

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**INVESTIGATION OF THE EFFECTS OF VARIOUS TYPES OF  
PLASTICIZERS ON THE PROPERTIES OF POLYESTER POLYOL BASED  
THERMOPLASTIC POLYURETHANE**

**M.Sc. THESIS**

**Bahar DURAK AKKOYUN**

**Department of Polymer Science and Technology**

**Polymer Science and Technology Programme**

**DECEMBER 2016**



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**Bahar DURAK AKKOYUN**  
**(515131028)**

**Department of Polymer Science and Technology**

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**Thesis Advisor: Prof. Dr. Nurseli UYANIK**

**DECEMBER 2016**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**FARKLI PLASTİFİYAN TİPLERİNİN, POLYESTER POLYOL BAZLI  
TERMOPLASTİK POLİÜRETAN ÜZERİNDEKİ ETKİLERİNİN  
ARAŞTIRILMASI**

**YÜKSEK LİSANS TEZİ**

**Bahar DURAK AKKOYUN  
(515131028)**

**Polimer Bilim ve Teknolojileri Bölümü**

**Polimer Bilim ve Teknolojileri Programı**

**Tez Danışmanı: Prof. Dr. Nurseli UYANIK**

**ARALIK 2016**



Bahar DURAK AKKOYUN, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515131028, successfully defended the thesis entitled “INVESTIGATION OF THE EFFECTS OF VARIOUS TYPES OF PLASTICIZERS ON THE PROPERTIES OF POLYESTER POLYOL BASED THERMOPLASTIC POLYURETHANE”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

**Thesis Advisor :**      **Prof. Dr. Nurseli UYANIK**      .....

Istanbul Technical University

**Jury Members :**      **Prof. Dr. Nilgün KIZILCAN**      .....

Istanbul Technical University

**Prof. Dr. Ayfer SARAÇ**      .....

Yıldız Technical University

**Date of Submission : 25 November 2016**

**Date of Defense : 21 December 2016**





*To my husband, father and beautiful mother,*



## **FOREWORD**

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December 2016

Bahar DURAK AKKOYUN  
(Chemical Engineer)



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## ABBREVIATIONS

<b>TPU</b>	: Thermoplastic Polyurethane
<b>REACH</b>	: Registration, Evaluation, Authorization and Restriction
<b>MFI</b>	: Melt Flow Index
<b>PU</b>	: Polyurethane
<b>SS</b>	: Soft Segment
<b>HS</b>	: Hard Segment
<b>TDI</b>	: Toluene Diisocyanates
<b>HDI</b>	: Hexamethylene Diisocyanate
<b>PTMEG</b>	: Poly(tetramethylene glycol)
<b>RIM</b>	: Reaction Injection Molding
<b>MDI</b>	: Methylene Diphenyl Diisocyanate
<b>TPE</b>	: Thermoplastic Elastomer
<b>MDA</b>	: Methylene Dianiline
<b>BZ</b>	: Benzoate Ester
<b>PH</b>	: Phthalate Ester
<b>CR</b>	: Tricresyl Phosphate
<b>DOA</b>	: Adipate Ester
<b>HE</b>	: Aliphatic Plasticizer Hexamoll DINCH
<b>AB</b>	: Absorption
<b>PVC</b>	: Poly(vinyl chloride)





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# **INVESTIGATION OF THE EFFECTS OF VARIOUS TYPES OF PLASTICIZERS ON THE PROPERTIES OF POLYESTER POLYOL BASED THERMOPLASTIC POLYURETHANE**

## **SUMMARY**

Thermoplastic polyurethane (TPU) elastomers offer a myriad of physical property combinations and processing applications. It's highly elastic, flexible and resistant to abrasion, impact and weather. At the same time, it has usage area in very different sectors due to its suitability for all kinds of shapes. The biggest advantage of polyurethanes compared to other materials is that products with very different hardness, density and elasticity can be obtained by changing formulations. This enables the production of suitable products for different usage areas by changing only raw materials in the same production line.

TPU is very important as a raw material input because of the fact that industrial and personal products are robust, economical and useful. The most important advantage of TPU is its high resistance to abrasion, its flexibility in a wide range of temperatures and good resistance to a large number of oils and greases. The TPU can be used in a wide range of temperatures. In short and long applications, it can be used at temperatures from -40 °C to 80 °C. All mechanical properties depend on the temperature and show a short time resistance to temperatures above 120 °C.

The thermoplastic polyurethane elastomers need to be dried to ensure good handling. Drying process is carried out in air circulating ovens at 100 -110 °C or in drying chambers for 1-2 hours. The amount of moisture contained in the granules should be as low as 0.1% by weight. They can be processed with methods used for thermoplastic materials such as injection, extrusion, overmolding and film lamination.

The thermoplastic polyurethanes have a minimum hardness value of 80 Shore A after they are processed if plasticizing agents are not used. Plasticizing agents are used to obtain the hardness values of 65-70-75 Shore A which is preferred especially in footwear applications. In this study, on the interaction of these agents with isocyanates and diols, which are the main raw materials in thermoplastic polyurethane production, percentage ratios of plasticizing agents and Shore values were determined. However, variations of thermoplastic polyurethane compatible and non plasticizing agents are also findings. Especially in the last years, it has been studied which agent can be used in thermoplastic polyurethane instead of phthalate based plasticizers which are likely to be on the list of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals).

Thermoplastic polyurethane materials can be produced by one-shot and two-step production methods. In the one-shot synthesis, polyol, diisocyanate and chain extender are added to the solvent at the same time and the system is heated to 80 °C. In some cases, catalysis is added to accelerate the reaction. However, one of the most

widely used routes for polyurethane synthesis is the two-step synthesis or pre-polymer synthesis route. In this method, the reaction of the isocyanate excess with the polyol occurs to synthesize the first-stage diisocyanate terminine oligomer intermediate.

Our work with the one-shot process has been completed. In addition to this, TPU material is also produced without plasticizing agent and absorbent is provided by putting plasticizing agent from outside. Results were obtained after 24 hours by mixing with 1 hour intervals. This was due to the fact that a plasticizer agent that could not enter the reaction with the one-shot process in the extrusion machine could have the same effect on the material as the absorption. However, the findings were that the one-shot process was more efficient.

Two procedure were used in that study. First one was extrusion and second one was absorption process. Phthalate ester, benzoate ester, adipate ester, 1,2-cyclohexane dicarboxylic acid diisononyl ester and tricresyl phosphate plasticizers were used and 15 samples were prepared with 10%-20%-30% percentages of each plasticizers and in each procedure. There were 30 sample in two procedures. They were taken the test after the preparing the samples.

TPU granules were made ready for characterizing of prepared samples in the injection molding machine. Tensile tests, tear tests, density, hardness, elongation, 100% and 300% strengths, massive melt flow index, abrasion resistance and warp index tests were applied.

In a polyurethane elastomer block, the hard segment of the copolymer is formed by the addition of the chain extender diisocyanate. The soft part comprises a long, flexible polyether or polyester chain. The hard, rigid part forms the vitreous or semi-crystalline areas, while the polyol soft part forms an amorphous or rubbery structure in which the hard parts are dispersed at different ratios. In this biphasic microstructure, the hard segments are the physical crosslinking point, while the soft segment is the elastic matrix. As a result of this microphase separation, they exhibit good physical and mechanical properties such as high modulus and high reversible deformation.

Mechanical tests have been applied to the materials in order to understand the effect of the plasticizing agents on these good properties and to know the difference between them. Tensile, elongation, modulus and tear tests were conducted to compare the mechanical properties of the materials. As a result, phthalate plasticizers were found to be the best benzoate esters and plasticizers.

The melt flow index is the most important property of TPU material. In order to be able to process, it is necessary to keep the melt flow value at optimum level. Abrasion resistance is a very good property that distinguishes TPU material from other thermoplastics. The abrasion resistance is very good and it is seen that the plasticizer agents used in the TPU materials preferred in the sector still have the best values for the ones with benzoate abatement.

Customers who use masterbatch in general in accordance with customer requirements, and those who will use transparent materials, regard the granules as transparent. In this case, the winding index becomes an important criterion. It was among the values we looked at in the thesis to make its processes easier. The result is that the phthalate materials have the best yellow color, followed by benzoate esters.

## FARKLI PLASTİFİYAN TİPLERİNİN, POLYESTER POLYOL BAZLI TERMOPLASTİK POLİÜRETAN ÜZERİNDEKİ ETKİLERİNİN ARAŞTIRILMASI

### ÖZET

TPU (termoplastik poliüretan) kırılmayan, aşınma direnci yüksek, esnek ve düzgün kalıp özelliği taşıyan sentetik bir malzemelerdir. Aynı zamanda her türlü şekle uygun özellik göstermesi sebebiyle çok farklı sektörlerde kullanım alanı bulur. Poliüretanın diğer malzemelere kıyasla en büyük avantajı, formülasyonların da değişiklik yapılarak birbirinden çok farklı sertlik, yoğunluk ve elastikiyete sahip ürünler elde edilebilmesidir. Bu da aynı üretim hattında, sadece hammadde değiştirilerek farklı kullanım alanlarına uygun ürün üretilbilmesine olanak vermektedir.

TPU, endüstriyel ve kişisel ürünlerin sağlam, ekonomik ve kullanışlı olması yönünden hammadde girdisi olarak en önemli tercih nedenidir. TPU'nun en önemli avantajı aşınma direncinin yüksek olması, geniş sıcaklık aralığında esneklik ile çok sayıda yağ ve greslere karşı iyi direnç göstermesidir. TPU geniş sıcaklık aralığında kullanılabilir, kısa ve uzun süreli uygulamalarda - 40°C ile 80 °C'ye kadar kullanılmakla beraber, tüm mekanik özellikler sıcaklığa bağlı olarak değişmektedir, 120 °C nin üzerindeki sıcaklıklara kısa süreli direnç göstermektedir.

Termoplastik poliüretan elastomerlerinin iyi işlenebilmeleri için kurutulmaları gereklidir. Kurutma işlemi, 100 -110 °C de hava sirkülasyonlu fırınlarda veya 1-2 saat kurutma odalarında tutularak yapılmaktadır. Granüllerin içerdiği nem miktarı ağırlıkça % 0,1 den düşük olmalıdır. Bunlar enjeksiyon, ekstrüzyon, kalıp üzerine kaplama (overmolding) ve film laminasyonu gibi termoplastik malzemeler için kullanılan metotlarla işlenebilmektedirler ve nem miktarı işlenebilmeyi yüksek oranda etkileyem bir özelliktir. Enjeksiyon için nem oranının %0,05'den düşük olması ve ekstrüzyon için %0,02 civarında olması gerekmektedir. En iyi şekilde nem oranını düşürmek için kurutma sisteminin uygun olmasına önem verilmesi gerekmektedir.

Termoplastik poliüretanlar plastikleştirici ajanlar kullanılmadığı takdirde proses edilmeleri sonucunda geldikleri en düşük sertlik değeri 80 Shore A olmaktadır. Özellikle ayakkabı tabanı uygulamalarında tercih edilen 65-70-75 Shore A sertlik değerlerini elde edebilmek için plastikleştirici ajanlar kullanılmaktadır.

Plastikleştirici ajanların termoplastik poliüretan üretiminde ana hammadde olan izosiyanat ve dioller ile etkileşimleri üzerine yaptığımız bu çalışma ile plastikleştirici ajanların yüzde oranları ile gelen sertlik değerleri tespit edilmiştir. Bununla birlikte termoplastik poliüretana uyumlu olan ve olmayan plastikleştirici ajan çeşitleri de bulgular arasındadır. Özellikle son yıllarda REACH (Kimyasalların Kaydı, Değerlendirilmesi, İzni ve Kısıtlanması) listesine girmesi muhtemel olan ftalat bazlı

plastikleştirici ajanların yerine termoplastik poliüretanda hangi ajanın kullanılabileceği çalışması yapılmıştır.

Termoplastik poliüretan malzemeler tek ve iki basamaklı üretim yöntemleri ile üretilirler. Tek basamaklı sentezde, aynı anda solvent içine poliöl, diizosiyanat ve zincir uzatıcı ilave edilir ve sistem 80 °C'nin üzerine ısıtılır. Bazı durumlarda reaksiyonu hızlandırmak için kataliz ilavesi yapılır. Bununla birlikte, poliüretan sentezi için en yaygın kullanılan yollardan biri iki basamaklı sentez veya pre-polimer sentezi yoludur. Bu metotta, ilk basamak diizosiyanat sonlu oligomer ara ürününü sentezlemek için poliöl ile izosiyanat fazlasının reaksiyonu sonucu oluşur.

Tez çalışmamızda tek basamak proses ile çalışmalarımız tamamlanmıştır. Bunun yanı sıra TPU malzemesi plastikleştirici ajan olmadan da üretilerek içerisine dışarıdan plastikleştirici ajan konularak absorpsiyonu sağlanmıştır. 1 saat aralıklar ile karıştırılarak 24 saat sonunda sonuçlar elde edilmiştir. Bunun nedeni tek basamaklı proses ile ekstrüzyon makinesinde reaksiyona giremeyen bir plastikleştirici ajanın, absorpsiyon ile malzeme üzerinde aynı etkiyi oluşturuyor olabileceğinin anlaşılmasıydı. Ancak alınan sonuçlarda tek basamaklı prosesin daha verimli olduğu bulgusu elde edilmiştir.

Bu çalışmada iki prosedür kullanılmıştır. Birincisi ekstrüzyon, ikincisi absorpsiyon prosesidir. Ftalat ester, benzoate ester, adipat ester, 1,2- sikloheksan dikarboksilik asit diizononil ester ve trikresil fosfat plastikleştirici ajanları kullanılmış ve her plastikleştiricilerden %10 -%20 -%30 oranında alınmış ve her prosedürden 15 numune hazırlanmıştır. İki prosedür için toplamda 30 örnek bulunmaktadır. Örnekler hazırlandıktan sonra numuneler test edilmiştir.

Alınan TPU granülleri enjeksiyon makinesinde karakterizasyona hazır hale getirilmiştir. Çekme testleri, yırtılma testleri, yoğunluk, sertlik, uzama, %100 ve %300 mukavemetler, kütlesek erime akış indeksi, aşınma dayanımları ve sararma indeksi testleri uygulanmıştır.

Bir poliüretan elastomer bloğunda, kopolimerin sert segmenti, zincir uzatıcının diizosiyanata katılmasıyla oluşur. Yumuşak kısım ise uzun, esnek polieter ya da poliester zinciri içerir. Sert, rijit kısım, camsı ya da yarı kristalin alanları oluştururken, poliöl yumuşak kısımları, sert kısımların farklı oranlarda dağıldığı amorf ya da kauçuğumsu yapıyı oluşturur. Bu iki fazlı mikro yapıda, sert kısımlar, fiziksel çapraz bağlanma noktası iken, yumuşak segment, elastik matrikstir. Bu mikro faz ayırımının neticesinde yüksek modül ve yüksek tersinir deformasyon gibi iyi fiziksel ve mekanik özellikler sergilerler.

Plastikleştirici ajanların bu iyi özelliklere ne yönde etki ettiğinin anlaşılması ve aradaki farkın bilinmesi için malzemelere mekanik testler uygulanmıştır. Çekme, uzama, modülüs ve yırtılma testleri malzemelerin mekanik özelliklerini karşılaştırmak için yapılmıştır. Sonuçta ftalatlı plastikleştiricilerin arkasından benzoat esteri plastikleştiricilerin en iyisi olduğu görülmüştür.

Erime akış indeksi TPU malzemesinin en önemli özelliğidir. Proses edilebilmesi için eriyik akış değerinin optimum düzeyde tutulması gerekmektedir. Aşınma dayanımı TPU malzemesini diğer termoplastiklerden ayıran çok iyi bir özelliğidir. Aşınma dayanımı çok iyi olarak sektörde tercih edilen TPU malzemesinde kullanılan plastikleştirici ajanlarda yine benzoat esteri olanlar en iyi değerlere sahip olduğu görülmüştür.



Müşteri gerekleri doğrultusunda genelde masterbatch kullanan müşteriler ve şeffaf malzeme kullanacak olanlar, granüllerin şeffaf olmasını önemsediklerinden sararma indisi önemli bir kıstas haline geliyor. Proseslerini de kolaylaştıracağı için tezde baktığımız değerler arasına girmiştir. Ftalatlı malzemelerin en iyi sararmaya sahip olduğu ve arkasından benzoat esterlerinin geldiği sonucuna varılmıştır. Plastikleştirici ajan kullanıldığın malzemenin camsı geçiş sıcaklığı ve erime sıcaklığına yaptıkları etkiler için test yapılmıştır ve kullanılan oranların belli değerlerde ancak yüksek farklılık yapmadan etki ettiği görülmüştür.



## 1. INTRODUCTION

Thermoplastic polyurethane (TPU) is a particular class of plastic created when a polyaddition reaction occurs between a diisocyanate and a number of diols. First developed in 1937, this versatile polymer is smooth and processable when heated, rough when cooled and in a position of being reprocessed more than one instances without shedding structural integrity. Used both as a malleable engineering plastic or as a substitute for tough rubber, TPU is famous for many matters including its high elongation and tensile strength, its elasticity, and to various levels, its potential to resist oil, grease, solvents, chemicals and abrasion. The general reaction of polyurethane reaction can be seen in Figure 1.1.



