İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

STARCH MODIFIED BIODEGRADABLE POLYURETHANE FILM

M.Sc. Thesis by
Pınar MUTLU

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

Thesis Supervisor: Prof. Dr. İ. Ersin SERHATLI

JUNE 2011

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

STARCH MODIFIED BIODEGRADABLE POLYURETHANE FILM

M.Sc. Thesis by
Pınar MUTLU
(515081016)

Date of submission : 06 May 2011
Date of defence examination: 10 June 2011

Supervisor (Chairman) : Prof. Dr. İ.Ersin SERHATLI (ITU)
Members of the Examining Committee : Prof. Dr. Ayşen ÖNEN (ITU)
Prof. Dr. Atilla GÜNGÖR (MU)

JUNE 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

NİŞASTA İLE MODİFİYE EDİLMİŞ BİYOBOZUNUR POLİÜRETAN FİLM

YÜKSEK LİSANS TEZİ
Pınar MUTLU
(515081016)

Tezin Savunulduğu Tarih : 6 Mayıs 2011
Tezin Enstitüye Verildiği Tarih : 10 Haziran 2011

Tez Danışmanı : Prof. Dr. İ.Ersin SERHATLI (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Ayşen ÖNEN (ITU)
Prof. Dr. Atilla GÜNGÖR (MU)

HAZİRAN 2011

FOREWORD

First of all, I would like to thank to my advisor, Prof. Dr. İ. Ersin SERHATLI, for his patience and guidance throughout this research and for his generosity for sharing his knowledges and experiences with me also for the opportunity to work in POLMAG Laboratory.

I also would like to thank to Prof. Dr. H. Ayşen ÖNEN for her guidance and invaluable technical support.

Moreover, I am grateful to have a chance to work with Bahadır GÜLER, Miray GÖKTAŞ, Ömer Faruk VURUR and Tuba Çakır ÇANAK also for their assistance and friendship.

In addition, I am thankful to my colleagues at Bosch Siemens Home Appliances for their support during my master.

I would like to give my special thanks to Atilla BEDEL for his caring, understanding and emotional support.

Finally and most of all, I would like to thank to my beloved parents and my brother; Neviye, Bülent MUTLU and Onur MUTLU for their endless love, patience, guidance and encouragement during all stages of my life.

May 2011

Pınar MUTLU

Polymer Science and Technology

TABLE OF CONTENTS

Page

ABBREVIATIONS

TDI : Tolyene diisocyanate
HDI : Hexamethylene diisocyanate
PTMG : Poly(tetramethylene glycol)
RIM : Reaction Injection Molding
TPU : Thermoplastic Polyurethane
PMDI : Polymeric Isocyanate
MDI : Methylenebis(phenyl isocyanate)
DMF : Dimethylformamide
CHDI : Cyclohexane - diisocyanate
TMXDI : Tetramethylxylene diisocyanate
IPDI : Isophorone diisocyanate
MDA : Methylenedianiline
PABA : *p*-aminobenzylamine
OABA : *o*-aminobenzylamine
PEG : Poly(ethylene glycol)
PPG : Poly(propylene glycol)
PTMG : Poly(tetramethylene glycol)
PO : Propylene oxide
DBTDL : Dibutyltin dilaurate
DBTDA : Dibutyltin diacetate
AP : Amylopectin

LIST OF TABLES

Page

LIST OF FIGURES

Page

STARCH MODIFIED BIODEGRADABLE POLYURETHANE FILM

SUMMARY

Polyurethane is an incredibly resilient, flexible, and durable manufactured material that can take the place of paint, cotton, rubber, metal, and wood in thousands of applications across all fields. Polyurethane might be hard, like fiberglass, squishy like upholstery foam, protective like varnish, bouncy like rubber wheels, or sticky like glue. Polyurethane is a substance categorized as a polymer based on its chemical structure. One way to manufacture polyurethane by combining a diisocyanate and a diol, two monomers, through a chemical reaction. This makes a basic material whose variations can be stretched, smashed, or scratched, and remain fairly indestructible. Depending on the different diisocyanates and diol or polyol constituents, the resulting polyurethane might take a liquid, foam, or solid form, each with advantages and limitations. On the other hand, starch that has been subjected to various types of processing to partially modify its original structure or properties, and starches have been modified and improved in various ways by modification to utilization as starting materials for industrial products. The basic structure of starch is a mixture of amylase consisting of α-D-glucose linked in a linear fashion by 1,4-bonds and amylopectin with the same in a branched structure, and modifications such as esterification utilizing hydroxyl groups in the structure. Similarly, bonding of starches hydroxyl groups with polyisocyanates has been proposed. This involves grafting of the starch resin and polyisocyanate. Combining isocyanate groups with starh hydroxyl groups is an attractive way to improve degradability of the material. Also termal stability of the film based on polyurethane can be decreased with increasing the starch content.

This work involves the sythesis of biodegradable starch-grafted polyurethane film sythesis. Blocked polyurethane was modified with corn and wheat starch and various starch amounts. The formulated compositions was polymerized by thermal polymerization method.

NİŞASTA İLE MODİFİYE EDİLMİŞ BİYOBOZUNUR POLİÜRETAN FİLM

ÖZET

Poliüretan; boya, pamuk, kauçuk, metal ve ahşap gibi birçok alanda binlerce uygulamaya sahip esnek, dayanıklı, elastik bir malzemedir. Poliüretan fiberglas gibi sert, izolasyon köpükleri gibi yumuşak, vernik gibi koruyucu, tekerlek gibi sekme özelliğine sahip, ya da yapıştırıcılar gibi yapışkan olabilir. Poliüretan kimyasal yapısına bağlı olarak kategorize edilen bir polimerdir. Poliüretan üretiminin bir yolu, iki monomerin, bir diizosiyanat ve bir diolün birleşiminin kimyasal reaksiyonu ile gerçekleşmektedir. Bu çok çeşitli varyasyonlarında esnek, parçalanan, çizilen ama genel özellikleriyle dayanıklı bir temel malzeme oluşturulmasını sağlar. Farklı izosiyanat ve diol veya polyol bileşenlerinin bağlı olarak ortaya çıkan poliüretan sıvı, köpük veya katı halde oluşabilir, hepsinin farklı avantajları ve sınırlamaları bulunmaktadır. Öte yandan, nişasta orjinal yapısı ve özelliklerini kısmi olarak modifiye etmek üzere çok çeşitli prosese tabi tutulmuş, nişasta sanayi ürünleri için başlangıç malzemesi olarak kullanılmak üzere çok çeşitli şekillerde modifiye edilmiş ve geliştirilmiştir. Nişastanın temel yapısı, amiloz alfa-glikoz monomer birimlerinin alfa-1,4 bağlantılarıyla lineer olarak bağlanmasıyla, amilopektininde amilozdan farklı olarak dallanmasıyla, yapıdaki hidroksil gruplarının esterleşme gibi modifikasyonuyla oluşur. Benzer şekilde nişastanın hidroksil gruplarıyla poliizosiyanatların birleşmesi sağlanmıştır. Bu nişasta ve poliizosiyanatın aşılanmasını sağlamaktadır. İzosiyanat ve nişasta hidroksil gruplarının birleştirilmesi malzemenin biyobozunurluğunu arttırıcı bir etkendir. Aynı zamanda poliüretan bazlı filmin termal kararlılığı içeriğindeki nişastanın artmasıyla azalmaktadır.

