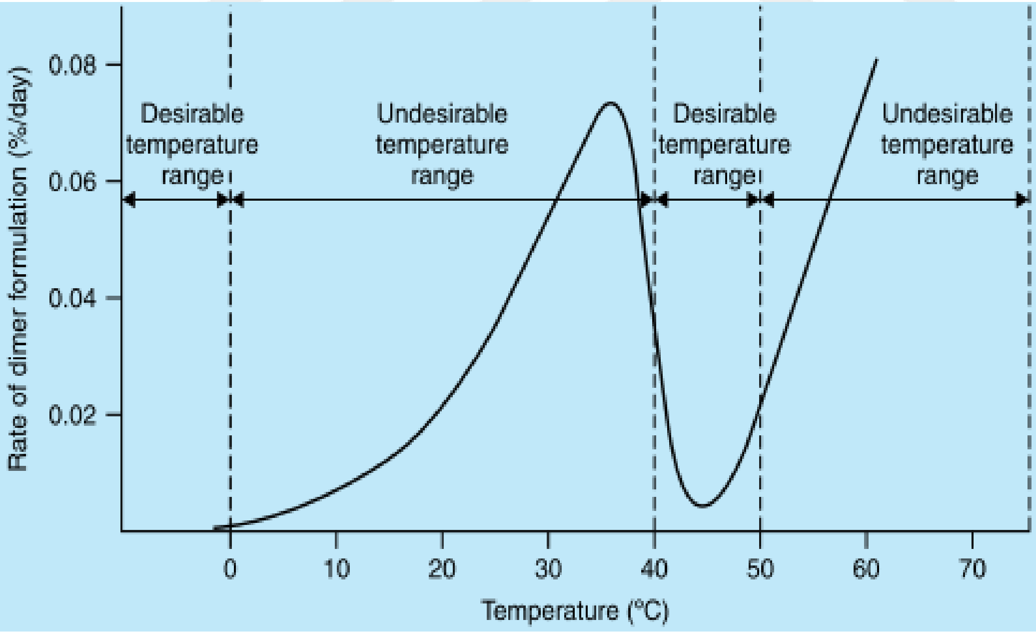


Figure 2. 17 Rate of dimerization of MDI with temperature [18].

Mdi isomers and possibilites of their dimerization

Stability and reactivity of dimers related to their monomer compositions. Isomers of MDI can be found in three different forms depending on the positions of isocyanate groups on benzene rings [2].

Isomer structures of MDI

o,o-MDI, o,p-MDI and p,p-MDI are considered as three isomer forms of MDI. Their optimized structure is shown in Figure 2.18.

Distance between nitrogen atoms of isocyanate groups calculated in three MDI isomers.

o,o-MDI: 7.96 Angström (closest position of isocyanate groups)

o,p-MDI: 11,04 Angström

p,p-MDI: 13,35 Angström (furthest position of isocyanate groups)

The reason for the difference in positions between isocyanate groups is related to the difference in benzene ring positions.

Isocyanate groups and benzene rings are located on the same plane. As a result of this positioning, electron delocalization occurs between the π orbitals of isocyanate groups and benzene rings. Therefore, a rigid system formed within the structure. Rigid structure rotates around the two sigma bonds of methylene groups [2].

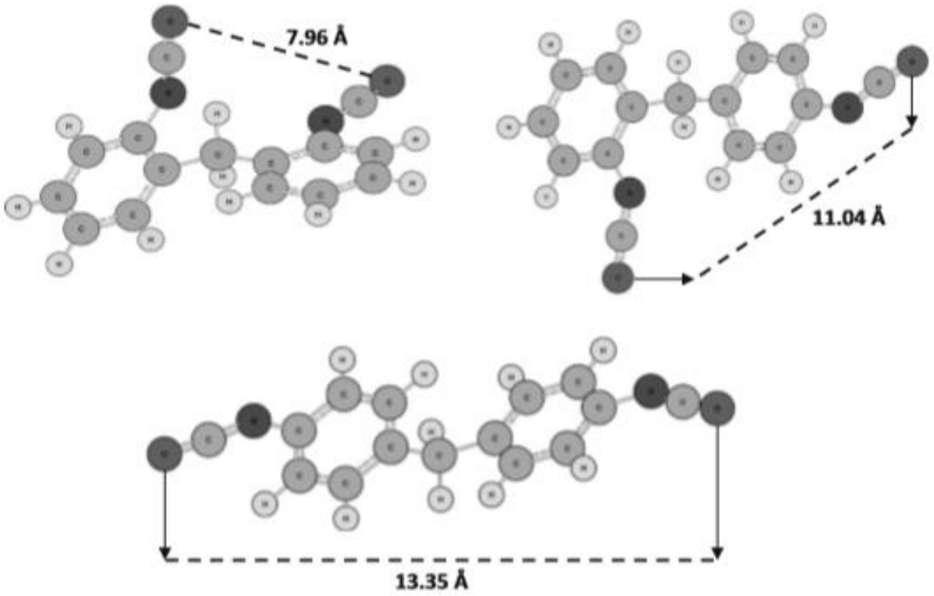


Figure 2. 18 Optimized structures of MDI at room temperature and in the gas phase obtained by M0-2X/6-31G (d,p) [2].

Molecular forces in isomers

There are generally three interactions in isocyanate structure which change the reactivity and possibility of dimerization.

The first interaction is known as Van der Waals interactions between a carbon atom of an isocyanate group and an oxygen atom of another isocyanate group. A partially positive carbon atom interacts with oxygen which has a negative charge. Van der Waals interaction is most likely to occur in o,o-MDI structure to its allowance for free rotation of isocyanate groups.

The second interaction is known as π stacking between two aromatic rings. This phenomenon happens between π bonds in aromatic rings. This interaction is considered the most observed interaction in isocyanates.

The third interaction is hydrogen bonding which occurs between the nitrogen atom in the isocyanate group and the hydrogen atom in the methylene group. This interaction reinforces the structure [2, 23, 24].

All three interactions are shown in Figure 2.18.

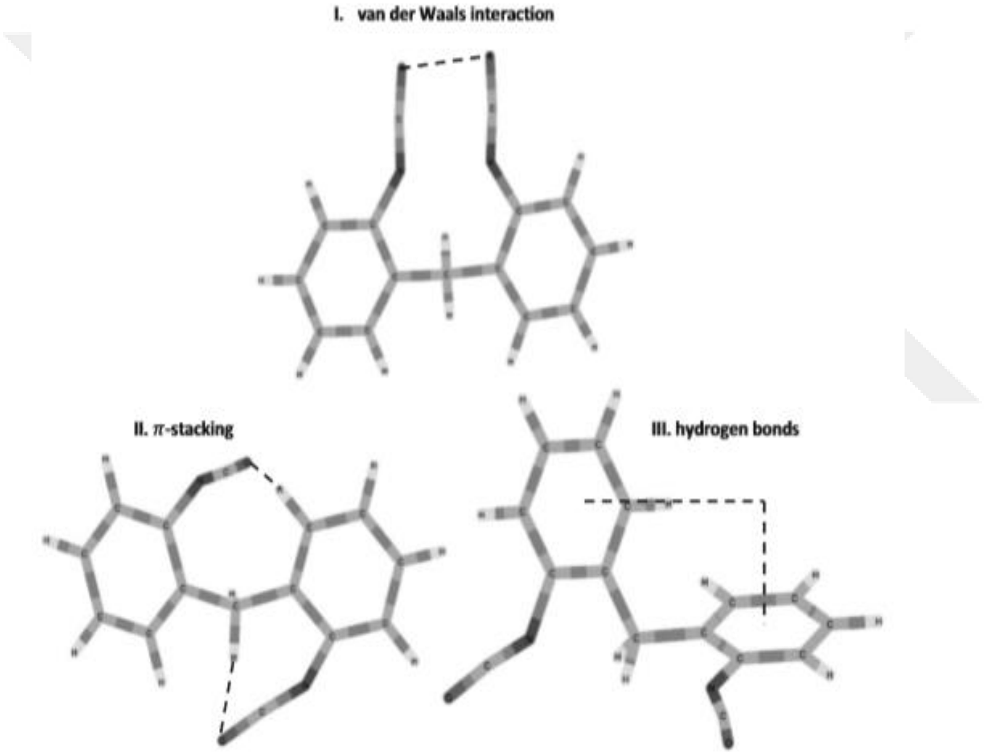


Figure 2. 19 Defined interactions between two isocyanate in o,o-MDI at room temperature and in the gas phase [2].

Dimers of isomers

Dimers from o,o-MDI isomer known for their instability. Methylene groups allow free rotation of benzene rings. Free rotation in benzene rings results in easily rotating isocyanate groups to form intrinsic interactions with each other. Neighbour isocyanate groups make Van der Waals interactions (weak interaction) which creates a steric hindrance in structure. This interaction occupies a volume in molecular space and causes destabilization for the dimer. Sterically the o,p-MDI dimer is more stable than o,o-MDI due to para positioned isocyanate groups which are more reactive and have less intention to create intrinsic interactions than ortho positioned isocyanate groups [2].

Possibility of dimer formation due to isomer structures

Reactivity of dimers related to the monomer structure. Positions of isocyanate groups differ on both least and most likely formed dimers.

Isocyanate groups are closest to each other in o,o-o,o-MDI dimer. The possibility of intrinsic interactions is much more than other dimers due to the easy movement of benzene rings. The interest of isocyanate groups is focused on intrinsic interactions rather than on other isocyanate groups, the possibility of dimer formation is quite low. Therefore, o,o-o,o- MDI dimer formation has the lowest possibility.

For p,p-p,o MDI dimers, isocyanate groups are farther from each other than o,o-o,o dimer. Therefore, intrinsic interactions are quite low.

For p,p-MDI, the isocyanate groups are furthest from each other compared to other dimers. These dimers are more reactive than others. This dimer structure has the highest possibility to form [2].

Dimer stability of isomers due to their molecular interactions

Isomer interactions directly affect their dimers. Dimers of o,o- or o,p- isomers are more stable than others. Due to the ortho position of methylene group, benzene rings can easily rotate around the methylene group and can create intrinsic interactions between isocyanate groups and can allow hydrogen bondings.

Dimers with p,p- or p,o- isomers are considered less stable due to the low possibility of intrinsic (weak) interactions. The methylene group is in the para position and in one plane with a four-membered ring which regulates the ring movement around the methylene group. For this reason, the number of occurring intrinsic interactions is very low.

Dimers with o,p- or p,p-isomers are unstable, since free isocyanate groups are in the para position. This conformation destabilizes the structure.

In addition, dimers with o,p- or p,p- isomers are unstable, as the free isocyanate group in the para-position destabilizes the structure.

The most stable dimer is considered as the p,o–o,p-MDI dimer while the least stable dimer is considered as the p,p-o,p-MDI dimer.

Most likely occurred p,p-p,o-MDI dimer structure and least likely occurred o,o-o,o-MDI dimer structure shown in Figure 2.19 [2].

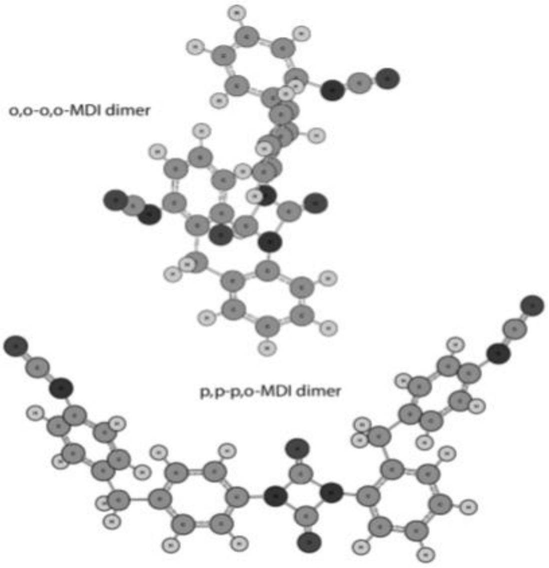


Figure 2. 20 Optimized structure of most and least likely formed products of the dimerization [2].

2.2 Polyols

Polyols are divided into two categories in polyurethane synthesis. The first group consists of propylene glycol, ethylene glycol, di propylene glycol, diethylene glycol, 1,4 butanediol, neopentyl glycol, triethanolamine and glycerol. They can serve as chain extenders (if they have two hydroxyl molecules per mol) or crosslinking agents (if they have more than two hydroxyl molecules per mol) in reactions [25, 26].

The second group of polyols are low molecular weight (maximum 10.000 dalton molecular weight) polymers with hydroxyl groups. They are called oligopolyols and their molecular weight is expressed as an average value like polymers. The general form of oligopolyol has been shown in Figure 2.20 [25, 27, 28].

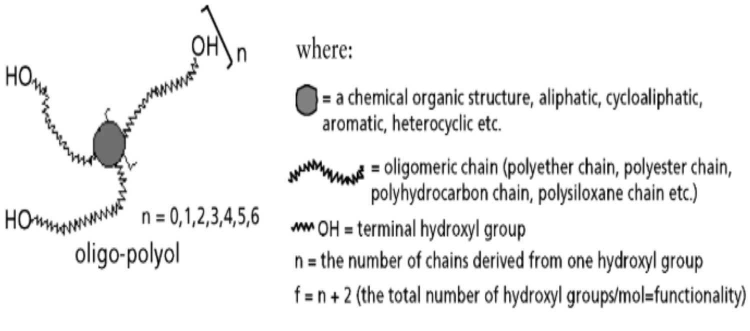


Figure 2. 21 The general formula of oligopolyols for polyurethanes [25].

Polyether and polyester polyol are classified as second group polyols [25].

2.2.1 Polyether polyols

Polyether polyols play an important part in polyurethane production. They are generally obtained from the addition polymerization of a monomeric epoxide [29].
Polyether polyols have low glass transition temperatures. This feature helps them to sustain their physical properties and compression strength in low temperatures. They are the best option for low-temperature applications.
Polytetramethylene glycol (PTMEG), polypropylene glycol (PPG) can be counted as the most used polyether polyols. Their synthesis is shown in Figure 2.21.

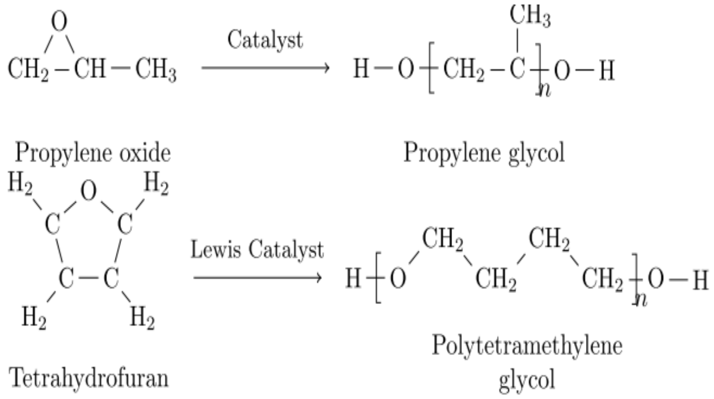


Figure 2. 22 Synthesis of propylene glycol and polytetramethylene glycol [29].

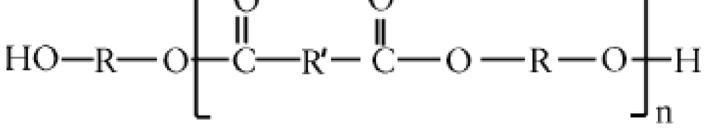
PTMEG is preferred in high-performance polyurethane elastomers.
Its properties consist of;

- excellent resilience against hydrolytic cleavage
- has good mechanical properties in low-temperature medium
- due to its soft segment’s strain induced crystallization, it can sustain good quality in mechanical properties in polyurethane systems with low acidity

PPG polyols are known for their good hydrolysis resistance. They can keep their properties in low temperatures. PPG is liquid at room temperature. Therefore, it is a good choice for room temperature systems.

2.2.2 Polyester polyols

Polyester polyols consist of ester groups and terminal hydroxyl groups. The chemical structure of polyester polyol is shown in Figure 2.22 [25, 30].



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

Figure 2. 23 Chemical structure of polyester polyol.

Polyester polyols are the second oligopolyol system preferred in polyurethane synthesis after polyether systems. They occupy 18 % of the polyurethane polyol market. This corresponds to 600.000 ton polyester polyol produced annually [31].

When added to polyurethane systems, polyester polyols provide more crystal structure than polyether systems due to secondary attractions in polyester chains.

They have superior thermal resistance and are less susceptible to solvent attack than polyether systems [25].

Polyester polyols have higher melting temperatures and viscosity than polyether and polycaprolactone systems. For this reason, they are more difficult to process [32].

Polyesters have more broad molecular weight distribution and a higher degree of acidity. Thus, it can affect the reactivity of catalysts.

Carboxylic acid monomers leave organic acid residues like adipic acid which disrupts hydrolytic balance since they autocatalyze the hydrolysis [32].

Final acidity is the most important factor in polyester polyol synthesis. Due to acidic residues coming from unreacted carboxyl groups, acidity in polyesters is higher than in polyether systems.

Most of the commercial polyester polyols have 2 mg KOH/g acidity while polyethers have 0.1 mg KOH/g acidity [25, 33].

Reaching 0.1 mg KOH/g in polyester systems is hard to obtain on an industrial scale since it requires a long reaction time.

The effect of catalysts has been examined to lower the reaction time. Without catalysts, the reaction completes in 25 hours with 0,9-1 mg KOH/g acidity while with tin catalysts reaction time drops to 11 hours with 0.4 mg KOH/g acidity. For this reason, catalysts are preferred in polyester polyol synthesis reactions.

Tin, titanium, lead or manganese catalysts can be used in synthesis. Especially tin catalyst is considered as the most efficient catalyst [25].

Polyester polyol synthesis is carried out in two steps:

1. Polycondesation reaction with the distillation of water (without catalyst)
2. Polycondensation after addition of catalyst

Most of the catalysts used in polyester polyols are susceptible to hydrolysis. For this reason, catalysts must be added after the first part (3-6 hours later) where most of the water has been eliminated from the reaction volume [25].Their applications include polyurethane elastomers (occupy 43 % of its consumption) and flexible foams (occupy 15 %-18 % of its consumption).

Besides these applications, they are also used in rigid foam, coatings, adhesives and synthetic leather [25].

2.2.2.1 Chemical synthesis of polyester polyols

Raw materials

A polyester polyol synthesis reaction is generally carried out with a polycondensation mechanism. The reaction involves a glycol (diol or tirol) reacting with a dicarboxylic acid to form polyester polyol.

Table 2.11 shows the most used glycols in polyester polyol reactions. Table 2.12 and Table 2.13 shows the most used aliphatic and aromatic dicarboxylic acids in polyester polyol synthesis respectively.

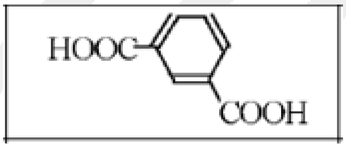
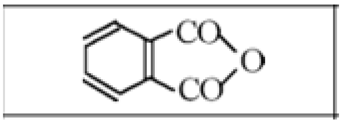
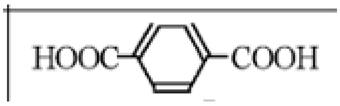
Table 2. 11 Most important diols and triols in polyester polyol synthesis [25].

No.	Polyol	Formula	MW, daltons	Hydroxyl number, mg KOH/g
		Diols		
1	Ethylene glycol (EG)	$HOCH_2OH$	62.07	1807.6
2	Diethylene glycol (DEG)	$(HOCH_2CH_2)O$	106.12	1057.2
3	1,2 Propyleneglycol (PG)	$HOCH_2CH(CH_3)OH$	76.10	1474.3
4	1,4 Butanediol (BD)	$HO\text{-}(CH2)_4\text{-}OH$	90.12	1245.0
5	Neopentyl glycol (NPG)	$(CH_3)_2C(CH_2OH)_2$	104.0	1078.8
6	1,6 Hexanediol (HD)	$HO\text{-}(CH_2)_6\text{-}OH$	118.18	949.3
		Triols		
1	Glycerol	$(HOCH_2)_2CHOH$	92.10	1827.3
2	Trimethylolpropane (TMP)	$(HOCH_2)_3CCH_2CH_3$	122	1379.5

Table 2. 12 Aliphatic dicarboxylic acids used for polyester polyol synthesis. [25].

No.	Polyol	Formula	MW, daltons	Acid number, mg KOH/g
1	Adipic acid (AA)	$HOOC(CH_2)_4COOH$	146.14	767.78
2	Glutaric acid	$HOOC(CH_2)_3COOH$	132.12	849.2
3	Succinic acid	$HOOC(CH_2)_2COOH$	118.09	950.1
4	Sebacic acid	$HOOC(CH_2)_8COOH$	202.0	555.4
5	Azelaic acid	$HOOC(CH_2)_7COOH$	186.0	603.2

Table 2. 13 Aromatic dicarboxylic acids used for Polyester polyol synthesis [25].

No.	Polyol	Formula	MW, daltons	Acid number, mg KOH/g
1	Isophtalic acid (IPA)		166.13	675.3
2	Pthalic anhydride		148.12	757.4
3	Teraphthalic acid		166.13	675.3

Reaction mechanisms

Polyester polyols can be synthesized in three methods. First method is the polycondensation reaction between dicarboxylic acid (or esters, anhydrates) and diols (or polyols). Adipate and pthalate based polyester synthesis can be given as an example [25, 34, 35, 36]. The general mechanism of the polycondensation reaction is shown in Figure 2.23. The second method is considered as the reaction of dicarboxylic acids or dimethyl esters (dimethyl adipate, dimethyl terephthalate, dimethyl carbonate or polyethylene terephthalate) of dibasic acid with glycols. The general reaction mechanism is shown in Figure 2.24. Polycarbonate diol synthesis can be given as an example [25, 36, 37].

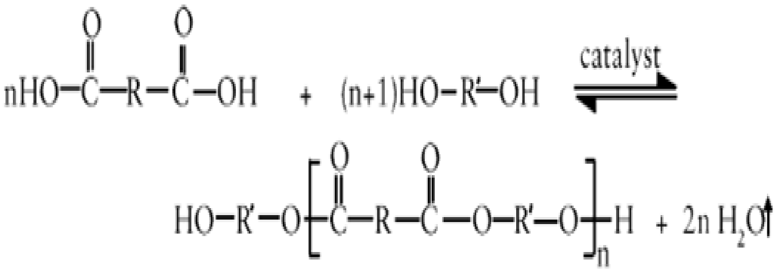


Figure 2. 24 Polycondensation reaction between dicarbocylic acid and diols [25].

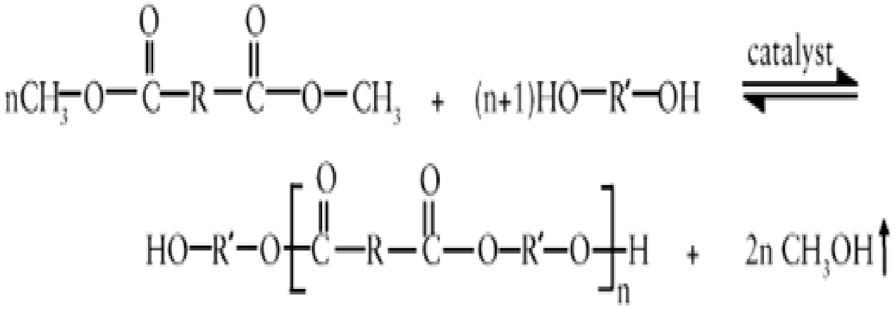


Figure 2. 25 Reaction of dimethyl esters and glycols [25].

The third method is the ring-opening reaction of cyclic esters (lactones, cyclic carbonates). Reaction steps involve the initiation of ε-caprolactone or cyclic carbonates (ethylene glycol carbonate, propylene glycol carbonate, neopentyl glycol carbonate) with diols followed by catalytic reaction. Polycaprolactone polyol synthesis can be given as an example in Figure 2.25 [25, 38].

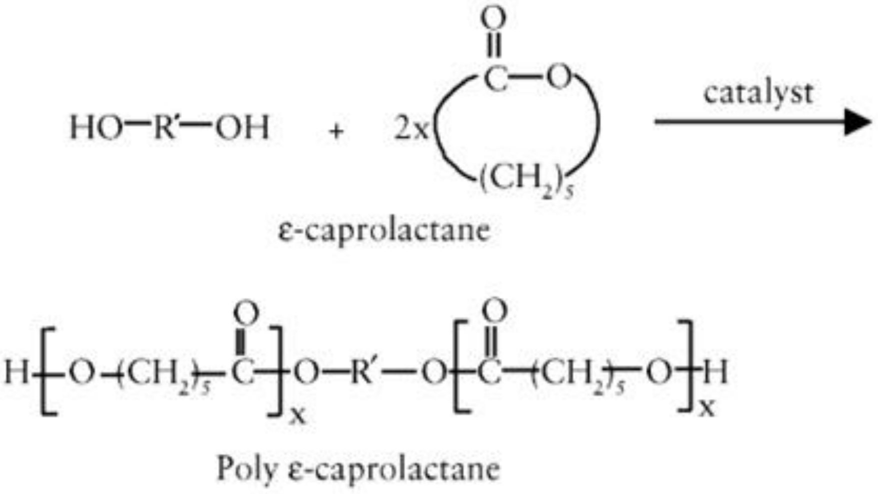


Figure 2. 26 Polycaprolactone polyol synthesis [25].