**Figure 1.1** : The general reaction of polyurethane (Ashida,2007).

These properties make TPU totally general throughout a variety of markets and applications. Inherently, it may be extruded or injection molded on conventional thermoplastic manufacturing apparatus to create solid components quite often for footwear, cable & wire, hose and tube, movie and sheet or different industry products. It can be compounded to create robust plastic moldings or processed using healthy solvents to form laminated textiles, protective coatings or practical adhesives.

TPU may also be produced in a number of approaches. The longest established construction system for thermoplastic polyurethane is reactive extrusion. For the reactive extrusion system, the monomers are separately fed to the extruder via a designated metering system. Within the extruder, reaction and transport take position, and the polymer fashioned is peletized on the die.

Plasticizers are the substances that usually low melting solids or high boiling organic liquids. When they are added to hard plastics, improve their flexibility and durability.

Plasticizers work by establish themselves between the chains of polymers, spacing them apart and thus making the plastic softer. There are many types of plasticizer. In the thesis, we investigate the best one for TPU. One thing is important for us, it is phthalate. Many types of phthalates are now regulated and restricted in many products.

Plasticizing agents are used to obtain the hardness values of 65-70-75 Shore A which is preferred especially in footwear applications. In this study on the interaction of these agents with isocyanates and diols, which are the main raw materials in thermoplastic polyurethane production, percentage ratios of plasticizing agents and Shore A values were determined. However, variations of thermoplastic polyurethane compatible and non plasticizing agents are also findings. Especially in the last years, it has been studied which agent can be used in thermoplastic polyurethane instead of phthalate based plasticizers which are likely to be on the list of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals).

Plasticizers effect the mechanical and physical properties on material. In this study, plasticized TPU is investigated that which plasticizer is more suitable according to REACH regulations and which one will effect in a good way with mechanical, rheological and physical properties. In that way, all the mechanical properties were investigated. MFI, hardness, yellowing index data, abrasion resistance and the other mechanical properties are given in the experimental part. In the theorotical part, the general information about TPUs, plasticizers, chemical structure of TPU, processing of TPU and the applications will be found.

## **2. THEOROTICAL PART**

In this part of the study, the main source of thermoplastic polyurethane, which constitutes the main theme of the work, is started from polyurethanes. The thermoplastic polyurethane, which is the bottom of the thermoplastic elastomer, was introduced. Main raw materials, chemistry and processes are explained. Explaining the plasticizers from the main points of the thesis, the types and theories used in the industry are mentioned.

### **2.1 Polyurethanes**

Polyurethane (PU) substances have been a main focus of research for many decades, since the first successful production by the pioneering german industrial chemist Otto Bayer in 1937. Since this first poly-addition reaction between poly-isocyanates and poly-alcohols, many various chemical compounds have been incorporated in PU materials in order to manage their very promising properties. PUs are multi block copolymer structures of the general type with their blocks held together by “urethane bonds” (R-NHCOO-R') and owe their versatility to the thermodynamic immiscibility of their unique units. The two different blocks are generally mentioned to as the “soft” (SS) and the “hard” (HS) segment respectively. Their immiscibility leads to a phase separation in the micro- scale, since the blocks are permanently engaged to each other with covalent bonds and they cannot phase separate macroscopically. This micro-phase separation in PUs has been the subject of countless studies conducted by scientists and engineers all over the globe, as an attempt to understand its main driving forces and afterwards control the final properties of each PU product. Precise concentration has been drawn over the years towards the family of thermoplastic polyurethanes (TPUs), which are PU samples that can be subjected to several heating-cooling cycles without significant alternations in their physical properties prior to their thermal degradation. The majority of the commercially available thermoplastic polyurethanes contain generally a low HS content, due to the

fact that their main applications in everyday life demand an elastomeric motion of the polymer at ambient temperatures. Therefore, the HS incorporation in a soft phase matrix of the copolymer is expected to act as a self-reinforcement agent for the polymer. Most of the synthesised polyurethanes contain a short alcohol unit, the chain extender (CE), which is mainly used to elongate the HS parts (Ashida,2007).

The polymers known as polyurethanes contain materials that incorporate the carbamate group, -NHCOO, as well as other functional groups, such as ester, ether, amide, and urea. The name polyurethane is reproduced from ethyl carbamate, known as urethane. Polyurethanes are generally produced by the reaction of a polyfunctional isocyanate with a macroglycol, a called polyol, or other reactants containing two or more groups reactive with isocyanates (Barikani,1986).

Polyurethanes are the synthetic macromolecules which find varied applications in every field of life, both domestic and industrial. Polyurethanes are widely used in many areas such as automotive (door panels, truck beds, mirror surrounds, seating, steering wheels and dashboards), construction (rigid foam and advanced wood composites), furniture (flexible foam), thermal insulation (rigid polyurethane foams), footwear (shoe soles, synthetic leather, seals) and as elastomers. Polyurethanes are organic polymers that include the urethane group in the constitution. They are typically made by the reaction of a polyol with a diisocyanate. Depending on initial reaction, the final product may require the addition of additives such as chain extenders, catalysts, and blowing agents. By careful stoichiometric calculations, polyurethane elastomers can be synthesized in one step or two steps methodology. (Szycher, 1999).

The rapid formation of high molecular weight urethane polymers from liquid monomers, which happens even at ambient temperature, is a unique feature of the polyaddition process, yielding products that range from crosslinked networks to linear fibers and elastomers.

The colossal versatility of the polyaddition method allowed the manufacture of a myriad of products for a wide variety of applications. The early German polyurethane products were based on toliene diisocyanate (TDI) and polyester polyols. In addition, a linear fiber, Perlon U, was produced from the aliphatic 1,6-hexamethylene diisocyanate (HDI) and 1,4-butanediol. Commercial production of

flexible polyurethane foam in the United States began in 1953. In 1956, DuPont introduced poly(tetramethylene glycol) (PTMG), the first commercial polyether polyol and the less expensive polyalkylene glycols appeared by 1957. The availability of the lower cost polyether polyols based on both ethylene and propylene oxides provided the foam manufacturers with a broad choice of suitable raw materials, which in turn afforded flexible foams with a wide range of physical properties. Polyether polyols provide foams with better hydrolytic stability whereas polyester polyols give superior tensile and tear force. The late 1950s saw the emergence of cast elastomers, which led to the development of reaction injection molding (RIM) at Bayer AG in Leverkusen, Germany, in 1964. Also, thermoplastic polyurethane elastomers and Spandex fibers were introduced in this time. In addition, urethane based synthetic leather was introduced by DuPont under the trade name Corfam in 1963.

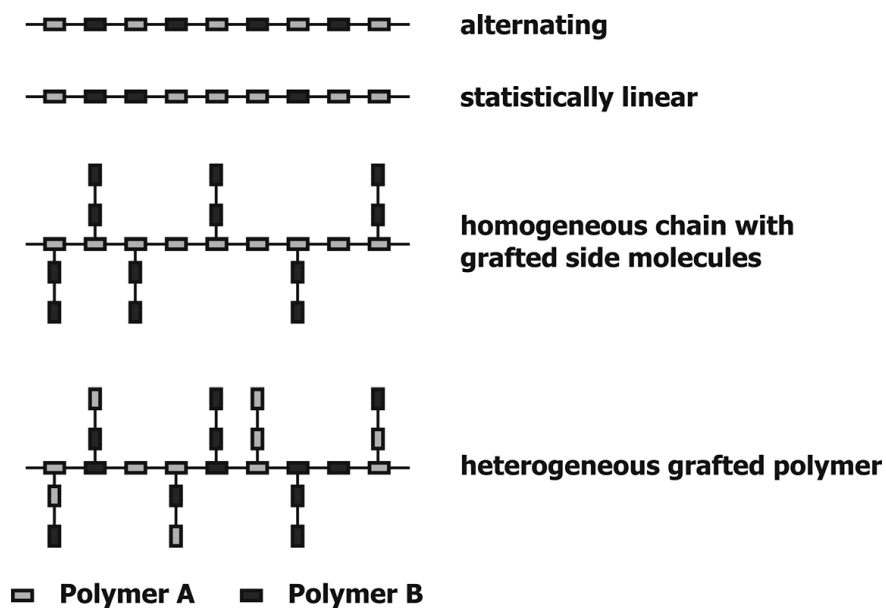
The late 1950s additionally witnessed the emergence of a new polymeric isocyanate (PMDI) based on the condensation of aniline with formaldehyde. This product was presented through the Carwin Co. in 1960 under the trade name PAPI. The superior heat resistance of rigid foams derived from PMDI prompted its exclusive use in rigid polyurethanes foams. The large scale production of PMDI made the coproduct 4,4'-methylene bis (phenyl isocyanate) (MDI) readily available, which has since been used almost exclusively in polyurethane elastomer applications. Liquid derivatives of MDI are used in RIM applications, and work has been accomplished on account that the 1990s to improve polyurethane elastomers with glass, graphite, boron, and aramid fibers, or mica flakes, to increase stiffness and curb thermal enlargement.

At present's global polyurethane industry has been reshaped by several mergers of the 1980s and 1990s. Some of the familiar players, such as ICI, Upjohn, Olin, Rhone Poulenc, Union Carbide, and Arco, sold their polyurethane businesses; Bayer, the principal global isocyanate producer, strengthened its position in polyether polyols by acquiring the Arco polyol business in 1999. Additionally, Dow, the other leading producer of polyether polyols, acquired Union Carbide in 1999, which further strengthened its position in polyols. The primary polyurethane players of the new millennium are Bayer, BASF, Dow, and Huntsman, the latter through the purchase of the global ICI business (Hepburn,1992).

## 2.2 Thermoplastic Elastomers

Thermoplastic elastomers are built to combine the physical properties of an “elastomer” and a “hard plastic” material. An elastomer has a low density of permanent crosslinks which account for its exceptional mechanical properties. A thermoplastic elastomer however, is a copolymer that includes both “softer” and “harder” polymeric chain parts that resemble the behaviour of an elastomer even without the existence of permanent crosslinks (Hepburn,1992).

Thermoplastic elastomers (TPEs) are elastic, flexible polymers with similar qualities as elastomers or rubber but of a thermoplastic nature. TPEs close the hole between stiff thermoplastics and vulcanized elastomers. As a result of the thermoplastic nature, TPEs can be processed to parts by extrusion and molding and can also be joined together or to other thermoplastic material by adhesive bonding, solvent bonding and welding processes or by coextrusion and multicomponent injection molding. Schematic type of copolymer can be seen in Figure 2.1.



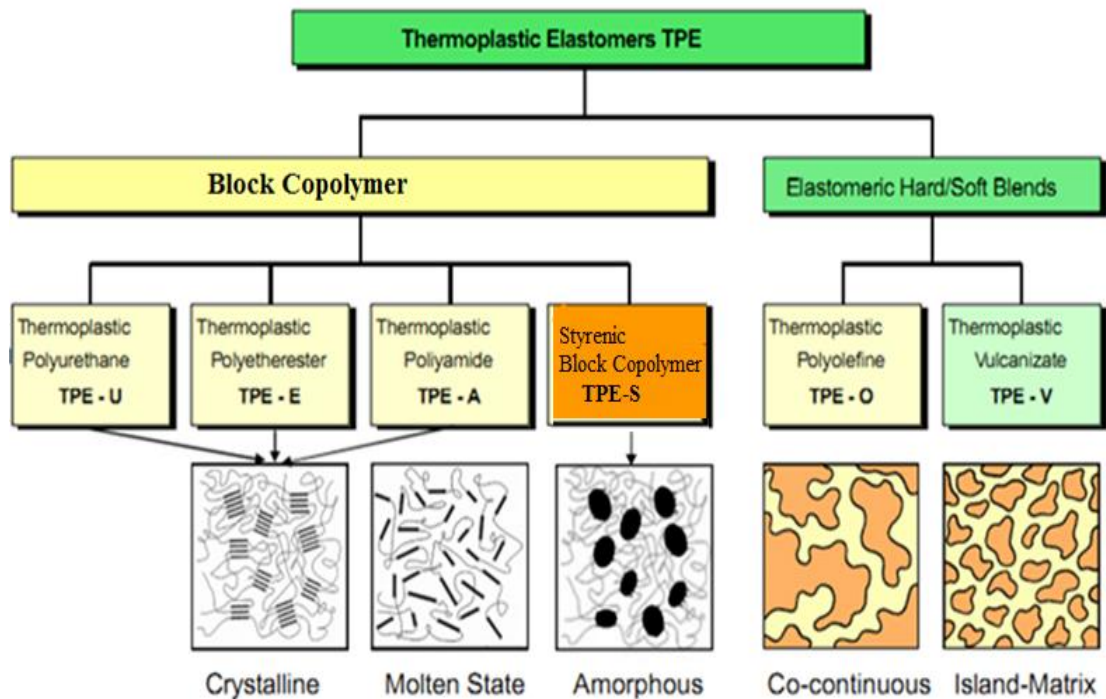
**Figure 2.1** : Schematic build up of copolymers (Holden et al.,1992).

In principal, the material group of TPEs contains two different base structures as a physical or chemical mixture, polymeric blends and block copolymers. Depending on the molecular structure given by the thermoplastic component, both of them could be amorphous or semicrystalline.

TPE is the comprehensive term used to describe a family of polymeric materials that can be processed as a thermoplastic, however show a number of characteristics as a



rule associated with typical thermoset rubbers. This family of materials, certainly those that are commercially available, can be divided into eight main classes that it can be seen Figure 2.2, based on their chemistry and morphology (Ehrenstein et al.,2001).



**Figure 2.2 :** Thermoplastic elastomers (Holden et al.,1996).

Thermoplastic elastomers (TPEs) have two enormous benefits over the conventional thermoset (vulcanized) elastomers. Those are ease and speed of processing. Other advantages of TPEs are recyclability of scrap, lower energy costs for processing, and the availability of standard, uniform grades (not generally available in thermosets). TPEs are molded or extruded on average plastics processing equipment in considerably shorter cycle times than those required for compression or transfer molding of conventional rubbers. They are made by copolymerizing two or more monomers, using either block or graft polymerization methods. One of the monomers provides the hard, or crystalline, polymer section that functions as a thermally stable component; the other monomer develops the soft or amorphous segment, which contributes the elastomeric or rubbery characteristic. Physical and chemical properties can be controlled by varying the ratio of the monomers and the length of the hard and soft segments. Block techniques create long-chain molecules that have various or alternating hard and soft segments (Saunders and Frisch, 1962). Graft

polymerization methods involve attaching one polymer chain to another as a branch. The properties that are affected by each phase can be generalized as follows:

➤ “hard phase” plastic properties:

\*processing temperatures

\*continuous use temperature

\*tensile strength

\*tear strength

\*chemical and fluid resistance

\*adhesion to inks, adhesives, and overmolding substrates

➤ “soft phase” elastomeric properties:

\*lower service temperature limits

\* hardness

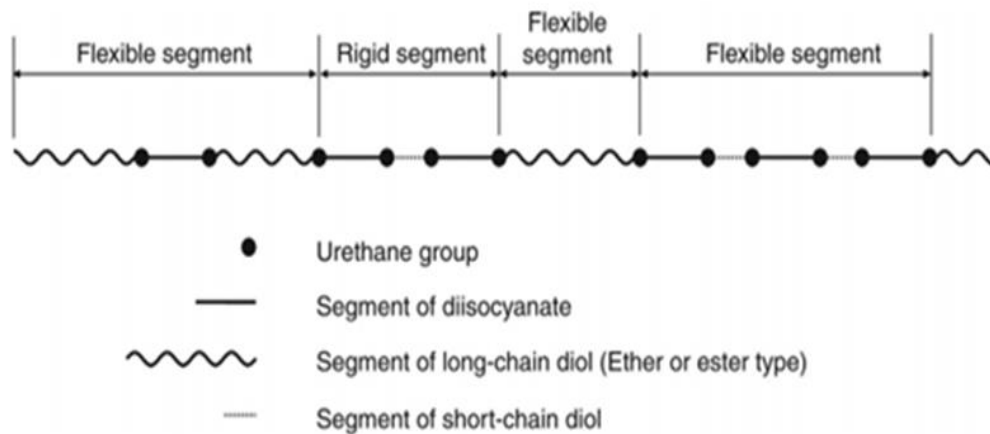
\*flexibility

\*compression set and tensile set

### **2.2.1 Thermoplastic polyurethanes**

Thermoplastic polyurethanes (TPUs) are linear multi-block co-polymers with a statistical distribution of hard segments (HS) and smooth segments (SS). The HS contains models of di-isocyanate “chain extended” by using low molecular weight alcohol units (chain extender). The SS is made from greater molecular weight alcohol chains (polyols). As far as mechanical characteristics of PU materials are concerned, they owe their flexibility and elasticity often to their SS and their rigidity to the HS. They have got been broadly used for the construction of many industrial merchandise by way of the years, covering a tremendous variety of functions and have consequently attracted a excellent deal of concentration from each educational and industrial study. Among different commercial merchandise, coatings, sealants, paints, fibres, foams and tough plastics were produced for the duration of the final decades and polyurethanes were given that regarded as a crucial part of the loved ones of highly versatile polymeric materials.