Bu çalışma biyobozunur nişasta aşılı poliüretan sentezini içermektedir. Blok poliüretan mısır ve buğday nişastası ve onların farklı oranlarıyla modifiye edilmiştir. Formüle edilmiş kompozisyonlar termal olarak polimerize edilmiştir.

1. INTRODUCTION

Recent years have seen an increased demand for active use of naturally derived, biodegradable raw materials with a low environmental load, from the standpoint of minimizing effects on the earth environment by improving waste treatment and lowering CO_2 emissions.

Typical naturally derived materials include modified starches such as polysaccharide starches or acetylated starches which have conventionally been used in the food and papermaking industries, but recently such starches have come into use as biodegradable plastic materials in the form of products for a wide range of fields including food containers, packaging materials, buffer material sheets, agricultural films, disposable diapers and the like [28].

Modification of the physical and chemical properties of these materials, through reaction or blending with other biodegradable and nonbiodegradable polymers, is often necessary to meet the required performances. As a biopolymer from agricultural resources, starch with multi-hydroxyl groups has been considered as an alternative material in developing degradable plastics because of its biodegradability, derivability, availability and low cost. [3]

Polyurethanes have revealed an unusual versality; their chemistry, as well as the chemistry of related intermediates (isocyanates among them), has been enormously developed and polyurethanes have one of the widest ranges of polymer applications throughout the world: fibres, elastomers, foams, skins, adhesives, coating [68].

The synthesis of biodegradable PU's is a relatively recent issue in PU chemistry. It is well known that polyester based PU's are much more susceptible to biodegradation than PUs derived from polyether diols. Polyurethanes obtained by reacting aliphatic and aromatic diisocyanates with poly (caprolactonediol)'s of various molecular weights were treated with microorganisms and enzymes [3]

This thesis will concern the preparation of starch containing polyurethane film which will contain blocked polyisocyanate and corn and wheat starch and their

polymerization by heat. Characterization of the films by analysis of various properties such as FTIR analysis, SEM analysis, stres-strain test, will be discussed. The thermal behaviour of the films are also evaluated.

2. THEORETICAL PART

2.1 Overview of Polyurethane

2.1.1 Introduction

The addition polymerization of diisocyanates with macroglycols to produce urethane polymers was pioneered in 1937 by O. Bayer [10]. The rapid formation of high molecular weight urethane polymers from liquid monomers, which occurs even at ambient temperature, is a unique feature of the polyaddition process, yielding products that range from cross-linked networks to linear fibers and elastomers. The enormous versatility of the polyaddition process allowed the manufacture of a myriad of products for a wide variety of applications.

The early German polyurethane products were based on tolyene diisocyanate (TDI) and polyester polyols. In addition, a linear fiber, PerlonU, 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 Germany a toluene diisocyanate consisting of an isomeric mixture of 65% 2,4-isomer and 35% 2,6-isomer was used in the manufacture of flexible foam, whereas in the United States the less expensive 80:20 isomer mixturewas used. In 1956, DuPont introduced poly(tetramethylene glycol) (PTMG), the first commercial polyether polyol; 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 strength. The development of new and superior catalysts, such as Dabco (triethylenediamine) and organotin compounds, has led to the so-called one-shot process in 1958, which eliminated the need for an intermediate prepolymer step. Prior to this development, part of the polyol was treated with excess isocyanate to give an isocyanateterminated prepolymer. Further reaction with water produced a flexible foam. 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 (TPU) elastomers and Spandex fibers were introduced during this time. In addition, urethane-based synthetic leather was introduced by DuPont under the trade name Corfam in 1963. The late 1950s also witnessed the emergence of a new polymeric isocyanate (PMDI) based on the condensation of aniline with formaldehyde. This product was introduced by the Carwin Co. (later Upjohn and Dow) in 1960 under the trade name PAPI. Similar products were introduced by Bayer and ICI in Europe in the early 1960s. The superior heat resistance of rigid foams derived from PMDI prompted its exclusive use in rigid polyurethane foams. The large-scale production of PMDI made the coproduct 4,4_,-methylenebis(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 done since the 1990s to reinforce polyurethane elastomers with glass, graphite, boron, and aramid fibers, or mica flakes, to increase stiffness and reduce thermal expansion. The higher modulus thermoset elastomers produced by reinforced reaction injection molding (RRIM) are also used in the automotive industry. In 1969 Bayer pioneered an all-plastic car having RIM-molded bumpers and fascia; in 1983 the first plastic-body commercial automobile (Pontiac Fiero) was produced in the United States. The polymerization step can be conducted in a mold, in an extruder (TPU production), or continuously on a conveyor (block foam production). Also, spraying of the monomers onto the surface of a substrate produces polyurethane coatings. The resulting polymers can be thermoplastic, which allows reprocessing by injection molding, extrusion, blow molding, and other remelting processes, or they are thermoset polymers as used in the RIM process in the molding of automotive bumpers, or in the manufacture of cellular polyurethanes. Polyurethanes are a primary component of the global polymer market. They amount to about 6% of the total world plastic use. The world consumption of polyurethanes in 2000 was about 8 million tons, with a global growth averaging around 3–4% a year.

Polyurethanes are among the most important class of specialty polymers. The term polyurethane leads to great deal of confusion. The term is more one of convernience than of accuracy, because polyurethanes are not derived from polymerizing a urethane monomer, nor are the polymers containing primarily urethane groups. Thus,

a typical polyurethane may contain, in addition to the urethane linkage, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, and isocyanurate groups.

The chemistry of urethanes makes use of the reactions of organic isocyanates with compounds containing active hydrogens. When polyfunctional isocyanates and intermadiates containing at least two active hydrogens per mole are reacted at proper ratios, a polymer results that can produce rigid or flexible foams, elastomers, coatings, adhesives and sealants. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkageas shown in Figure 2.1

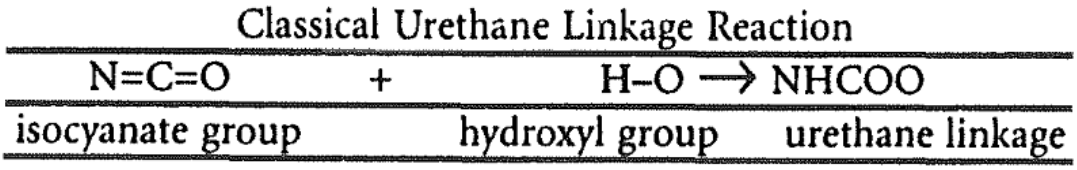


Figure 2.1 : Classical urethane linkage reaction

The isocyanates also react with amines to form substituted urea linkages; they will react with water to form carbamic acid, which is an unstable intermmediate, and it decomposes readily to evolvecarbon dioxide and an amine. This amine, in turn, reacts with additional isocyanate to form disustituted urea. In addition, a number of cross-linking reactions may take place, depending on the reaction conditions such as temperatur, the presence of catalys, the structure of the isocyanate, alcohols, and amines involved. These reactions form linkages of allphanate (reaction between urethane-isocyanate), biuret (reaction between substituted urea and isocyanate), and isosyanurate (trimerization of isocyanate groups). Isocyanates can also be polymerized to form dimers (uretidine diones), carbodiimide, and 1-nylon.