2.2.2.2 Classes of polyester polyols

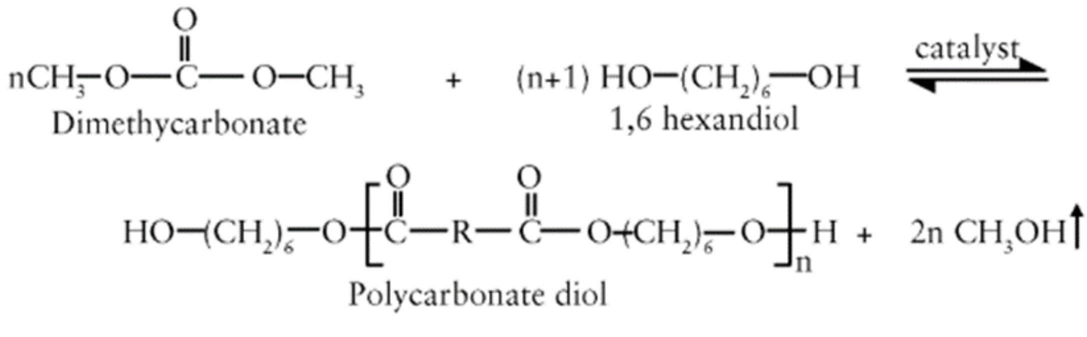
Adipate and pthalate based polyesters

The reaction between dicarboxylic acids and glycols is considered a polycondensation reaction. In a typical condensation reaction, glycol and dicarboxylic acid reacts and produce polyester polyol with water. Since the reaction is reversible, in each step the water must be eliminated to obtain a high yield of polyester polyol. Excess usage of glycol is necessary to guarantee terminal hydroxyl groups of polyol [25].

In general, the reaction is carried out in a non-catalyst way due to the catalytic behavior of acidic carboxyl groups. However, for lower reaction time and final acidity, the aid of specific catalysts is necessary. These catalysts can be p-toluene sulfonic acid, tin compounds (stannous octate), antimony, titanium (tetrabuyltitane), zinc (zinc acetate), manganese (manganese acetate) or lead compounds [25].

Polycarbonate diols

Polycarbonate diols are considered linear, aliphatic polyols with carbonate bonds. Aliphatic polycarbonates produced with transesterification reaction between dialkyl carbonates and aliphatic diols. A common example is a reaction between dimethyl carbonate and 1,6-hexanediol shown in Figure 2.26.



$$nCH_3{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3 + (n+1)\,HO{-}(CH_2)_6{-}OH \xrightleftharpoons{catalyst} HO{-}(CH_2)_6{-}O{-}\left[\overset{\overset{\displaystyle O}{\|}}{C}{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}(CH_2)_6{-}O\right]_n{-}H + 2n\,CH_3OH\uparrow$$

Figure 2. 27 Reaction between dimethyl carbonate and 1,6-hexanediol.

Polycarbonate diols have a better hydrolytic balance than typical polyester systems due to high-temperature hydrolysis without CO_2 evolution and a lower level of moisture. Since there are no acid residues in the reaction medium hydrolytic balance will be better than typical polyester systems with adipic acid residues [32].

Polycarbonate diols form the next generation of polyester polyols. For this reason, they are considered high-performance polyols.

They are superior due to their;

- good hydrolytic balance
- good abrasion resistance
- good UV resistance
- excellent high-temperature durability
- good chemical resistance

than other polyols [32].

Polycaprolactone polyols

Polycaprolactone (PCL) polyester polyols are made by a ring-opening reaction of cyclic carbonates with a glycol initiator. In the following steps, catalysis of reaction results with polycarbonate diol. The initiator can be taken as diol or triol with low molecular weight [32]. The general reaction mechanism is shown in Figure 2.27.

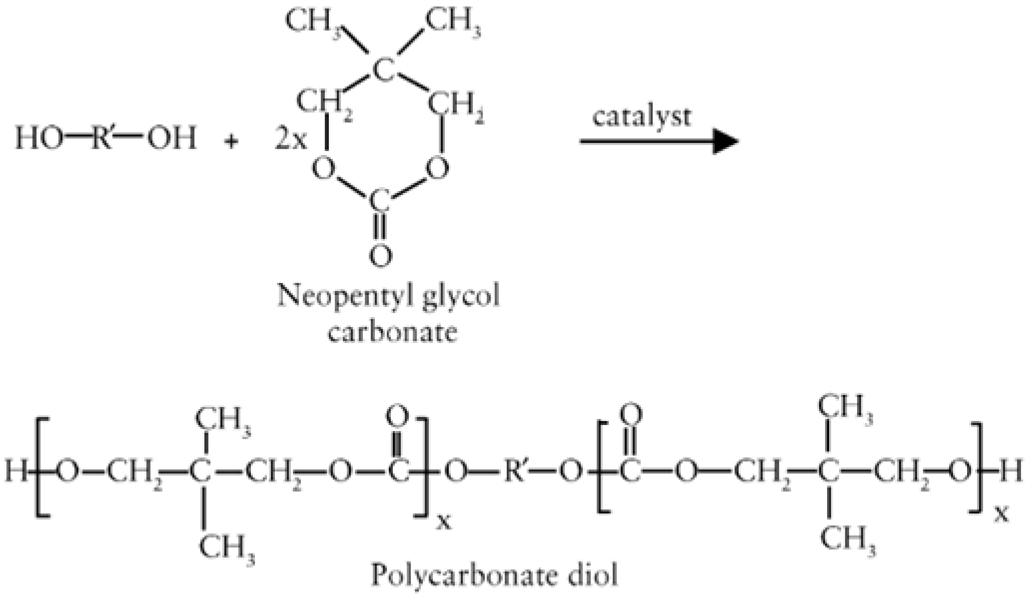


Figure 2. 28 Ring opening reaction of cyclic carbonates with a glycol initator [32].

PCL polyester polyols have long (-$(CH_2)_5$-) hydrophobic hydrocarbon segments, giving them good hydrolysis resistance. Their effects on polyurethane elastomer can be arranged with glycol initiators [25].

Reaction carries out in lower temperatures and no acidic residue evolved in the reaction medium. For this reason, PCL polyols have lower acidity [32].

PCL polyols have lower polydispersity, resulting in lower viscosity and better processibility [32].

PCL polyesters;

- can perform in a wide temperature spectrum
- have good durability
- have good hydrolysis resistance
- have a good tensile strength

2.3 Prepolymers

Prepolymers are obtained by a reaction between polyols and isocyanates. Isocyanate and polyol react to form a urethane bond and unreacted NCO groups form the terminal part of the chain. Polyurethane synthesis follows the prepolymer formation. The general mechanism is shown in Figure 2.28 [15].

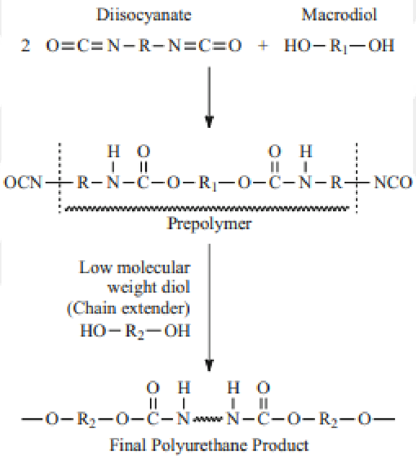


Figure 2. 29 Synthesis of prepolymer and polyurethane structures [15].

The viscosity of a prepolymer increases with a polyol- isocyanate reaction [19]. Chain length of prepolymer increases during the urethane bond formation [19]. The viscosity buildup mechanism is shown in Figure 2.29.

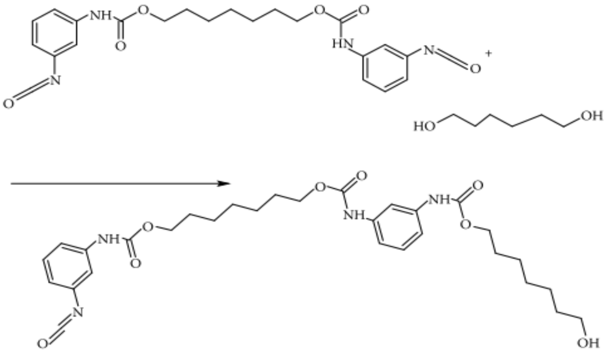


Figure 2. 30 Viscosity buildup in prepolymer [19].

Prepolymer synthesis

Prepolymers are generally synthesized with a 2:1 iso/poly molar ratio to guarantee isocyanate terminal groups. If the ratio is high as 4:1 then this formation is named quasi prepolymer. High ratios mean more unreacted isocyanates and more toxicity in the system. Increasing toxicity and less stable structure limit the application areas for prepolymer [13].

In industry, prepolymers can have different stoichiometric ratios of free isocyanates in the prepolymer. This ratio is generally between 2-20 %. Shoe sole microcellular applications use 20 % NCO while in sealant and hot melt adhesives this value could be 2 % [13].There are three main rules to apply during the prepolymer synthesis.

1. Reaction should take place with an excess of isocyanate to guarantee isocyanate terminal groups [29].
2. Polyols are viscous materials. For this reason, polyol should be added slowly to achieve the right viscosity and final free isocyanate level [29].
3. Polyols prepared with alkaline catalysts have catalysts in low amounts. Even this can cause faster reaction and gelation. For this reason, the acid/base balance of the compound should be investigated [29].

Most polyurethane systems are known for their glass surface adhesion during synthesis. For this reason, anchor type mixer is preferable since it applies spreading to prevent adhesion [29].First diisocyanates are put into a flask. Then, additional ingredients to control acidity or to catalyze reaction are put into the system. Diisocyanate heat in starting temperature with gentle agitation. Polyols are put slowly to control reaction exotherm and to minimize side reactions. Reaction temperature should be kept between 60-90 °C . After all ingredients were added, the reaction was kept at the final temperature to achieve the final product. Reaction finalizes in 1-2 hours. At the end of the reaction, unreacted diisocyanate should be degassed from the system to prevent gelation [29].

In case of alkaline presence in prepolymers, to increase the shelf life of prepolymers acids like benzoyl chloride, acetyl chloride or para (p)-toluenesulfonic acid can be added to the system [13].The reaction can be monitored in three ways:

1. Titration

NCO level can be monitored with classic titration. At the start, the NCO value will be higher and all of it will come from diisocyanate. However, after the reaction starts between polyol and isocyanate, most of the NCO groups will be converted to urethane bonds. During chain growth, the free NCO level will be decreased. When the reaction finalizes, the free NCO level will be fixed in a value [29].

2.Cone or plate viscosimeter

The reaction can be monitored with a cone or plate viscosimeter. As the chain starts to grow viscosity will show an increase. At the end of the reaction, the viscosity will be fixed in a value. Furthermore, side reactions can be spotted with fast viscosity increases. An example of viscosity monitoring is seen in Figure 2.30 [29].

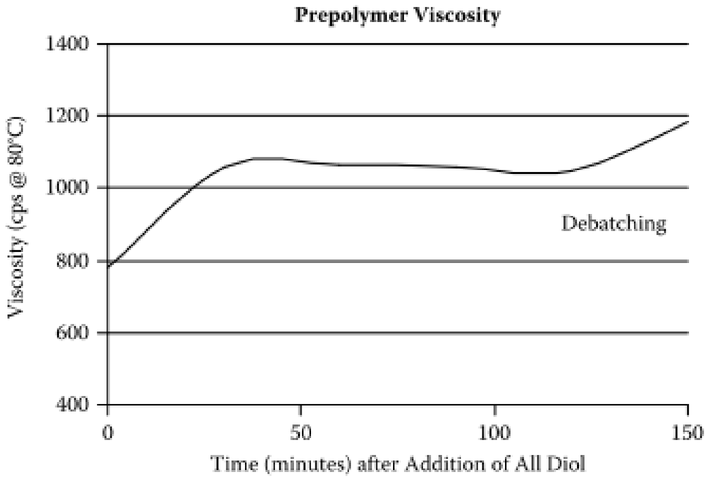


Figure 2. 31 Monitoring prepolymer reaction according to viscosity [29].

3.Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is another technique to monitor the reaction. Completion can be observed with drop at hydroxyl peak, formation of urethane band at 1739, maximum drop of NCO band at 2273. Balance in the NCO band indicates the chain growth step of the reaction [29].

Final properties of prepolymers can be adjusted with polyols [29]. For example, hydrophilic polyols like poly (ethylene oxide) or poly (propylene oxide) can create prepolymers with hydrophilic character [39].

The final reactivity of prepolymers can be adjusted with isocyanates since the free NCO level is the indicator of active isocyanate potential in the system [29].

Processibility is an important factor for prepolymers as any polymer. Viscosity and free NCO level are important criteria for this matter. Prepolymer viscosity is inversely proportional to the free level of NCO. A high level of free NCO means less reactive diisocyanates used during synthesis. For example, MDI is a more reactive isocyanate than TDI and IPDI. Therefore, MDI-based prepolymers are more reactive and have higher viscosity with broad molecular weight distribution. TDI and IPDI based prepolymers have less viscosity with narrow molecular weight distribution [13].

Some prepolymer and polyol systems for different applications are summarized in Table 2.14 [40].

Table 2. 14 Application and choices of prepolymer system [40].

Property	Best Choice	Second Best Choice	Poorest Option
Abrasion resistance	Ester system	Caprolactone	Ether
Compression set	PTMEG/TDI/E300	PTMEG/TDI/MOCA	PPG/MDI/BDO
Erosion resistance	MDI ether	PTMEG/TDI	Ester system
Food	PTMEG/MDI/BDO	Hydroxyl	Amine-cureed systems
Heat aging	Ester system	Caprolactone	Ester system
Heat buildup	PTMEG/MDI/BDO	PTMEG/TDI/M-CDEA	Standard ester
High temperature properties	PTMEG/PPDI/M-CDEA	PTMEG/TDI/MOCA plus heat treatment	Caprolactone
Hydrolysis	PTMEG/MDI/BDO	PTMEG/MDI/BDO	Standard ester
Low temperature	PTMEG/MDI/BDO	PTMEG/TDI/E300	Standard ester
Oil resistance	Ester system	Caprolactone	Ether
Processing	Low cost ether	Quasiprepolymers	Standard ester
Resiliance	PTMEG/MDI/BDO	PTEMG/TDI/M-CDEA	Standard ester
Very low hardness	Ester/TDI	Ester/TDI	Low cost ether

2.4 Polyurethane

The first work on polyurethane synthesis was the formation of the urethane group which is made by Wurtz in 1849. The reaction made between isocyanate and alcohol is seen in Figure 2.31 [25, 41, 42].

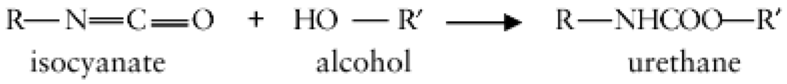


Figure 2. 32 Formation of urethane group [25].

In 1937 Dr.Otto Bayer synthesized the first polyurethane by a new method called polyaddition reaction between diisocyanate and polyester diol (which has two terminal hydroxyl groups) as seen in Figure 2.32.

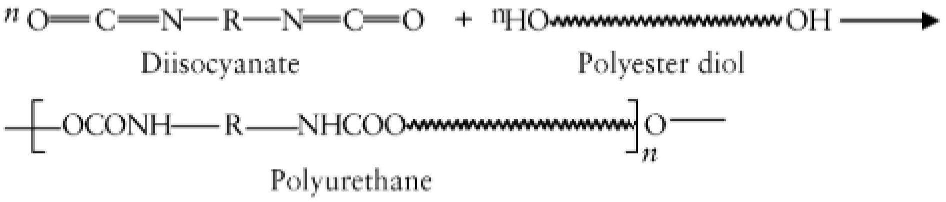


Figure 2. 33 Formation of polyurethane [25].

In classical polycondensation reaction products were polymer, accompanied by small molecules like water, alcohol. Polyaddition made a huge step-up since most of the reaction product was polymer itself [25].

In the 2nd World War, polyurethane was used at coatings and was an alternative to rubber. After the war polyurethane passed to an industrial scale and was used in various applications. Starting as rigid foams, adhesives, coatings in the ’50s and by the invention of polyether polyols, flexible polyurethane foams are used in households since it creates comfort in beds.

Today with further modifications and innovations in formulations, polyurethanes occupy most of our daily life materials like desks, chairs, cars, footwear, insulations [43].

Polyurethane synthesis is done by three major components which they are polyols, isocyanates and chain extenders.

The most used synthesis method is the prepolymer method. This method is common since it creates polyurethane coating materials which have a huge place in the polyurethane market [25, 43].

The first step of reaction involves a reaction between isocyanate and polyether or polyester diols and the formation of a prepolymer which has a polymerization degree between 2 or 5. Excess of diisocyanate will be used to terminate end groups of the final product.

The last step is the reaction of this prepolymer with a chain extender to create a high molecular weight polyurethane polymer [25]. The reaction mechanism is shown in Figure 2.33.

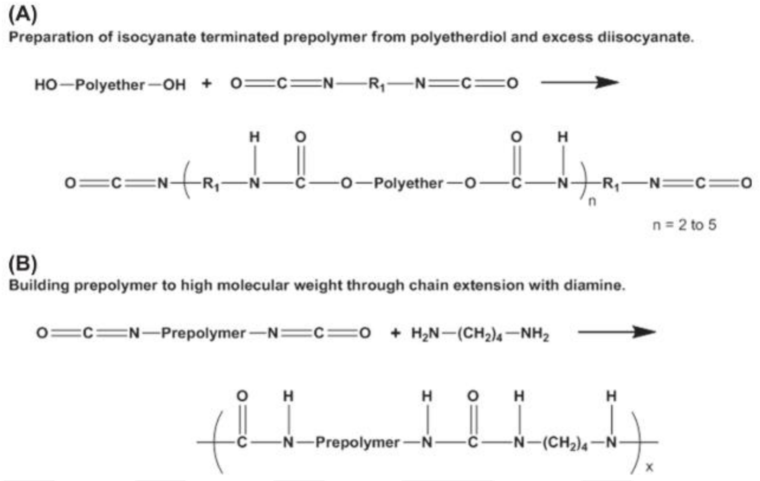


Figure 2. 34 Two-step synthesis of a polyurethane block copolymer: (A) Isocyanate-terminated prepolymer synthesis from excess diisocyanate and polyether diol; (B) Reaction of prepolymer with diamines to build high molecular weight polyurethane chains [44].

In the case of applications, polyurethanes can be investigated into two groups named elastic polyurethanes and rigid polyurethanes as seen in Figure 2.34 [25].

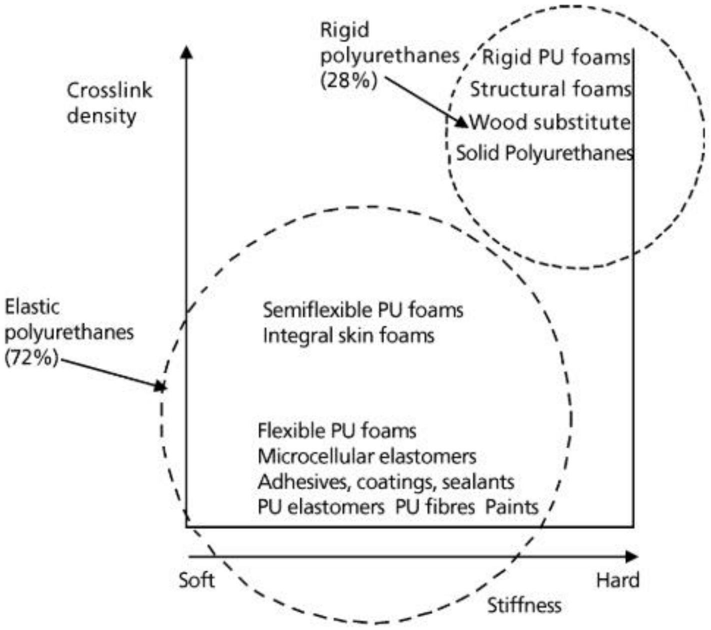


Figure 2. 35 Classification of polyurethanes as function of crosslink density and stiffness [25].

This difference is caused by the polyols used in the synthesis reaction. The functionality and molecular weight of polyols change the crosslink density. Low functionality (2-3 hydroxyl groups) and high molecular weight (2000-10000 Da) polyol creates a lower crosslinking; causing the formation of elastic polyurethanes. However, a polyol with a low molecular weight (150-1000 daltons) and with high functionality (3-8 hydroxyl groups) creates a higher crosslinking; causing the formation of rigid polyurethanes [25]. Both principles are shown in Figure 2.35.

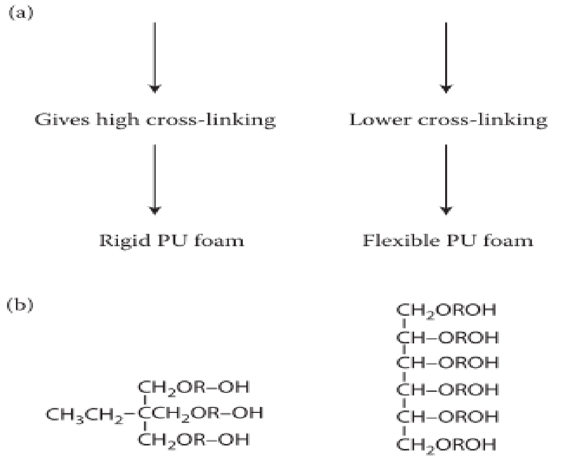


Figure 2. 36 (a) Cross-linking requirements. (b) Triol (left) and hexol (right) [14].

Polyether and polyester polyols are the most used polyol classes in the synthesis. They can be synthesized with ring-opening polymerization and polycondensation reaction [43].

Isocyanate shows high reactivity and in the case of moisture, it will react with water. This creates a complex situation when isocyanates react with polyhydroxyl compounds in conditions where moisture is an element. As a product, an unstable carbamic acid is formed. In further steps, carbamic acid disintegrates to amine and carbon dioxide. Foam formation follows gas formation [14]. Gas formation due to chemical reaction is an indication of water is acting as a blowing agent [45]. The formation of carbon dioxide is shown in Figure 2.36.

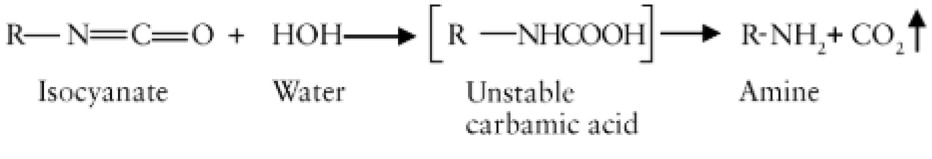


Figure 2. 37 Formation of CO_2 [25].

As the reaction progresses isocyanate reacts with the amine to form urea groups. Urea formation is shown in Figure 2.37.

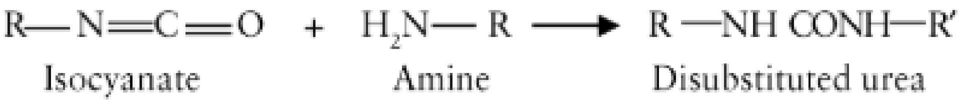


Figure 2. 38 Formation of urea group [25].

Aromatic and aliphatic isocyanates are mostly used in the synthesis of polyurethane. Commercially used isocyanates are methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI) [43] as shown in Figure 2.38.

Polyurethane is a thermoset material however it shows different characteristics compared to other classic thermosets. Due to the phase incompatibility between polyols and isocyanates, the structure follows a segmented order. This segmented structure allows the formation of thermoplastic elastomers [44].

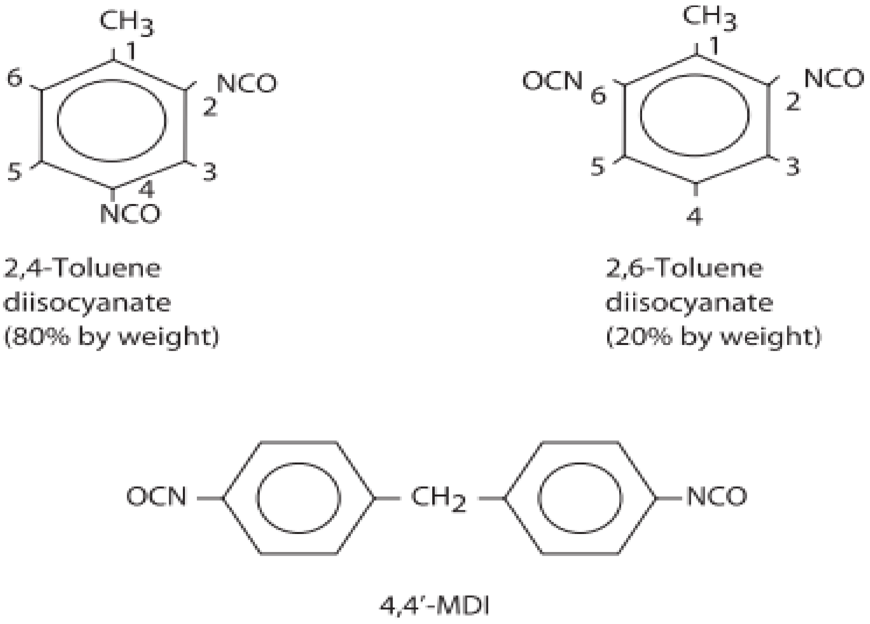


Figure 2. 39 Difunctional aromatic isocyanates [14].