Considering their initial discovery with the aid of the German industrial chemist Otto Bayer in 1937 by way of a polyaddition reaction of poly-isocyanates and polyalcohols, curiosity has been primarily concerned with the change of their chemistry. This led to a very huge form of PUs concentrating on special utility fields. Quite simple alternations within the chemical architectures of the PUs can tremendously adjust their bodily properties and as a result duvet the constantly expanding demands of the polymer enterprise (Barikani, 1996). It can be seen in Figure 2.3 that molecular structure of TPU.

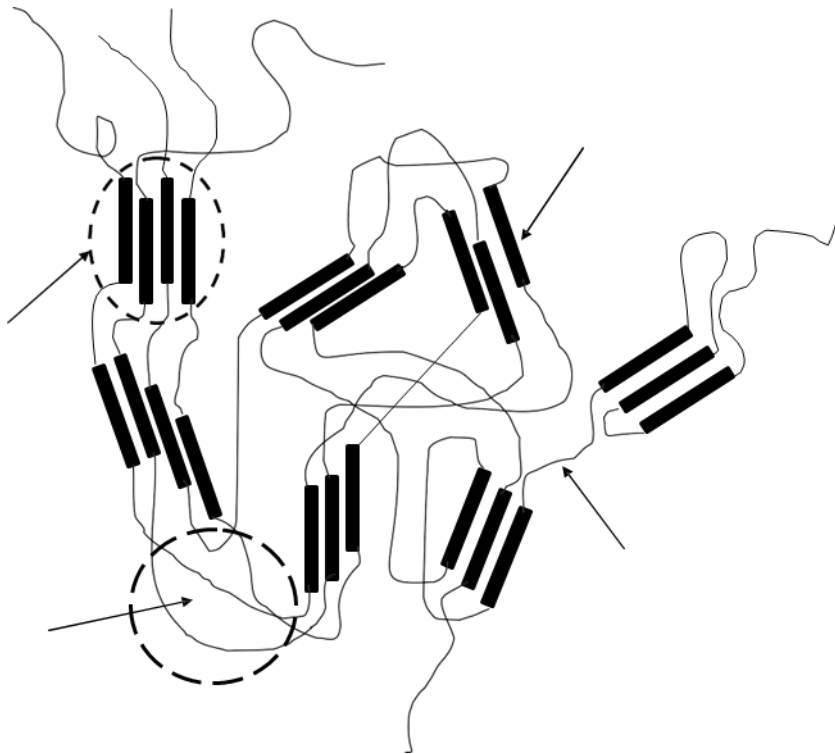


**Figure 2.3 :** Molecular structure of a thermoplastic polyurethane elastomer (Hepburn,1992).

One of the most important residences of the PUs include; just right compression set, excessive resilience, resistance to influence, tear, abrasion and climate. Their nice houses together with high hardness, modulus, abrasion and chemical resistance, just right mechanical conduct and have blood and tissue compatibility. Consequently, a PU system, in property terms, stands someplace in between average rubber and original “hard” plastics. PU products can have high flexibility (in some circumstances even in “harder” substances), with out the usage of supportive supplies like plasticizers, and additionally, high elasticity and an awfully huge range of hardness. They are able to also be welded, colored, sterilised and readily processed.

As the main riding force in the back of the flexibility of PUs is the micro-phase separation between the one of a kind blocks of the co-polymers that may be visible in determine the Figure 2.4, scientists and engineers have been making an attempt for a long time to use blocks with unique chemistry, as a way to manipulate the desirable

and thermodynamically driven section separation. This might be comprehensive with the aid of affecting the shut packing of the polymeric chains of polyurethanes and their bonding mechanisms via steric, electrostatic, amphiphilic and other forms of interactions, controlling the measure of crystallinity of the certain polyurethane accessories, altering the molecular weights of the distinctive segments, applying outside forces and distinctive thermal histories.



**Figure 2.4 :** Representation of the thermodynamically driven micro-phase separation occurring in linear, thermoplastic polyurethane systems (Krol,2007).

### 2.2.2 Basic chemical components of TPU

Thermoplastic polyurethane elastomers (TPU) belong to thermoplastic elastomers (TPE) that mix the mechanical homes of vulcanised rubber with the processability of thermoplastic polymers. They can be repeatedly melted and processed because of the absence of the chemical networks that in most cases exist in rubber. TPU were the first homogeneous, thermoplastically processable elastomers. In these days, they continue to play an principal role within the quickly growing loved ones of thermoplastic elastomers and their application can be located in practically all industrial branches. It is well identified that TPU are linear segmented block copolymers having difficult segments and delicate segments. The HS are comprised of diisocyanate, e.q. diphenylmethane 4,4-diisocyanate (MDI), by way of addition of

a sequence extender, e.g. Butanediol. The SS consist of the lengthy flexible polyether or polyester chains which interconnect two difficult segments. The hard segments act as multifunctional tie elements functioning both as bodily crosslinks and reinforcing fillers, at the same time the soft segments type an elastomer matrix which money owed for the elastic homes of TPU. At room temperature, the low melting SS are incompatible with the polar high melting HS, which ends up in a microphase separation and, for that reason, a site structure. One reason for the phase separation is because of the development of HS crystallites (Leunget al.1985).

### **2.2.2.1 Diisocyanates**

Diisocyanates used in polyurethane production have two types aromatic diisocyanates and aliphatic diisocyanates. Aromatic TPUs based on isocyanates like MDI are workhorse products and can be used in applications that require flexibility, strength and toughness. Aliphatic TPUs based on isocyanates like MDI, HDI and IPDI are light stable and offer excellent optical clarity. They are commonly employed in automotive interior and exterior applications and as laminating films to bond glass and polycarbonate together in the glazing industry. They are also used in projects where attributes like optical clarity, adhesion and surface protection are required.

#### ➤ Aromatic diisocyanates

##### \*Diphenylmethane Diisocyanate (MDI)

It was developed within the early 1960s. It is a white stable at room temperature that melts at 38 °C. It is acquired from the condensation of aniline with formaldehyde to produce methylene dianiline (MDA), which is in flip reacted with phosgene to kind MDI. Commercial MDI consists of over 98% 4,4'-MDI with small amounts of 2,4'-isomer (Oertel,1993).

##### \*Toluene Diisocyanate (TDI)

It was improved prior to the Second World War. The commercial product, a distilled colorless liquid, is a mixture of the 2,4- and 2,6-isomers. The major TDI product has a composition of 80:20 of the two isomers, but 65:35, 95:5 and pure 2,4-isomer are also available. It is obtained by nitration of toluene; hydrogenation of dinitrotoluene

is then obtained to produce toluendiamine (TDA), which is in turn reacted with phosgene to form TDI. (Oertel,1993).

➤ Aliphatic diisocyanates

\*Hexamethylene Diisocyanates (HDI)

This is the classical aliphatic diisocyanate, improved prior to the Second World War. It is a liquid at room temperature, with a freezing point of -55 °C. The starting chemical for HDI is Hexamethylene diamine, the monomer for nylon-6,6, which is reacted with phosgene to form HDI (Mills, 2007).

\*Isophorone Diisocyanate (IPDI)

It is based on Isophorone chemistry. Isophorone is reacted with HCN and afterwards the cyanoketone obtained is reduced by amination to form isophorone diamine (IPDA), which in turn is reacted with phosgene to form IPDI. It is a liquid at room temperature. Commercial IPDI is a mixture of cis and trans isomers with a 75:25 compositions.

\*Dicyclohexylmethane -4,4'-Diisocyanate (H<sub>12</sub>MDI)

This is hydrogenated MDI. Methylene dianiline (MDA) is hydrogenated and afterwards, the obtained product is reacted with phosgene to form H<sub>12</sub>MDI. It is a liquid at room temperature with a melting range of 19-23 °C.

\*Meta-Tetramethylxylylene Diisocyanate (TMXDI) and Trans-Cyclohexane Diisocyanate (CHDI)

### 2.2.2.2 Long chain diols (polyols)

Major part of the PU is composed of polyols which specify the properties of the final PU polymer. There are many varieties of polyols which have made PU the most versatile family of polymeric materials. Chemically these polyols are the compound which have hydroxyl group which react with diisocyanate to produce PU polymer. Typically, polyols are produced with 2 and 8 reactive groups having average molecular mass ranges 200-8000 g mol<sup>-1</sup>. Selection of polyols is based on the end use application and especially it should be cost effective. The varieties of polyols used are hydroxy terminated polyester polyols, hydroxy terminated polyether polyols and miscellaneous polyols including hydroxy terminated polybutadienes. Some

other types of polyol are also available under the heading of modified polyols such as PHD and PIPA polyols. (Lonescu,2005).

As described earlier, polyurethanes occur of hard and soft segments. These soft segments are improved with the help of polyols. The chemical nature of polyols has determined the physical behavior of polyurethanes.

There are four main types of long-chain diols used in the production of polyurethanes. These are:

\*Polyesters

\*Polycaprolactones

\*Polyethers

\*Polycarbonates

For polyesters; these are low molecular weight polyesters made by the condensation reaction between glycols and dicarboxylic acid (generally adipic acid). As the esterification proceeds the water produced is removed from the reaction and finally, the elimination of glycol under decreased pressure results in polyester with the desired molecular weight. Polybutanediol adipate is the most common polyester in the polyurethane production. It is very crystalline and solid at room temperature with a melting point of about 50 °C. Polyethylene adipate and copolyesters with a mixture of different glycols are also used.

For polycaprolactone; these are a peculiar type of polyesters produced by the ring-opening polymerization of  $\epsilon$ -caprolactone. They have a lower viscosity than the polyadipates of the same molecular weight, due to their narrower molecular weight distribution. They are nearly the same to polybutanediol adipate in both crystallinity and melting point (about 45-50 °C). They have an excellent temperature resistance, being more water resistant than polybutanediol adipate. For polyethers; the main polyethers used in polyurethane production are:

\*Polytetramethylene Ether Glycol (PTMEG)

This is a waxy, low crystalline solid that melts near room temperature. It is produced by polymerization of tetrahydrofuran. Compared to polycaprolactones and adipate-polyesters, it has lower crystallinity, a lower melting point and lower viscosity. This is the most used polyether in TPUs production.

#### \*Polyoxypropylene glycols (PPG)

These are liquid, amorphous polyethers produced by the polymerization of propylene oxide. They are mainly used in the production of polyurethane prepolymers and polyurethane emulsions.

#### \*Polyoxyethylene glycols (PEG)

These are from oily liquids to waxy, low crystalline solids depending on their molecular weight. They are produced by polymerization of ethylene oxide. They are soluble in water and are used for producing polyurethanes that need this characteristic.

For polycarbonates; these are white, crystalline solids produced by polycondensation reaction of diethyl or dimethylcarbonate with a diol, generally 1,6-hexanediol. Their melting point is in the range of 35-50 °C, depending on their molecular weight (Sickey et al.,2002).

### **2.2.2.3 Chain extenders**

Chain extenders are low molecular weight monomers employed to bond the prepolymer species for the duration of the synthesis of polyurethane. Any chemical compound which is difunctional can also be viewed as a chain extender, at the same time polyfunctional compounds are considered as move-linkers. These chain extenders and move-linkers are traditionally termed as chain extenders, bearing lively hydrogen agencies. Polyurethane chain extenders are categorized into two lessons: aliphatic diols and diamines. Traditionally, when polyurethane chains are multiplied with an aliphatic diol or diamine a softer fabric than do their fragrant chain elevated counterparts' outcome since these are introduced within the rough segments which ultimately controls the mechanical, thermal and hydrolytic steadiness of completed products. There are some examples of the chain extenders given below that Table 2.1 (Tsiatos,2012).



**Table 2.1** : Some chain extender types (Tsiatos,2002).

Material	Formula
1,4-Butanediol	(HO CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)
1,6-Hexanediol	(HO CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)
Ethylene diamine	(H <sub>2</sub> N CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> )
Ethylene glycol	(HO CH <sub>2</sub> CH <sub>2</sub> OH)

#### 2.2.2.4 Catalysts

A catalyst is a compound that alterations the cost of a reaction, but emerges from the reaction apparently unchanged and this phenomenon is referred to as catalysis. The catalyst will also be considered because the controlling agent of the reaction. Commonly, tertiary amines, organometallic salts of Sn, Pb and Hg and carboxylic acid salts are used as catalyst in the synthesis of polyurethanes.

Amines catalyses the -NCO and -OH reactions. Amines like tertiary amines are essentially the most reactive ones and exhibit extra full of life reaction with water than polyols. Amines are favorably used as blowing catalyst for polyurethane foams.

Organometallic salts of Sn, Pb and Hg and many others. Act as catalysts, which can be polyurethane unique e.q. Organometallic salts of Hg and Pb play a vital position in the synthesis of elastomers and inflexible spray foams, respectively. Nevertheless, both mercury and lead catalysts have negative hazard homes, so choices are perpetually being sought. Organometallic salts of Sn are essentially the most largely used catalyst and are more potential for the hydroxal agencies of polyols than water. Potassium and sodium carboxylic acid salts and quaternary ammonium carboxylic acid salts are used mainly in isocyanurate. Organotins like dibutyltin dilaurate (DBTDL) has been used for catalyzing the synthesis of polyurethane elasomers (Szycher, 1999). In this dissertation, the proposed mechanism of Sn (IV) is described because DBTDL catalyst was used during the synthesis of polyurethane elastomers. Dialkyltin dicarbonates through alcoholysis converted in to tin alkoxide, which under go intra rearrangement and react subsequently with isocyanate and resulted as N-stannylurethane complex. This complex again undergoes alcoholysis and

converted in to urethane and tin alkoxide. The various steps of the reaction mechanism have been shown monomerically for convenience in Fig. 2.3, but in there is still not a generally accepted mechanism (Szycher, 1999).

### 2.2.3 Chemical classes of TPU

Urethanes are a reaction product of a diisocyanate and long and brief chain polyether, polyester, or caprolactone glycols. The polyols and the shortchain diols react with the diisocyanates to form linear polyurethane molecules. This combination of diisocyanate and short-chain diol produces the inflexible or tough segment. The polyols form the flexible or smooth phase of the final molecule. There are three main chemical classes of TPU: polyester, polyether and a smaller class known as polycaprolactone.

- Polyester TPUs are compatible with PVC and other polar plastics. Offering value in the form of enhanced properties they are unaffected by oils and chemicals, provide excellent abrasion resistance, offer a good balance of physical properties and are perfect for use in polyblends.
- Polyether TPUs are slightly lower in specific gravity than polyester and polycaprolactone grades. They offer low temperature flexibility and good abrasion resistance and tear resilience. They are also durable against microbial attack and have excellent hydrolysis resistance making them suitable for applications where water is a consideration.
- Polycaprolactone TPUs have the inherent toughness and resistance of polyester-based TPUs combined with low-temperature performance and high resistance to hydrolysis. They are an ideal raw material for hydraulic and pneumatic seals.

TPUs can also be subdivided into aromatic and aliphatic varieties:

- Aromatic TPUs based on isocyanates like MDI are workhorse products and can be used in applications that require flexibility, strength and toughness.
- Aliphatic TPUs based on isocyanates like H<sub>12</sub>MDI, HDI and IPDI are light stable and offer excellent optical clarity. They are commonly employed in car interior and exterior functions and as laminating films to bond glass and polycarbonate together within the glazing industry. They are also utilized in

projects where attributes like optical clarity, adhesion and surface protection are required (Petrovic,1998).

The foremost change between each forms is their resistance to daylight. Uncovered to an ultraviolet radiation within the presence of oxygen, similar to an incidental sunlight radiation, fragrant polyurethanes suffer an ultraviolet initiated auto oxidation degradation, with a deepening colour of the uncovered polyurethane which alterations from colorless to yellow and to amber and, on large exposures, even to a brown color, with lack of mechanical houses. This is due to the fact that the aromatic ring, beneath such stipulations, is auto oxidized to a chromophore akin to a quinoneimine structure. Aliphatic diisocyanates can not undergo such quinoid formation, yielding polyurethanes that exhibit a sophisticated balance to ultraviolet radiation and as a result superior colour balance and good mechanical property retention.

On the contrary aromatic polyurethanes have better thermal resistance (in the absence of oxygen) than aliphatic polyurethanes. This is an important point, as the urethane group is the least thermal resistants in the polyurethane structure. Thermooxidation resistance is great influenced by the type of long-chain diol, more than by the difference between aliphatic or aromatic diisocyanate (Szycher,1999).

The properties of the resin depend on the nature of the raw materials, the reaction conditions, and the ratio of the starting raw materials. The polyols used have a huge influence on certain properties of the TPU. Both polyether and polyester polyols are used to produce many products. The polyester-based TPUs have the following characteristic features:

- good oil/solvent resistance
- good UV resistance
- abrasion resistance
- good heat resistance
- mechanical properties

The polyether-based TPUs have the following characteristic features:

- fungus resistance

- low-temperature flexibility
- excellent hydrolytic stability
- acid/base resistance

In addition to the basic components described earlier, most resin formulations contain additives to provide production and processability. Other additives can also be included such as:

- demolding agents
- flame retardants
- heat/UV stabilizers
- plasticizers

The polyether types are quite more luxurious and have better hydrolytic steadiness and low temperature flexibility than the polyester varieties. Applications and end makes use of incorporate the clinical thin-walled, bendy tubing, catheters, connectors, luers, and stopcocks, movies and material coatings, component housings, smooth contact grips, dental components, automobile battery cables, ski goggles, ski boot shells, snowboard surfaces, and sporting events shoe soles.