The repeating urethane linkage is the basis for the generic name: polyurethane. However, the use of the generic term polyurethane is deceiving in that all useful polyurethane polymers contain a minority of urethane functional groups. Thus, polyurethane is more a term of convenience rather than accuracy, since these polymers are not derived by polymerizing a monomeric urethane reactant, nor are theypolymers containing primarily urethane linkages. In fact, other groups such as ethers, amides, biurets, and allophanates are the majority linkages in the molecular chain. Urethane linkges represent the minority of functional groups as long as the

polymers contain a significant number of urethane linkages. The name polyurethane may be correctly ascribed to these polymers.

Polyurethanes and the closely related polyureas are the products of the reaction of isocyanates (-N—C—O) with the active hydrogen compounds (R-OH) or (R-NH_2). [67]

2.1.2 Synthesis of polyurethanes

The synthesis of polyurethanes is usually presented as proceeding via the formation of carbamate (urethane) linkages by the reaction of isocyanates and alcohols:

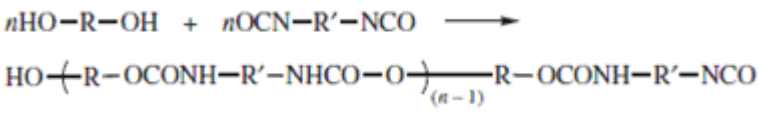


Figure 2.2 : Reaction of isocyanates and alcohols

However, this is an over simplification since other reactions are also usually involved [6-9]. Foamed products such as seat cushions and bedding are the largest applications of polyurethanes. Water is often deliberately added in the production of flexible polyurethane foams. Isocyanate groups react with water to form urea linkages in the polymer chain with the evolution of carbon dioxide.

Figure 2.3 : Form of urea linkages

The carbon dioxide acts as the blowing agent to form the foamed structure of the final product. (Low-boiling solvents such as fluorotrichloromethane are usually added to act as blowing agents in the synthesis of rigid polyurethane foamed products.) Many polyurethanes are synthesized using mixtures of diols and diamines. The diamines react with isocyanate groups to introduce additional urea linkages into the polymer.

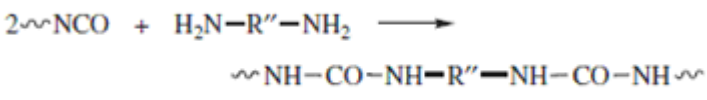


Figure 2.4 : Forming additional urea linkages

Thus, the typical polyurethane actually contains both urethane and urea repeat units. (There are even some instances where only diamines are used in the synthesis. The polymer is then a polyurea although the manufacturer typically refers to it as a polyurethane.) The situation is even more complex since the N-H bonds of both urethane and urea linkages add to isocyanate groups to form allophanate and biuret linkages, respectively. These reactions result in branching and crosslinking of the polymer. Figure 2.5 shows how a diisocyanate crosslinks the urethane and urea groups from two different polymer chains.

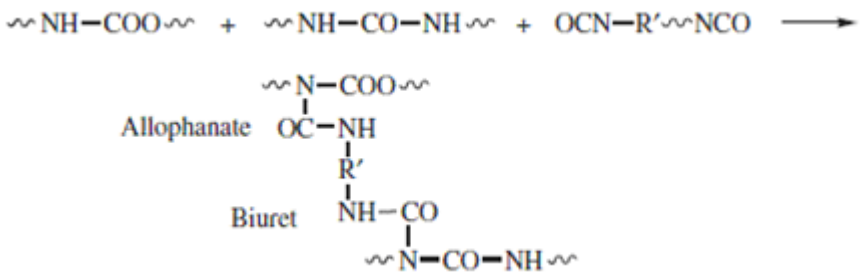


Figure 2.5 : Crosslinking of urethane and urea groups

The relative amounts of allophanate and biuret crosslinks in the polymer depend on the relative amounts of urea and urethane groups (which, in turn, depends on the relative amounts of diamine and diol) and reaction conditions. There is a greater tendency to biuret linkages since the urea N-H is more reactive than the urethane N-H. Trimerization of isocyanate groups to form isocyanurates also occurs and serves as an additional source of branching and crosslinking:

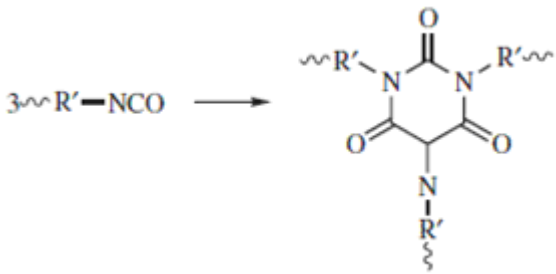


Figure 2.6 : Forming isocyanurates

These reactions present a complexity in carrying out polymerization. Simultaneously, we have the ability to vary polymer properties over a wide range by control of the relative amounts of reactants and the polymerization conditions. Further control of the final product is achieved by choice of monomers. Most polyurethanes involve a

macroglycol (a low-molecular-weight polymer with hydroxyl end groups), diol or diamine, and diisocyanate. The macroglycol (also referred to as a polyol) is a polyether or polyester synthesized under conditions that result in two or more hydroxyl end groups. The diol monomers include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and p-di(2-hydroxyethoxy)benzene. The diamine monomers include diethyltoluenediamine, methylenebis(p-aminobenzene), and 3,30-dichloro-4,40-diaminodiphenylmethane. The diisocyanate monomers include hexamethylene diisocyanate, toluene 2,4- and 2,6-diisocyanates, and naphthalene 1,5-diisocyanate. Alcohol and isocyanate reactants with functionlity greater than 2 are also employed.

The extent of crosslinking in polyurethanes depends on a combination of the amount of polyfunctional monomers present and the extent of biuret, allophanate, and trimerization reactions [16]. The latter reactions are controlled by the overall stoichiometry and the specific catalyst present. Stannous and other metal carboxylates as well as tertiary amines are catalysts for the various reactions. Proper choice of the specific catalyst result in differences in the relative amounts of each reaction. Temperature also affects the extents of the different reactions. Polymerization temperatures are moderate, often near ambient and usually no higher than 100–120ºC. Significantly higher temperatures are avoided because polyurethanes undergo several different types of degradation reactions, such as;

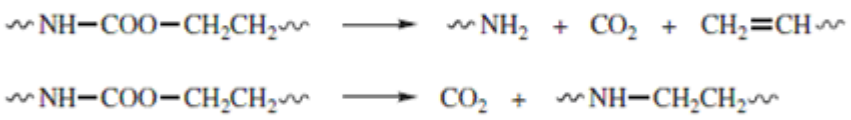


Figure 2.7 : Degradation reactions of polyurethanes

as well as decomposition back to the alcohol and isocyanate monomers. Overall control in the synthesis of polyurethane foamed products also requires a balance between the polymerization–crosslinking and blowing processes. An imbalance between the chemical and physical processes can result in a collapse of the foamed structures (before solidification by crosslinking and/or cooling) or imperfections in the foam structures, which yields poor mechanical strength and performance. The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives. Polyurethanes possess good abrasion, tear, and impact

resistance coupled with oil and grease resistance. The global production of polyurethanes was more than 15 billion pounds in 1997. Flexible foamed products include upholstered furniture and auto parts (cushions, backs, and arms), mattresses, and carpet underlay. Rigid foamed products with a closedcell morphology possess excellent insulating properties and find extensive use in commercial roofing, residential sheathing, and insulation for water heaters, tanks, pipes, refrigerators, and freezers. Solid elastomeric products include forklift tires, skateboard wheels, automobile parts (bumpers, fascia, fenders, door panels, gaskets for trunk, windows, windshield, steering wheel, instrument panel), and sporting goods (golf balls, ski boots, football cleats). Many of these foam and solid products are made by reaction injection molding (RIM), a process in which a mixture of the monomers is injected into a mold cavity where polymerization and crosslinking take place to form the product. Reaction injection molding of polyurethanes, involving low-viscosity reaction mixtures and moderate reaction temperatures, is well suited for the economical molding of large objects such as automobile fenders. [48]

2.1.3 Isocyanates

The synthesis, reactions, and manufacture of isocyanates were reviewed in 1997 [71], and the chemistry and technology of isocyanates is the subject of a recent book [72]. The standard method of synthesis of isocyanates is the phosgenation of amines or amine salts. The phosgenation of amines to isocyanates was pioneered by Hentschel in 1884 [24]. Using this method, a solution of the diamines in chlorobenzene is added to excess phosgene in the same solvent below 20◦C.