High molecular weight, highly mobile polyols create a soft segment which shows rubbery (elastic) character while isocyanates and chain extenders create a crystalline rigid segment which shows reinforcing filler characteristics [25, 44]. The hard segment has physical crosslinks besides covalent crosslinks and it is due to secondary bonds like hydrogen bonds [25, 44]. Hard domain, soft domain and formation of hydrogen bonding are shown in Figure 2.39.

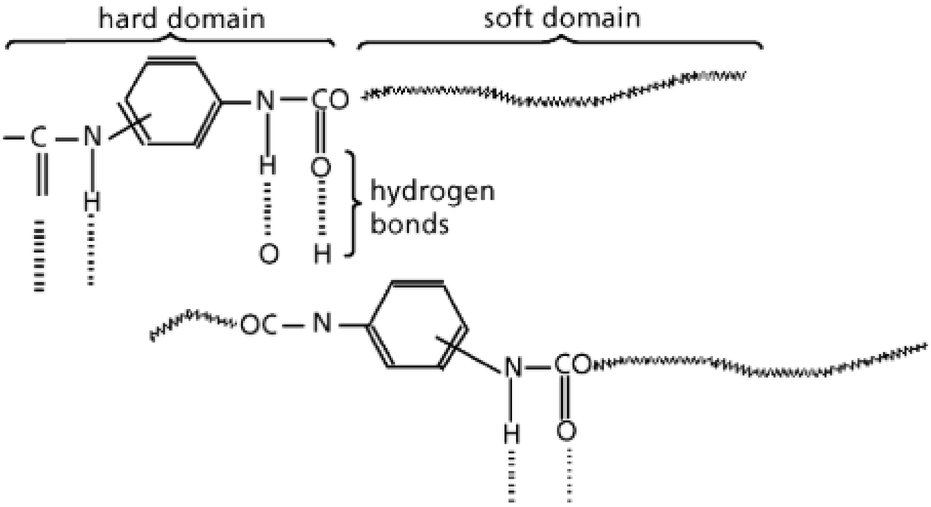


Figure 2. 40 The ‘hard domains’ and ‘soft domains’ of polyurethane elastomers [25].

Physical crosslinks are also called virtual crosslinks since they can be destroyed at high temperatures and create linear polyurethane elastomer melt which can be processed similar to thermoplastics (thermoplastic elastomers) [25]. Virtually crosslink structure is shown in Figure 2.40.

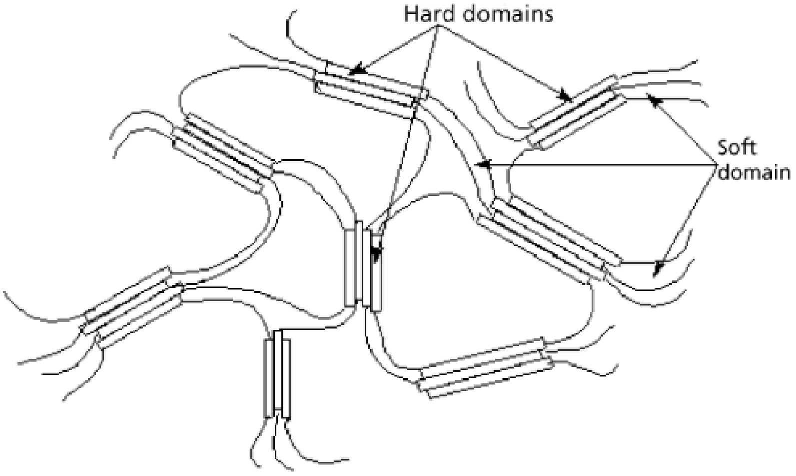


Figure 2. 41 Virtually’ crosslinked polyurethane elastomers [25].

Chain extenders are diamines or short aliphatic diols that have 2 or 6 carbons and they are used in the last step of synthesis to create a high molecular weight polyurethane polymer [44].

Other than this three major components catalysts, additives (pigments, flame retardants, smoke retardants, surfactants, fillers) can be added to create various polyurethane formulations [43].

3. EXPERIMENTAL PART

This section contains the procedure of experiments and reaction conditions. In addition, the brand and model information of the prepolymers and equipment used are included in this section.

3.1 Materials

4,4’-Diphenylmethane diisocyanate: Millionate MT
50 % - 50 % Mixture of 2,4’- and 4,4’- diphenylmethane diisocyanate (OP50): Millionate MR 200
Base Polyester Polyol : Flokser Chemical
Dipropylene glycol: SKC Chemicals
Neopentyl glycol: Ataman Kimya
Diethylene glycol: Petkim Petrokimya
Adipic acid: Lanxess AG
Trimethylol propane: PERSTORP AB
Carboiimide modified diphenylmethane diisocyanate: Wannate CDMDI

3.2 Equipments

This chapter involves general information about the synthesis and analysis equipments during the study.

3.2.1 Production equipments

Hot Water Bath: BM 402
Mixing head: Heidolph R7R 2102 Control
Viscosimeter: Brookfield DV-2 Pro
Free NCO Amount Measurement: Metrohm 916
Polyurethane Casting Machine: AMA GUSBERTI PU ROTARY MACHINE

3.2.1.1 Free NCO percentage measurement

Dibutylamine (DBA) can react with hydrochloric acid. Blank NCO percentage can be obtained from the reaction between DBA and hydrochloric acid. NCO groups in prepolymer will react with DBA and it will occupy some of the reactive end groups in DBA. Therefore, the absence of pre-reacting end groups of DBA can be monitored from its loss of reactivity with hydrochloric acid. These pre-reacted groups correspond to free, reactive NCO end groups of prepolymer and are taken as free NCO percentages.

For measurement of blank NCO percentage, 19.5 mL dibutylene amine solution which consists of dibutylene amine-chlorobenzene and 100 mL methanol added and mixed in flask.

Later, the weight of the sample was recorded and the mixture was put into the system. Recorded weight of sample written down as sample size. After sample size configuration, the analysis started. Blank NCO percentage read from the screen after analysis. This value should be between 19 - 19.15.

After blank NCO analysis, a base value of NCO was created in the analysis database.

For measurement of prepolymer NCO percentage, 19.5 mL dibutylene amine solution which consists of dibutylene amine-chlorobenzene, 2 g prepolymer sample. Obtained solution mixed for 2 minutes. Later on, 100 mL methanol was added and mixed in a flask. Obtained solution mixed for 1 minute.

Later, the weight of the prepolymer was recorded and the mixture was put into the system. Recorded weight of prepolymer written down as sample size. After sample size configuration, the analysis started.

Prepolymer NCO percentage read from the screen after analysis.

As final step, obtained blank and prepolymer NCO percentages compared in a formulation 3.1;

$$\%NCO = \frac{(Vblank - Vprepolymer) * factor * NCO\ value}{Taken\ prepolymer\ weight} \quad (3.1)$$

V_{blank} : NCO percentage of blank solution

$V_{prepolymer}$: NCO percentage of prepolymer

factor: taken as 0.99

NCO value: taken as 4.2

3.2.1.2 Polyurethane casting machine

Polyurethane synthesis is done in a shoe sole polyurethane casting machine. Polyol and isocyanate were loaded in two separate tanks at 45 °C . After loading, both of the materials were mixed in 1/1 iso/poly ratio in the head of the machine before casting to form polyurethane. After mixing, penetration in synthesized polyurethanes was measured to find the working iso/poly ratio of polyurethane. After finding the lowest penetration value, polyurethanes were cast into a mold with 60 °C temperature in the molded density of 270-290 kg/m^3 (typical molded density of polyurethane slippers). After casting demoulding time was observed on polyurethane from its easy separation from the mold.

Finally, polyurethane slippers are taken from the mold.

The casting of polyurethane done by AMA GUSBERTI PU ROTARY MACHINE is shown in Figure 3.1.

Figure 3. 1 Polyurethane casting machine.

3.2.2 Testing equipment

3.2.2.1 DSC (Differential Scanning Calorimetry)

DSC (differential scanning calorimetry) is a thermal analysis instrument. It pinpoints the specific phase change zones by analyzing necessary heat flow to keep the temperature difference at zero for reference and sample.

Normally it will create a baseline of heat flow at zero since both the sample and reference will be in applied temperature. However, due to phase transitions in the sample, the sample will get cold or hot according to the thermal characteristic of the transition. This phenomenon will create a difference in necessary heat flow to balance the temperature of the sample and reference. As a result, this change will disrupt the baseline of heat flow and will create a peak. By this rule, it signalizes and pinpoints the phase transition temperature.

Glass transition temperature, melting, crystallization, specific heat capacity, cure process, purity, oxidation behavior and thermal stability can be measured with DSC analysis.

DSC can be applied on polymers, plastics, composites, adhesives, coatings, pharmaceuticals and many more materials.

DSC thermograms were obtained by PerkinElmer DSC 4000, the heating and cooling rate was 5 °C/min. DSC equipment is shown in Figure 3.2.

Applied temperature program summarized below:

1) Heating from -20.00 °C to 80.00 °C at 5.00 °C/minute

2) Cooling from 80.00 °C to -20.00 °C at 5.00 °C/minute

3) Holding for 20 minutes at -20.00 °C

4) Heating from -20.00 °C to 80.00 °C at 5.00 °C/minute

5) Cooling from 80.00 °C to -20.00 °C at 5.00 °C/minute

Figure 3. 2 DSC device.

3.2.2.2 FTIR (Fourier Transform Infrared)

Fourier transform infrared is a well-known infrared technique. It is sometimes considered as a first step to discovering an unknown material.

FTIR applies infrared radiation to samples, collects the absorption zones of radiation in different wavelengths and finally compiles them into a graph.

In different compounds, covalent bonds in structure differ by their absorptions of applied radiation in different wavelengths. The absorption of radiation significantly changes the vibrational energy of the bond. This phenomenon can be observed as stretching or bending of bonds.

Points of absorption were recorded by the device and turned into graphical data where x-axis stands for wavenumber (cm^{-1}) while y-axis stands for transmittance.

FT-IR spectra were performed using THERMO NICOLET IS50 FT-IR seen in Figure 3.3.

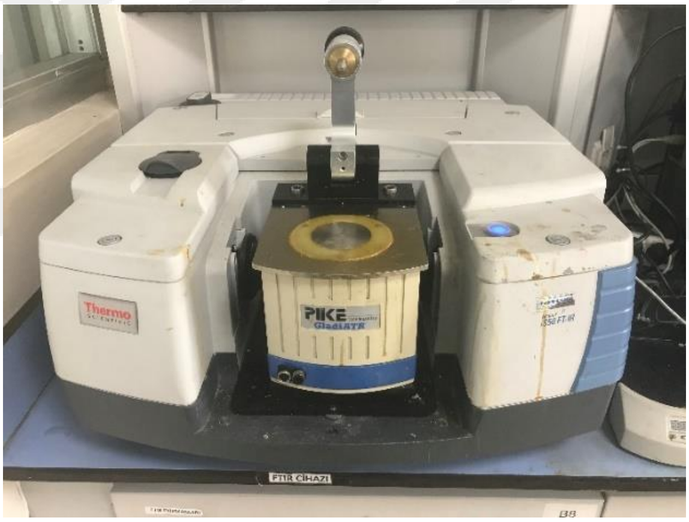


Figure 3. 3 FTIR device.

3.2.2.3 Compression set test

In compression set analysis, specimens which have been cut into cubic forms and their initial heights recorded before analysis. After recording, samples are placed in an oven at 70-80 °C where they will be compressed to 50 % of their initial heights for 1 day. After 1 day, samples were removed from the oven and waited outside for 30 minutes. After 30 minutes new height values of samples were recorded and the percentage of permanent deformation was found in the formula 3.2 and 3.3.

$$Height\ of\ compression = \frac{Initial\ height\ of\ sample}{2} \tag{3.2}$$

$$Percentage\ of\ permanent\ deformation = \frac{H_I - H_C}{H_I} * 100 \qquad (3.3)$$

H_I: Initial height of sample (cm)
H_C: Height of sample after compression (cm)
Analysis done according to ASTM D395 standart

3.2.2.4 Tensile strength and tear resistance test

In tensile strength analysis, the sample is clamped between two arms while arms apply force to break the sample. Applied force by arms and elongation at sample recorded to the software and turned into a graph. Y-axis represents the applied force in MPa while the x-axis represents the elongation in percentage.

Tensile strength, elongation at break, modulus can be found from tensile strength analysis.

In tear resistance analysis, the sample is clamped between two arms while arms apply force to tear the sample. The most resistant time of material must be found for the right analysis. Most resistant behavior of sample considered as the point before the tear. The maximum applied force observed in this point is used to evaluate tear resistance. Y-axis represents the applied force in N while the x-axis represents the elongation in percentage. The maximum point of applied force is taken as the tear resistance of the material.

Tensile strength and tear resistance test applied with Instron 3300 series Universal Testing System in Figure 3.4. Tensile strength analysis was done according to the ASTM D412 standard. Tear strength analysis done according to ASTM D624 standard.

Figure 3. 4 Tensile strength and tear resistance analysis device.

3.3 Experimental Procedure

3.3.1 Synthesis of prepolymers

Hot water bath temperature set to 63 °C . After it reached 63 °C three glass reactors were placed in a hot water bath.

The reaction set of synthesis is shown in Figure 3.5.

Figure 3. 5 Reaction set of synthesis.

3.3.1.1 Synthesis prepolymers with 4,4’-MDI, carbodiimide modified MDI, OP50 MDI and base polyester polyol

In the first reactor (PREP1) (Reference Formulation);

65-72 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 3-7 % percentage of weight carbodiimide modified MDI was added. As the final ingredient, 23-30 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

In the second reactor (PREP2);

61-68 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 5-10 % percentage of weight carbodiimide modified MDI and 1-4 % percentage of weight OP50 MDI added. As the final ingredient, 23-30 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

In the third reactor (PREP3);

61-68 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 1-4 % percentage of weight carbodiimide modified MDI and 5-10 % percentage of weight OP50 MDI added. As the final ingredient, 23-30 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

Each reaction ended in 1 hour. Synthesized samples PREP1, PREP2 and PREP3 are shown in Figure 3.6.

Figure 3. 6 Obtained prepolymer samples.

3.3.1.2 synthesis of prepolymers with 4,4’-MDI, carbodiimide modified MDI, OP50 MDI and base polyester polyol

In the first reactor (PREP4);

61-68 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 7-12 % percentage of weight carbodiimide modified MDI was added. As the final ingredient, 23-30 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

In the second reactor (PREP5);

61-68 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 3-7 % percentage of weight carbodiimide modified MDI and 2-6 % percentage of weight OP50 MDI added. As the final ingredient, 23-30 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

In the third reactor (PREP6);

63-70 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 3-7 % percentage of weight carbodiimide modified MDI was added. As the final ingredient, 25-32 % percentage of weight base polyester polyol was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

Each reaction ended in 1 hour. Synthesized samples PREP4, PREP5 and PREP6 are shown in Figure 3.7.

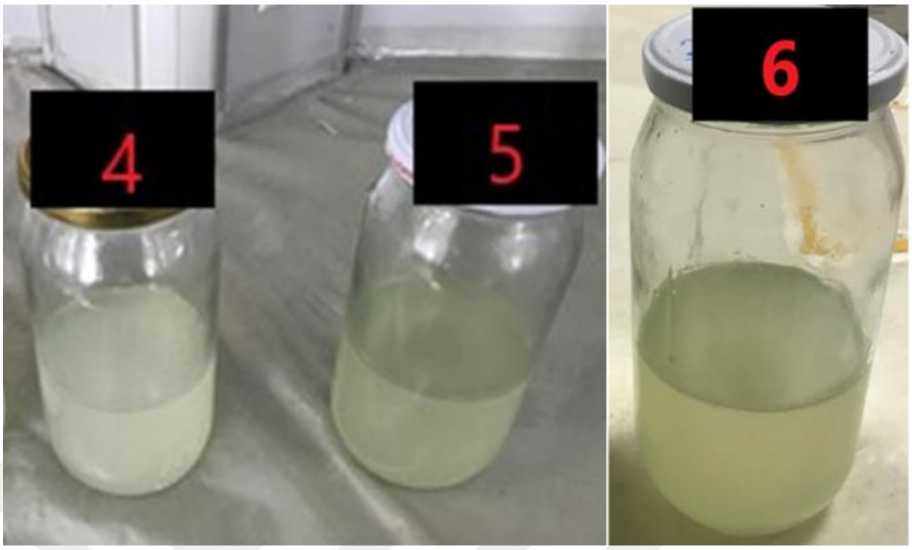


Figure 3. 7 Obtained prepolymer samples.

3.3.1.3 Synthesis of prepolymers with 4,4’-MDI, carbodiimide modified MDI, base polyester polyol or noepentyl glycol added base polyester polyol and dipropylene glycol

In the first reactor (PREP7);

65- 72 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 3-7 % percentage of weight carbodiimide modified MDI was added. As the final ingredient, 23-30 % percentage of weight polyester polyol with neopentyl glycol (NPG) was added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

In the second reactor (PREP8);

65- 72 % percentage of weight 4,4’- MDI added and mixing started. The rate of mixing was 130 rpm. Later, 3-7 % percentage of weight carbodiimide modified MDI was added. As the final ingredient, 22-29 % percentage of weight base polyester polyol and 0.1-0.7 % percentage of weight di propylene glycol (DPG) were added to the mixture gently to prevent gelation and to ensure the same free NCO amounts in all samples.

Each reaction ended in 1 hour. Synthesized samples PREP7, PREP8 are shown in Figure 3.8.

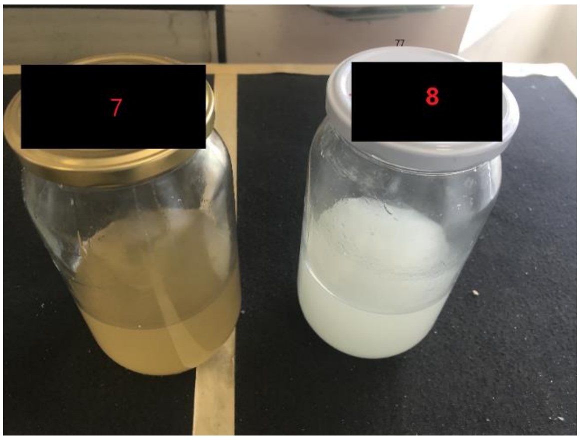


Figure 3. 8 Obtained prepolymer samples.

3.3.2 Synthesis of polyester polyol with neopentyl glycol

Synthesis steps of the polyester polyol with neopentyl glycol are summarized below.

1..Before the heating, 560 g trimethylolpropane, 4 kg diethylene glycol and 300 g neopentyl glycol have been put into the reactor and the mixer turned on.

2. Heating set 100 °C to prevent the escape of glycol from the reaction medium. 8 kg adipic acid was added to the reactor.

3. When the acid value reached between 70-60 mg KOH/g, a 2 g tin catalyst was added to the reactor.

4. By observing the upper column temperature vacuum increased slowly and kept in 680-730 mmHg intervals.

5.Cooling sequence started after completion.

After the synthesis obtained polyester polyol has an OH value of 62.7 mg KOH/g while having an acid value of 0.05 mg KOH/g.

The polyester polyol reactor system is shown in Figure 3.9.

Figure 3. 9 Polyester polyol reactor.

4. RESULT AND DISCUSSIONS

4.1 Synthesis Prepolymers With 4,4’-MDI, Carbodiimide Modified MDI, OP50 MDI and Base Polyester Polyol

The reaction between 4,4’- MDI, carbodiimide modified MDI and base polyester polyol shown in Figure 4.1.

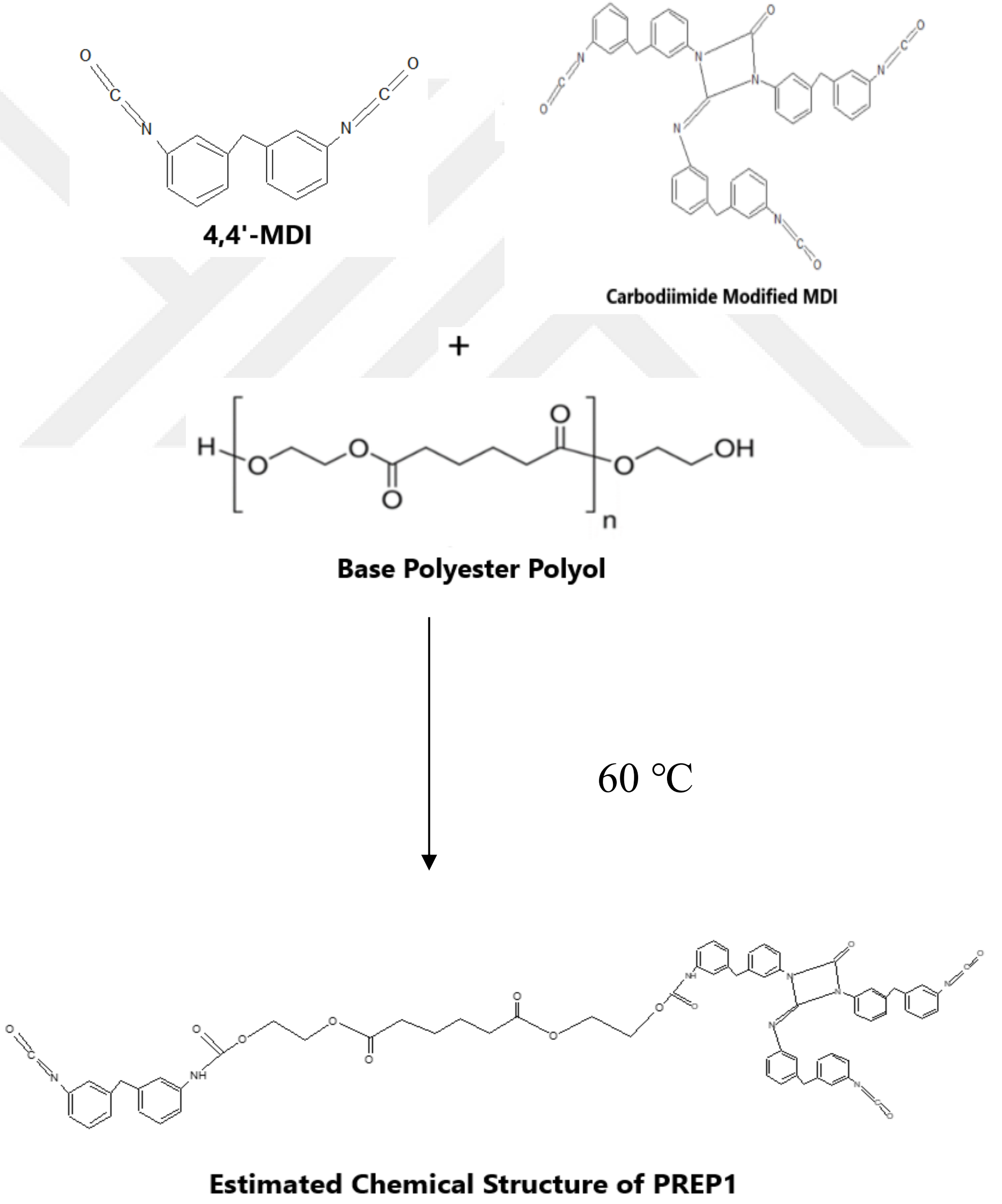


Figure 4. 1 Prepolymer synthesis reaction between 4,4’- MDI, modified MDI and base polyester polyol.

The reaction between 4,4’- MDI, carbodiimide modified MDI , OP50 and base polyester polyol shown in Figure 4.2.