The hydrolysis reaction of an ester group follows the three-centre mechanism and is catalyzed by both acid and bases; since a free acid is liberated as a result of the hydrolysis of ester bonds, this reaction becomes autocatalytic. Therefore, polyethers TPUs have much better hydrolysis resistance than polyester and polycaprolactone TPUs (Verhoeven,2004). As a summary, the hydrolysis resistances of the types of TPU were given as follows:

Polyether TPU >>>Polycaprolactone TPU> Polyester TPU

Polyether TPUs have much better microbial resistance than polyester and polycaprolactone TPUs. In other words:

Polyether TPU >>>Polycaprolactone TPU= Polyester TPU

Oxidation in most cases begins with attacking the hydrocarbon chains to provide radicals, which in turn, develop several reactions until chain scission (a normal oxidation mechanism). The more the hydrocarbon chain has labile hydrogen atoms,

the less the polymer has thermooxidative balance. In ethers the hydrogen bonded to the carbon adjoining to the oxygen is especially sensitive to oxidation, with ease forming peroxides. By contrast, the ester bonds are those TPUs moieties most resistant to oxidation. To sum it up, thermooxidative stability:

Polycaprolactone TPU= Polyester TPU>>>Polyether TPU

A schematic summary of the resistances properties of TPU types are given Table 2.2.

**Table 2.2 :** Comparison of different based TPUs (Zia,2008).

Parameter	Polyester based TPUs	Polycaprolactone based TPUs	Polyether based TPUs
Hydrolysis resistance	--	-	++
Microbial stability	--	--	+
Adhesion strength	+	++	-
Thermooxidative resistance	+	+	-
Low temperature flexibility	o	+	++
Mechanical properties	++	++	+
Oil and grease resistance	++	+	-
Injectability (cycle time)	+	++	o

(++ excellent; + good; o acceptable; - poor; -- very poor)

#### 2.2.4 Chemistry of TPU

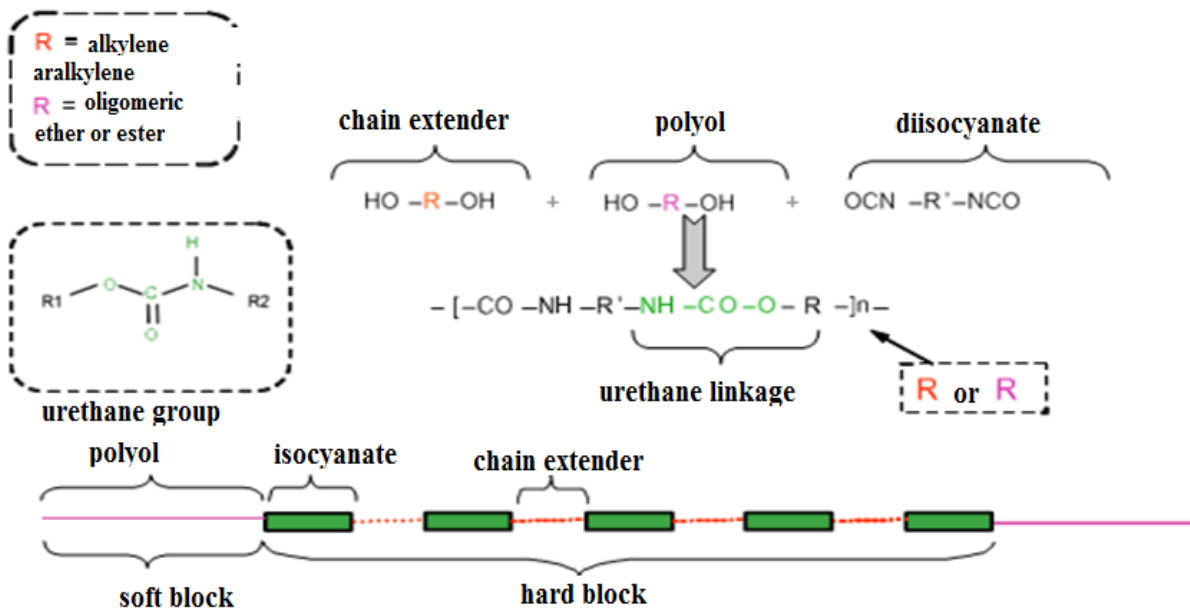
A TPU is a multi-phase block copolymer that is created when three basic raw materials are combined together in a specific way. The individual components required to produce a TPU are:

\*a polyol or long-chain diol

\*a chain extender or short-chain diol

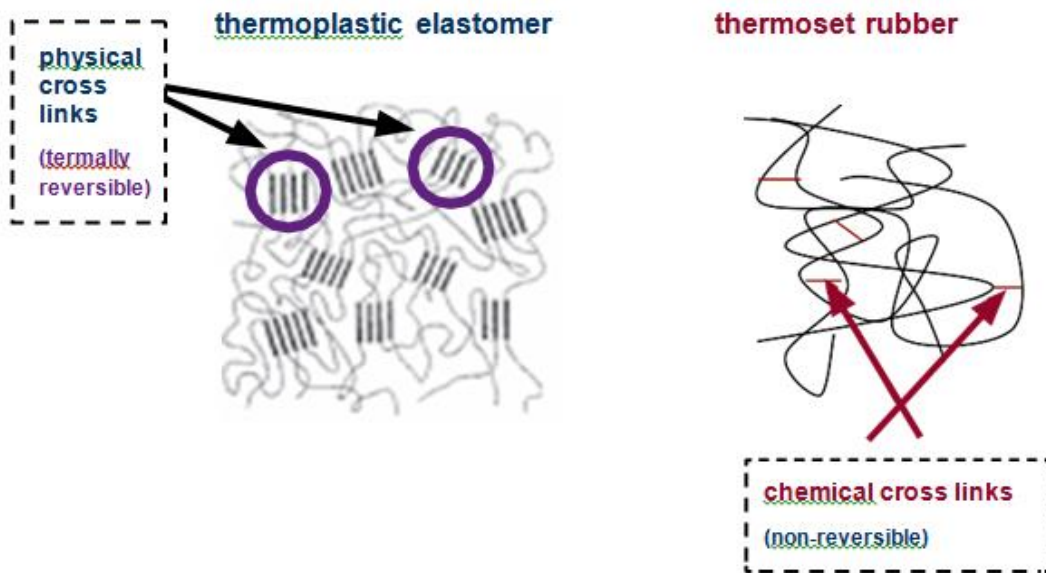
\*a diisocyanate

Basic chemistry of TPU can be seen in below in Figure 2.5, 2.6 and 2.7.



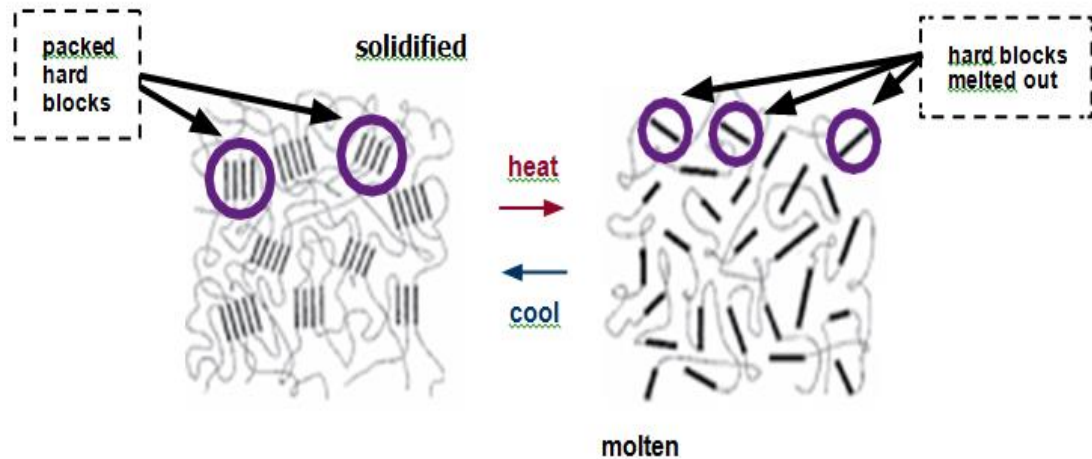
**Figure 2.5 :** Basic chemistry of TPU (Sickey et al.,2002)

The smooth block, constructed out of a polyol and an isocyanate, is dependable for the flexibility and elastomeric persona of a TPU. The hard block, constructed from a chain extender and isocyanate, gives a TPU its toughness and physical performance properties.



**Figure 2.6 :** Cross-linking structure of a thermoplastic elastomer versus a thermoset rubber (Sickey et al.,2002).

It shows that there are no chemical cross-links in TPUs unlike thermoset rubbers or casted polyurethane systems.



**Figure 2.7 :** Graphic illustration of the morphology of a TPU (Sickey et al.,2002).

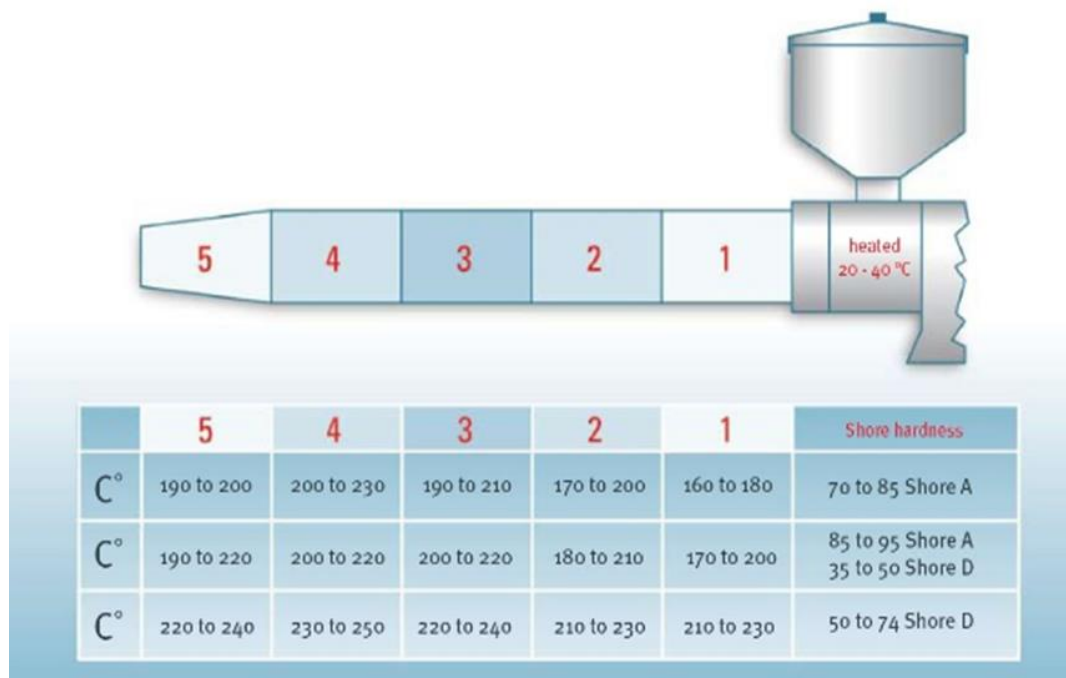
It shows how physical cross-links melt out under heat and repack when the material is cooled.

### 2.2.5 Processing of TPU

In processing TPUs, water at elevated temperatures reacts with the isocyanate one of the building blocks of urethanes. One of the by-products of the reaction of TPUs with water is carbon dioxide. Urethanes that are processed "wet" will tend to foam or bubble during processing and that will be manifested in the final part. While many resin manufacturers recommend that the moisture content of TPUs be less than or equal to 0.05% for molding and 0.02% for extrusion, experience dictates that they be even dryer. However, when parts made from resin with a moisture content of less than 0.05% when molded and 0.02% when extruded may appear fine, their physical properties probably are not optimized. Elongation, impact strength, tensile modulus, and other properties can be negatively affected. In addition, it is not just the percentage of moisture content that's important, but also how one gets to it. If not dried properly, TPUs will degrade. If the resin is dried too lengthy, it is going to oxidize; if it is dried at too excessive a temperature, the polymer chains will probably be severed. Once the resin is dry, the material must not be exposed to air for increased durations of time as it will swiftly take in moisture again (Wilkinson, 1999).

TPU should be processed at melt temperatures of between 190 and 220 °C. With some hard grades, a melt temperature of up to 240 °C may be needed. Figure 2.8

shows guide values for the settings for cylinder and nozzle heating in relation to the Shore hardness. As a rule, small injection molding machines need a higher temperature setting than large ones.



**Figure 2.8 :** Temperature profile according to hardness (Wilkinson,1999).

The mold temperature has a major influence on the quality of the surface and the demolding behavior. It also affects shrinkage and internal (frozen-in) stresses in the final component. Mold temperatures of between 20 and 40 °C are generally employed. A number of modified and glassfiber grades require mold temperatures of up to 60 °C in order to achieve an optimum surface finish. With thick-walled articles, cooling down to approximately 5 °C can bring a reduction in cycle time.

### 2.2.5.1 One-Shot process

One-shot polymerization is established by simultaneous addition of a polyol, a diisocyanate, and a chain extender stoichiometrically. Polymerization methodology either bulk or solution determine the use of solvent. Solvent is recommended for solution polymerization. Common solvents used in urethane synthesis are dipolar aprotic solvents including N, N'-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and dimethyl formamide (DMF). The reaction mixture is heated above 80-100°C to prepare the polyurethane elastomers. In some cases, catalysts are also recommended especially when aliphatic isocyanates are used (Mills,2007).



### **2.2.5.2 Two-Step process**

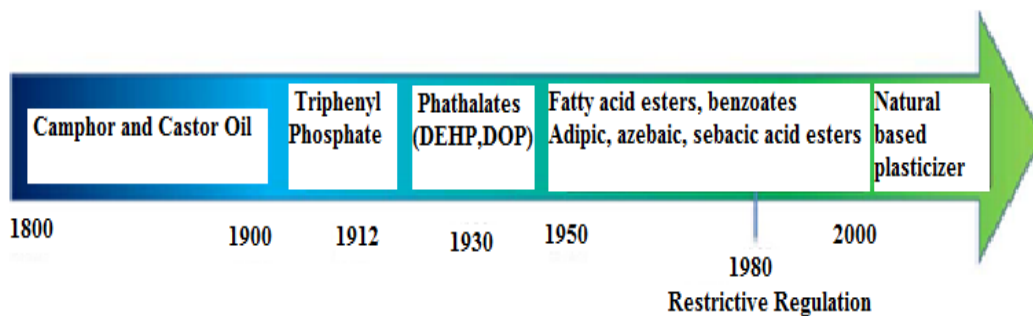
However, two-step synthesis is an extra long-established route for manufacturing the polyurethane. This method can be termed as the prepolymer method. In step one, a polyol is reacted with excess of diisocyanate to form a NCO terminated oligomer of excessive molecular mass referred to as prepolymer, relying upon the polyol's molecular weight and the ratio between these two reactants. The prepolymer that is formed is almost always a sticky liquid, which is without problems saved. Within the 2d step, prepolymer is changed in to the final polyurethane by reacting with a diol or diamine performing as chain extender and mainly referred to as the chain extension step.

Because the tender phase influences the elasticity and low temperature efficiency limit and in addition contributes toward hardness, tear strength and modulus. However, difficult section especially impact modulus, hardness and tear force and also verify the upper use limit of temperature. So, a polyurethane constitution made by using the 2-step process is extra systematic than one-shot procedure. This structural regularity determines the easier mechanical homes to the polyurethane. (Hepburn, 1992).

## **2.3 Plasticizers**

In step with the IUPAC council, a plasticizer is outlined as “a substance or a material integrated right into a plastic to develop its flexibility, workability or distensibility.” nonetheless countless other definitions of plasticizers are based on the molecular weight, the nonvolatile personality of the compounds. Plasticizers comprise many healthy compounds: oil derivatives, animal fat, vegetable oils. The foremost position of plasticizers is to increase the flexibility and the processability of polymers by using reducing the glass transition temperature ( $T_g$ ). Plasticizers enable processing on different types of apparatus (injection molding, extrusion, calendaring), optimizing experimental parameters, shortening the blending time, and the stress of extrusion. They also scale back physical properties like hardness, elastic modulus, and expand fracture and impact resistance. Viscosity, density and dielectric constant are additionally impacted by the polymer chain flexibility. Numerous other properties are affected by means of plasticizers: crystallization, melting and gelation temperatures,

interactions with water, firebehavior, gas permeability, degradation rate. The evolution of plasticizers can be seen in Figure 2.9.