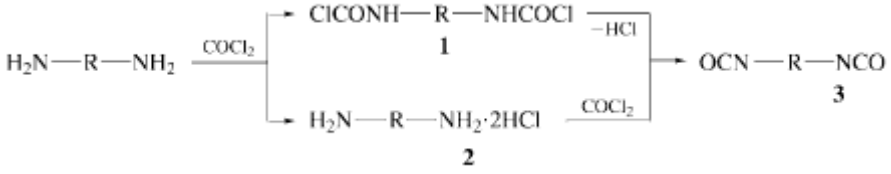


Figure 2.8 : Phosgenation of amines

The resultant slurry consisting of the dicarbamoyl chloride (1) and the diamine dihydrochloride (2) is treated with excess phosgene at temperatures up to 130ºC. Upon heating above 65ºC the dicarbamoyl chloride dissociates to generate diisocyanate (3). The conversion of 2 is very slow, and the use of polar solvents or higher pressures increases the rate of reaction.

In the laboratory a slurry of the diamine salts, obtained by treating a solution of the diamines with hydrogen chloride or carbon dioxide, is treated above 100 ºC until a clear solution is obtained. Instead of the toxic phosgene gas, the liquid trichloromethyl chloroformate (diphosgene) [33] or the solid bistrichloromethyl carbonate [15] (triphosgene) can be used in the laboratory. The phosgene oligomers have to be used with caution because the toxic monomer can be generated readily and all reactions have to be performed under a fume hood. In the continuous manufacture of diisocyanates, the by-products (hydrogen chloride and excess phosgene) are vented and separated. The recovered phosgene is recycled and part of the hydrogen chloride is used in the aniline/formaldehyde condensation. The solvents used in the phosgenation of the diamines are aromatic hydrocarbons, especially chlorobenzene and *o*-dichlorobenzene. Occasionally, more polar solvents, such as ethyl acetate, dioxane, nitrobenzene, or dimethylsulfone, are used. Excess phosgene can also be used as solvent if the reaction is conducted under high pressure. Dimethylformamide (DMF) and phenyltetramethylguanidine catalyze the phosgenation reaction [56].

Aliphatic diamines are also phosgenated in a two-phase reaction using methylene chloride and aqueous sodium hydroxide. The diamine and phosgene are dissolved in methylene chloride and the form 2 is instantaneously neutralized with sodium hydroxide. The generated diisocyanate remains in the solvent phase, and excess phosgene is also neutralized with sodium hydroxide, which enhances the safety of phosgene handling. The highly exothermic reaction requires efficient cooling. A disadvantage of this process is the use of a slight excess of phosgene, which cannot be recovered.

Instead of phosgene and its oligomers, oligomeric *t*-butylcarbonates are also used to convert diamines into diisocyanates. For example, sterically hindered aromatic diamines react with di-*t*-butyldicarbonate in the presence of dimethylaminopyridine in acetonitrile at room temperature to give sterically hindered aromatic diisocyanates. In this manner 3,6-3,6-tetramethyl MDI is obtained in 93% yield [30]. Also, aliphatic diamines react with di-*t*-butyltricarbonate at room temperature to give a high yield of the corresponding diisocyanates [50].

Since the early 1970’s, attempts have been made by the principal global producers of isocyanates to avoid the use of the toxic phosgene in the manufacture of isocyanates.

Attempts to produce TDI and PMDI by nonphosgene processes have failed. However, two aliphatic diisocyanates, CHDI and TMXDI, are manufactured using nonphosgene processes. H¨ uls and BASF have also announced plans to use nonphosgene processes for the manufacture of IPDI in their new plants which are under construction. In the new, nonphosgene chemistry, isocyanic acid, generated by thermolysis of urea, reacts with diamines to give a bis-urea derivative. Subsequent reaction with diethylamine affords tri-substituted urea derivatives, which are thermolyzed in an inert solvent in the presence of an acidic catalyst to give the diisocyanate [60]. Gaseous ammonia is the only by-product in this process. Also, reaction of aliphatic diamines with carbon dioxide, in the presence of triethylamine, affords biscarbamate salts, which can be dehydrated with phosphoryl chloride to give the diisocyanate [80].

Another laboratory method of synthesis of diisocyanates is the thermolysis of bisacylazides (4) (Curtius reaction). For example, dicarboxylic acid chlorides react with trimethylsilyl azide to give (4), which is thermolyzed in an inert solvent to give the diisocyanates (5), [49].

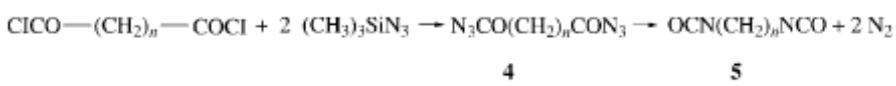


Figure 2.9 : Sythesis of diisocyanates

The preparation of aliphatic diisocyanates, using bisacylazides, has to be conducted with caution because an explosion occurred in the preparation of ethylene diisocyanate by using this method [38]. Ethylene diisocyanate is readily obtained by dehydrochlorination of a heterocyclic allophanoyl chloride derivative obtained in the phosgenation of ethyleneurea [73]. The commodity aromatic isocyanates TDI and PMDI/MDI are most widely used in the manufacture of urethane polymers. Tolylene diisocyanate, TDI, is a distilled 80:20 mixture of 2,4- and 2,6-isomers. However, pure 2,4-TDI and a 65:35 mixture of the 2,4- and 2,6-isomers are also commercially available. Pure 2,4- TDI, mp 19.5–21◦C, is obtained on cooling of 80:20 TDI. The manufacture of TDI involves nitration of toluene, hydrogenation to the diamines, and phosgenation. Separation of the undesired ortho derivatives, such as 2,3- and 3,4-dinitrotoluene, is necessary because their presence interferes with the polymerization

of TDI [57]. The other commodity isocyanate, PMDI/MDI, is based on benzene. Mononitration of benzene, catalytic reduction to aniline, followed by condensation of aniline with formaldehyde produces oligomeric amines, which are phosgenated to give mixtures of PMDI and MDI. MDI is separated from PMDI by continuous thin-film vacuum distillation. PMDIs are crude products that vary in exact composition. The main constituents are 40–60% MDI; the remainder is the other isomers of MDI, triisocyanates, and higher molecular weight oligomers. Important product variables are functionality and acidity. Rigid polyurethane foams are mainly manufactured from PMDI. The so-called pure MDI is a low melting solid that is used for high performance polyurethane elastomers and spandex fibers. Liquid MDI (Isonate 143-L) is produced by converting some of the isocyanate groups in MDI to carbodiimide groups, which react with the excess isocyanate present to form a small amount of the trifunctional four-membered ring cycloadduct [18]. The presence of the cycloadduct lowers the melting point of MDI to give a liquid product. In most applications the trifunctional cycloadduct will dissociate into difunctional monomers; therefore, this type of liquid MDI can be used in the manufacture of linear polyurethanes. Liquid MDI products are also made by reaction of the diisocyanate with small amounts of glycols. These products are called prepolymers. MDI products enriched in 2,4-MDI are also available. The latter are used in the manufacture of flexible MDI foams. The manufacture of the oligomeric amine precursors for PMDI/MDI is conducted by continuously adding formaldehyde to aniline in the presence of less than the stoichiometric amount of hydrochloric acid at room temperature in agitated reactors. The reaction mixture is gradually heated to 100◦C over a period of several hours. The reaction can also be conducted under pressure at higher temperatures in order to increase the rate of reaction. However, the oligomeric amines produced in this manner contain higher amounts of 2,2- and 2,4-methylenedianiline (MDA). The acid-catalyzed aniline/formaldehyde reaction proceeds in two steps.