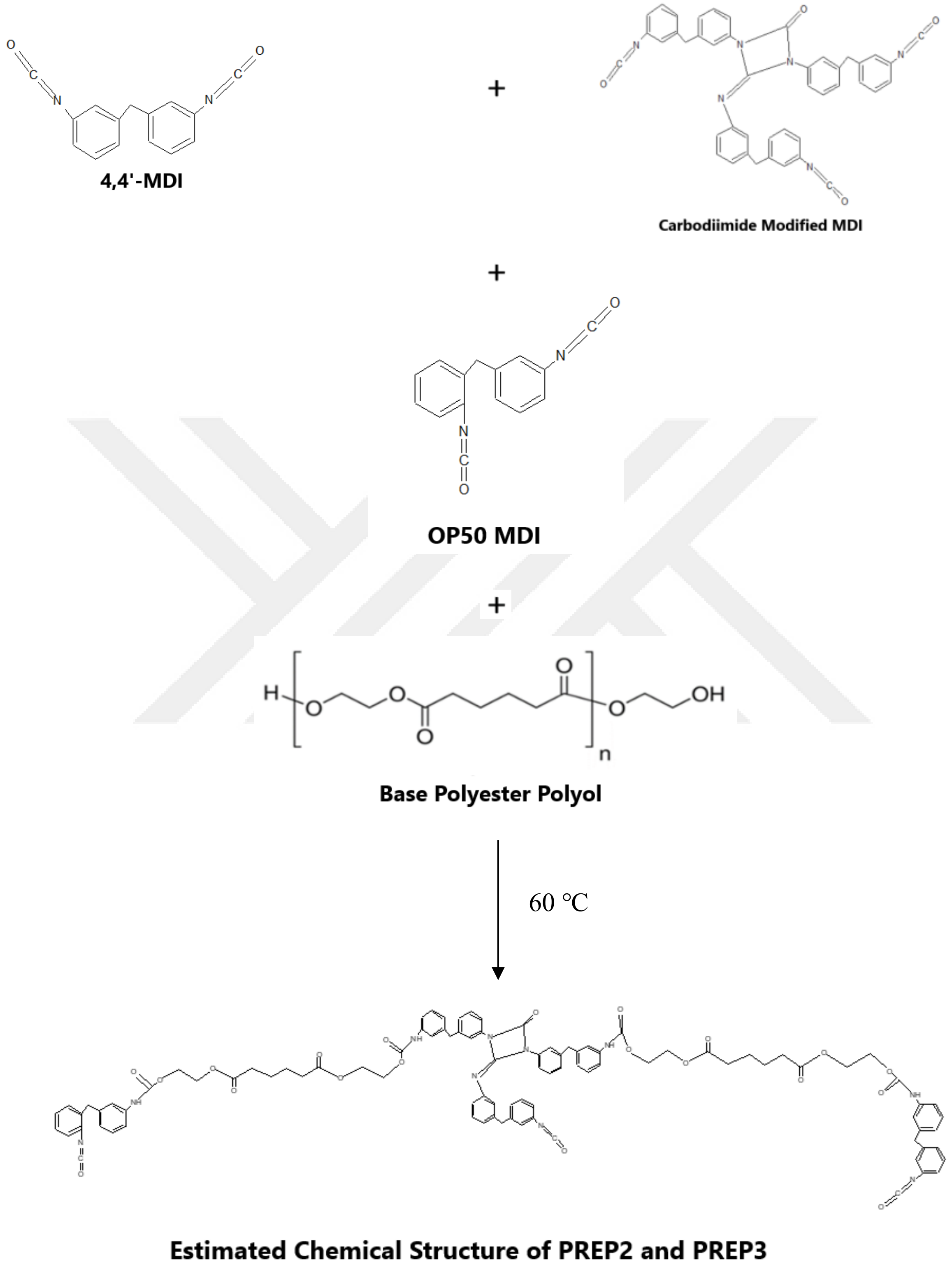


Figure 4. 2 Prepolymer Synthesis Reaction between 4,4’- MDI, modified MDI, OP50 and base polyester polyol.

Compositions of synthesized prepolymers are summarized in Table 4.1.

Table 4. 1 Composition of PREP1,PREP2 and PREP3.

Prepolymer No.	4,4’- MDI	Carbodiimide Modified MDI	OP50 MDI	Base polyester polyol
PREP1 (Ref)	65-72 %	3-7 %	0 %	23-30 %
PREP2	61-68 %	5-10 %	1-4 %	23-30 %
PREP3	61-68 %	1-4 %	5-10 %	23-30 %

After the synthesis, the specimen’s free NCO percentage and viscosity at 40 °C were measured. Results are shown in Table 4.2.

Table 4. 2 Viscosity and free NCO amount of PREP1,PREP2 and PREP3.

Prepolymer No.	Viscosity (40°C) (CPa)	Free NCO Percentage (%)
PREP1	300	22.40
PREP2	335	22.54
PREP3	320	22.53

To observe the effect of the arrangement of carbodiimide and OP50 in the prepolymer, NCO percentages should be similar to each other. Different NCO percentages, especially lower values, will affect the crystallinity and lower the total MDI content in the prepolymer. Therefore, observations won’t be consistent for analysis.

Besides free NCO percentage, isocyanate amount can be monitored from IR spectroscopy by looking at 2250 cm^{-1} isocyanate (N=C=O) peak. According to the IR spectrum in Figure 4.3, all samples show the same height of the peak at 2245 cm^{-1}. At 1730 cm^{-1} strong C=O stretching was observed due to carbonyl groups contributed to prepolymer backbone by polyester polyol. At 1522 cm^{-1} strong N-O stretching peak of nitro compounds was observed due to H-N-O urethane bonds found in the prepolymer backbone. At 1350 and 1380 cm^{-1} C-H and C-O stretching was observed due to polyester polyol.

From the results in Table 4.2 and IR spectrum, free NCO percentages were found similar to each other. After reaching this conclusion, DSC analysis was applied to samples to obtain crystallization and melting temperatures.

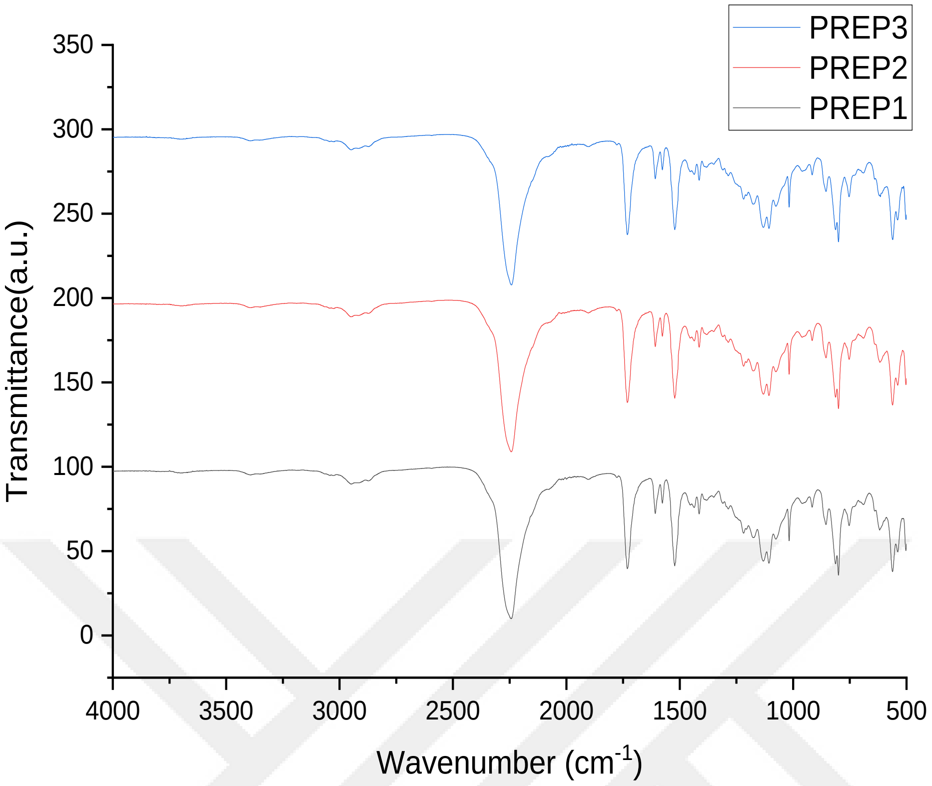


Figure 4. 3 IR Spectrum of PREP1, PREP2 and PREP3.

Tm, Tc starting point of crystallization and melting obtained from the DSC analysis. From Figure 4.4, 1.61 °C Tc of PREP1 decreased in PREP2 to -4.55 °C . This value increased in PREP3 to 7.39 °C .

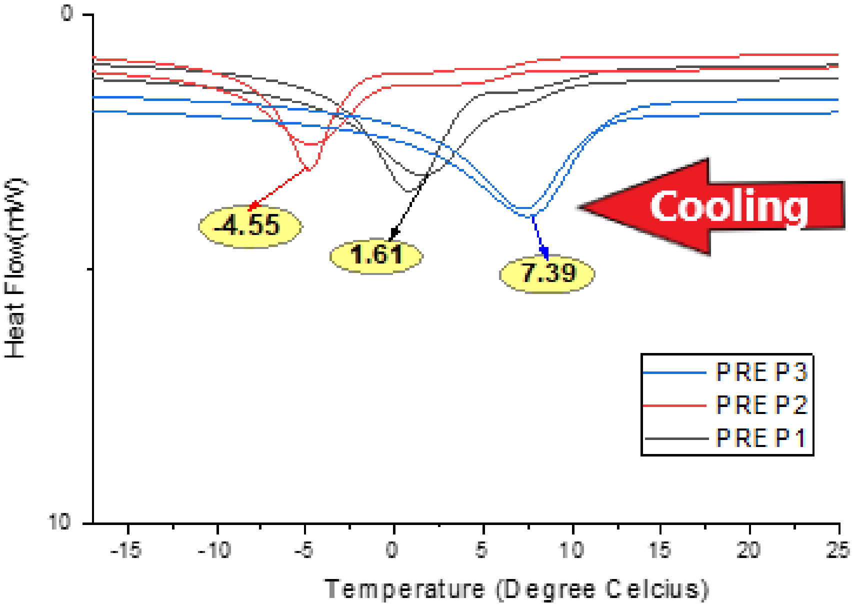


Figure 4. 4 Tc values of PREP1, PREP2 and PREP3.

From Figure 4.5, 29.81°C Tm of PREP1 decreased in PREP2 to 27.90 °C . This value increased in PREP3 to 31.31 °C .

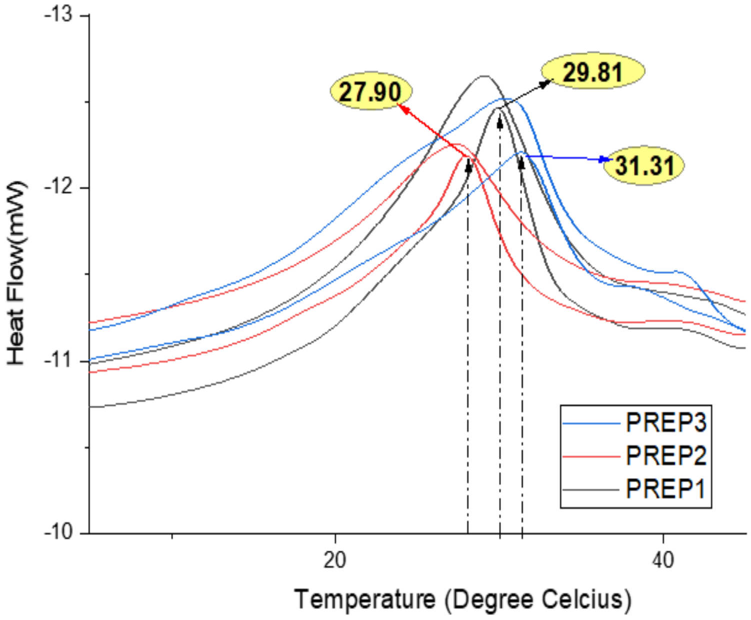


Figure 4. 5 Tm values of PREP1, PREP2 and PREP3.

Starting points of melting and crystallization of PREP1, PREP2 and PREP3 are shown in Figure 4.6, Figure 4.7, Figure 4.8, Figure 4.9, Figure 4.10 and Figure 4.11 respectively.

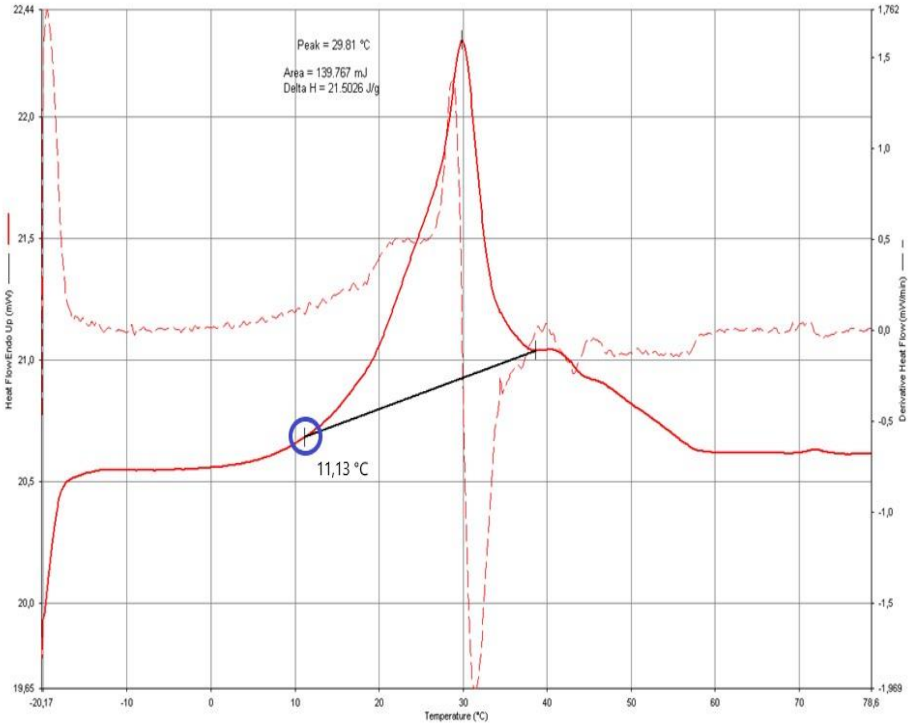


Figure 4. 6 Starting point of melting in PREP1.

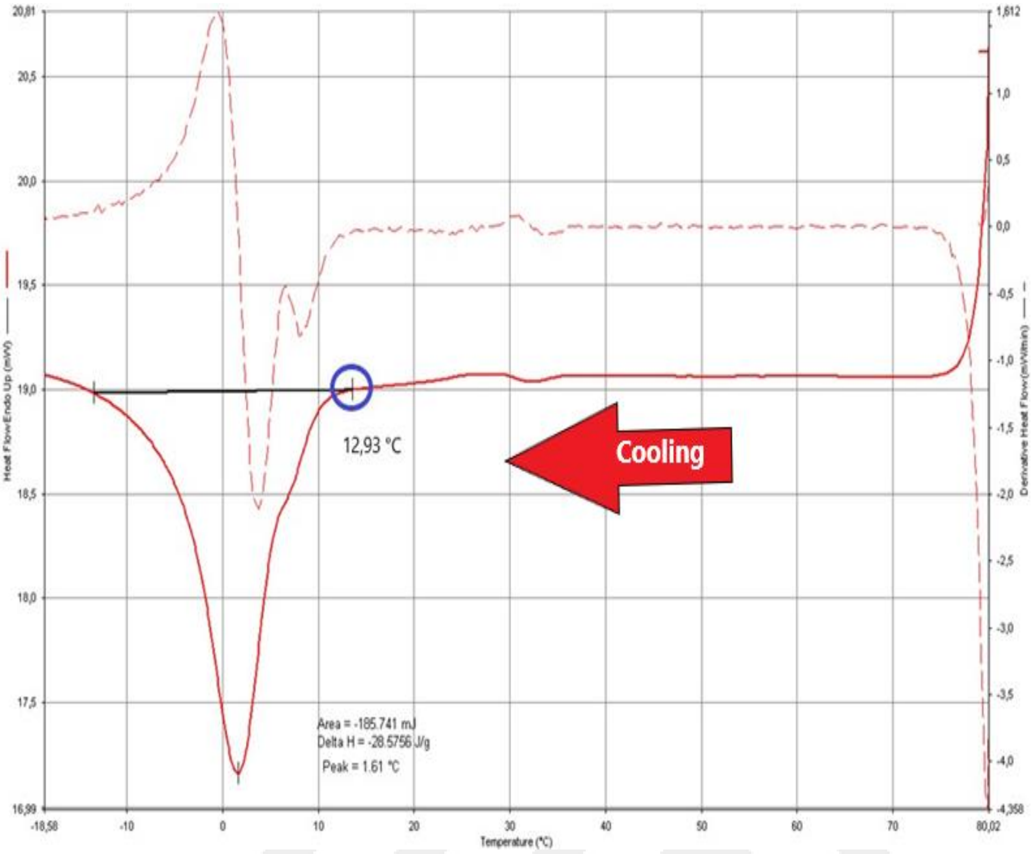


Figure 4. 7 Starting point of crystallization in PREP1.

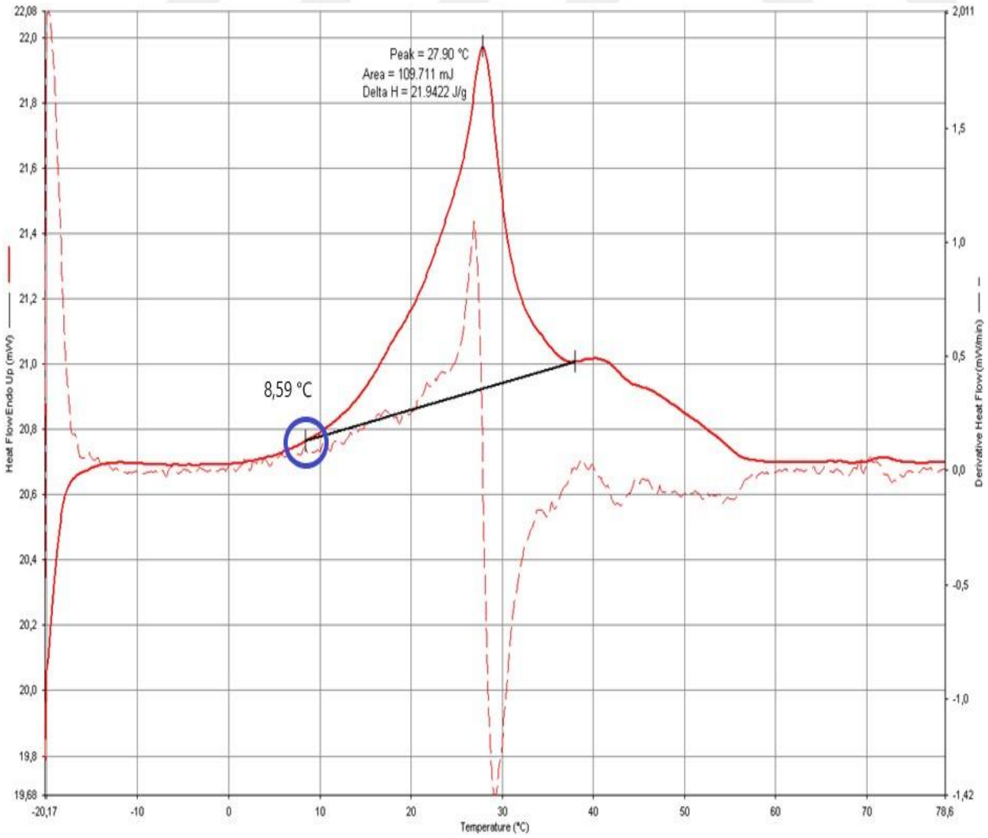


Figure 4. 8 Starting point of melting in PREP2.

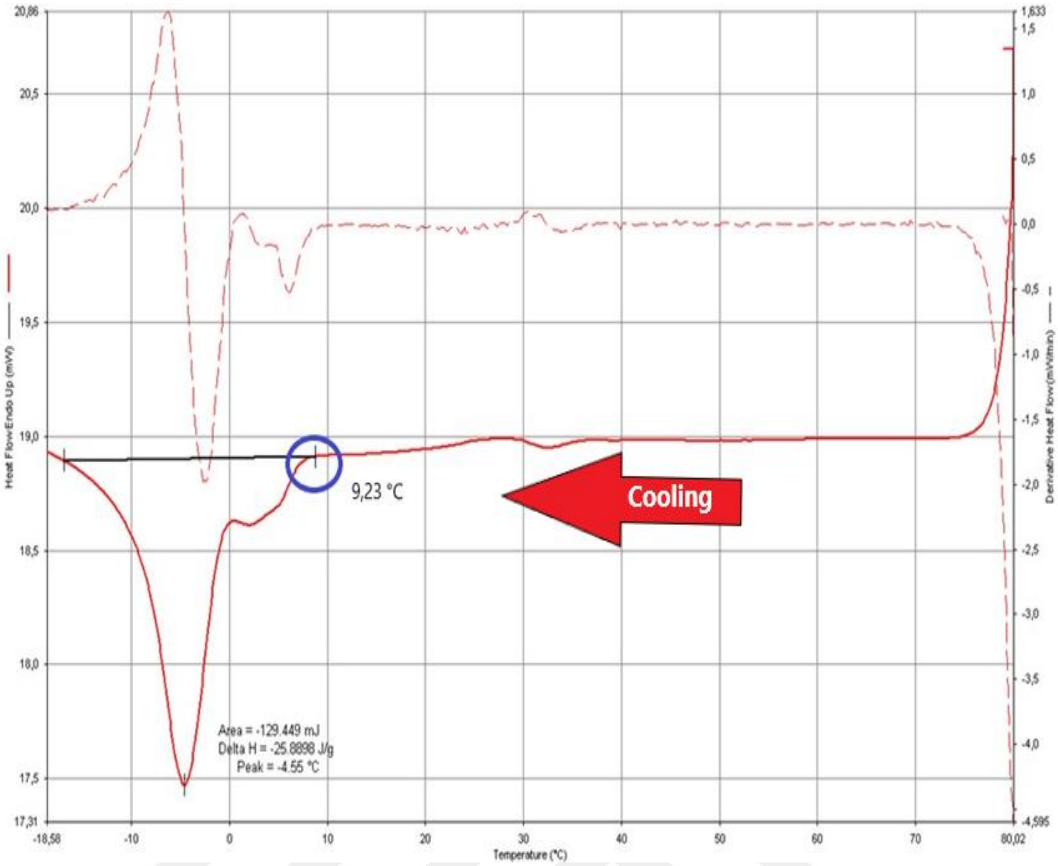


Figure 4. 9 Starting point of crystallization in PREP2.

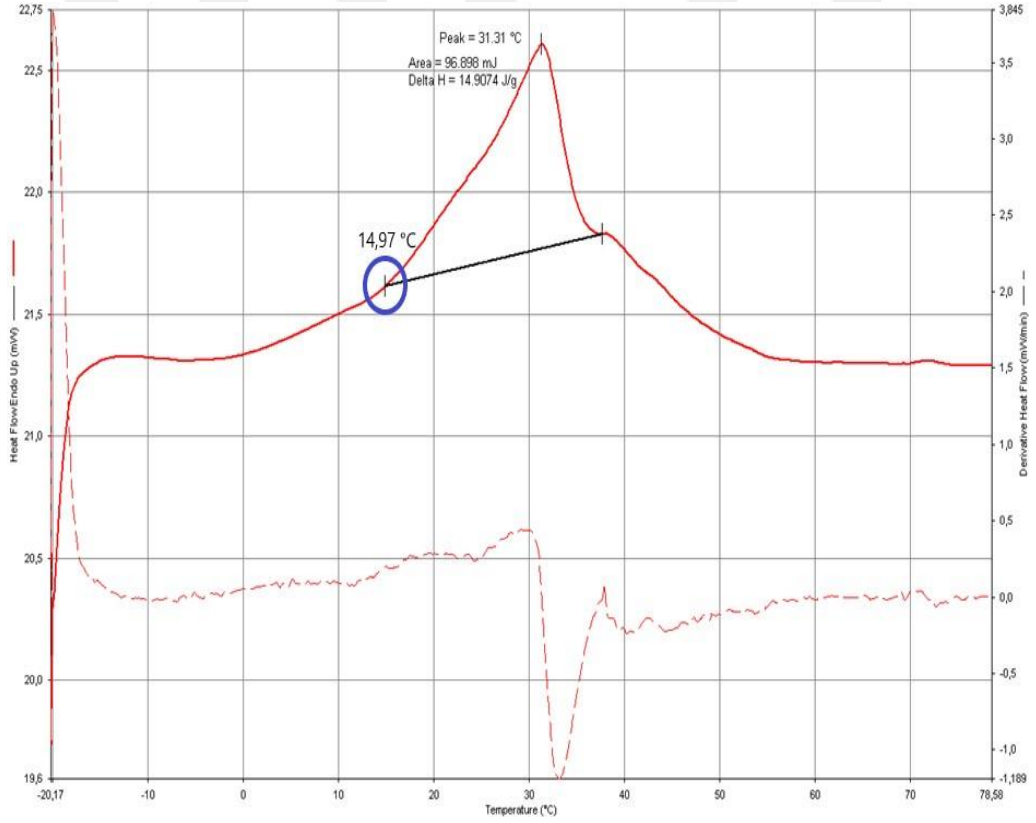


Figure 4. 10 Starting point of melting in PREP3.

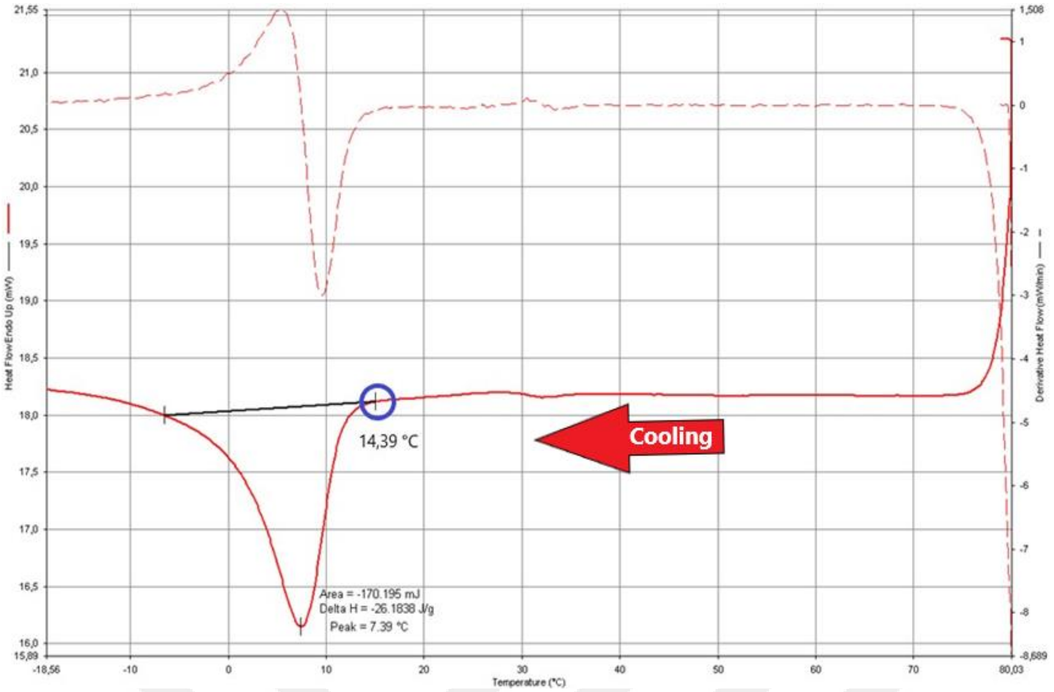


Figure 4. 11 Starting point of crystallization in PREP3.