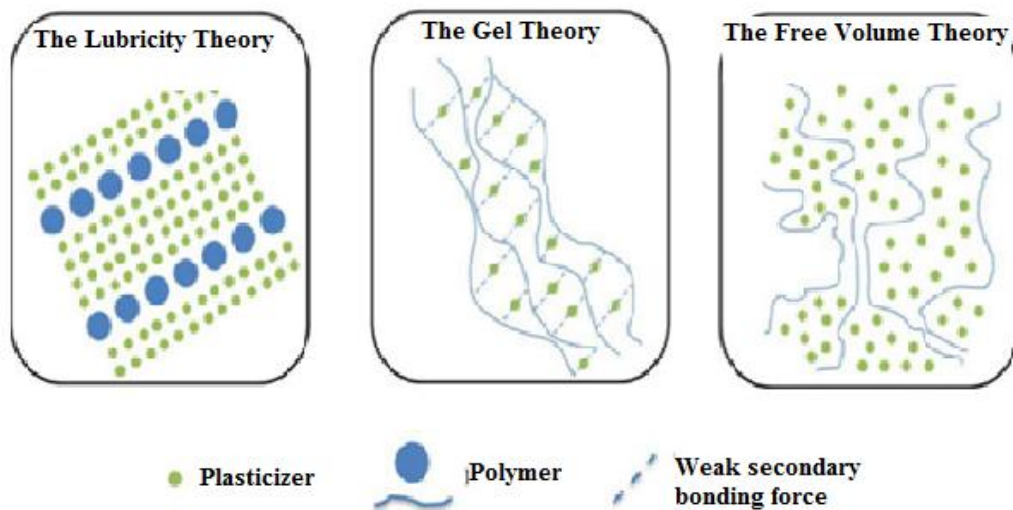
**Figure 2.9 :** Evolution of plasticizers (Benaniba,2010).

There are presently about 100 different plasticizers produced worldwide, although only about 50 of these are important. Of these 50 products, just 7 plasticizers comprise more than 80% of the global plasticizer market. Approximately 90% of all plasticizers are used in the production of plasticized or flexible PVC materials. For this reason, the majority of the information discussed in this chapter will focus on PVC plasticizers. Other polymer systems that use small amounts of plasticizers include poly(vinyl butyral) or PVB, acrylic polymers, poly(vinylidene chloride), nylon, polyolefins, polyurethanes, and certain fluoroplastics. The estimated worldwide production of plasticizers in 2014 was about 14 billion pounds with the majority of the plasticizer consumption taking place in Asia Pacific, predominately China. About 75% of this volume is phthalate ester plasticizers (Gil,2006).

### 2.3.1 Mechanism of plasticizers

The primary plasticization theories have been developed in 1930–1950. Three of them are nonetheless used nowadays: the lubricity idea and the gel thought that had been developed in a parallel means, and ultimately the free quantity concept which originated some years later than the other two. Mainly it is well-known that the low molecular weight of a plasticizer allows decreasing secondary forces (hydrogen bonding, vander waals forces etc.) between the polymer chains by means of occupying intermolecular spaces. Therefore, plasticizers change the molecular institution of polymers, lowering the power required for molecular movement.

The lubricity theory supplies that the plasticizer diffuses into the polymer, inserting into the polymer chains and decreasing the intermolecular frictions. The macromolecules slip over every other when a plastic part is flexed. Then, the plasticizer lubricates the movement of the molecules decreasing their internal resistance to slide and to avert the reformation of the inflexible matrix. As a consequence, consistent with this thought, a plasticized plastic can also be represented as parallel alternating layers of polymer and plasticizer (Gil,2006). The lubricating theory of plasticization holds that plasticizers act as molecular lubricants to facilitate polymer chain movement when a force is applied to the plastic. It starts with the assumption that the unplasticized polymer chains do not move freely because of surface irregularities and van der waals attractive forces. As the method is heated and blended, the plasticizer molecules diffuse into the polymer and weaken the polymer–polymer interactions. Portions of the plasticizer molecule are strongly drawn to the polymer even as other materials of the plasticizer molecule can preserve the polymer chain and act as a lubricant. This discount in intermolecular or van der waals forces among the polymer chains raises the flexibility, softness, and elongation of the polymer. It can be seen in Figure 2.10 of the theories.



**Figure 2.10 :** Mapping of plastication theories (Gil,2006).

The gel theory is based on the assumption that the plasticized polymer is considered to be a three-dimensional network with plasticizer molecules bonded to resin chains by weak secondary forces. The plasticizer acts by breaking the polymer–polymer bonds and interactions, masking these centers of attachment from each other and

preventing their reformation. To sum up, the lubricity theory assumes that the tension of polymers comes from interior frictions and that plasticizers act by way of lubricating the layers of polymer whereas the gel thought supposes that it comes from elements of attachments of polymer to polymer and that plasticizers reduce the quantity of those sites. The gel idea considers the plasticized polymer to be neither solid nor liquid however an intermediate state, loosely held collectively through a three-dimensional community of vulnerable secondary bonding forces. This network or gel might be shaped by everlasting intermolecular ties or by means of ties that form in a dynamic state, as plasticizers partner and disassociate with the polymer. In result the plasticizer supplies the position of a bridge between two polymer chains. The bonding forces performing between plasticizer and polymer are conveniently overcome through utilized external stresses permitting the plasticized polymer to flex, elongate, or compress (Wypych,2004).

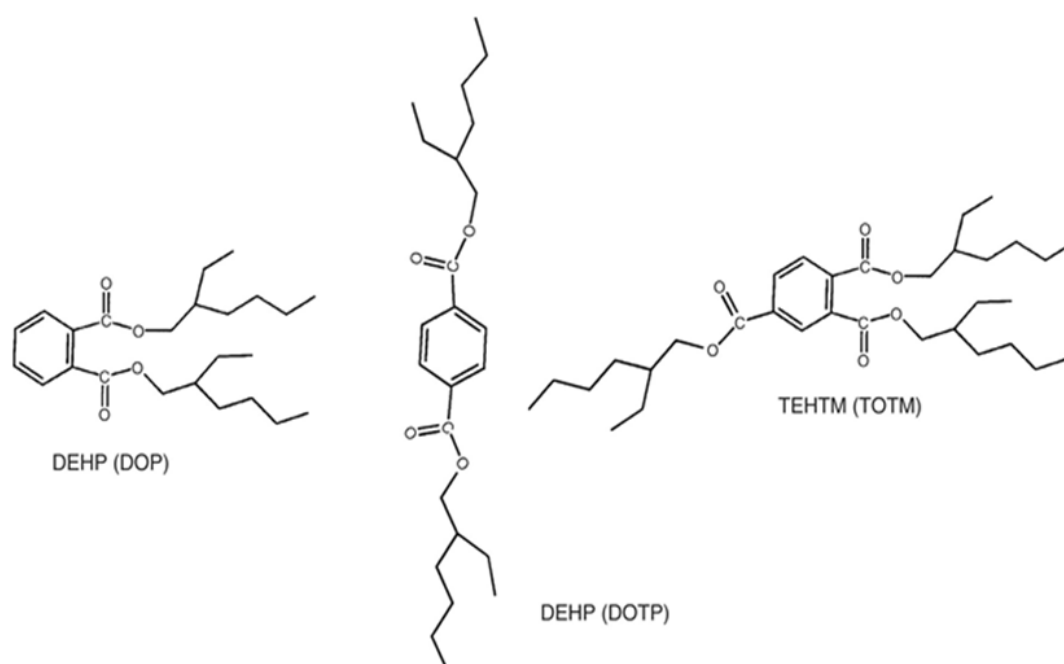
The free volume is the internal space available within a polymer. A rigid polymer possesses very little free volume. When a plasticizer is added, it increases the free volume making the polymer soft and rubbery, increasing motion of polymer molecules. This free volume is maintained when the resin-plasticizer mixture is cooled down after melting. Free volume comes from three principal sources: motion of chain ends, motion of side chains and motion of the main chain (Wypych, 2004). Free volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided by molecule or polymer chain movement, making the polymer system more flexible. In the unplasticized polymer, free volume arises from movement of polymer end groups, polymer side chains, and internal polymer motions, while in the amorphous region (Maruru,2002).

### **2.3.2 Types of plasticizers**

Plasticizers can be characterized by the concentrations in which they are used. Primary plasticizers are the products that are either used as the sole plasticizer in the system, or the major plasticizer that is used in plasticizer blends. Secondary plasticizers are used in smaller quantities in a blend with a primary plasticizer. Secondary plasticizers are generally added to improve a specific property such as low temperature flexibility, reduced flammability, improved processing, or reduced costs.

### 2.3.2.1 Phthalate esters

Phthalate esters continue to represent the largest chemical class of plasticizers, with DEHP and DINP as the two most commonly used plasticizers globally. Phthalate esters are used by the esterification of phthalic anhydride with 2 molar equivalents of an alcohol or an alcohol blends. Although almost any alcohol can be used to make a phthalate ester, it is usually only the esters of the C<sub>6</sub> to C<sub>13</sub> alcohols that are useful as PVC plasticizers. Improvements in plasticizer performance can be obtained through the choices in the level of branching of the alcohol used to come together phthalate esters. Figure 2.11 shows the structure of three plasticizers.



**Figure 2.11 :** Structures of the phthalate, terephthalate, and trimellitate esters of 2-ethylhexanol (Maruru,2002).

### 2.3.2.2 Terephthalate esters

The terephthalate plasticizer DEHTP, first commercialized around 1975 as Eastman DOTP, is very similar in structure to DEHP except that the substitution of the aromatic ring is at the 1,4 position versus the 1,2 position of the aromatic ring. The structure of DEHTP is also shown in Fig. 2.12. Terephthalates are prepared by the esterification of terephthalic acid or by the transesterification of dimethyl terephthalate with aliphatic alcohols such as butanol or 2-ethyl hexanol. Terephthalate esters will not be as suitable as phthalates with PVC and more elaborate to method. Today there may be very nearly just one predominant

terephthalate plasticizer commercially on hand, DEHTP, as terephthalate esters of C<sub>9</sub> and C<sub>10</sub> alcohols have compatibility issues (Gil,2006).

### **2.3.2.3 Dibasic acid esters**

Aliphatic dicarboxylic acid esters are prepared by the esterification of diacids such as adipic, succinic, and azelaic acid with C<sub>6</sub> to C<sub>10</sub> monohydric alcohols. Most of the more commercially important products are based on 2-ethyl hexanol. This class of plasticizers was first introduced in the 1940s and these products are generally used to help extend the useful temperature range of plasticized PVC products by providing increased flexibility at lower temperatures. Di-2-ethylhexyl adipate (DEHA), which is prepared by the esterification of one mole of adipic acid with two moles of 2-ethyl hexanol, is the most important plasticizer in this class. Another important adipate is diisononyl adipate (DINA), which offers greater permanence over DEHA. Di-2-ethylhexyl azelate (DEHZ) and diisodecyl adipate (DIDA) are used for demanding low temperature applications or low temperature applications requiring plasticizers with lower volatility than DEHA or DINA. DEHA is also used in a number of food contact approved applications, including film. Generally, these dibasic acid esters are not used as phthalate replacements or phthalate alternatives except in a few situations; this is because the properties of the finished PVC product are too different, the processing of flexible PVC with these products is different, and these esters are much more expensive than the GP phthalates and many phthalate alternatives.

### **2.3.2.4 Epoxy plasticizers**

The consumption of epoxy plasticizers has grown in the past few years because of the interest in vegetable oil derived plasticizers. Vegetable oils and other natural oils are not compatible with PVC and will get over time; consequently, chemical modification of these products is required to make these oils compatible with PVC. Techniques such as elimination of a double bond through conversion to an epoxide or through conversion of hydroxyl functionalities into esters such as acetate esters are often used. The product epoxidized soybean oil (ESO) was introduced as an alternative for the primary plasticizer DEHP more than 50 years ago. Because it was offered at lower costs, had significant improvements in plasticizer permanence, and provided a secondary benefit of improved PVC stabilization, ESO developed a

number of commercial applications. Consequently, the use of ESO as a primary plasticizer rapidly decreased while its use, and the use of other alkyl epoxy stearates, increased as costabilizers for PVC. The PVC stabilizer market still get the most important application for epoxy esters (Bananiba,2010).

### **2.3.2.5 Benzoate esters**

Like many of the phthalate alternatives, benzoic acid situated plasticizers have additionally been commercially on hand for greater than 50 years. Despite the fact that there are a type of extraordinary forms, most can be categorised as dibenzoate esters or monobenzoate esters. Dibenzoate esters are ready with the aid of the esterification of 2 molar equivalents of benzoic acid with a glycol reminiscent of diethylene glycol or dipropylene glycol. These esters and benzoate ester combo present rapid fusing performance and to find a style of functions in plastisol tactics like spread coating, rotomolding, spraying, and dipping, either as the primary plasticizer or as a speedy-fusing secondary plasticizer utilized in blends with plasticizers equivalent to DINP or DEHTP. The advantages benzoate plasticizers convey are multiplied processability, extended stain resistance, and better UV steadiness; regrettably they have got bigger densities, are more unstable than GP plasticizers, and give decreased low temperature flexibility and bigger plastisol viscosities.

Monobenzoate esters are prepared by the esterification of benzoic acid with one molar equivalent of alcohol, usually 2-ethylhexanol, isononanol, or isodecanol. Monobenzoates are not used as primary plasticizers but as secondary plasticizers where they help reduce plastisol viscosities, lower the fusion or processing temperatures, and give a boost to stain resistance in formulations based on GP plasticizers. Both mono and dibenzoate esters can be used in non- PVC materials such as acrylic films and caulks, latex coatings, polysulfide sealants and coatings, and polyurethanes (Benaniba,2010).

### **2.3.2.6 Trimellitate esters**

Trimellitate esters are used as primary plasticizers in those applications where greater permanence is required. These esters, prepared by the esterification of trimellitic anhydride with 3 molar equivalents of alcohol, are similar in structure to both the lactic acid esters and terephthalic acid esters of Fig. 2.12, but with a third ester

functionality on the aromatic ring. This third ester group increases the molecular weight and improves the plasticizer compatibility with PVC. Trimellitate esters offer advantages in greater plasticizer permanence, either by reduced volatility losses or losses attributed to lower migration rates into other materials. Trimellitate esters prepared with linear alcohols in the C<sub>6</sub> to C<sub>8</sub> range show improved resistance to outdoor weathering and are used in automotive instrument panels. (Benaniba,2010).

### **2.3.2.7 Phosphate esters**

One of the very first plasticizers proposed for PVC was the phosphate ester tricresyl phosphate. This plasticizer was later used for its flame-resistant properties in the first commercial PVC electrical wire insulation materials. Today the majority of the phosphate esters used as plasticizers are the alkyl diaryl phosphates, which are prepared with mixtures of various phenols and alcohols and often used in combination with GP plasticizers such as DINP, DIDP, or DPHP. Phosphate esters provide significant improvement in flame retarding properties and for some products, reduced smoke generation. This property helps enable flexible PVC materials to be used in plenum cables, data and communication cables, and electronics. Phosphates such as isodecyl diphenyl phosphate can also be used in transportation fabrics and wall coverings where some level of flame retardant properties is required (Wypych, 2004).

## **2.4 Literature Review**

Thermoplastic polyurethanes (TPU) are a commercially predominant type of thermoplastic elastomers, which have an inherent nanostructured morphology. The urethane linkage is formed through the reaction between an isocyanate workforce and a hydroxyl team. Preliminary reports into these polymers excited by forming linear polyurethanes via reacting diisocyanates with diols, but it was very speedily realized that a multitude of polymers with vast-ranging properties would be produced. Early work occupied with polyester-founded polyols; nonetheless, the improved hydrolytic stability and big versatility afforded through polyether-founded polyols saw them grow to be a preferred precursor in polyurethane synthesis. Nowadays, the massive resolution of polyols, isocyanates, and chain extenders allows polyurethanes to be diverse from soft thermoplastic elastomers to adhesives,



coatings, flexible foams, and rigid thermosets. TPUs are normally known as 'segmented polyurethane block copolymers,' and kind a subset of a big and commercially essential loved ones of thermoplastic elastomers comprising styrene block copolymers, thermoplastic olefins, thermoplastic vulcanizates, and copolyester elastomers. TPEs combine the pliability and resilience of rubbers with the processability of plastics. (Martin, 2012).

Some usual purposes for TPUs incorporate car interiors, footwear, flexible hose and tubing, mobile buttons, closures, seals and o-rings, adhesives, cable jacketing, activity and enjoyment objects, textiles and textile coatings, implantable scientific device accessories, mining and mineral processing equipment, laminates for affect glazing, photovoltaic phone encapsulation, and wastewater therapy apparatus, simply to name a few (Tereshatov,2014).

Recent screening studies in industrialized countries for contaminants in human urine samples have published the huge exposure of folks to the group of phthalate plasticizers. In view that phthalates are not chemically certain to the products they quite simply diffuse to the encompassing media throughout its existence-time, important reasons from the atmosphere that cause the aging of the especially those with high fat content material. As a consequence, phthalates contaminate indoor environments and human food and belong to the ubiquitous environmental contaminants and present difficulties in toys. Several phthalates and especially diethyl hexylphthalate (DEHP) is well known as di-octyl phthalate, (DOP, as well) are suspected of having bad health effects. In 2008, dibutyl phthalate (DBP), DEHP, and benzyl butyl phthalate (BBP) were ordered within the SVHC (Substances of Very High Concern) by ECHA (European Chemicals Agency), as toxic for human infertility. Recently, many plasticizer producers promoted several products for alternative in order to substitute DEHP due to the health effects as a shift from low to high molecular phthalates or even to other compound classes (adipates, succinates, glutarates, terephthalates, trimellitates, and citrates) has taken place for the use in TPU and PVC applications.

The migration behavior of plasticizers is of value on account that the phthalates soon will come to be out of use with the intention to alleviate the environmental illness problems and ensure compliance with the contemporary environmental and

wellbeing rules of European Union. On this gain knowledge of, it's searched about the to find the substitute plasticizer for TPU (Demir and Ulutan,2012).