At room temperature aniline reacts with formaldehyde to form N-substituted carbonium ions which attack aniline in the para- and ortho-position to give a mixture of *p*-aminobenzylamine (PABA), (6), *o*-aminobenzylamine (OABA), (7), and oligomeric benzylamines. Subsequent heating affects dissociation of the benzylamines to give C-bonded carbonium ions, which form another C-C bond in their reaction with aniline.

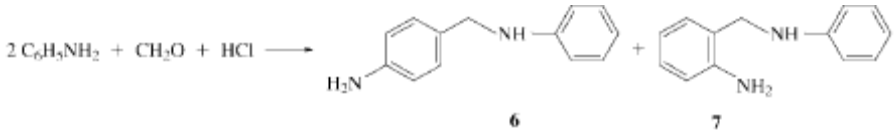


Figure 2.10 : Reaction of formaldehyde with aniline

The variables affecting the product distribution are aniline concentration, hydrochloric acid concentration, and temperature. The higher the excess of aniline, the higher is the diamine concentration. Higher hydrochloric acid concentration and lower initial temperature favor the formation of 4,4_-MDA. Attempts were made over the years to replace the aqueous hydrochloric acid catalyst with slower reacting solid acidic clay catalysts, but the obtained product distribution was different, and therefore this approach was never used. The commercial manufacture of TDI and PMDI/MDI is the continuous phosgenation under pressure of the amine precursors in an inert solvent at elevated temperatures. The by-products, hydrogen chloride and excess phosgene, are continuously vented and separated. The recovered phosgene is recycled and the hydrogen chloride is used in the aniline/formaldehyde condensation, or it is sold or reoxidized to chlorine to be reused in the manufacture of phosgene. In case of the manufacture of PMDI, some of the diisocyanate (MDI) is separated by continuous vacuum distillation using a wiped film evaporator. In this operation the residual PMDI, which still contains MDI, is only subjected to a short heat treatment. The advantage of the simultaneous manufacture of both isocyanates is a quantitative yield because the by-products of the phosgenation reaction are contained in the residual PMDI. The current prices of the commodity aromatic isocyanates (DM/kg) are TDI: 3.6; PMDI: 2.8; MDI: 4.3. The light-stable aliphatic isocyanates are somewhat more expensive.

Several higher-priced aromatic diisocyanates, such as *p*-phenylene diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), and bitolylene diisocyanate (TODI), are also available. These symmetrical high melting diisocyanates give high melting hard segments in polyurethane elastomers. Aromatic diisocyanates are also obtained in the coupling of suitable monoisocyanates. For example, reaction of 4-isocyanatobenzoyl chloride (8) with a trimethylsiloxy-substituted isocyanate (9) affords diisocyanato benzoates (10) [43].

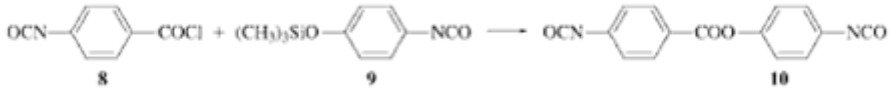


Figure 2.11 : Formation of diisocyanato benzoates

Triad diisocyanates (12) are obtained in the reaction of two equivalents of 4-isocyanatobenzoyl chloride with the silylated hydroquinone derivative (11) [44].

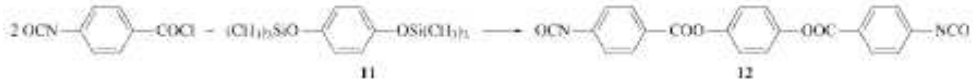


Figure 2.12 : Reaction of triad diisocyanates

The aromatic triisocyanate (13) is obtained in the reaction of 4-nitrophenol and thiophosphoryl chloride, followed by reduction and phosgenation. [25]. This triisocyanate is sold under the trade name Desmodur RF (Bayer) as a glue for rubber adhesive solutions.

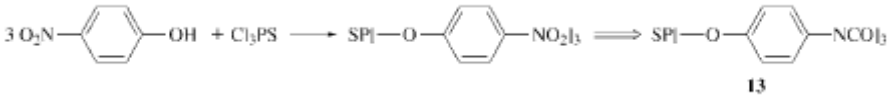


Figure 2.13 : Reaction of aromatic triisocyanate

Aromatic triisocyanates as cross-linkers are more readily obtained by trimerizing 2,4-TDI. In this reaction the more reactive isocyanate group in the 4-position undergoes trimerization to produce a triisocyanate [31]. Also, aromatic polyisocyanates are obtained in the copolymerization of styrene with cinnamoyl azide [36]. Blocked polyisocyanates (14) are obtained from *p*-nitrostyrene and carbon monoxide in methanol, using a ruthenium catalyst [21].

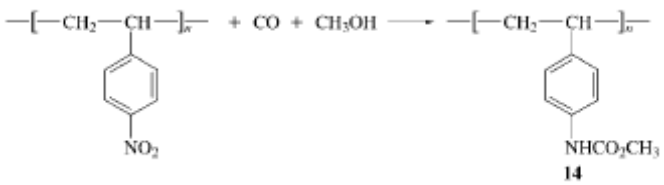


Figure 2.14 : Formation of blocked polyisocyanates

Polyurethanes obtained from aromatic diisocyanates undergo slow oxidation in the presence of air and light causing discoloration, which is unacceptable in some applications. In contrast, polyurethanes obtained from aliphatic diisocyanates are color stable, although it is necessary to add antioxidants and uvstabilizers to the formulations to maintain the physical properties of the polymers with time. The elusive parent diisocyanate, is only stable at −75◦C, and therefore it is not suitable as a monomer for polyurethanes [40]. The least costly aliphatic diisocyanate is hexamethylene diisocyanate (HDI), which is obtained by phosgenating the nylon intermediate hexamethylenediamine (HDA). Because of its low boiling point, HDI is mostly used in the form of its derivatives, such as biurets, allophanates, dimers, or trimers [35]. Isophorone diisocyanate (IPDI) and its derivatives are also used in the formulation of rigid coatings, while hydrogenated MDI (HMDI) and cyclohexane diisocyanate (CHDI) are used in the formulation of flexible coatings and polyurethane elastomers. HDA is commercially produced from adipic acid or butadiene. The catalytic hydrogenation of adiponitrile to HDA is common in both routes. The phosgenation of the diamine is conducted continuously in chlorobenzene. In Table 1 the advantages and disadvantages of several phosgenation processes for aliphatic diisocyanates are shown.