All of the obtained values summarized in Table 4.3 and Table 4.4.

Table 4. 3 Tm, Tc, ΔHm and ΔHC of PREP1, PREP2 and PREP3.

Prepolymer No.	Melting Point (°C)	Enthalpy of melting (ΔH) (J/g)	Crystallization Point (°C)	Enthalpy of Crystallization (ΔH) (J/g)
PREP1	29.81	21.5026	1.61	-28.5766
PREP2	27.90	21.9422	-4.55	-25.8898
PREP3	31.31	14.9074	7.39	-26.1838

Table 4. 4 Starting point of melting and crystallization in PREP1, PREP2 and PREP3.

Prepolymer No.	Starting point of crystallization (°C)	Starting point of melting (°C)
PREP1	12.93	11.13
PREP2	9.23	8.59
PREP3	14.39	14.97

According to results, the carbodiimide modified MDI both decreased melting and crystallization points significantly while lowering starting points of melting and crystallization. However, OP50 MDI increased both melting and crystallization point while increasing starting points of melting and crystallization.

4.2 Synthesis of Prepolymers With 4,4’-MDI, Carbodiimide Modified MDI, OP50 MDI and Base Polyester Polyol

The reaction between 4,4’- MDI, carbodiimide modified MDI and base polyester polyol is shown in Figure 4.12.

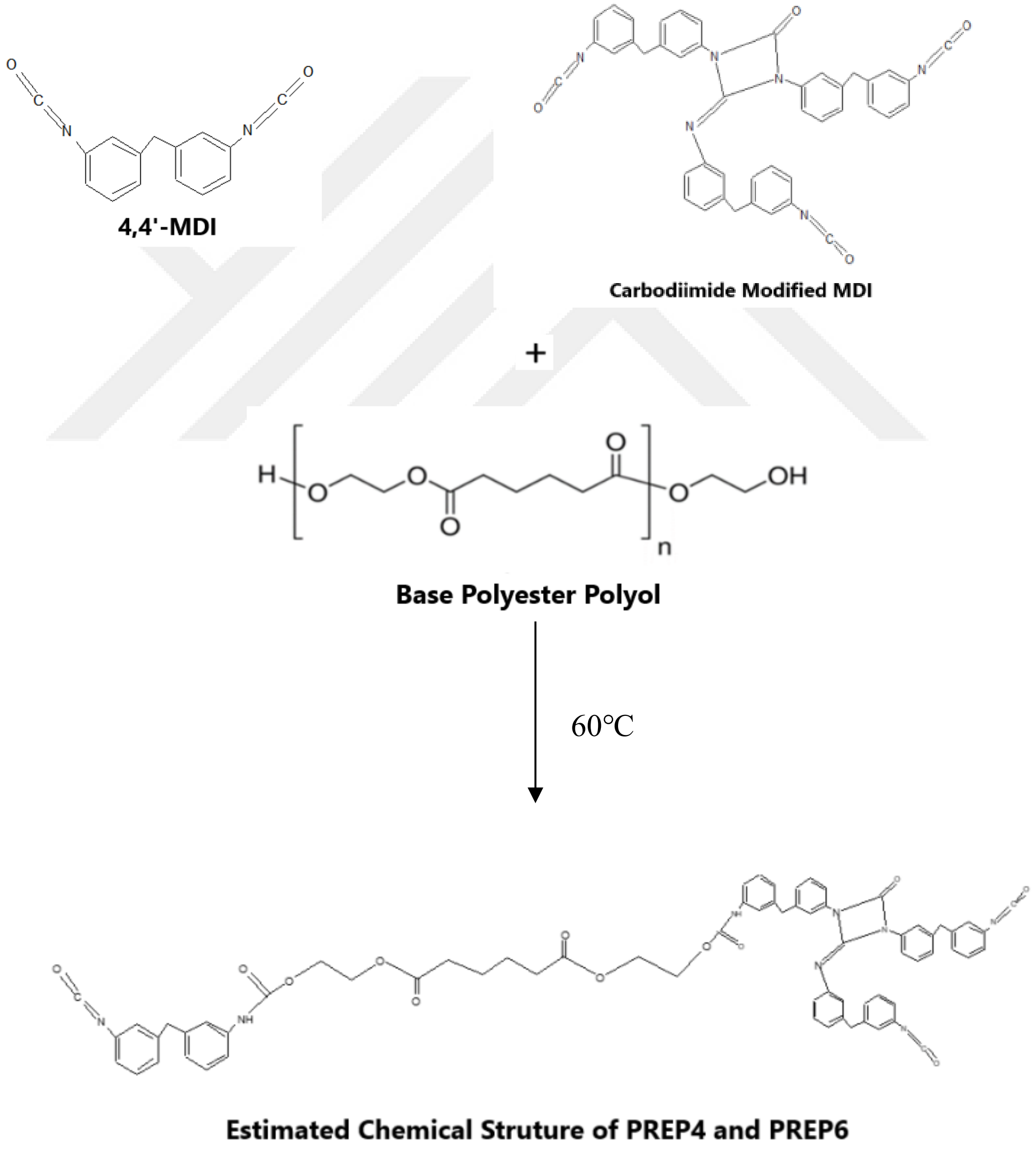


Figure 4. 12 Prepolymer Synthesis Reaction between 4,4’- MDI, modified MDI and base polyester polyol.

The reaction between 4,4’- MDI, carbodiimide modified MDI, OP50 and the base polyester polyol is shown in Figure 4.13.

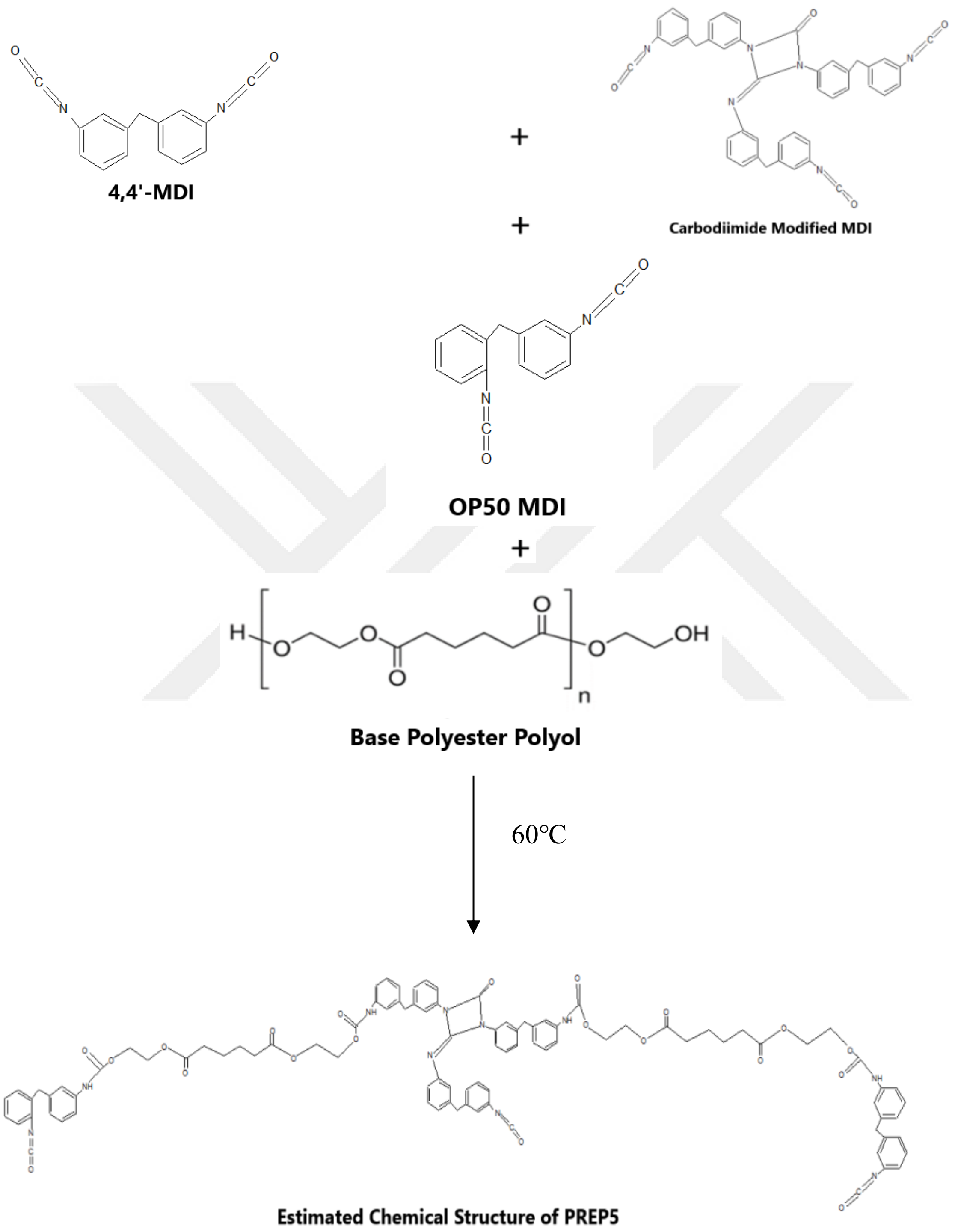


Figure 4. 13 Prepolymer Synthesis Reaction between 4,4’- MDI, modified MDI, OP50 and base polyester polyol.

Compositions of synthesized prepolymers are summarized in Table 4.5.

Table 4. 5 Composition of PREP4,PREP5 and PREP6.

Prepolymer No.	4,4’-MDI	Carbodiimide Modified MDI	OP50 MDI	Base polyester polyol
PREP4	61-68 %	7-12 %	0 %	23-30 %
PREP5	61-68 %	3-7 %	2-6 %	23-30 %
PREP6	63-70 %	3-7 %	0 %	25-32 %

After the synthesis, the specimen’s free NCO percentage and viscosity at 40 °C were measured. Results are shown in Table 4.6.

Table 4. 6 Viscosity and free NCO amount of PREP4, PREP5 and PREP6.

Prepolymer No.	Viscosity (40°C) (CPa)	Free NCO Percentage (%)
PREP4	305	22.68
PREP5	305	22.72
PREP6	435	21.58

According to the IR spectrum in Figure 4.14, all samples show the same height of the peak at 2245 cm^{-1}. At 1730 cm^{-1} strong C=O stretching was observed due to carbonyl groups contributing to prepolymer backbone by polyester polyol. At 1522 cm^{-1} strong N-O stretching peak of nitro compounds was observed due to H-N-O urethane bonds found in the prepolymer backbone. At 1350 and 1380 cm^{-1} C-H and C-O stretching was observed due to polyester polyol.

From the results in Table 23, Table 24 and IR spectrum, free NCO amounts were found similar to each other.

After reaching this conclusion, DSC analysis was applied to samples to obtain crystallization and melting temperatures. Tm, Tc starting point of crystallization and melting obtained from the DSC analysis.

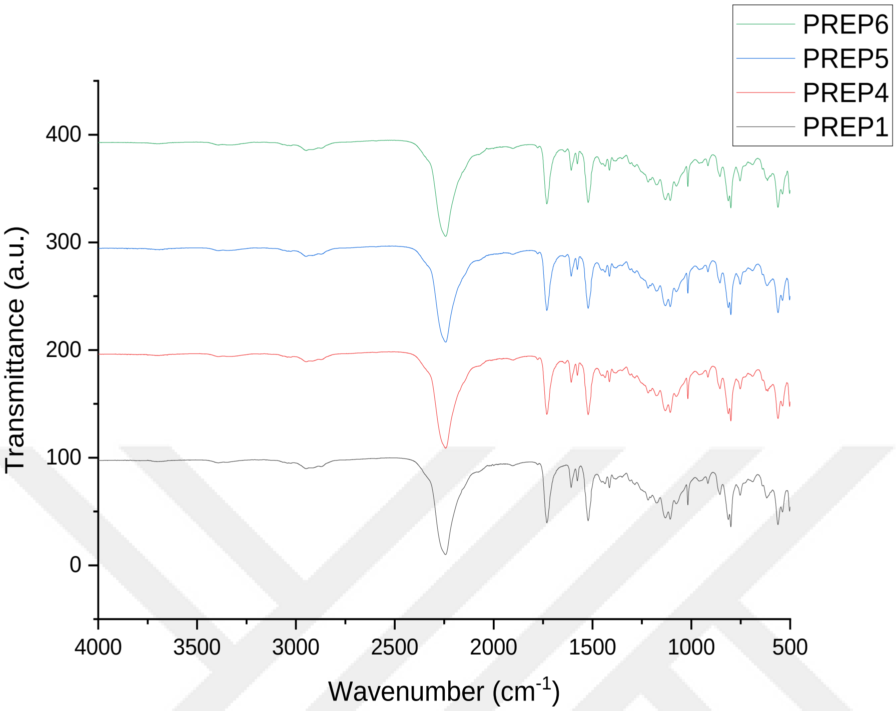


Figure 4. 14 IR Spectrum of PREP1, PREP4, PREP5 and PREP6.

From Figure 4.15, 1.61 °C Tc of PREP1 decreased in PREP4 to -6.47 °C . PREP5 decreased the Tc to -1.18 °C . By lowering the free NCO amount by 1 point (PREP6) Tc decreased to -2.23 °C .

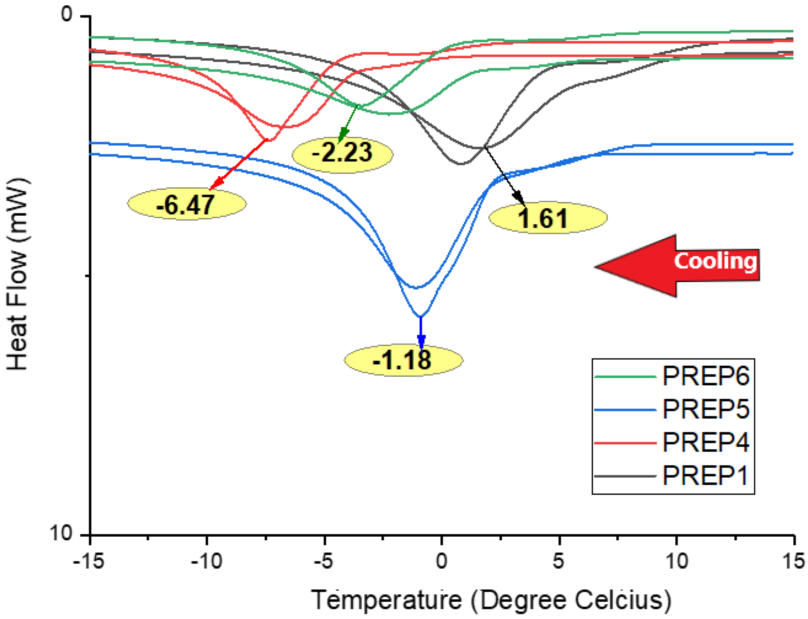


Figure 4. 15 Tc values of PREP1, PREP4, PREP5 and PREP6.

From Figure 4.16, 29.81 °C Tm of PREP1 decreased in PREP4 to 27.23 °C . PREP5 decreased the Tm to 27.97 °C . By lowering the free NCO amount by 1 point (PREP6) Tm decreased to 28.99 °C .

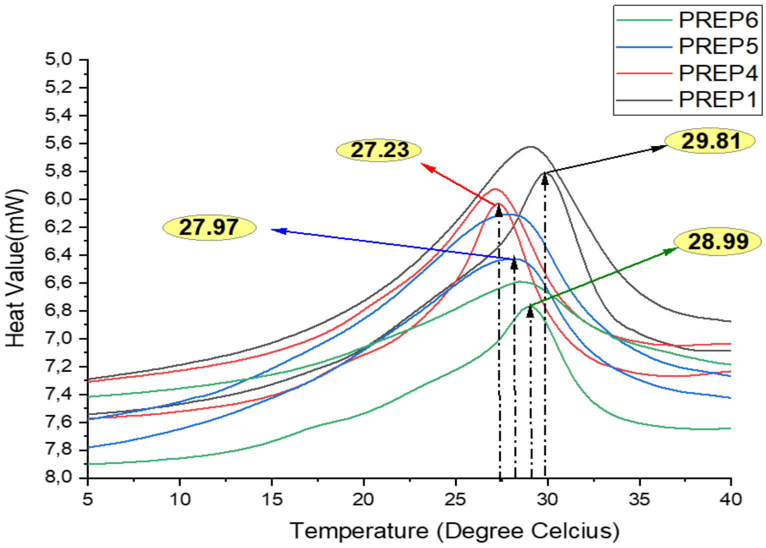


Figure 4. 16 Tm values of PREP1, PREP4, PREP5 and PREP6.

Starting points of melting and crystallization of PREP4, PREP5 and PREP6 are shown in Figure 4.17, Figure 4.18, Figure 4.19, Figure 4.20, Figure 4.21 and Figure 4.22 respectively.

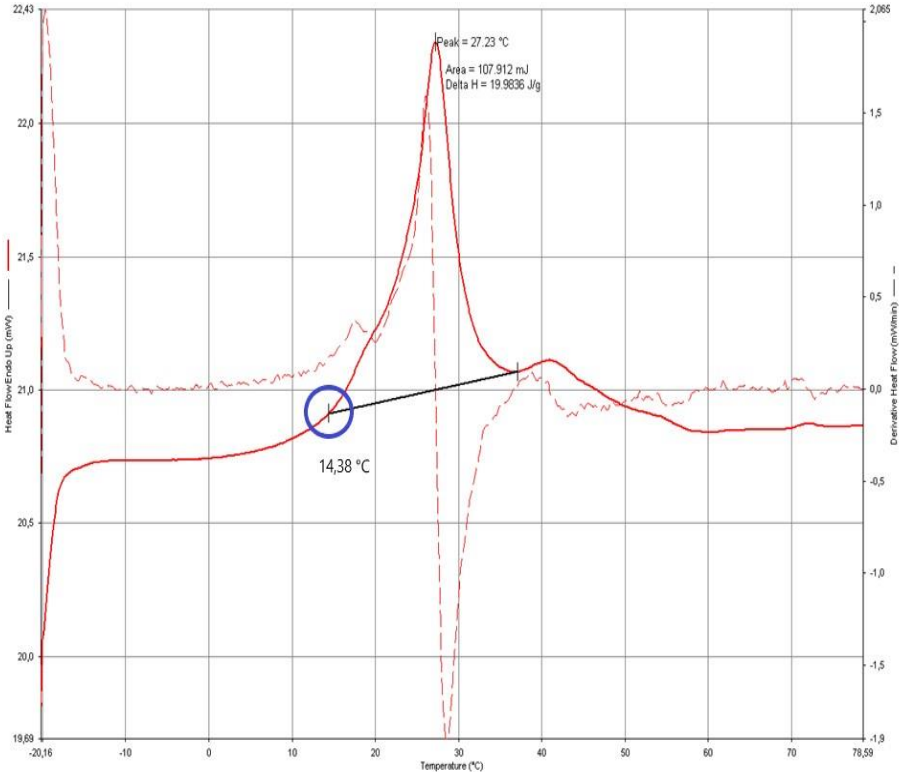


Figure 4. 17 Starting point of melting in PREP4.

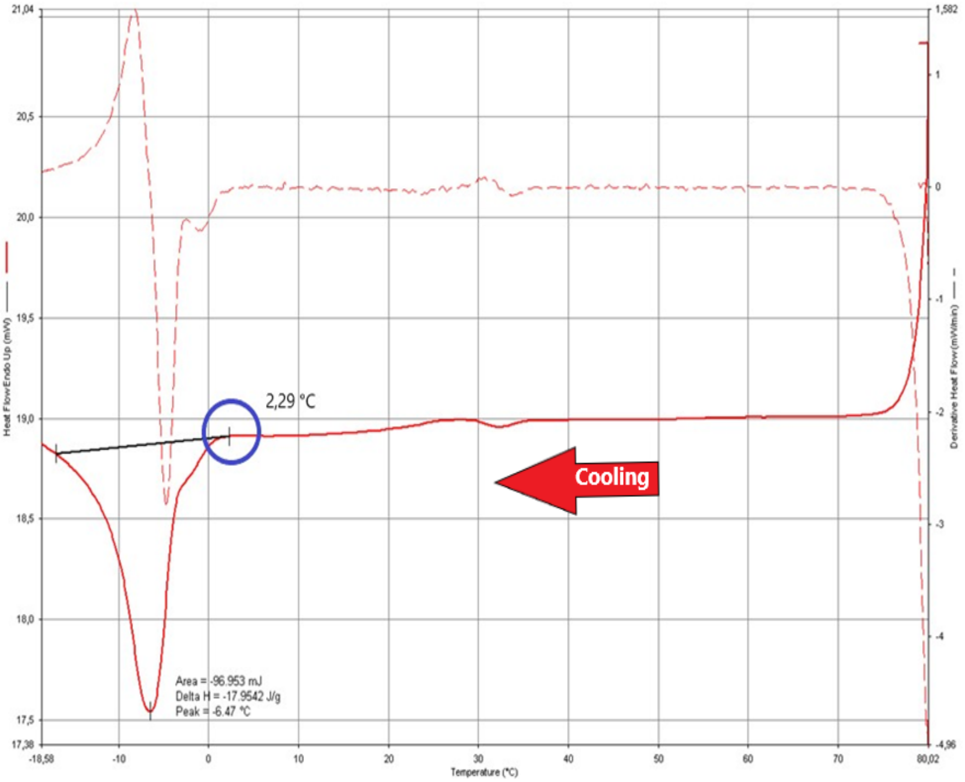


Figure 4. 18 Starting point of crystallization in PREP4.

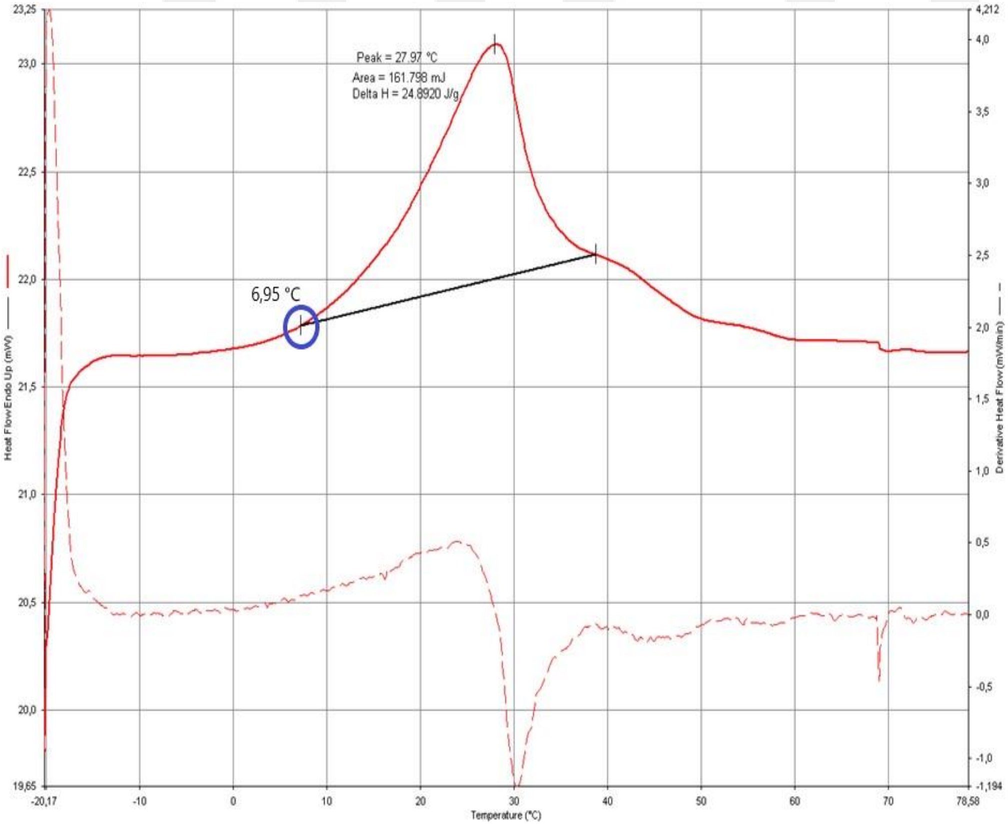


Figure 4. 19 Starting point of melting in PREP5.