Within the contemporary be trained of Kim et al., it's investigated for the plasticized TPU/PC blends. Thermoplastic polyurethane (TPU) is likely one of the most versatile engineering thermoplastics with elastomeric properties. The TPUs possess bigger tensile modulus in comparison to rubber, excessive abrasion resistance, and resistance to oil and plenty of solvents. TPUs are characterized via a two-phase morphology in which a tender section containing either polyesters or polyethers is strengthened via condensation, with a tough area together with an aromatic diisocyanate elevated with a brief-chain diol. Via various the quantities of the difficult and tender segment, the residences may also be assorted over a extensive range, and houses of blends additionally will also be influenced. TPUs are used as nonmigrating plasticizer in poly(vinyl chloride) (PVC) and not using a shrink of physical properties (Kim et al.,1998).

In 2004, Leonard G. Krauskopf research about the alternative plasticizer instead of phthalate. In summation, over 200 chemical structures have been evaluated as plasticizers for PVC. Possibly one many of them have met commercial desires. But, the key 'common rationale' plasticizers consist of not up to six or seven dialkyl phthalates. Price anal total performance in PC are the imperative standards. This paper summarizes the criteria required for any candidate plasticizer to meet, in an effort to be potential as a substitute to 'common rationale Phthalate Plasticizers.' not one of the substances reviewed on this paper appears to qualify, which is not to say that future raw materials and innovations is not going to make it possible.

Applications that chiefly require another to phthalate plasticizers is also satisfied via choices from the chemical courses described in this paper. However, in comparison with flexible percentmerchandise made with common motive phthalate plasticizers, the formulator should expect performance compromises and higher fees (Krauskopf,2003).

### **3. EXPERIMENTAL**

In this part of the study, the test procedure, materials, equipment used are indicated. The work that constitutes the main structure of the thesis is explained in this section.

#### **3.1 Materials**

##### **3.1.1 Ravathane 130A65**

Ravathane® is the brand name for Thermoplastic Polyurethanes in Ravago Petrokimya Üretim A.Ş. The most outstanding advantage of polyurethane in comparison with other materials is that products with very different hardness, density and elasticity can be produced by modifying their formulations. This allows producing products suitable for different areas of usage just by changing the raw material.

Ravathane 130A65 (R130A65) is a plasticized thermoplastic polyurethane based on polyester having strong resilience and tear resistance, excellent abrasion resistance, higher resistance to hydrolysis failure and oxidation, good stability towards solvents and light. It is for injection molding.

In this study, R130A65 was made with non-plasticizer and 10%-20%-30% plasticizer with one-shot process-reactive extrusion in extruder. The beginning was the mixing of MDI as diisocyanate, 1,4- butanediol, polyester polyol (produced from Ravago named SPX56E00) and tetra isopropyl titanate as catalyst. If it is non-plasticizer, the pellets were get after the extrusion directly but if it plasticizer will be added, they are feed into 9th zone and pellets were obtained. Absorption process were started with the non-plasticized R130A65. The plasticizers were added externally to the granules and the granules were mixed with the plasticizers.

The typical properties of non-plasticized and plasticized R130A65 can be seen in Table 3.1 and Table 3.2.

**Table 3.1** : Typical properties of plasticized R130A65

Properties	Test Method	Units	Values
Hardness	ISO 868	Shore A	67
Density	ISO 1183-1A	gr/cm <sup>3</sup>	1.15
Tensile stress at:			
-100% Elongation	ISO 37	MPa	2.14
-200% Elongation	ISO 37	MPa	5.0
Tensile Strength at Break	ISO 37	MPa	25
Elongation at Break	ISO 37	%	900
Tear Strength	ISO 34-1 B/b	N/mm	80
Abrasion Resistance	ISO 4649	Mm <sup>3</sup>	40

**Table 3.2** : Typical properties of non-plasticized R130A65

Properties	Test Method	Units	Values
Hardness	ISO 868	Shore A	82
Density	ISO 1183-1A	gr/cm <sup>3</sup>	1.19
Tensile stress at:			
-100% Elongation	ISO 37	MPa	4.9
-200% Elongation	ISO 37	MPa	10.0
Tensile Strength at Break	ISO 37	MPa	38
Elongation at Break	ISO 37	%	620
Tear Strength	ISO 34-1 B/b	N/mm	126
Abrasion Resistance	ISO 4649	Mm <sup>3</sup>	30

### 3.1.2 Benzoate ester plasticizer (BZ)

Benzoflex™ 9-88 is a high solvating plasticizer that has been used for many years in a wide variety of polymer systems and applications. Its diverse uses include resilient flooring, adhesives, artificial leather cloth and caulk. It is supplied from Estman company. Physical properties declared by company datasheet are given in Table 3.3.

**Table 3.3** : Physical properties

Property	Typical Value, Units
Boiling Point @760 mmHg	347 °C
APHA Color, Pt-Co Scale	40-80
Flash Point Setaflashed Closed Cup	182 °C
Odor	Mild
Pour Point	-19 °C
Refractive Index @25 °C	1.52
Solubility in Water @25 °C	Negligible
Specific Gravity @25°C/25 °C	1.12
Vapor Pressure @20 °C	<0.00001 torr
Viscosity <sup>a</sup> @25 °C	105 MPa.s

### 3.1.3 Phthalate ester plasticizer (PH)

Santicizer 261A is a fast fusing phthalate plasticizer that supplied from Valtris company. Used in acrylic coatings. Possesses very good resistance to extraction, low initial viscosity, good shelf life and flow properties. Provides very good durability, anti-fogging properties, good adhesion to metal undercoats, improved weatherability and good solvent-craze resistance. Offers gloss, good flow characteristics and flexibility without brittleness for a long, handsome coating life. There are many advantages;

- High solvating plasticizer with low volatility, extremely low moisture and excellent permanence
- Compatible in multiple polymers offering versatility in formulating
- Fast-fusing plasticizer in PVC systems to boost throughput and energy saving
- Calendering and extrusion: combination of the efficiency of monomeric esters with permanence approaching that of low molecular weight polymeric plasticizers
- Extraction resistance against alcohol and kerosene is comparable to low molecular weight polymeric plasticizers
- Improved foam structure, dimensional stability and better blowing ratio in chemically and mechanically blown foams
- Excellent compatibility in PU, providing viscosity control, permanence and tolerating high filler levels because of its superior wet-out characteristics
- In acrylic coatings, excellent durability, permanence, excellent adhesion to metal undercoats, combined with excellent gloss, water resistance, providing good flow characteristics and flexibility without brittleness for a long coating life.

Typical properties of phthalate ester are given Table 3.4.

**Table 3.4 : Typical properties of PH**

Property	Typical Value,Units
Appearance	Clear, oily liquid
Acidity (meq KOH/100g)	0.25 max.
Color (APHA)	75 max.
Moisture (byKF, wt%)	0.03 max.
Specific Gravity @25°C/25°C	1.059
Viscosity <sup>a</sup> @25°C	101

**3.1.4 Adipate plasticizer (DOA)**

Eastman™ DOA plasticizer (Bis(2-Ethylhexyl) Adipate) is a light colored, oily liquid generally used as a plasticizer for PVC. It can be used alone or blended with other plasticizers, such as DOP or DOTP. In PVC, Eastman™ DOA features flexibility at low temperatures, good electrical properties, good resistance to weathering, and good stability to heat. Eastman™ DOA is used to produce clear films for food packaging applications. In addition to PVC, Eastman™ DOA is compatible with nitrocellulose, ethyl cellulose, most synthetic rubbers, and high butyryl cellulose acetate butyrates. Table 3.5 gives the physical properties of DOA.

**Table 3.5 : Physical properties of DOA**

Property	Typical Value,Units
Acidity (wt%)	0.02 max.
Color, Pt-Co Scale	10 max.
Flash Point Setaflashed Closed Cup	196 °C
Refractive Index @25 °C	1.447
Specific Gravity @25°C/25 °C	0.927
Boiling Point	417 °C
Freezing Point	<-70 °C
Vapor Pressure @20 °C	<0.00001 torr
Viscosity <sup>a</sup> @25 °C	105 MPa.s

**3.1.5 1,2-Cyclohexane dicarboxylic acid diisononyl ester (HE)**

1,2-Cyclohexane dicarboxylic acid diisononyl ester is an aliphatic plasticizer for the manufacture of flexible plastic articles in sensitive application areas such as toys, medical devices and food packaging. From a chemical point of view, it belongs to the group of aliphatic esters. Hexamoll® DINCH® is the trusted non-phthalate plasticizer especially developed for applications with close human contact. It is

supplied from BASF. Therefore, it is the ideal solution when it comes to high safety and quality standards for use in many sensitive goods. Hexamoll® DINCH® is recommended whenever people are in close contact with PVC products that contain plasticizers. The two commercial routes to manufacture 1,2-cyclohexane dicarboxylic acid diisononyl ester are the catalytic hydrogenation of diisononyl phthalate and the Diels-Alder reaction of a maleic acid ester with 1,3-butadiene followed by hydrogenation. In the case of the catalytic hydrogenation the aromatic part of the diisononyl phthalate is transformed to a cyclohexane ring by a formal addition of 6 hydrogen atoms while the alkyl and ester groups are not affected by the hydrogenation.

### **3.1.6 Tricresyl phosphate plasticizer (CR)**

Tricresyl phosphate, is an organophosphate compound that is used as a plasticizer and diverse other applications. It is a colourless, viscous liquid, although commercial samples are typically yellow. It is supplied from Acar Kimya Company. It is virtually insoluble in water. Tricresyl phosphate is manufactured by reaction of cresols with phosphorus oxychloride. The cresol is a mixture of three isomers (ortho, meta, and para). The fact that tricresyl phosphate is derived from a mixture and itself is a mixture ensures that it remains liquid over a wide span of temperatures. Tricresyl phosphate is used as a plasticizer in nitrocellulose, acrylate lacquers, varnishes, and in polyvinyl chloride. It is a flame retardant in plastics and rubbers. It is used as a gasoline additive as a lead scavenger for tetraethyllead. It is a hydraulic fluid and a heat exchange medium. It is also used by the U.S. Navy in its pure form as a lubricant in cryogenic liquid pumps. Exploiting its hydrophobic properties, it is used for the waterproofing of materials. It is a solvent for extractions, a solvent for nitrocellulose and other polymers. It is used as an antiwear and extreme pressure additive in lubricants and hydraulic fluids.

## **3.2 Equipments**

### **3.2.1 Coperion extrusion machine**

TPU can be produced in several ways. The most common production method for thermoplastic polyurethane is reactive extrusion. For the reactive extrusion process, the monomers are separately fed to the extruder by a precise metering system. In the

extruder, reaction and transport take place, and the polymer formed is pelletized at the die. In the thesis, we use the extruder that brand name is Coperion. The temperature profile while the processing of R130A65 was given in Table 3.6.

**Table 3.6 :** Temperature profile of R130A65 in extrusion machine

Zones	Temperature (°C)
Zone 01	180
Zone 02	200
Zone 03	210
Zone 04	210
Zone 05	220
Zone 06	220
Zone 07	220
Zone 08	220
Zone 09	220
Zone 10	210
Zone 11	160
Zone 12	150
Zone 13	150
Zone 14	150

Extrusion machine properties are:

\* screw diameter is 58 mm,

\*screw speed is 300 rpm

\*output pressure is between 30-50 bar

\*there is conveyor and mixing blocks in extruder,

\*co-rotate twin screw,

\*14 zones,

\*exothermic reaction occurs while processing of TPU,

\*cooling water temperature is 5 °C

\*reaction starts in 3th zone and finish in the 7th zone. In 10th zone, plasticizer is added.

The machine can be seen in Figure 3.1.





**Figure 3.1 : Extrusion machine**

### **3.2.2 Haitan MA-900 injection molding machine**

Haitan MA900 is a injection molding machine that te test plaques were getting from it. The parameters:

- \*Screw diameter: 38 mm
- \*L/D ratio: 20
- \*Maximum injection pressure: 165
- \*Screw speed: 0-187 rpm
- \*Clamp pressure: 1000
- \*Motor power: 11 kW
- \*Oil tank: 180 lt
- \*Noise level: 72,5 dB

The injection molding properties of R130A65 are shown in Table 3.7. The injection molding machine picture can be seen in Figure 3.2. In this study, non plasticized and plasticized R130A65 was made. While the non-plasticized were making, the mold

temperature was 25-35 °C but while the plasticized were making, the mold temperature was 20-30 °C.

**Table 3.7 :** Application guideline for injection molding of Ravathane 130 A65

Nozzle (°C)	Metering (°C)	Compression (°C)	Feed (°C)
180-190	175-185	170-180	170-180



**Figure 3.2 :** Injection molding machine.

Mold shape can be seen in Figure 3.3.



**Figure 3.3 :** The mold shape in injection molding machine

Mechanical tests were made from the plaques that get from injection molding that seen in Figure 3.15. In injection molding, the temperature scale in feeding was 180 °C and nozzle was 190 °C. In the mold we get mechanical test plaques and from it, abrasion test, hardness and density were seen. Yellowing index data were taken from granules. The test specimens after the molding can be seen in Figure 3.4.

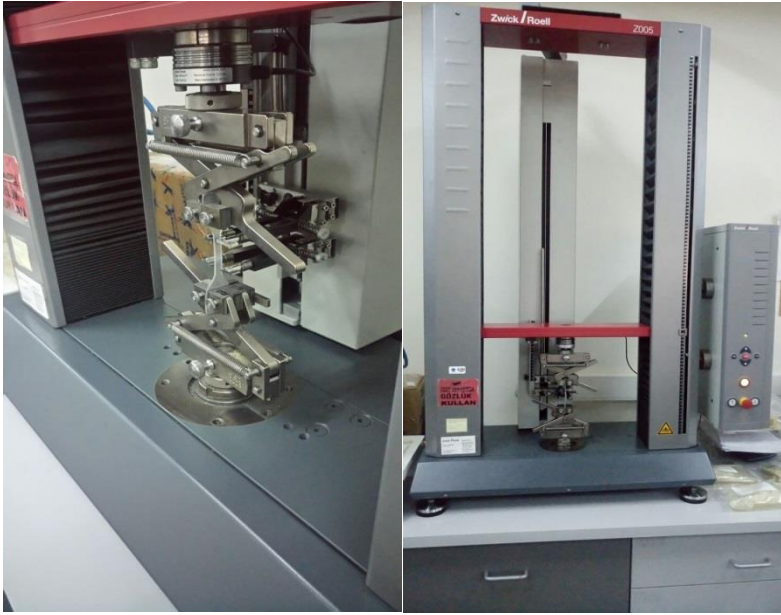


**Figure 3.4 :** The test specimens after the molding

### 3.2.3 Zwick/Roell Z005 - tensile test

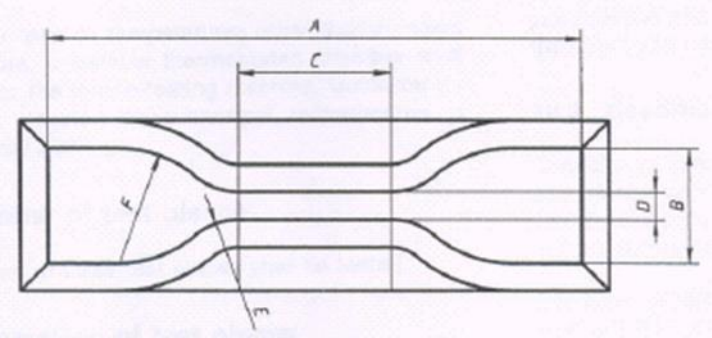
The tensile test is a standardized materials testing procedure for determining yield point, tensile strength, strain at break and other characteristic values of materials.

Tensile tests are performed in quality assurance and research and development in virtually all industries, the most common tensile tests being those on plastics and metals. Figure 3.5 shows the device.



**Figure 3.5 :** Tensile test device

There are many values were get from this machine. It is performed for 100% modulus (MPa), 300% modulus (MPa), tensile strenght (MPa), and ultimate elongation (%). The dinamometer is 1kN for the making tests. The test speed is  $500 \pm 50$  mm/dk. The test aparatus is prepared with hydrolic mold and special cutting system. The test specimen must be like in Figure 3.6. Test specimens were taken from 2mm thickness plaques.



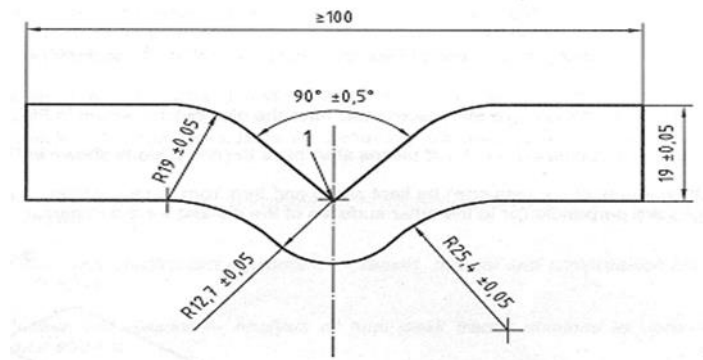
**Figure 3.6 :** Test specimen for tensile test

**3.2.4 Zwick/Roell Z005 – tear strength**

It is used the same machine for measuring the tear strength of samples. Tear strength is a measure of how well a material can withstand the effects of tearing. More

specifically however it is how well a material resists the growth of any cuts when under tension, it is usually measured in kN/m. In the project, we measure the tear strength of materials in N/mm in zwich machine.