In a recent patent a nonphosgene synthesis of HDI is described [4]. The other significant aliphatic diisocyanate, IPDI, is based on isophorone chemistry. Trimerization of acetone gives isophorone (15), which on reaction with HCN affords the *β*-cyanoketone (16). Reductive amination of (16) to the diamine (17), followed by phosgenation, gives IPDI (18).

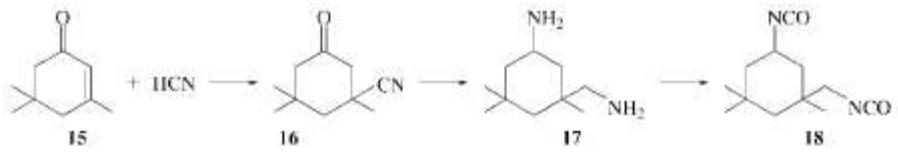


Figure 2.15 : Formation of isophorone, *β*-cyanoketone, IPDI

An example of a nonphosgene route to IPDI is the reaction of 17 with urea and *n*-butanol in the presence of dibutyl carbonate at 210–220◦C. Thermolysis of the biscarbamate at 270–280◦C at 30 mbar affords 18 [5]. IPDI is a mixture of 72% cis isomers and 28% trans isomers [53].

HMDI was originally produced by DuPont as a coproduct in the manufacture of Quiana fiber. After terminating Quiana production DuPont sold the product to Bayer. Today, a crude mixture of the diamines obtained in the acid-catalyzed aniline/formaldehyde reaction is supplied by Bayer to Air Products, which is performing the ring hydrogenation. The phosgenation of the ring hydrogenated diamines is performed by Bayer. Commercial HMDI is a mixture of three stereo isomers (trans–trans, mp 65◦C; cis–trans, mp 36◦C; and cis–cis, mp 61◦C). The direct formation of a blocked HMDI is conducted by ring hydrogenation of caprolactam blocked MDI [76]. Semicommercial aliphatic diisocyanates include *trans*-cyclohexane-1,4- diisocyanate (CHDI) and*m*-tetramethylxylylene diisocyanate (TMXDI). A coproduct in the production of TMXDI is *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI), which can be copolymerized with other olefins to give aliphatic polyisocyanates.

These aliphatic diisocyanates are manufactured using nonphosgene routes. Akzo has developed the CHDI process based on scrap polyester fiber. Ring hydrogenation of dimethyl terephthalate (DMT), transesterification with diethylene glycol, followed by reaction with ammonia provides a diamide, which is N-chlorinated. Hofmann rearrangement in the presence of diethylamine produces the blocked diisocyanate, which is subsequently deblocked on heating in the presence of hydrogen chloride [88]. Cyclohexyl diisocyanate (CHDA) can also be obtained by catalytic hydrogenation of *p*-phenylenediamine. Most likely, this approach has economic advantages over the multistep process based on fiber scrap. The manufacture of TMXDI, developed by American Cyanamid, is based on the reaction of *m*-isopropylidenebenzene (19) with ethyl carbamate to give the blocked diisocyanate (20). Thermolysis affords a mixture of TMXDI (21) and the monoisocyanate (TMI) (22) [63] .

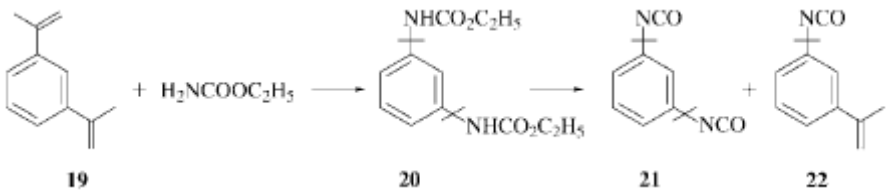


Figure 2.16 : M-isopropylidenebenzene, blocked diisocyanate, TMXDI and TMI

The coupling of ω-isocyanatocarboxylic acid chlorides (23) with silylated aliphatic hydroxy-isocyanates (24) is another method of synthesis of aliphatic diisocyanates (25), containing ester groups in their structure [42].

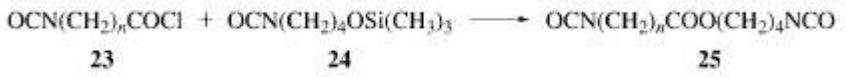


Figure 2.17 : W-isocyanatocarboxylic acid chlorides, silylated hydroxy-isocyanates

2.1.3.1 Blocked isocyanates

The urethane linkage is thermally reversible to R-OH and R'-N=C=0. Depending on the nature of [R], the presence of catalyst, and the presence of active hydrogen compounds, this reaction can be utilized to block or mask isocyanates such that the blocked isocyanate is stable in the presence of active hydrogens at room temperature but unblocks to liberate free isocyanate at elevated temperature, shown in Table 2.1.

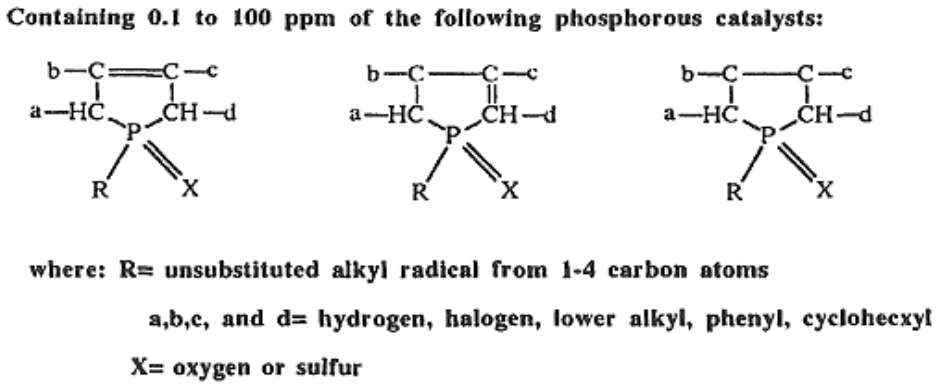


Figure 2.18 : Storage-stable, carbodiimide-containing diisocyanate [19]

It should be noted that both isocyanate moieties do not have to be blocked at once. One isocyanate may be blocked and subsequently deblocked at a higher temperature. An elegant example of this technique is provided by Stallman. This invention relates to organic diisocyanates in which one of the isocyanate groups is hindered or blocked to render it unreactive with most compounds having active hydrogen- containing functional groups below temperatures of about 85° C. It is therefore an object of the present invention to reduce the activity of one of the -NCO groups in organic diisocyanates at temperatures below about 85° C.