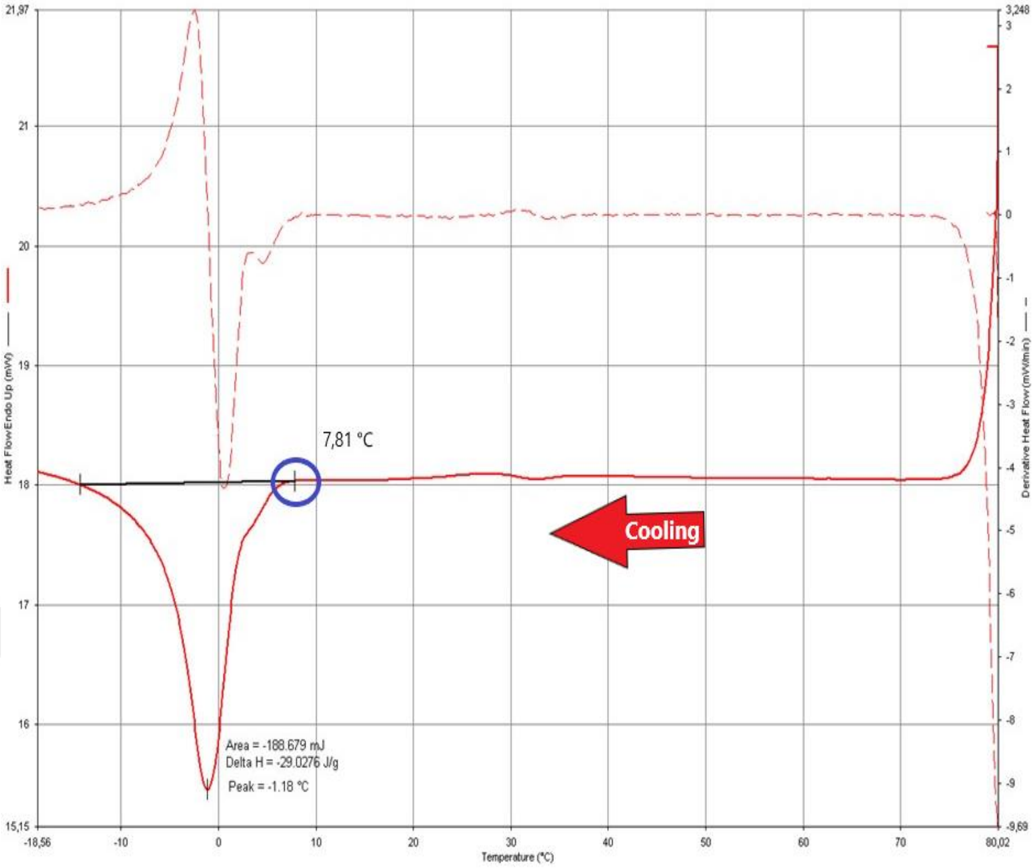


Figure 4. 20 Starting point of crystallization in PREP5.

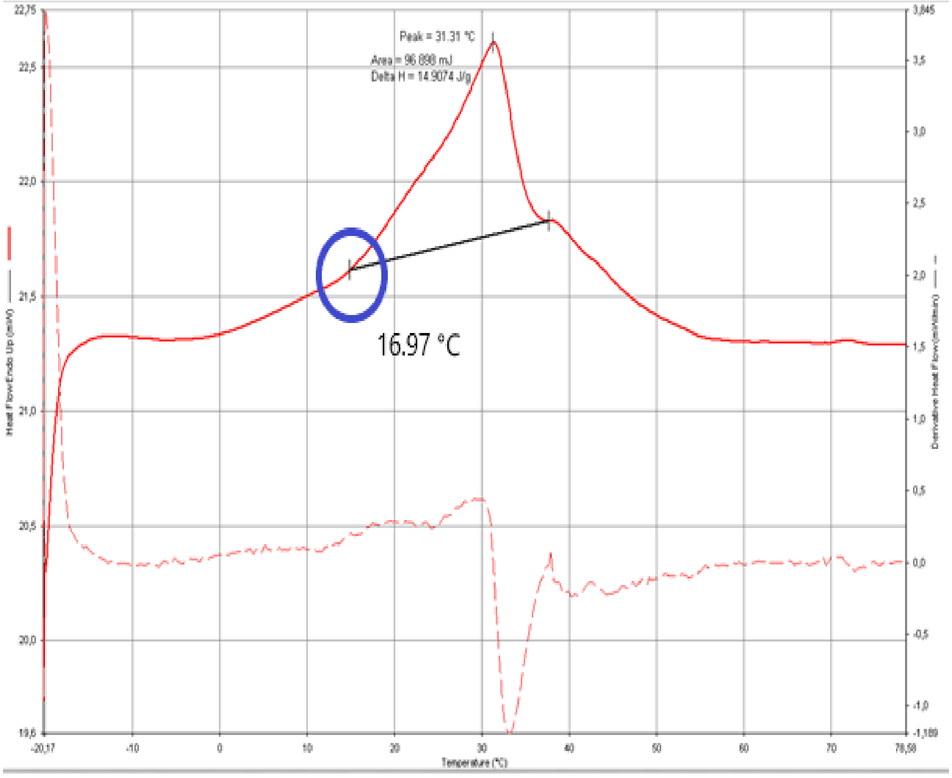


Figure 4. 21 Starting point of melting in PREP6.

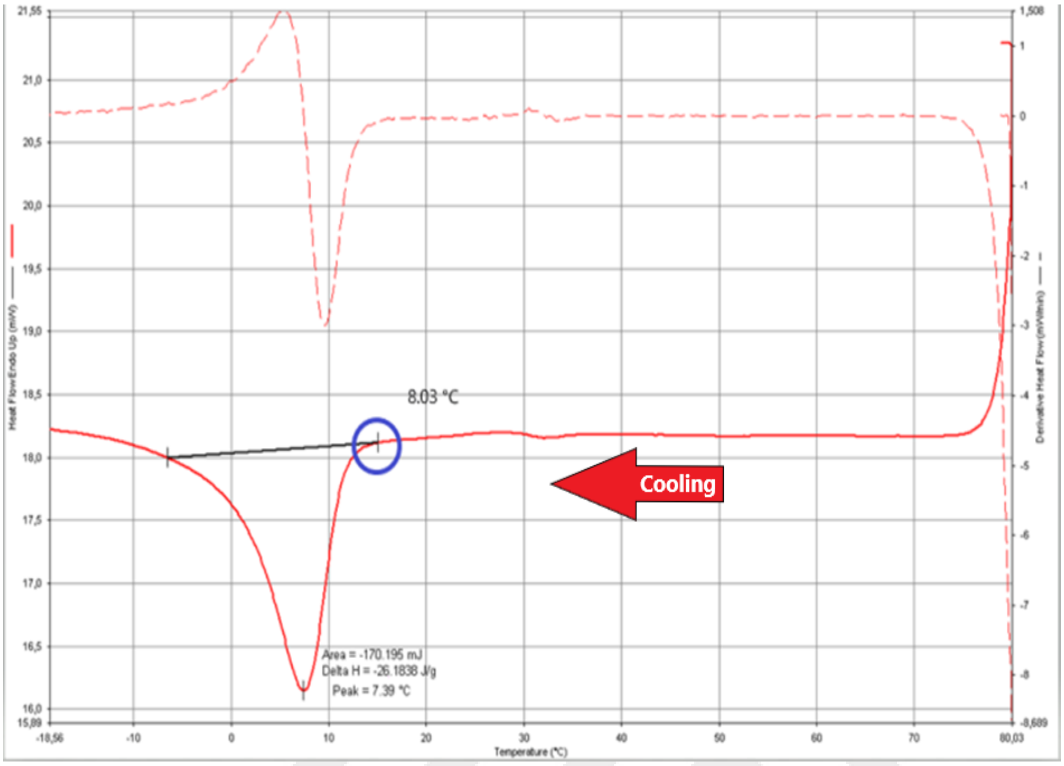


Figure 4. 22 Starting point of crystallization in PREP6.

All of the obtained values are summarized in Table 4.7 and Table 4.8.

Table 4. 7 Tm, Tc, ΔHm and ΔHC of Samples PREP1, PREP4, PREP5 and PREP6.

Prepolymer No.	Melting Point (°C)	Enthalpy of melting (ΔH) (J/g)	Crystallization Point (°C)	Enthalpy of crystallization (ΔH) (J/g)
PREP1	29.81	21.5026	1.61	-28.5766
PREP4	27.23	19.9836	-6.47	-17.9542
PREP5	27.97	24.892	-1.18	-29.0276
PREP6	28.99	13.1557	-2.23	-17.8322

Table 4. 8 Starting point of melting and crystallization in Samples PREP1, PREP4, PREP5 and PREP6.

Prepolymer No.	Starting point of crystallization (°C)	Starting point of melting (°C)
PREP1	12.93	11.13
PREP4	2.29	14.38
PREP5	7.81	6.95
PREP6	8.03	16.97

According to results, the addition of carbodiimide modified MDI in 7-12 % percentage of weight to prepolymer decreased both the melting and crystallization point to the lowest temperatures. Lowering the free NCO amount by 1 point significantly decreased the crystallization and melting point while lowering starting point of crystallization. However, it increased the starting point of melting.

Besides melting and crystallization points, starting points seem to be important to get an accurate analysis of effects.

4.3 Synthesis of Prepolymers With 4,4’-MDI, Carbodiimide Modified MDI, Base Polyester Polyol or Noepentyl Glycol Added Base Polyester Polyol and Dipropylene Glycol

The reaction between 4,4’- MDI, carbodiimide modified MDI and polyester polyol with neopentyl glycol is shown in Figure 4.23.

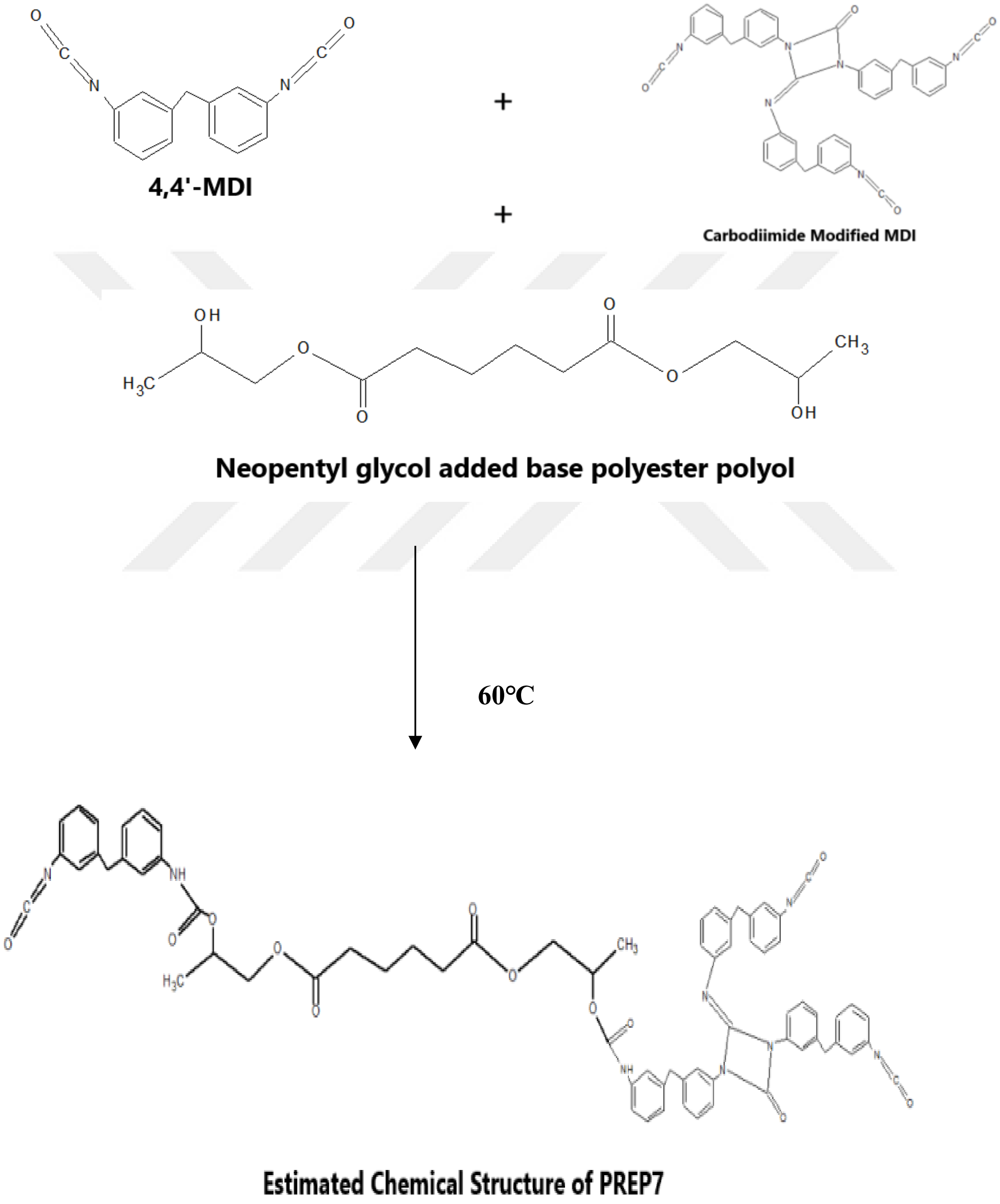


Figure 4. 23 Prepolymer Synthesis Reaction between 4,4’- MDI, modified MDI and polyester polyol with neopentyl glycol.

The reaction between 4,4’- MDI, carbodiimide modified MDI base polyester polyol and dipropylene glycol is shown in Figure 4.24.

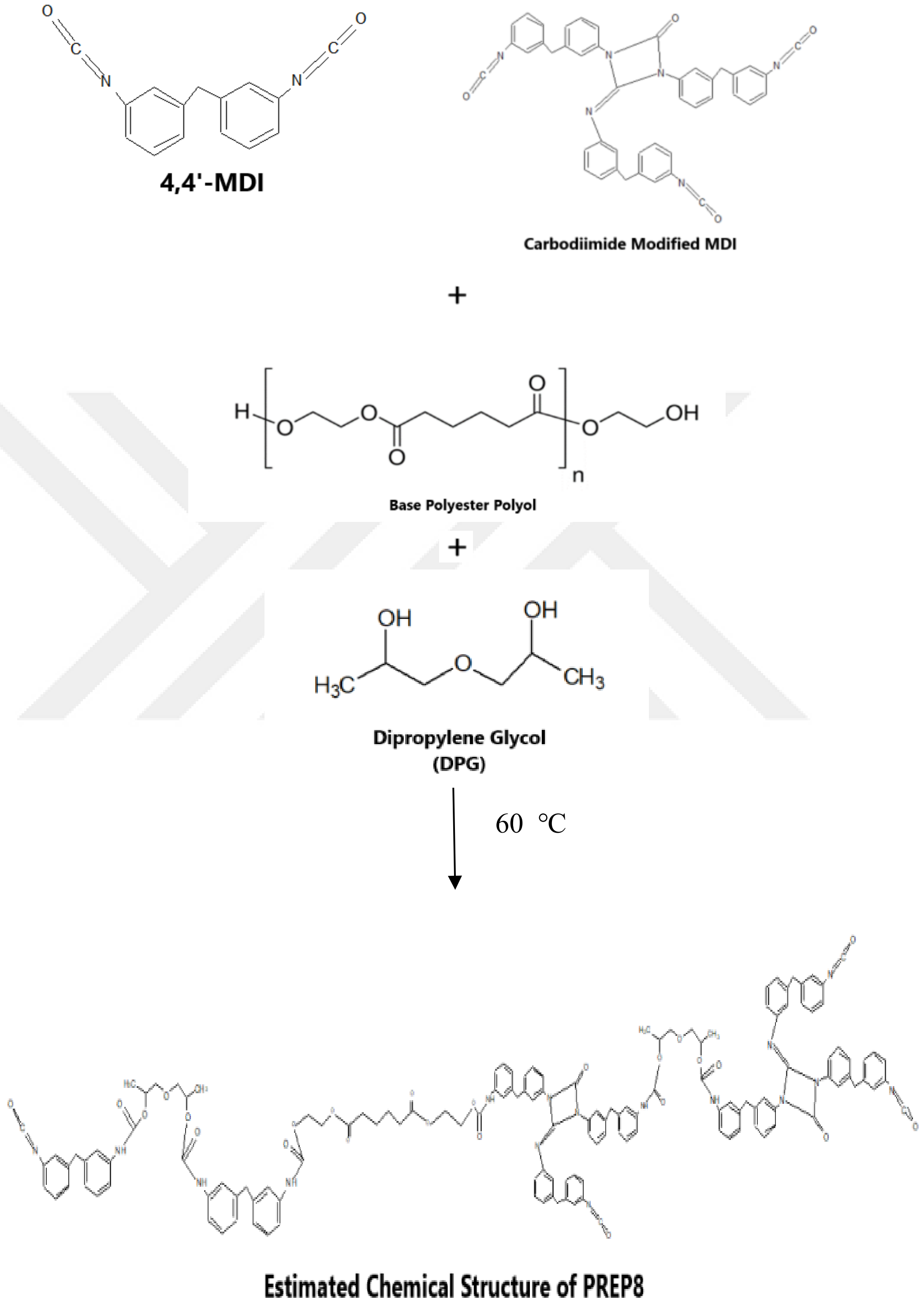


Figure 4. 24 Prepolymer Synthesis Reaction between 4,4’- MDI, modified MDI, base polyester polyol and DPG.

Compositions of synthesized prepolymers are summarized in Table 4.9.

Table 4. 9 Composition of PREP7 and PREP8.

Prepolymer No.	4,4’-MDI	Carbodiimide Modified MDI	OP50 MDI	Base polyester polyol	Neopentyl Glycol Added Base Polyester Polyol	Dipropylene Glycol
PREP7	65-72 %	3-7 %	0 %	0 %	23-30 %	0 %
PREP8	61-68 %	5-10 %	1-4 %	23-30 %	0 %	0.1-0.7 %

After the synthesis, the specimen’s free NCO percentage and viscosity at 40 °C were measured. Results are shown in Table 4.10.

Table 4. 10 Viscosity and free NCO amount of Samples PREP7 and PREP8.

Prepolymer No.	Viscosity (40°C) (CPa)	Free NCO Percentage (%)
PREP7	285	22.88
PREP8	365	22.44

According to the IR spectrum in Figure 4.25, PREP1 and PREP8 show the same height of the peak at 2245 cm^{-1} however due to the different OH value in polyester polyol with neopentyl glycol difference in isocyanate peak estimated. At 1730 cm^{-1} strong C=O stretching was observed due to carbonyl groups contributed to prepolymer backbone by polyester polyol. At 1522 cm^{-1} strong N-O stretching peak of nitro compounds was observed due to H-N-O urethane bonds found in the prepolymer backbone. At 1350 and 1380 cm^{-1} C-H and C-O stretching was observed due to polyester polyol. At 1176-1218 cm^{-1} stronger C-O stretching was observed due to bonds between tertiary carbons and OH end groups in neopentyl glycols.

At 1076 cm^{-1} C-O stretches in primary alcohols. Since base polyester polyol has more primary carbons than neopentyl glycol peak at 1076 cm^{-1} is sharper in PREP1 and PREP8 than PREP7.

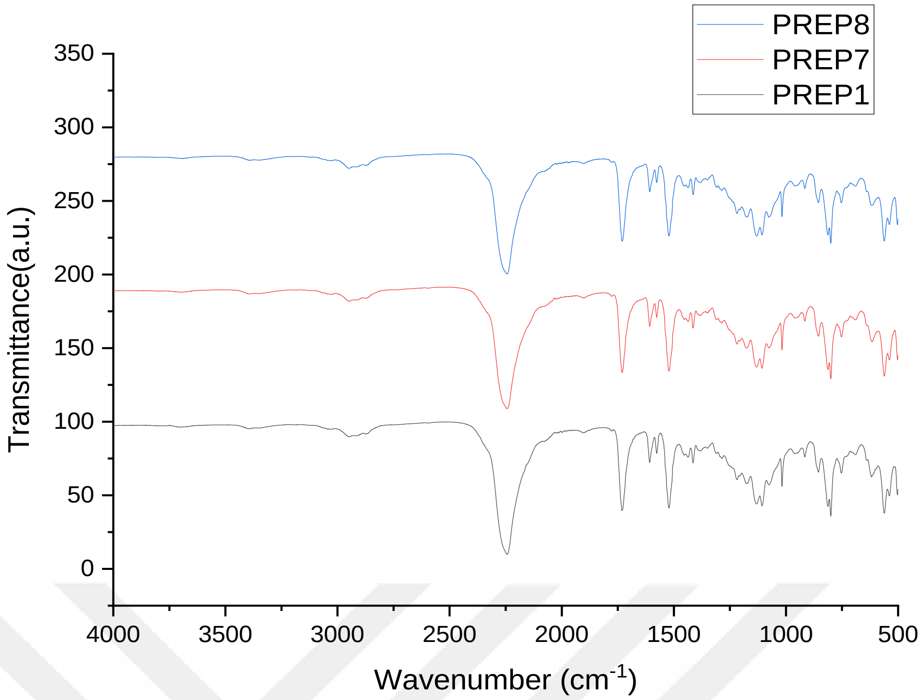


Figure 4. 25 IR Spectrum of PREP1, PREP7 and PREP8.

From the results in Table 27, Table 28 and IR spectrum, free NCO amounts were found similar to each other. After reaching this conclusion, DSC analysis was applied to samples to obtain crystallization and melting temperatures.

Tm, Tc starting point of crystallization and melting obtained from the DSC analysis. From Figure 4.26, 1.61 °C Tc of PREP1 increased to 2.36 °C in PREP7. This value decreased from PREP8 to 0.05 °C .

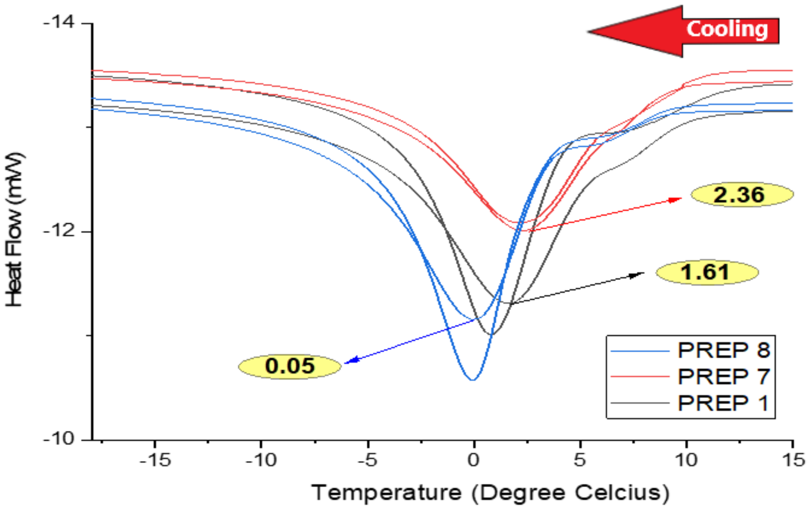


Figure 4. 26 Tc values of PREP1, PREP7 and PREP8.

From Figure 4.27, 29.81°C Tm of PREP1 increased to 30.15 °C in PREP7. This value decreased in PREP8 to 29.06 °C .

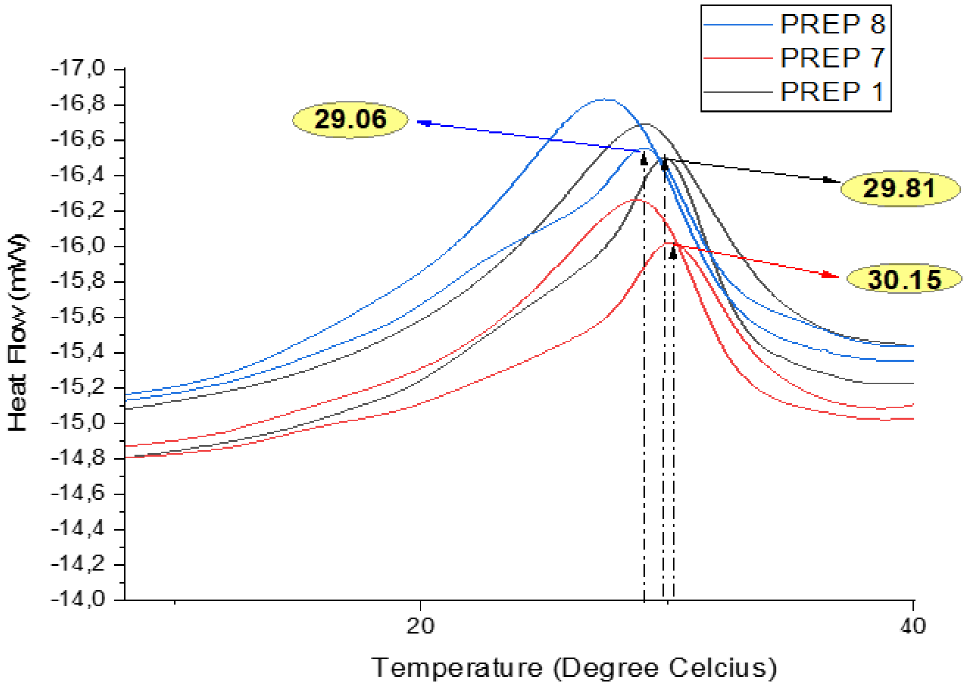


Figure 4. 27 Tm values of PREP1, PREP7 and PREP8.