The dinamometer is 1kN for the making tests. The test speed is  $500 \pm 50$  mm/dk. The test specimen is shown in Figure 3.7. Test specimens were taken from 2 mm thickness plaques.



**Figure 3.7 :** The tear strength test specimen

### 3.2.5 Zwick/Roel – hardness

These shore electronic hardness testers are used for determining the hardness of plastics and rubber to ISO 7619-1, ASTM D2240, ISO 868, NFT 51109 and BS 903 Part A26. Hardness value determination after dwell times of 3 seconds (ISO 7619-1) and 1 second (ISO 868) can be accommodated with digital hardness testing instruments. Shore A and Shore D can be measured. In this project we made our measurements in ISO 868 that seen the device in Figure 3.8.



**Figure 3.8 :** Hardness testing device

### 3.2.6 Precisa XB 220A - density

The machine is used for the determine the density of thermoplastic materials in ISO 1183-1. Precision scale was used in 0,1 mg sensitivity. The test is made in  $23\pm 2$  °C or  $27\pm 2$  °C condition. Before making the test, the calibration must be done. It is seen the device in Fiure 3.9.



**Figure 3.9 :** The density device

### 3.2.7 Instron ceast MF20 – melt flow index

The purpose of this test, which is applied at certain temperatures and weights in thermoplastic materials, is to determine the mass melt flow rates of the materials. Before the test, samples must be dry in 100 °C for 1 hour. In that project, Ravathane 130 A 65 material is tested in 190 °C with 2,16 kg load. Preheating time is 300 seconds, then the load must be put and give the pressure on it. when the loading finish, the piston spontanouslt descents. The machine can be seen below in Figure 3.10.



**Figure 3.10 :** Melt Flow index test device

### **3.2.8 Abrasion resistance**

Abrasion defines the volume loss under specified conditions in  $\text{mm}^3$ . On the one hand, the test piece is tested at a certain distance and the weight loss is determined by winding the abrasive paper cylinder under constant load and constant speed. The level of abrasive is determined by weight loss as a result of applying the same procedure to the standard rubber sample. This value is taken as the standard abrasive value. The abrasion test is made in ISO 4649. The shape of the test sample should be cylindrical. The diameter should be  $16 \pm 0.2$  mm and the thickness should be 6 mm minimum. The mold shown below in Figure 3.11 is used to prepare the sample.



**Figure 3.11 :** Test specimen of abrasion resistance

The test sample carrier should be centered and should stand upright. The test sample shall be applied with  $10 \pm 0.2$  N (1000 gr) force on the abrasive. The sample carrier should not be vibrated during the test. The abrasion size must be normally  $40 \pm 0.2$

mt. The thickness of the abrasive material is allowed to be 1 mm. and it makes 84 turns. It is seen below the abrasion resistance device in Figure 3.12.



**Figure 3.12 :** Abrasion resistance device

### 3.2.9 Konica minolta spectrophotometer

The CM-5 is a very versatile bench-top spectrophotometer to measure the colour of solid, pasty granular and liquid samples either in reflectance or transmittance. The top-port concept, offering various aperture sizes, allows measurement of almost any kind of samples. Aperture size from 3 – 30 mm, different Petri-dishes, different cell paths and a large transmittance chamber offer a unique flexibility. We are getting the yellowing index values from the device that can be seen in Figure 3.13.



**Figure 3.13 :** The device for yellowing index



### 3.2.10 Nüve FN500- oven

After the get the pellets from extruder, it must be dried in oven 2 hours in 100 °C. Thermoplastic polyurethanes are living polymers so they must be made good drying for stop the polymerization. Nüve oven has 120 lt capacity and ambient temperature is +5 °C / +200 °C. Power consumption is 1500 W. It can be seen below in Figure 3.14.



**Figure 3.14 :** Nuve- FN 500 for drying the pellets.

### 3.2.11 Differential scanning calorimetry (DSC)

The DSC measurements were performed with a Perkin Elmer DSC 4000 calorimeter. The samples were heated from -40 to 230 °C at the heating rate of 10 °C/min and held at this temperature for 1 min, then cooled to -40 °C at a cooling rate of 10 °C/min and held for 1 min, then again heated to 230 °C. The second cycle was used to evaluate the thermal behavior of sample.

## 3.3 Experimental Procedure

### 3.3.1 Preparation of samples

In this study, 5 types of plasticizer were used. They are the benzoate ester, phthalate ester, phosphate ester, adipate ester and cyclohexane ester. DOA and HE are the aliphatic ones, the others are aromatic type plasticizers. Experiments were made with two procedures. First one is extrusion process and second one is absorption processes. The idea was to prepare 30 samples, 15 samples by reactive extrusion and 15 samples by absorption processes.

### 3.3.1.1 Preparation of samples with extrusion process

In this study, coperion extrusion machine were used for the extrusion process. MDI, 1,4-butanediol, polyester polyol and catalyst were put in the same time in extrusion that is called reactive extrusion. They are all in liquid forms. In extrusion there are 14 zones and the plasticizers were given from the 9th zone to the extruder. In the extruder, temperature profile is; 180/ 200/ 210/ 210/ 220/ 220/ 220/ 220/ 220/ 210 / 160/ 150/ 150/ 150 °C. Cooling water is 5 °C. 10%, 20% and 30% by weight of all 5 types of plasticizers were added. After the extruder, the pellets were obtained from pelletizer. The samples were put into the hopper of injection machine and they dried in 120 °C and 30 minutes with an air circulating dryer. After drying, the samples were molded for all tests. 1 hour they were put in oven in 80 °C and then 1 hour they were put in room temperature for conditioning. They can be tested after 2 hours. Preparation properties of the can be seen in Table 3.8.

**Table 3.8 :** The names, explanations and quantites of samples in extrusion process

Name	Explanation	Quantity
BZ01	reactive extrusion with 10% BZ plasticizer	90 kg R130A65 + 10 kg BZ
BZ02	reactive extrusion with 20% BZ plasticizer	80 kg R130A65 + 20 kg BZ
BZ03	reactive extrusion with 30% BZ plasticizer	70 kg R130A65 + 30 kg BZ
PH01	reactive extrusion with 10% PH plasticizer	90 kg R130A65 + 10 kg PH
PH02	reactive extrusion with 20% PH plasticizer	80 kg R130A65 + 20 kg PH
PH03	reactive extrusion with 30% PH plasticizer	70 kg R130A65 + 30 kg PH
DOA01	reactive extrusion with 10% DOA plasticizer	90 kg R130A65 + 10 kg DOA
DOA02	reactive extrusion with 20% DOA plasticizer	80 kg R130A65 + 20 kg DOA
DOA03	reactive extrusion with 30% DOA plasticizer	70 kg R130A65 + 30 kg DOA
HE01	reactive extrusion with 10% HE plasticizer	90 kg R130A65 + 10 kg HE
HE02	reactive extrusion with 20% HE plasticizer	80 kg R130A65 + 20 kg HE
HE03	reactive extrusion with 30% HE plasticizer	70 kg R130A65 + 30 kg HE
CR01	reactive extrusion with 10% CR plasticizer	90 kg R130A65 + 10 kg CR
CR02	reactive extrusion with 20% CR plasticizer	80 kg R130A65 + 20 kg CR
CR03	reactive extrusion with 30% CR plasticizer	70 kg R130A65 + 30 kg CR

### 3.3.1.2 Preparation of samples with absorption process

Non-plasticized R130A65 were made in extrusion. That prepared pellets were used in absorption process. 10%, 20% and 30% percentages of all 5 types of plasticizers were added. Absorption process were made in 20 kg pails. Firstly, the pellets were put and the plasticizers were put on them. They were mixed very well and we must

wait for the pellets must absorb them. They were put in oven at 80 °C and they were mixed in every 2 hours. After 24 hours, they were tested. The names, explanations and quantities for tests were given below Table 3.9.

**Table 3.9 :** The names, explanations and quantities of samples in absorption process

Name	Explanation	Quantity
BZAB01	absorption process with 10% BZ plasticizer	2.7 kg R130A65 + 0.3 kg BZ
BZAB02	absorption process with 20% BZ plasticizer	2.4 kg R130A65 + 0.6 kg BZ
BZAB03	absorption process with 30% BZ plasticizer	2.1 kg R130A65 + 0.9 kg BZ
PHAB01	absorption process with 10% PH plasticizer	2.7 kg R130A65 + 0.3 kg PH
PHAB02	absorption process with 20% PH plasticizer	2.4 kg R130A65 + 0.6 kg PH
PHAB03	absorption process with 30% PH plasticizer	2.1 kg R130A65 + 0.9 kg PH
DOAAB01	absorption process with 10% DOA plasticizer	2.7 kg R130A65 + 0.3 kg DOA
DOAAB02	absorption process with 20% DOA plasticizer	2.4 kg R130A65 + 0.6 kg DOA
DOAAB03	absorption process with 30% DOA plasticizer	2.1 kg R130A65 + 0.9 kg DOA
HEAB01	absorption process with 10% HE plasticizer	2.7 kg R130A65 + 0.3 kg HE
HEAB02	absorption process with 20% HE plasticizer	2.4 kg R130A65 + 0.6 kg HE
HEAB03	absorption process with 30% HE plasticizer	2.1 kg R130A65 + 0.9 kg HE
CRAB01	absorption process with 10% CR plasticizer	2.7 kg R130A65 + 0.3 kg CR
CRAB02	absorption process with 20% CR plasticizer	2.4 kg R130A65 + 0.6 kg CR
CRAB03	absorption process with 30% CR plasticizer	2.1 kg R130A65 + 0.9 kg CR

### 3.3.2 Hardness and density characterization

Hardness is important for plasticized TPU materials. Non plasticized TPU can be minimum 80 Shore A because of including types of hard and soft segments. When it is plasticized, Shore value and density must be decrease. Plasticizers will effect the hard blocks and softer them, prevent to link and occur physical crooslinks, so density and Shore value must be decrease. Density is measured with Precision that scale was used in 0.1 mg sensitivity. The test is made in 23±2 °C or 27±2 °C condition. Before making the test, the calibration must be done and the tests were made in ISO 1183-1. Hardness is measured in Zwick/Roell hardness device. In this project we made our measurements in ISO 868.

### 3.3.3 Mechanical property characterization

Specimens were prepared as DIN 53504 method with Zwick/Roell Z005 test device. Then dimensional measurements, which are width and thickness, were taken place.

Suitable specimens were placed between gauge. From the stress-strain graph, tensile strength, elongation, 100% modulus and 300% modulus were calculated. ISO 34 1/B method were used for tear strength. Stress in MPa and elongation values gave us the results of tear strength. After the extrusion and absorption process, the samples were prepared for injection molding process and the dog bones obtained after injection molding. The plaques were dried for 1 hour at 80 °C and after that they were waited for 1 hour at room temperature. Mechanical tests were made after that drying procedure.

### **3.3.4 Abrasion property characterization**

The level of abrasive is determined by weight loss as a result of applying the same procedure to the standard rubber sample. This value is taken as the standard abrasive value. The abrasion test is made in ISO 4649. The shape of the test sample should be cylindrical. The diameter should be 16 +0 / -0.2 mm and the thickness should be 6 mm minimum. The test sample shall be applied with 10 +/- 0.2 N (1000 gr) force on the abrasive. The sample carrier should not be vibrated during the test. The results were given in mm<sup>3</sup> values.

### **3.3.5 Melt flow index characterization**

Before the test, samples must be dry in 100 °C for 1 hour. In that project, Ravathane 130 A 65 material is tested in 190 °C with 2.16 kg load. Preheating time is 300 seconds, then the load must be put and give the pressure on it. When the loading finish, the piston spontaneously descends. Melt flow index is very important for TPU. When processing, it can be known that there is any problem for reaction. If the MFI is very high, it can be concluded that there is something wrong and degradation can occur. If it is very low, the process will be very difficult and granules will be different. They will meet high shear in screw and they will be more small.

### **3.3.6 Yellowing index characterization**

Generally, TPU turns yellow. Usage of polyol, chain extender and isocyanates and their percentages effect all of the reaction. Usage of catalyst is important for yellowing index. The pellets were put the apparatus of yellowing index device. The details of the used apparatus were given in section 3.2.9. The results are given from the screen.

### **3.3.7 Differential scanning calorimetry characterization**

Plasticizers are small molecules which get in between the polymer chains, and space them out from each other. We call this increasing the free volume. When this happens they can slide past each other more easily. When they slide past each other more easily, they can move around at lower temperatures than they would without the plasticizer. In this way, the T<sub>g</sub> of a polymer can be lowered, to make a polymer more pliable, and easier to work with.

The samples were heated from -40 to 230 °C at the heating rate of 10 °C/min and held at this temperature for 1 min, then cooled to -40 °C at a cooling rate of 10 °C/min and held for 1 min, then again heated to 230 °C. The second cycle was used to evaluate the thermal behavior of sample.



## **4. RESULTS AND DISCUSSION**

In this part of the study, the characterizations of the prepared samples were made, the results were obtained. This section contains the results of the thesis and shows the importance of studying the outcoming evaluation.

### **4.1 Evaluation of Results**

Two procedure were used in that study. First one was extrusion and second one was absorption process. Phthalate ester (PH), benzoate ester (BZ), adipate ester (DOA), 1,2-cyclohexane dicarboxylic acid diisononyl ester (HE) and tricresyl phosphate (CR) plasticizers were used and 15 samples were tried to prepare with 10%-20%-30% by weight of each plasticizers and in each procedure. The idea was to prepare 30 samples in two procedures. The prepared ones were tested and characterized.

During the preparation process of the samples, it was realized that, CR plasticizer could not be used neither by absorption nor extrusion processes. In the extrusion processes, degradation could occur in TPU pellets and did not get any plastic shaped material out from the extruder. Samples with DOA and HE were not prepared by absorption process even at 80 °C oven for 3 nights. Although this period is also very long time for absorption process. The absorption can not occur at any concentration for these additives. The TPU sample pellets obtained by extrusion by using DOA and HE at 10% only. The higher percentages addition to the extruder showed the similar problem by using CR in extruder. 15 samples could be prepared including non plasticized one.

#### **4.1.1 Hardness and density test results**

Is is seen on the Table 4.1 that, when we add more plasticizer, hardness is decreasing and at the same time density is decreasing. Normally, hardness is a mechanical measurement but the results were seen that they were compatible to each other and results of density and hardness were given in the same table. It was showed from the

table that phthalate ester plasticizers are more suitable for TPU and than benzoate esters. When we compare the samples, the BZAB03 ve BZ03 samples by hardness and density values are more suitable. In PHAB03 and PH03 there is no difference as two processes used. When we look at the DOA01 and HE01, plasticizers effect the materials. The expected results should be no more changes in density to reach 75 Shore A. Some samples are very good according to the point of view.