Table 2.1: Typical blocked isocyanates

Isocyanate	Blocking Agent	Unblocking Temperature (°C)
TDI	Nonyl phenol	150
TDI	Phenol	150
TDI	Butanone oxime	125
MDI	Butanone oxime	140
HDI	Butanone oxime	150
IPDI	Butanone oxime	150
HDI	Caprolactam	150

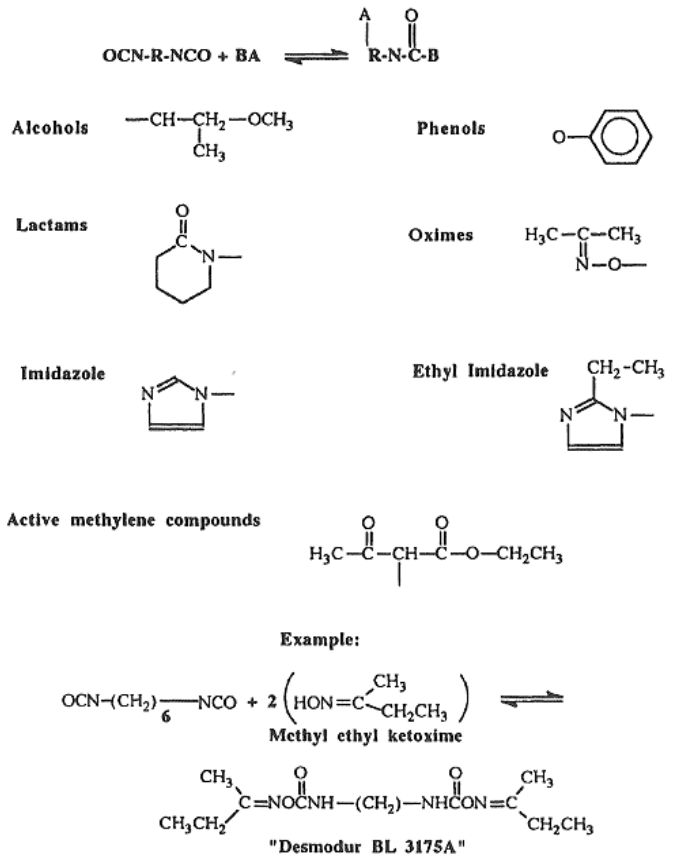


Figure 2.19 : The structure of some commonly used blocking agents.

Due to their chemical nature, isocyanates are very reactive with groups containing an active hydrogen such as -OH, -COOH, -NH_2, etc. In carrying out the reactions with the isocyanates, extreme care must be exercised to prevent undesirable reactions by carefully controlling the various steps such as order of addition, temperature, pressure, presence of moisture, and so on to avoid undesirable side reactions.

Many attempts have been made to reduce the activity of the diisocyanates by various means including blocking or hindering one of the -NCO groups. One such suggested method involves reacting the isocyanate group with a phenol or a compound containing methylene hydrogen, such as a malonic ester, to form adducts that regenerate the -NCO group on heating to about 150 to 180° C. Among the compounds that may be used to form mono adducts of diisocyanates are aceto-acetic ester; diethyl malonate; mercaptans such as 2-mercapto benzothiazole; lactams; imides such as succinimide, phthal- imide, and the like; tertiary amyl alcohol; dimethyl phenyl carbinol; and secondary amines such as diphenylamine. These adducts regenerate -NCO groups on heating to 100 to 150° C. It is also known that dimeric aromatic isocyanates such as the dimer of phenyl isocyanate regenerate the original isocyanate on heating to 150 to 180° C. However, it is frequently impossible, due to various reasons (such as shape and dimensions of the object containing them) that preclude placing the object in an oven, or due to the adverse effect on the objects by high temperatures. These requirements for the liberation of the -NCO group obviously place restrictions and inconvenience on their use [67].

Factors on deblocking reaction of blocked isocyanates

A blocked isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed insuch a way as to regenerate the isocyanate and the blocking agent. The regenerated isocyanate could react with a co-reactant containing the hydroxyl functional groups to form urethane with thermally more stable bonds.

There are several variables which affect the rate and extent of the deblocking reaction such as: the structure of the blocking agent and the polyisocyanate used, the structure of substituent, presence of catalysts, effects of solvents, temperature.

The deblocking temperature of the blocked isocyanates depends on the structures of the blocking agents and structures of the isocyanates. Several compounds namely phenols, oximes, amides, imides, imidazoles, amindines and related compounds, pyrazoles, 1,2,4- triazoles, hydroxamic acid esters, and active methylene compounds have been reported as blocking agents [83]. Among these blocking agents, phenols are the most studied blocking agents because of the possibilities of introducing number of substituents on the benzene ring. Generally, the dissociation or deblocking temperatures (Td°C) of blocked polyisocyanates based on commercially utilised blocking agents decrease in the order: alcohols > e-caprolactam > phenols > methyl ethyl ketoxime > active methylene compounds [59].

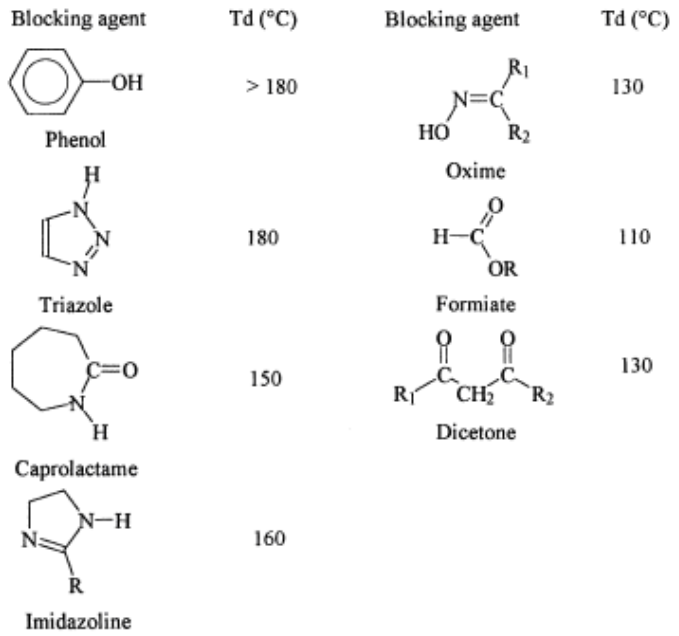


Figure 2.20 : Blocking agents and deeblocking temperatures of isocyanates

The substituent being a strong influencing factor on the deblocking temperature of blocked isocyanates. Substitutents present in the phenolic aromatic ring with electron-withdrawing tendency decrease the deblocking temperature while electron releasing groups increase the deblocking temperature [23][32]. The structures of isocyanates also have major effect on the deblocking temperatures; the isocyanate structure has additional effect on urethane formation reaction. In general, blocked aromatic isocyanates deblock at lower temperatures than aliphatic isocyanates.

Isocyanate structure can strongly affect the strength of the labile bond formed during the blocking reaction, and hence the deblocking temperature. If the blocked isocyanate is based on aromatic isocyanate, the aromatic ring drains the electron density of the nitrogen atom of isocyanate moiety and makes the labile bond formed between the isocyanate and blocking agent more labile. The vice versa is true for the cases of blocked isocyanates based on aliphatic isocyanates [54].

Urethane forming reactions from blocked isocyanates

There are two urethane forming reaction mechanisms by which a blocked isocyanate can react with a nucleophile (NuH). In the elimination-addition reaction(Figure 2.21.), the blocked isocyanate decomposes to the free isocyanate and the blocking group (BH). The isocyanate then reacts with a nucleophile to form a final product. In the addition-elimination reaction (Figure 2.22.), the nucleophile reacts directly with the blocked isocyanate to yield a tetrahedral intermediate followed by elimination of the blocking agent [83].