Starting points of melting and crystallization of PREP7 and PREP8 are shown in Figure 4.28, Figure 4.29, Figure 4.30 and Figure 4.31 respectively.

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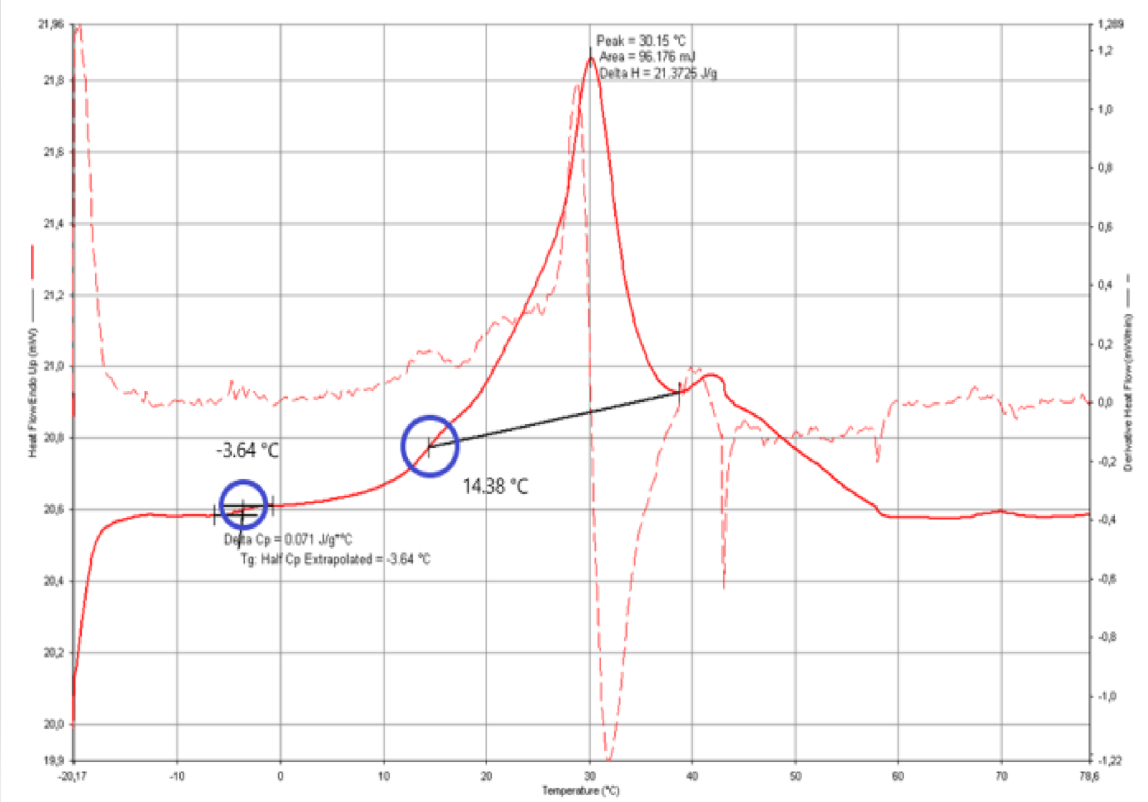


Figure 4. 28 Starting point of melting and Tg in PREP7.

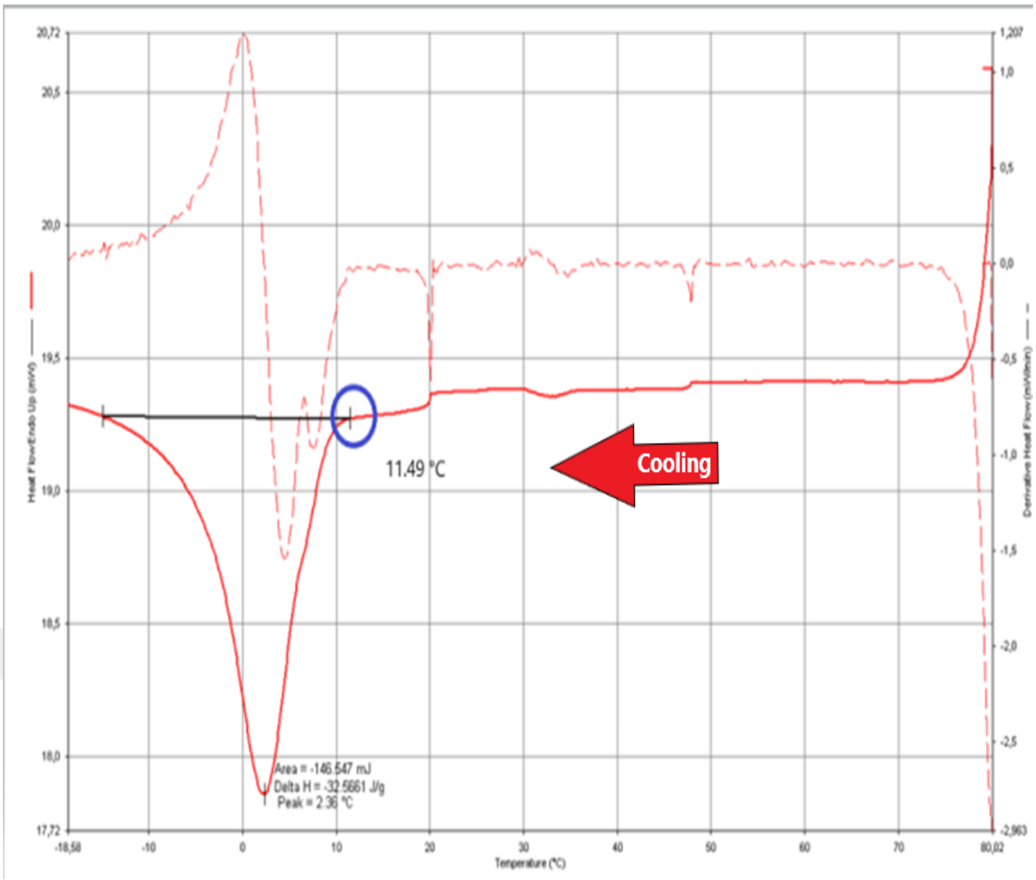


Figure 4. 29 Starting point of crystallization in PREP7.

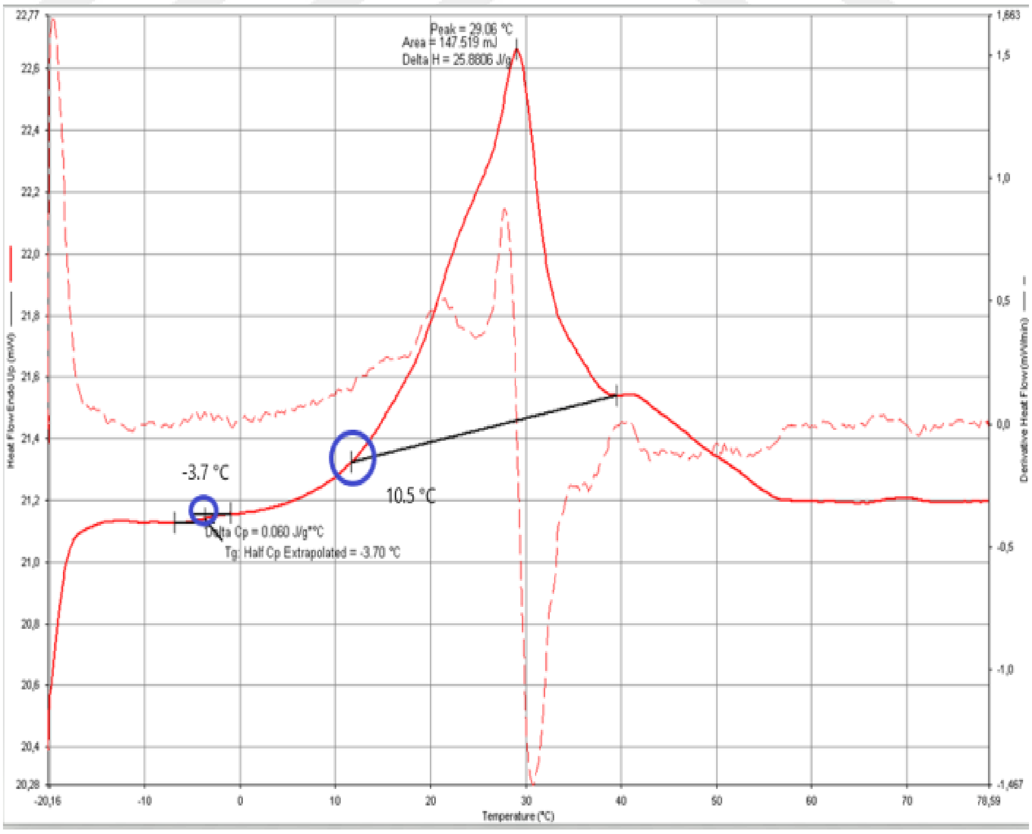


Figure 4. 30 Starting point of melting and Tg in PREP8.

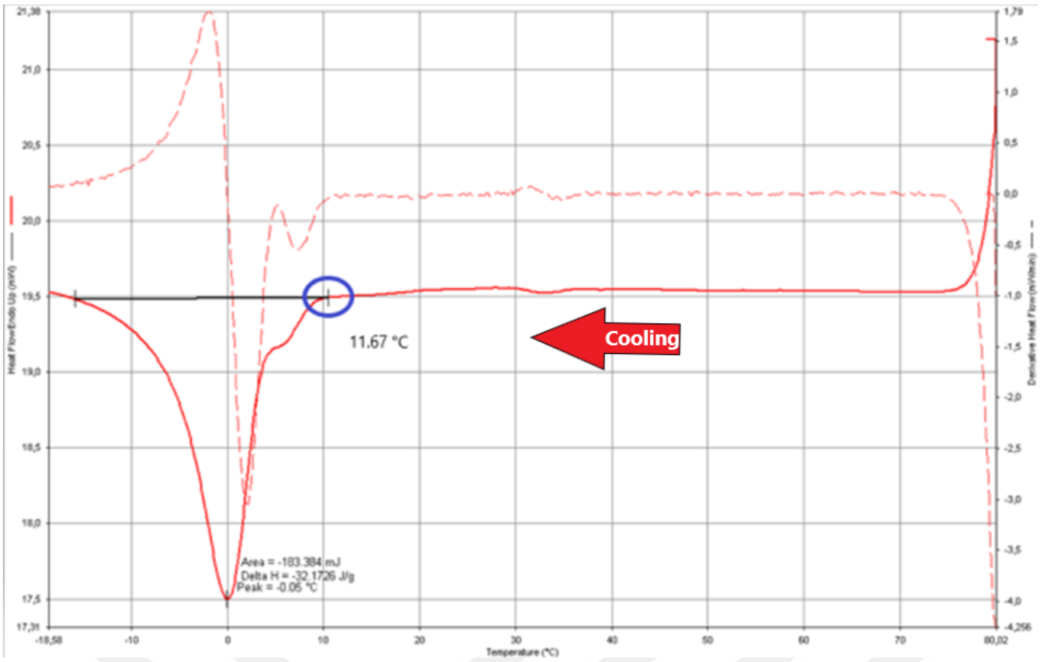


Figure 4. 31 Starting point of crystallization in PREP8.

All of the obtained values are summarized in Table 4.11 and Table 4.12.

Table 4. 11 Tm, Tc, ΔHm and ΔHC of Samples PREP1, PREP7 and PREP8.

Prepolymer No.	Melting Point (°C)	Enthalpy of Melting (ΔH) (J/g)	Crystallization Point (°C)	Enthalpy of Crystallization (ΔH) (J/g)
PREP1	29.81	21.5026	1.61	-28.5766
PREP7	30.15	21.3725	2.36	-32.5661
PREP8	29.06	25.8806	-0.05	-32.1726

Table 4. 12 Starting point of melting and crystallization in Samples PREP1, PREP7 and PREP8.

Prepolymer No.	Starting point of crystallization (°C)	Starting point of melting (°C)
PREP1	12.93	11.13
PREP7	11.49	14.38
PREP8	11.67	10.5

According to the results in Table 30, the addition of neopentyl glycol to prepolymer decreased the starting point of crystallization and increased the starting point of melting. The addition of DPG to prepolymer decreased both the crystallization and melting temperature.

Besides Tm and Tc, Tg was observed in DSC analysis and summarized in Table 4.13.

Table 4. 13 Tg and ΔCp of Samples PREP7 and PREP8.

Prepolymer No.	Glass Transition Temperature (°C)	ΔC_p (J/g**C)
PREP7	-3.64	0.071
PREP8	-3.7	0.060

4.4 Polyurethane Synthesis

After the examination of crystallization, polyurethane synthesized from PREP1 (PU1) and PREP4 (PU2), PREP2 (PU3) and PREP6 (PU4) to observe different scenarios in effect on mechanical properties.

For PU1;

Prepolymer and polyester polyol mixed in 1/1 ratio at 45 °C in shoe sole polyurethane casting machine. Working iso/poly ratio found as 118/100 in 6.2 mm penetration value.

For PU2;

Prepolymer and polyester polyol mixed in 1/1 ratio at 45 °C in shoe sole polyurethane casting machine. Working iso/poly ratio found as 119/100 in 5.5 mm penetration value.

For PU3;

Prepolymer and polyester polyol mixed in 1/1 ratio at 45 °C in shoe sole polyurethane casting machine. Working iso/poly ratio found as 119/100 in 6.7 mm penetration value.

For PU4;

Prepolymer and polyester polyol mixed in 1/1 ratio at 45 °C in shoe sole polyurethane casting machine. Working iso/poly ratio found as 120/100 in 6.9 mm penetration value.

Specific properties are recorded in Table 4.14 for PU1, PU2, PU3 and PU4 respectively.

Table 4. 14 Properties of PU1,PU2, PU3 and PU4.

Properties	PU1	PU2	PU3	PU4
Ratio (Iso/poly)	118/100	119/100	119/100	120/100
Cream time (second)	6	5	5.5	6
Tack Free Time (second)	27	25	27	28
Rise Time (second)	36	35	36	36
Free Rise Density (kg/m^3)	205	205	195	198
Molded Density (kg/m^3)	270-290	270-290	270-290	270-290

Synthesized polyurethane slipper sole is shown in Figure 4.32.

Figure 4. 32 Polyurethane slipper sole.

4.5 Mechanical Analysis

After the synthesis, polyurethanes are put into mechanical tests (compression set, tensile strength, tear resistance).

4.5.1 Compression set

Samples were prepared in the standard cubic form to take compression homogeneously. Samples are shown in Figure 4.33.

Figure 4. 33 Compresion set samples.

The initial height of samples was recorded as 16.88 cm for PU1 and PU2. 23.35 cm for PU3 and PU4 according to the method shown in Figure 4.34.

After the prepared samples were put into an oven at 70 °C with compression set equipment.

Figure 4. 34 Measurement method of height before compression.

Samples compressed at 50 % of their measured lengths. 50 % compression height is found in the formula below. PU1 and PU2 compressed to 8.40 cm and PU3 and PU4 compressed to 11.67 cm as shown in Figure 4.35.

$$Compression\ height\ for\ PU1\ and\ PU2 = \frac{(16.88 + 16.73)}{4} = 8.40\ cm$$

$$Compression\ height\ for\ PU3\ and\ PU4 = \frac{(23.40 + 23.30)}{4} = 11.67\ cm$$

Figure 4. 35 Compressed samples.

Samples were kept in a compression set for 24 hours. After 24 hours samples were taken from the oven and waited in ambient conditions for 30 minutes for recovery of elastic deformation. After 30 minutes, the height of samples was recorded according to the method shown in Figure 4.36.

Figure 4. 36 Measurement method of height after compression.

Permanent deformation of samples calculated from heights at initial and after compression.

For PU1;

$$Percentage\ of\ permanent\ deformation = \frac{(16.73 - 13.84)}{16.73} * 100 = 17.27\%$$

For PU2;

$$Percentage\ of\ permanent\ deformation = \frac{(16.88 - 13.98)}{16.88} * 100 = 17.18\%$$

For PU3;

$$Percentage\ of\ permanent\ deformation = \frac{(23.40 - 19.34)}{23.40} * 100 = 17.35\%$$

For PU4;

$$Percentage\ of\ permanent\ deformation = \frac{(23.30 - 17.87)}{23.30} * 100 = 23.30\%$$

According to the results, adding carbodiimide modified MDI and isomeric MDI did not create a significant change in the compression set. However, due to the softer structure since PU4 has fewer isocyanate hard segments (causes lower level of reinforcement and rebound) permanently deformed area seems to be increased.

4.5.2 Tensile test

Polyurethane samples were prepared for the tensile strength test as shown in Figure 4.37.

Figure 4. 37 Tensile test sample.

After the prepared samples were mounted on a tensile test mechanism. PU1, PU2, PU3 and PU4 during elongation and during the break shown in Figure 4.38, Figure 4.39, Figure 4.40 and Figure 4.41 respectively.

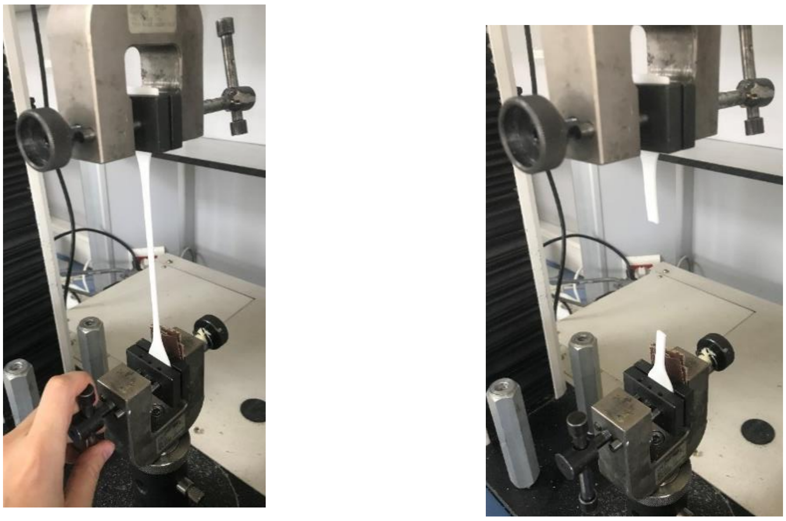


Figure 4. 38 PU1 sample during elongation and after breakage.

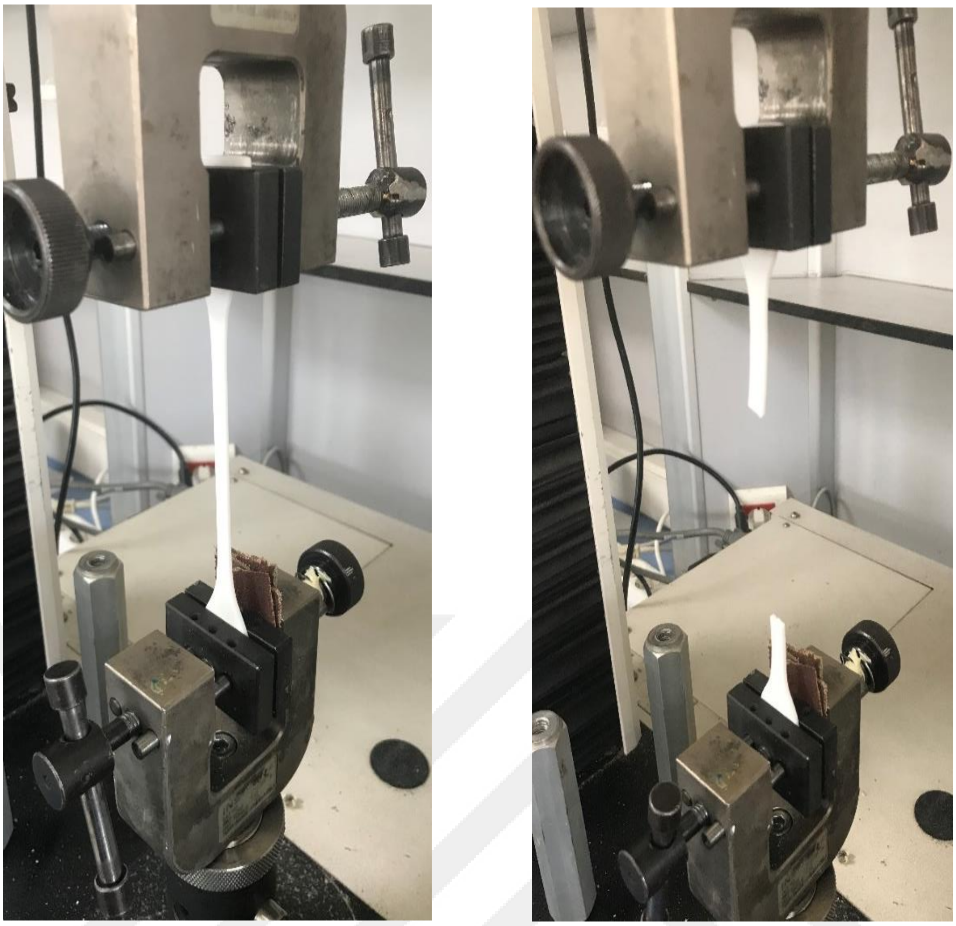


Figure 4. 39 PU2 sample during elongation and after breakage.

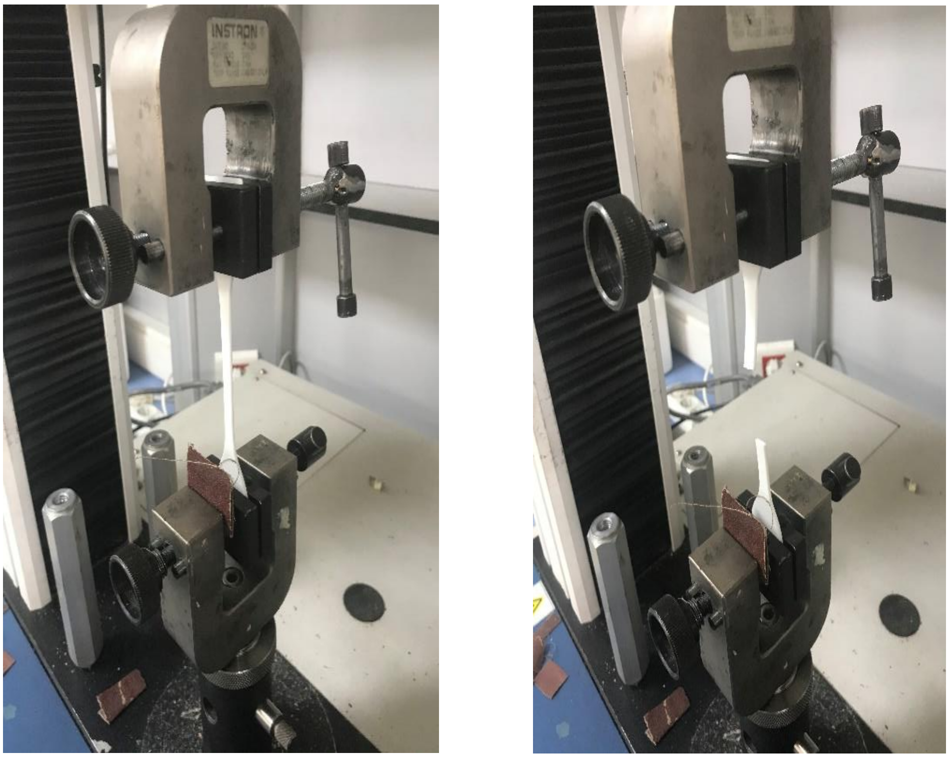


Figure 4. 40 PU3 sample during elongation and after breakage.