**Table 4.1 : Results of hardness and density**

Sample	Hardness ( Shore A)	Density (gr/cm <sup>3</sup> )
Non plasticizer	82.0	1.19
BZAB01	78.5	1.17
BZAB02	76.0	1.17
BZAB03	69.0	1.16
PHAB01	78.5	1.18
PHAB02	72.6	1.16
PHAB03	65.0	1.16
BZ01	75.5	1.18
BZ02	72.0	1.18
BZ03	65.0	1.17
PH01	77.5	1.17
PH02	72.0	1.16
PH03	65.0	1.15
DOA01	76.5	1.15
HE01	77.0	1.16

#### 4.1.2 Mechanical test results

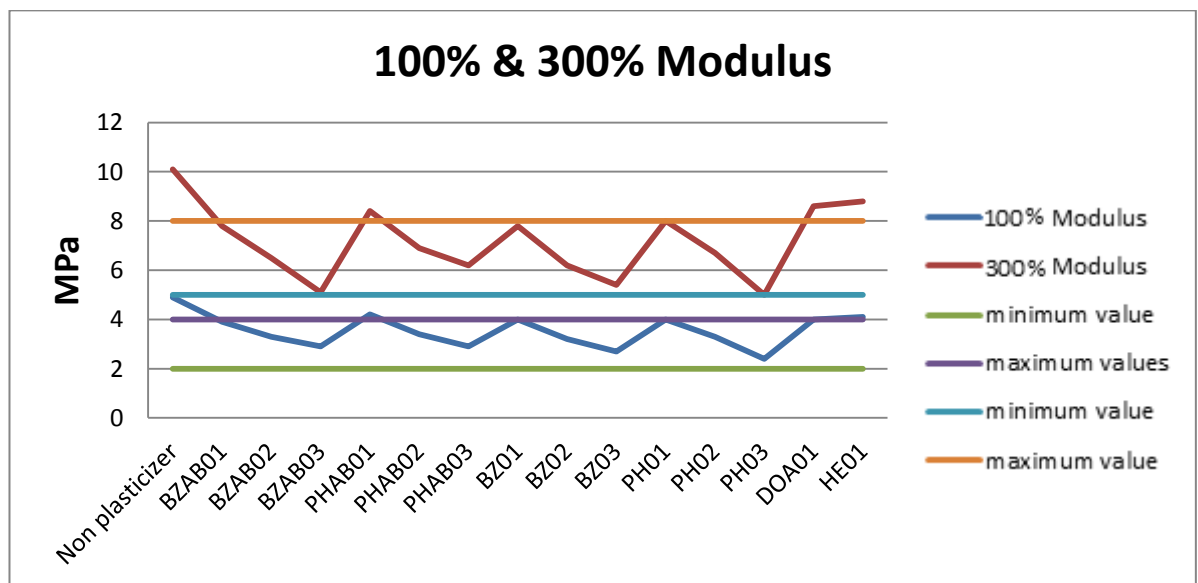
All the results can be seen in Table 4.2. Minimum and maximum exceptable values of each results were put in Figure 4.1, Figure 4.2, Figure 4.3, and Figure 4.4. According to the results of the all plasticize samples, tensile strength, 100%, and 300% modulus are decreased simultaneously, when they are compared with the non plasticized TPU. Phthalate esters containing samples give the best results on the mechanical properties. When we compare the samples obtained from the absorption and the reactive extrusion proseses, they have the same effect on the tensile strength, 100% modulus, and 300% modulus. For ultimate elongation, when the plasticizer added in absorption, elongation is decreasing. In reactive extrusion, when the plasticizer added to the samples, elongation is increasing in a huge difference. These differences are significant in BZAB series. When we compare the samples containing DOA and HE with the others, they have good 300% modulus even in 10%



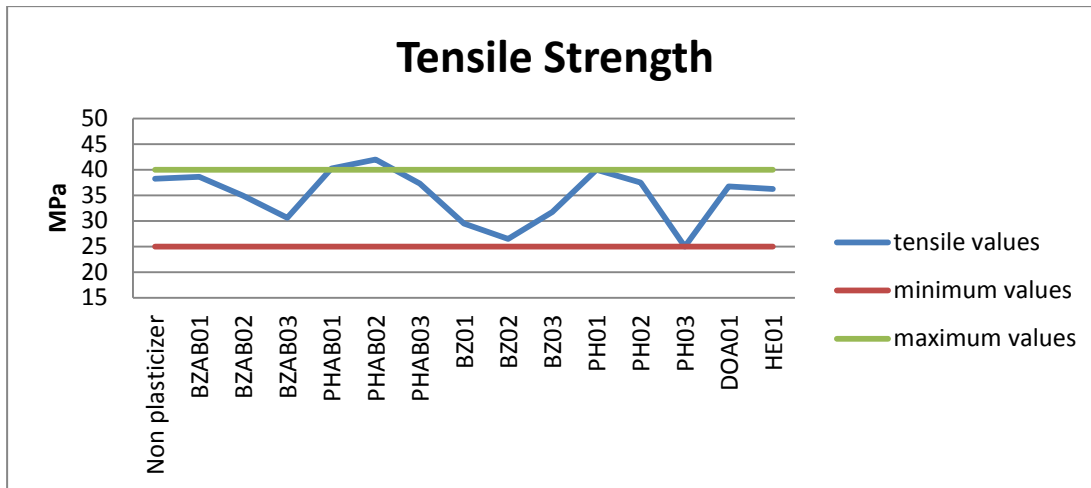
percentage. According to the tear strength results, all the samples are better than the minimum acceptable value except the sample no. BZAB03.

**Table 4.2 : Results of mechanical tests**

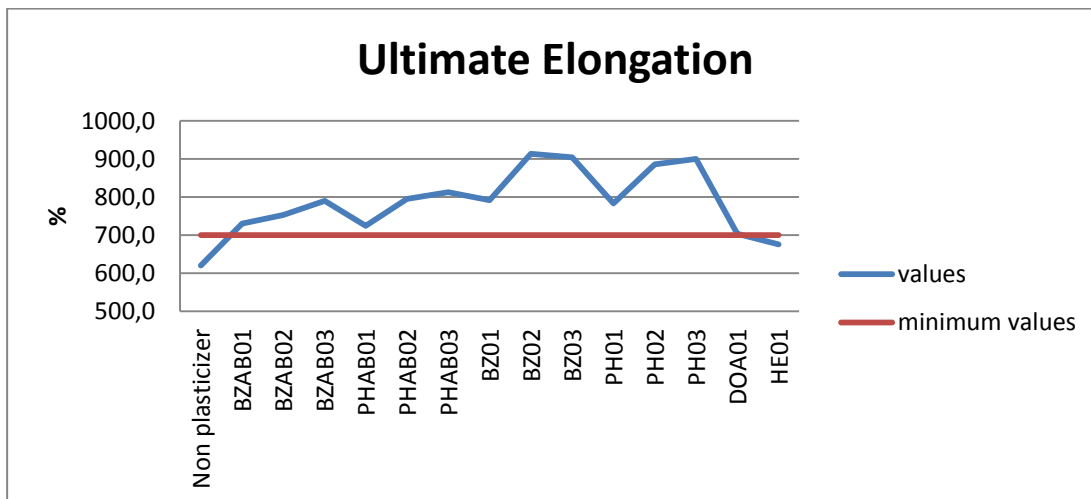
Sample	100% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Ultimate Elongation (%)	Tear Strength (N/mm)
Non plasticizer	4.9	10.1	38.2	620	126.9
BZAB01	3.9	7.8	38.6	730	94.3
BZAB02	3.3	6.5	34.9	753	89.4
BZAB03	2.9	5.1	30.6	790	66.6
PHAB01	4.2	8.4	42.0	780	101.9
PHAB02	3.4	6.9	40.0	724	93.2
PHAB03	2.9	6.2	37.3	812	81.7
BZ01	4.0	7.8	29.5	791	98.5
BZ02	3.2	6.2	26.5	913	95.8
BZ03	2.7	5.4	31.7	904	82.6
PH01	4.0	8.0	40.0	783	103.5
PH02	3.3	6.7	37.5	885	94.4
PH03	2.4	5.0	25.0	900	80.0
DOA01	4.0	8.6	36.7	703	98.7
HE01	4.1	8.8	36.2	675	102.0



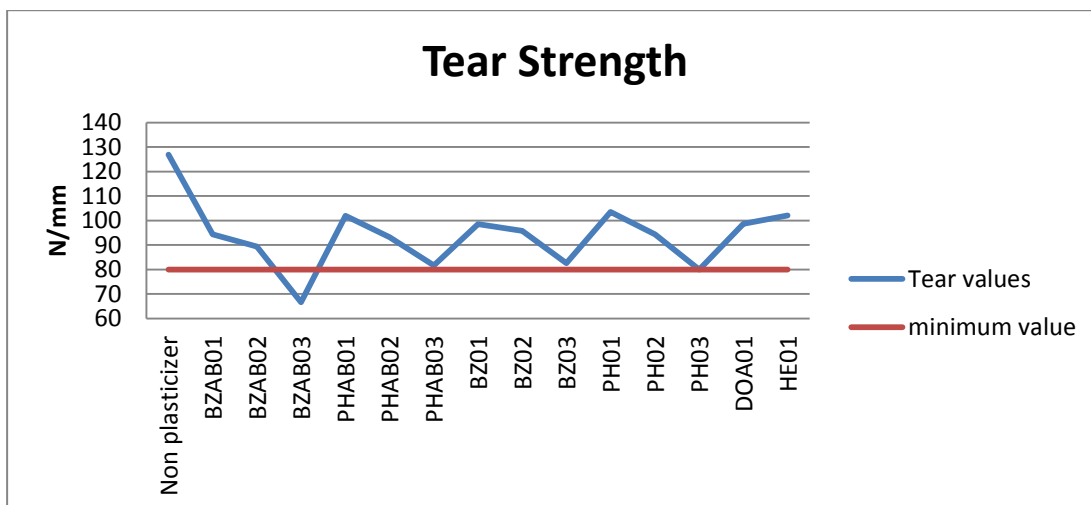
**Figure 4.1 : Results of modulus test**



**Figure 4.2 :** Results of tensile test



**Figure 4.3 :** Results of elongation test



**Figure 4.4 :** Tear strength test results

### 4.1.3 Abrasion resistance test results

Abrasion resistance is very important for TPU materials. Good abrasion properties provide an opportunity for comparison with the other thermoplastics. In the results, we can see that the abrasion results are good, although, phthalate esters containing samples show different results by absorption and reactive extrusion processes. In absorption, when the plasticizer percentage increase, abrasion goes to the very good results. In extrusion, when the plasticizer percentage increase, abrasion goes to bad for these samples. For benzoates containing samples, the results are the same for the two processes. The best results are get from the 30% percentage of phthalate. It can be seen in Table 4.3.

**Table 4.3 :** The abrasion test results

Sample	Abrasion (mm <sup>3</sup> )
Non plasticizer	30
BZAB01	41
BZAB02	48
BZAB03	62
PHAB01	33
PHAB02	32
PHAB03	26
BZ01	46
BZ02	56
BZ03	58
PH01	21
PH02	27
PH03	40
DOA01	17
HE01	14

### 4.1.4 Melt flow index test results

The melt flow index is also very important property for TPU material. In order to be able to process, it is necessary to keep the melt flow value at optimum level. When we look at the results, adding of plasticizer effects the MFI and when plasticizer percentage increase, MFI will increase too. When we look the samples of BZ and PH, in extrusion, their MFI values is very good from the point of processability. MFI test results can be seen in Table 4.4.

**Table 4.4 : Melt flow index test results**

Sample	Compression Set
Non plasticizer	MFI:3
BZAB01	MFI:17
BZAB02	MFI:16
BZAB03	MFI:31
PHAB01	MFI:6
PHAB02	MFI:20
PHAB03	MFI:25
BZ01	MFI:17
BZ02	MFI:34
BZ03	MFI:41
PH01	MFI:5
PH02	MFI:10
PH03	MFI:25
DOA01	MFI:8
HE01	MFI:8

#### 4.1.5 Yellowing index test results

It can be seen that the plasticizers do not effect very much to the yellowing index values for TPU granules. If the yellowing index is small, granules are more transparent. If the yellowing index is high, it means that the granules are yellowish. In some cases, when the usage of yellowish granules, it can effect the masterbatch efficiency and the percentage of transparency. So, from the Table 4.5, we can say that phthale esters in reactive extrusion are very good about the yellowish. In absorption process, all results are very high and it means that the granules are yellow. When we compare the procedures, extrusion process is better rather than the absorption process. The most different result is the sample HE01. The sample HE01 has a good yellowing index value and it has very good transparency. From that results, when the 10% HE plasticizers are used, it will give good transparency and no yellowish effect.

**Table 4.5 : Yellowing index test results**

Sample	Yellowing Index
Non plasticizer	12.7
BZAB01	14.7
BZAB02	17.2
BZAB03	17.9
PHAB01	12.7
PHAB02	18.2
PHAB03	15.2
BZ01	17.7
BZ02	21.4
BZ03	24.4
PH01	17.6
PH02	14.2
PH03	10.0
DOA01	11.0
HE01	9.0

#### 4.1.6 Differential scanning calorimetry test results

Differential scanning calorimetry test were made for the examine to finding of Tg and Tm values of samples prepared with two different procedures. These results can be seen in the Table 4.6 and Table 4.7, by extrusion process and by absorption process respectively. Plasticizers effect the Tg and Tm values. When the plasticizer ratio increase, the Tg values are increased and the Tm values are decreased.

**Table 4.6 : Tg and Tm values of samples from extrusion process**

Sample	Tg (°C)	Tm (°C)
Non-Plasticizer	16.7	154.1
BZ01	21.8	155.8
BZ02	21.0	150.1
BZ03	24.0	147.5
PH01	30.5	158.6
PH02	31.9	156.2
PH03	32.0	153.8
DOA01	18.4	149.3
HE01	56.4	160.7

**Table 4.7** : Tg and Tm values of samples from absorption process

Sample	Tg (°C)	Tm (°C)
Non-Plasticizer	16.7	154.1
BZAB01	60.2	147.7
BZAB02	63.8	147.8
BZAB03	93.6	146.6
PHAB01	64.2	131.2
PHAB02	63.0	130.7
PHAB03	77.8	130.1

The plasticizers were used to modify the TPU and enhancing their utilities. Each of the plasticizers has a compatibility with a specific type of a polymer. Plasticizers can disperse between the soft segments. When we compare the samples of BZ and PH, in two procedures the different results were obtained. When the plasticizer ratio increases in BZ containing TPU samples for the extrusion process, Tg values increase while Tm values decrease. For PH containing TPU samples obtained by extrusion process, when the plasticizer ratio increase, Tg values have no change while Tm values decrease. For the absorption processes results showed that for both BZ and PH containing samples, Tg values increase while the additive content ratios increase. The interesting results found that, in the absorption processes samples of BZ and PH, when the additive ratios increases there is no change on Tm values. Moreover, the sample HE01 has the highest Tg and Tm values.

## 5. CONCLUSION

In this study, effects of different types of plasticizers to TPU were investigated. Two procedures were used in this study. First one was reactive extrusion and second one was absorption processes. Phthalate ester (PH), benzoate ester (BZ), adipate ester (DOA), 1,2-cyclohexane dicarboxylic acid diisononyl ester (HE) and tricresyl phosphate (CR) plasticizers were used and 15 samples can be prepared with 10%-20%-30% by weight of each plasticizers by using the mentioned procedures. In reactive extrusion process, Ravathane 130 A65 TPU material were made with the starting materials as MDI, 1,4-butanediol, polyester polyol and catalyst. During extrusion process, plasticizers were put into the extruder from 9th zone. CR was not possible to process by extrusion. On the other hand, in the absorption process, the TPU granules could not absorb the DOA, HE and CR plasticizers. On the other hand, DOA and HE can be added to TPU by extrusion only 10%.

The test devices that Zwick/Roell Z005 for mechanical tests, Zwick/Roell for hardness, Presica XB 220A for density, Instron Ceast MF20 for melt flow index, abrasion resistance, Konica Minolta spectrophotometer for yellowing index, Nüve FN500 for oven were used. Haitan MA900 were used for injection molding and copierion extrusion machine were used for production. The values of T<sub>g</sub> and T<sub>m</sub> of the samples were determined by DSC measurements using Perkin Elmer DSC 4000 calorimeter.

Different results were obtained from this study. 5 types of plasticizer used and finally two types of plasticizers for TPU as phthalate esters and benzoate esters were found suitable. The other plasticizers could not reach good results. If the phthalate esters can not be allowed for usage in TPU due to REACH regulations, it can be replaced by benzoate esters. Because there is not big differences in results for the samples containing BZ and PH. Hardness and density values are similar each other according to the same percentages. When we compare the processes, we can see the BZAB03 ve BZ03 that reactive extrusion is more suitable for hardness and density values. In

PHAB03 and PH03 there is no important difference between two processes. When we look at the results of samples including DOA01 and HE01, the 75 Shore A TPU material can be prepared from these plasticizers.

According to the mechanical results, in all plasticized samples obtained by these two processes, the tensile strength, 100%, and 300% modulus are decreased simultaneously while percent ratio in the samples are increased. Phthalate esters containing samples give the best results about the mechanical properties. For ultimate elongation of the samples, when the plasticizer added in both processes, elongation increase as expected. When we compare the samples of DOA and HE with the others, they have the best result in 300% modulus, especially. Adding the plasticizers to TPU samples, tear strength is decreased rapidly in all materials. In reactive extrusion process, tear strength values are a little better than the absorption process.

Abrasion resistance test results showed that BZ containing samples have high abrasion while PH containing ones have better abrasion resistance results than that of non plasticized sample except sample no. PH03. The best abrasion resistance results are belong to DOA01 and HE01 samples.

The melt flow index is the most important property of TPU material. In order to be able to process, it must be necessary to keep the melt flow value at optimum level. When we look the results, plasticizers effect the MFI values of the samples. When plasticizer percentages increase, MFI values increase. When we look at the samples containing BZ and PH additives, extrusion process is more suitable than the absorption process.

Determining of the yellowing index values were made by spectrophotometer. Yellowing index datum are very closer with each other, but it is known that if the yellowing index of a material is less than 13, it is available for preparing clear TPU samples. Samples of DOA and HE have the best results. It showed that, if the 75-80 Shore A TPU materials can be made by using the DOA and HE plasticizers to obtain a transparent pellets.

DSC results were examined because of the understanding the effect of plasticizers to the molecular structure and the T<sub>g</sub> and T<sub>m</sub> values of prepared samples. For all the samples have higher T<sub>g</sub> values than that of non plasticized one and T<sub>m</sub> values of the



samples produced by absorption process are lower than that of non plasticized sample. Moreover, the sample HE01 has the highest Tg and Tm values.

In this study, isocyanates and diols, which are the main raw materials in thermoplastic polyurethane production, the interaction between these agents with plasticizers determine the important properties required. Especially in the last years, it has been worked on valuable studies, which plasticizing agent can be used in thermoplastic polyurethane instead of phthalate based plasticizers due to REACH regulations. Many properties of BZ containing TPUs are found that better than that of phthalate ester plasticizer, therefore benzoate ester plasticizer can be replaced to phthalate ester plasticizer.



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## CURRICULUM VITAE



**Name Surname** : Bahar DURAK AKKOYUN  
**Place and Date of Birth** : İstanbul- 17.01.1989  
**E-Mail** : bahardurak@gmail.com  
**Adress** : Soğuksu mahallesi, karadut sokak, kardelen  
konutları, BB blok K:3 D:8 Beykoz/İstanbul

## EDUCATION

- **B.Sc.** : 2012, Kocaeli University, Engineering Faculty,  
Environment Engineer
- **B.Sc.** : 2013, Kocaeli University, Engineering Faculty,  
Chemical Engineer
- **M.Sc.** : Istanbul Technical University, Polymer Science and  
Technology