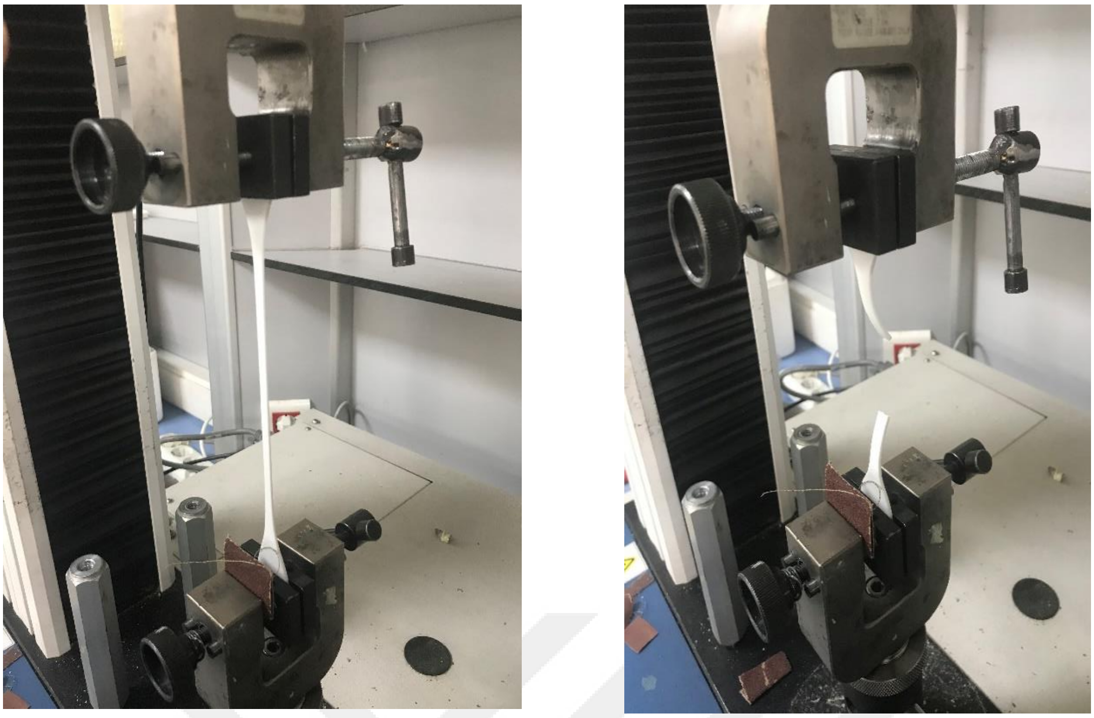
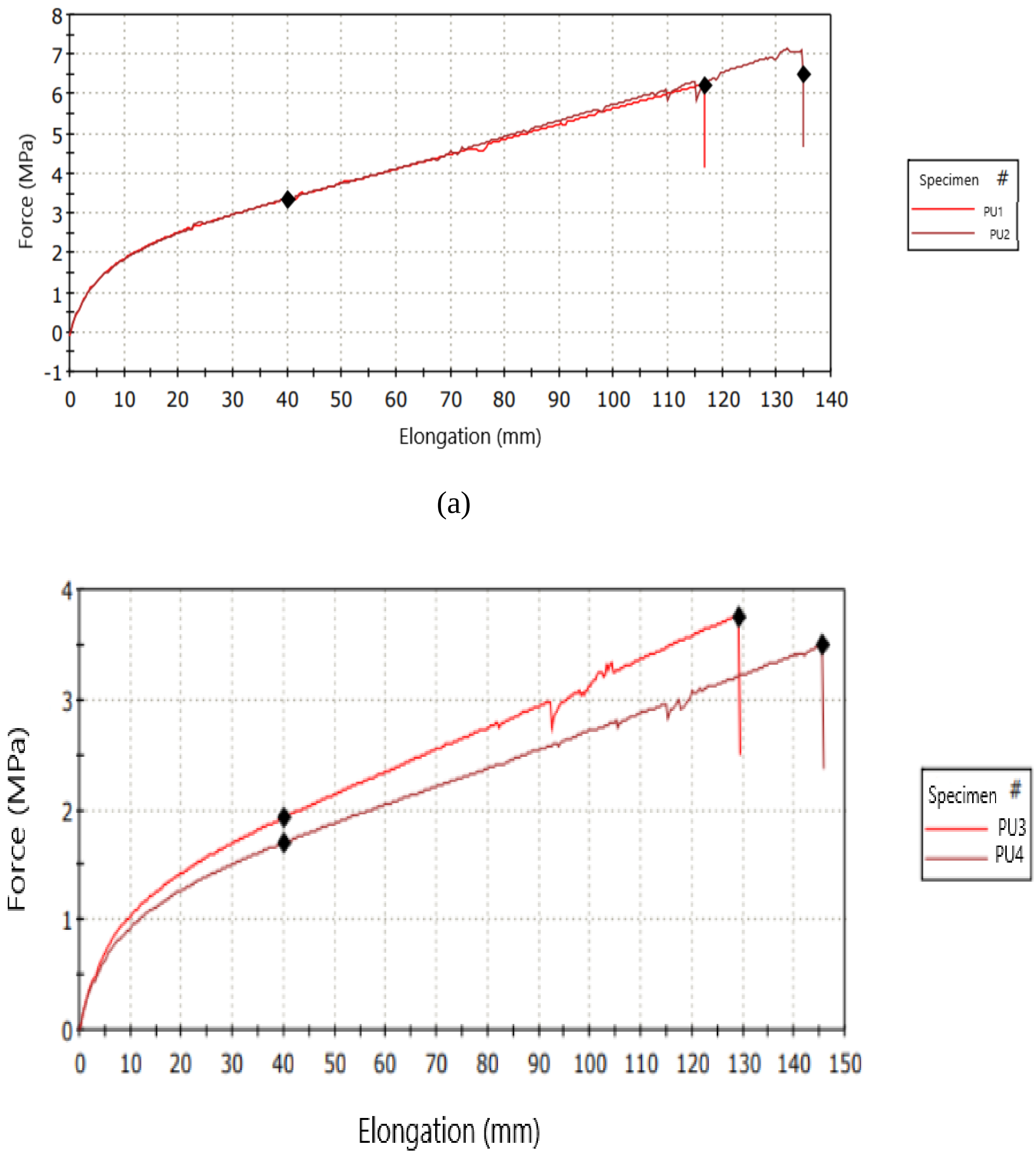


Figure 4. 41 PU4 sample during elongation and after breakage.

100 % Modulus, elongation at break and tensile strength values recorded after analysis. Graphs obtained from the software of the Instron analysis device are shown in Figure 4.42. Summary of properties shown in Table 4.15.

Table 4. 15 %100 Modulus, elongation at break and tensile strength results of PU1, PU2, PU3 and PU4.

Properties	PU1 Specimen	PU2 Specimen	PU3 Specimen	PU4 Specimen
% 100 Modulus (MPa) (Modulus)	3.357	3.318	1.924	1.697
Elongation at Break (%)	291.667	337.500	323.333	364.167
Tensile Strength (MPa)	6.211	6.507	3.746	3.489



(a)

(b)

Figure 4. 42 Tensile analysis graph of (a) PU1 and PU2 (b) PU3 and PU4.

According to results, modulus dropped significantly in PU3 and PU4 which has OP50 and 1 % of NCO percentage dropped prepolymers respectively. Significant decrease thought as less reactivity or lower level of hard segment formation since modulus related with brittleness and crystallinity.

Elongation at break increased in PU2, PU3 and PU4. The highest level of elongation was achieved in PU4 where polyurethane has a higher portion of elastic segments due to fewer isocyanates at present. The second best result was obtained for PU2.

The highest tensile strength was obtained in PU2 and the lowest value was achieved in PU4.

4.5.3 Tear resistance

Polyurethane samples were prepared for the tear resistance test as shown in Figure 4.43.

Figure 4. 43 . Tear resistance samples.

Samples prepared for tear resistance analysis mounted on mechanism. PU1, PU2, PU3 and PU4 at initial and after rupture are shown in Figure 4.44, Figure 4.45, Figure 4.46 and Figure 4.47 respectively.

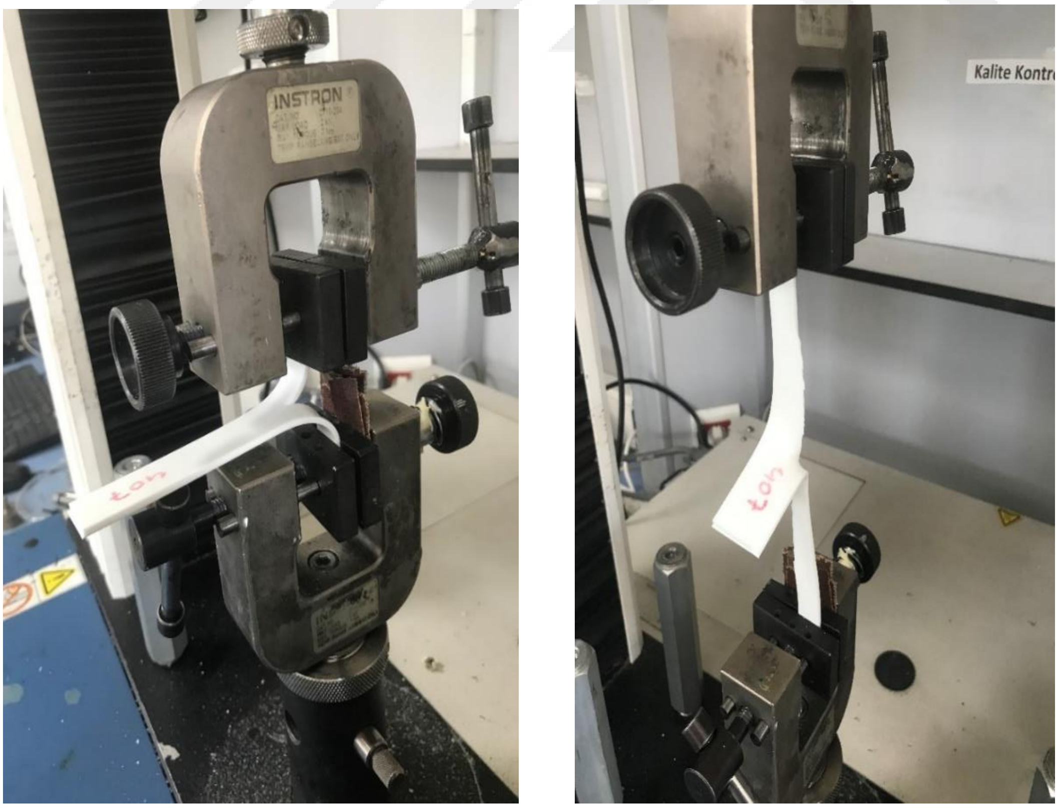


Figure 4. 44 PU1 sample at initial stage and after rupture.

Figure 4. 45 PU2 Sample at inital stage and after rupture.

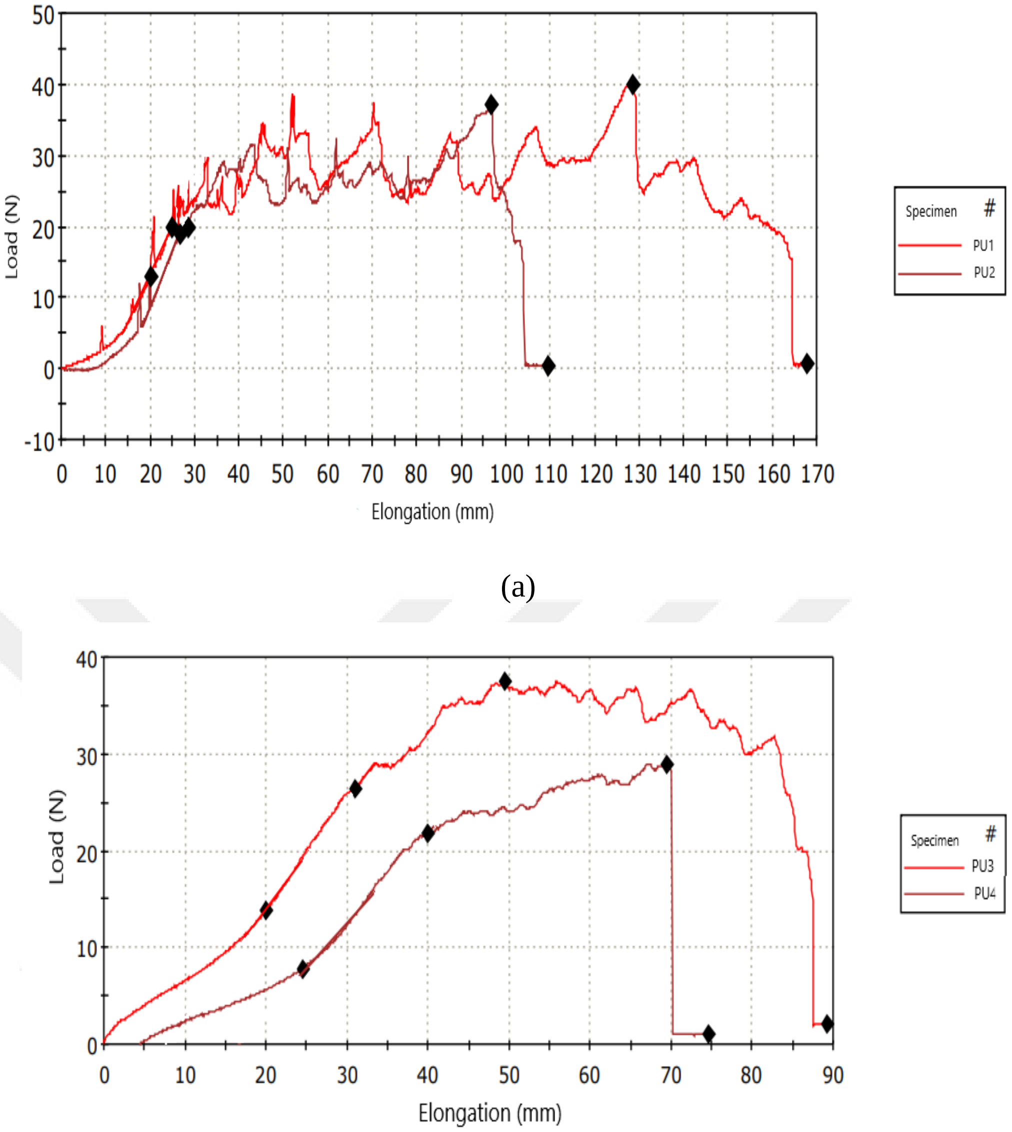
Figure 4. 46 PU3 Sample at inital stage and after rupture.

Figure 4. 47 PU4 Sample at inital stage and after rupture.

Maximum load at the weight (N), pressure at breakage (W/mm^2) values were recorded after analysis. Graph of samples obtained from the software of Instron analysis device shown in Figure 4.48. Summary of properties shown in Table 4.16.

Table 4. 16 Maximum load at weight, pressure at breakage, tear resistance of PU1, PU2, PU3 and PU4.

Specimen Name	PU1 Sample	PU2 Sample	PU3 Sample	PU4 Sample
Maximum load at weight (N)	40.095	37.010	37.435	28.910
Pressure at breakage (W/mm^2)	0.018	0.016	0.024	0.011
Tear resistance (N/ mm^2)	6.63	6.1	6.2	4.8



(a)

(b)

Figure 4. 48 Tear analysis graph of (a) PU1 and PU2 (b) PU3 and PU4.

According to results, tear resistance which is proportionally related to maximum load at weight value, did not show a significant change in PU2 and PU3. However, tear resistance dropped in PU4 which has a lower level of reinforcing hard segments.

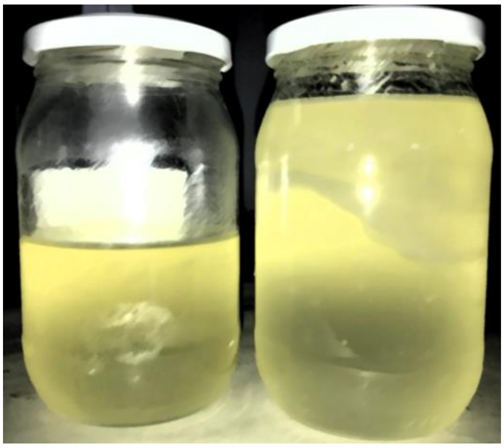
4.6 Shelf Life Examination of Reference and Improved Formulation

As a result of observations, PREP4 was chosen as the most stable formulation because of its lowest crystallization point, low percentage of crystallinity and lowest starting temperature of crystallization.

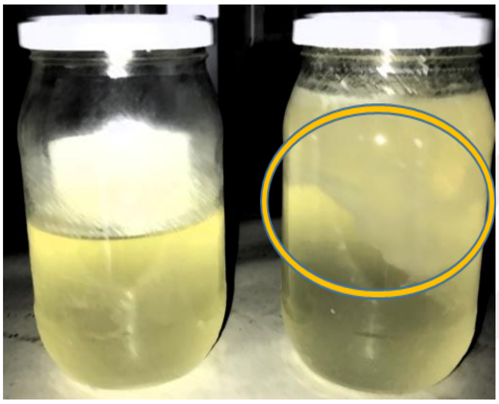
PREP1 and PREP4 were taken to jars at 21 °C for appearance shelf life examination. The appearances of samples are shown in Figure 4.49.


R-99-A iyileştirme
CO: 22.55
s. 283
9. 08-2021
CR-99-A Orjinal
NCO = 22.98
Vis = 295
19.08.2021

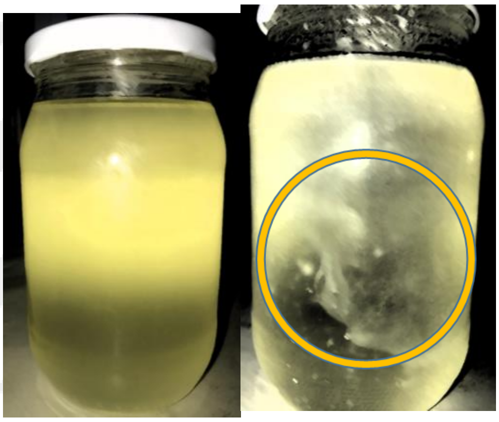
(a)



(b)

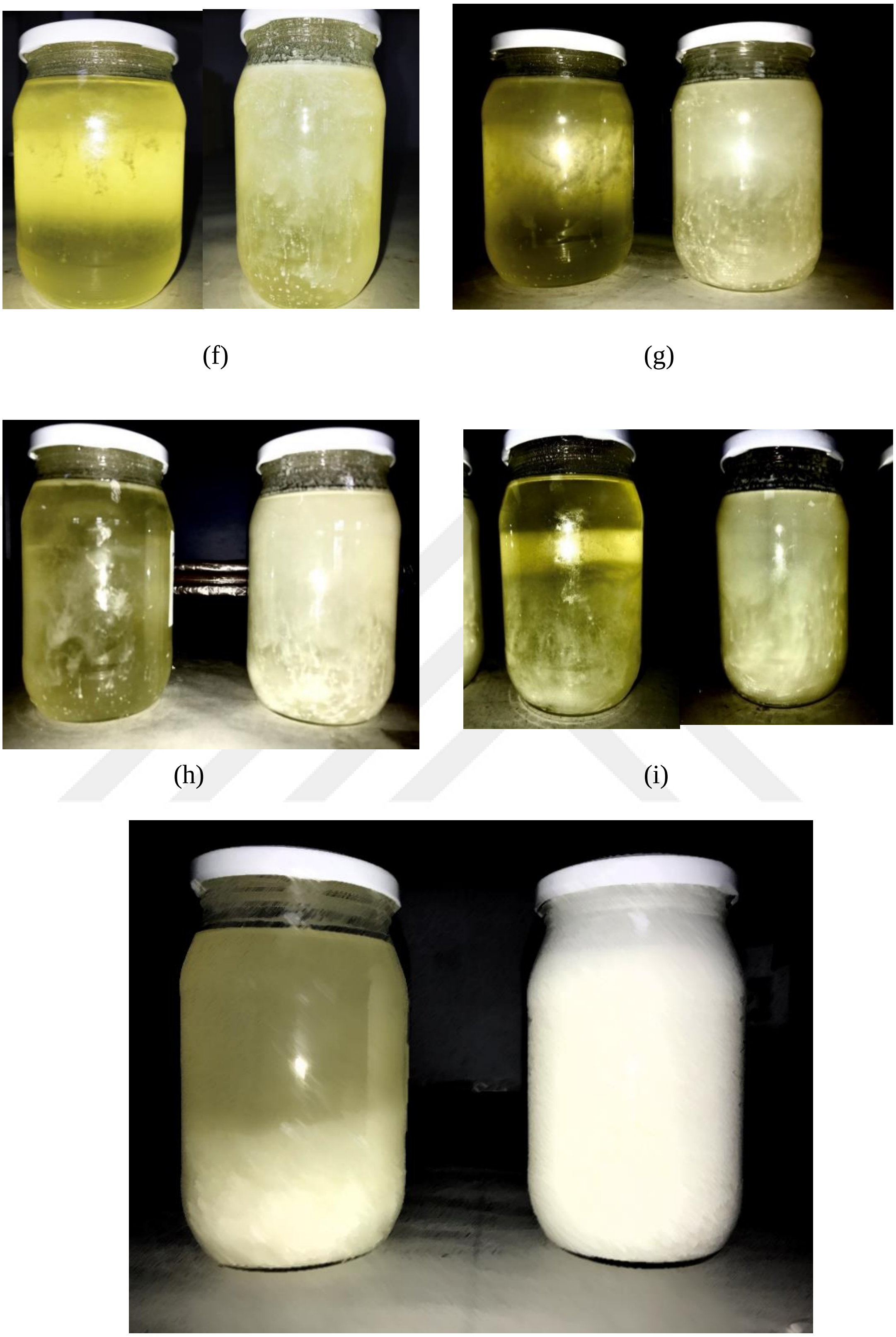


(c)



(d)

(e)



(f)

(g)

(h)

(i)

(j)

Figure 4. 49 Observations of PREP4 and PREP1 formulations in (a) day of synthesis, (b) 19 days, (c) 22 days, (d) 25 days, (e) 27 days, (f) 38 days, (g) 39 days, (h) 63 days, (i) 118 days, (j) 150 days respectively.

Observations are summarized below.

- At day of synthesis, both of the samples were tranpsarent and no sign of haziness observed.
- After 19 days of synthesis, signs of freezing at the top of the jar observed in PREP1. PREP4 stayed transparent.
- After 22 days of synthesis, the frozen region in prepolymer enlarged towards the middle section of the jar in PREP1 while PREP4 stayed transparent.
- After 25 days of synthesis, increased regularity of frozen regions was observed in PREP1 while PREP4 stayed transparent.
- After 27 days of synthesis, frozen regions in PREP1 increased. Frozen particles were observed on the prepolymer. PREP4 stayed transparent.
- After 38 days of synthesis, both the numbers of frozen particles and frozen zones increased in PREP1. PREP4 started to freeze at the top region.
- After 39 days of synthesis, both the number of frozen particles and frozen zones increased in PREP1.The frozen zone started to expand to lower levels. The freezing zone in the top level of PREP4 shows expansion.
- After 63 days of synthesis, more freezing particles were observed in PREP1. Freezing propagated to lower levels of PREP4.
- After 118 days of synthesis, more freezing particles were observed in PREP1. Freezing occupied half of the PREP4.
- After 150 days of synthesis, PREP1 completely frozen while PREP4 stayed in liquid form.

5. CONCLUSION

According to results, freezing point of prepolymer decreased proportionally with increasing carbodiimide modified MDI in the isocyanate component.

The accuracy of the study was confirmed by analysis of free NCO percentage.

Both from DSC analysis, PREP4 shows the lowest freezing temperature, starting point of freezing, the starting point of melting, melting temperature.

OP50 can decrease both crystallization and melting temperature when it is combined with carbodiimide modified MDI in 3-7 % percentage of weight. However, it cannot be used alone or cannot be used in higher amounts as 5-10 % percentage of weight .

Dipropylene glycol addition in prepolymer chain and neopentyl glycol addition to polyester polyol to increase branching in prepolymer does not show significant improvement on both freezing and melting points of the prepolymer.

PREP4 is observed as the best prepolymer formulation which can withstand storage conditions due to its lowest freezing temperature.

However, enhancement in shelf life is known for its negative effect on mechanical properties. For this reason, mechanical tests were applied for polyurethanes made from PREP1 (PU1) and PREP4 (PU2).

According to tensile strength analysis, improvement at elongation at break was observed due to a decrease in the degree of crystallization with carbodiimide modified MDI in PU2.

Decrease in modulus related with the low level of brittle crystalline 4,4'- MDI and low level of brittle hydrogen bonds in PU2.

Tear resistance is less in PU2 than PU1 due to a lower level of hydrogen bonding (lower level of reinforcing effect) and lower level of crystalline 4,4'- MDI.

According to the compression set, PU2 showed a lower percentage of permanent deformation due to a lower level of crystallinity.

From observations, increasing modified carbodiimide MDI in formulation increases general elasticity while decreasing reinforcing capability since it has lower level of 4,4'- MDI. However, there are no significant differences in both tear resistance and modulus.

Besides mechanical observations of PREP1 and PREP4, the other two best prepolymers which are PREP5 and PREP6 also observed for their projections on mechanical behaviors when they are added. Same mechanical tests were applied for polyurethanes made from PREP5 (PU3) and PREP6 (PU4).

PU3 and PU4 were made from second and third best prepolymer formulation which was PREP2 and PREP6 according to DSC analysis. And besides PU4, both of these prepolymers were observed for their effects on the mechanical properties of polyurethane.

In PU3 and PU4, from mechanical analysis, PU3 did not show any significant changes besides modulus. However, PU4 shows significant losses both in modulus and compression set analysis.

After observing no significant negative effect on mechanical properties, shelf life of PREP4 and PREP1 was observed.

From the shelf life test, PREP1 started to freeze 19 days after synthesis while PREP4 started to freeze 38 days after synthesis. Besides, propagation of freezing in PREP4 also shows a slower trend than PREP9. At the end of 150 days, PREP1 completely frozen while PREP4 stayed in liquid form. From both mechanical, thermal and shelf life analysis results, PREP4 has a better storage resistance and can be used in polyurethane formulations.

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- **Tibet Hüten, Nilgün Kızılcan, Ahmet Akar, Kerim Can Ünlü, Kübra Ortaç** 4-6 November 2021. Improving Storage Stability Of 4,4-Diphenylmethane Diisocyanate Based Prepolymers By Decreasing Melting And Crystallization Temperature, *KOMPEGE V, 5. International Ege Composite Materials Symposium*, Pg. 388-408. (Research Article)