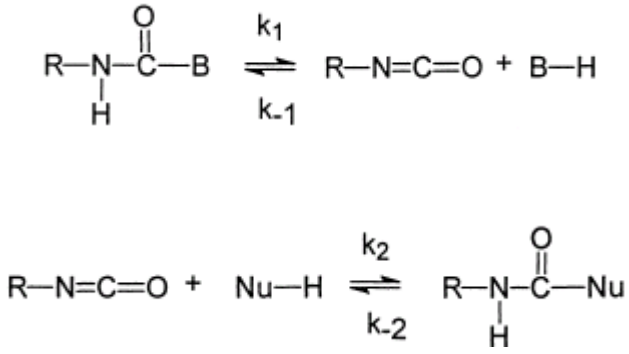


Figure 2.21 : Elimination-addition reaction

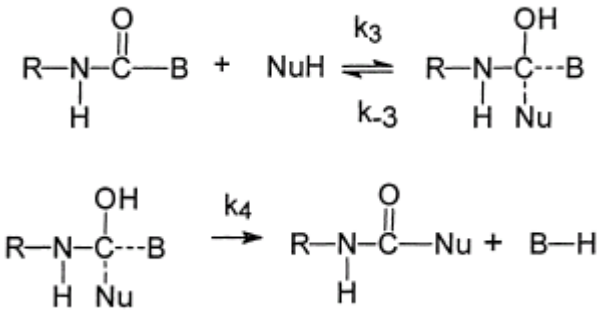


Figure 2.22 : Addition- elimination reaction

In general, crosslinking is more rapid in the presence of a NuH that can react rapidly with the isocyanate; for example, amines react much more rapidly than alcohols. The differences in reactivity depend on the structures of the amines, alcohols, and blocking agent. Primary amines react more rapidly than secondary amines. Thus, blends of oxime blocked isocyanates and secondary amine-functional polymers increase in viscosity more slowly than those with primary amine-functional polymers [37].

During the curing process, low molecular weight blocking agents can evaporate from the film. Those that can diffuse more rapidly through the crosslinking film and volatilize more rapidly from the surface give more rapid (or lower temperature) cure than other blocking agents of the same class that diffuse and evaporate more slowly. For example, methyl, ethyl, and isopropyl alcohol blocked TMXDI and an acrylic polyol with a tin catalyst gave crosslinked films in increasing times in the order listed [26].

The curing schedule required for crosslinking of blocked polyisocyanates with polynucleophiles is dependent on many variables including [82]:

- structures of the isocyanate, blocking agent, and nucleophile,
- relative rate of reaction of the nucleophile with the isocyanate compared to the reverse reaction rate of the isocyanate with the blocking agent,
- the rates of diffusion and evaporation of the blocking agent,
- polarity and hydrogen bonding potential of the reaction medium (solvents or coreactant),
- concentrations of reactive groups,
- type and concentration of catalysts,
- extent of side reactions and whether they lead to crosslinking or termination,
- the extent of crosslinking required to achieve film proper

2.1.4 Polyols

Polyols are reactants which contains as functional groups hydroxyl groups. In urethane reactions primary hydroxyl groups, such as derived from ethylene oxide are faster reacting with an isocyanate than secondary hydroxyl groups, for example propylene oxide derived groups. Polyether polyols contain in the polymer backbone ether groups. These polyether polyols are very stable to hydrolysis under basic conditions, but can be attacked in an acidic environment. Polyether polyols are the main stay of the polyurethane market, they are used in foams, elastomers and coatings. Polyether polyols can be di-functional (diol) or they can be of higher functionality. In applications where high flexibility and elongation is required diols are used to create highly flexible and soft polyurethanes. Highly functional polyols are used in the preparation of hard or rigid polyurethanes. The products made this way are highly crosslinked and not soluble in a solvent. Besides polyether also polyester polyols are used in the preparation of polyurethanes. The ester linkage in the polyester makes the polyurethanes more sensitive to hydrolysis, but it is possible to prepare polyurethanes with improved exterior durability [51]

2.1.4.1 Polyether polyols

The polyether polyols used in the manufacture of polyurethanes are hydroxy terminated macromolecules, with molecular weights ranging from 250 to 8000. Lyondell/Bayer has provided pilot plant diols/triols having molecular weights of 10,000 to 15,000 for lubricant and surfactant applications. The hydroxy functionality can range from 2 to 8. The economically attractive polyether polyols based on alkylene oxides are listed in Table 2.2.

Other speciality initiators derived from natural products are also manufactured. Examples include formose, lactose, α-methyl glucoside, and soybean-derived polyols. Propoxylation of dairy waste also affords polyether polyols.

DuPont has developed a fermentation process to convert glucose into 1,3-propanediol, a useful polyurethane extender. The alkylene oxide polymerization is usually initiated by alkaline hydroxides, especially potassium hydroxide. In the base-catalyzed polymerization of propylene oxide (PO), some rearrangement occurs to give allyl alcohol. Further reaction of allyl alcohol with PO produces a monofunctional alcohol. Therefore, polyether polyols derived from PO are not truly

difunctional. By using zinc hexacyano cobaltate as catalyst, a more difunctional polyol is obtained [64].

Table 2.2: Commercial polyether polyols

Product	Nominal Functionality	Initiator	Cyclic Ether
Poly(ethylene glycol) (PEG)	2	Water or EG	EO
Poly(propylene glycol) (PPG)	2	Water or PG	PO
PPG/ PEG	2	Water or PG	PO / EO
Poly(tetramethylene glycol) (PTMG)	2	Water	THF
Glycerol adduct	3	Glycerol	PO
Trimethylolpropane adduct	3	TMP	PO
Pentaerythritol adduct	4	Pentaerythritol	PO
Ethylenediamine adduct	4	Ethylenediamine	PO
Phenolic resin adduct	4	Phenolic Resin	PO
Diethylenetriamine adduct	5	DETA	PO
Sorbitol adduct	6	Sorbitol	PO
Sucrose adduct	6	Sucrose	PO

Ethylene oxide is manufactured by direct oxidation of ethylene, in contrast PO is only obtained in coproduct processes. The classical process, chlorination of propylene, is still used by Dow, one of the world's largest producer of polyether polyols. In contrast, all other producers use the Halcon process, based on the simultaneous production of PO and styrene monomer or *t*-butyl alcohol. In view of the demise of MTBE (methyl-*t*-butyl ether based on *t*-butyl alcohol) as a fuel additive, the styrene coproduct process (POSM) will remain as the economically viable route to PO. A recent example is the new (SMPO) plant of Basell at Moerdijk in the Netherlands. The backbone of the polyether polyols are either PO homopolymers or random or block copolymers with ethylene oxide. Important characteristics of the polyol are their hydroxy functionality, hydroxy equivalent weight, and their reactivity and compatibility with the other components used in the polyurethane formulation. Blending of polyols of different functionality, molecular

weight, and reactivity can be used to tailor a polyol for a specific application. Since primary hydroxy groups are more reactive than secondary hydroxy groups, it is advantageous to produce block copolymers with terminal primary hydroxyl groups by using ethylene oxide last in a block copolymer. Capping with ε - caprolactone also produces primary hydroxyl groups. Trichlorobutylene oxidederived polyols are used as fire retardants. The hydrophobicity of polyether polyols can be modified by homo- or copolymerization with 1,2-butylene oxide or styrene oxide. The higher molecular weight polyether polyols are soluble in organic solvents. Poly(PO) is soluble in water up to a molecular weight of 760, and copolymerization with ethylene oxide expands the range of water solubility. Random copolymers are obtained by polymerizing mixtures of PO and ethylene oxide. The viscosity of polyether polyols increases with hydroxyl equivalent weight. With amine initiators the so-called self-catalyzed polyols are obtained, which are used in the formulation of rigid spray foam systems. The rigidity or stiffness of a foam is increased by aromatic initiators, such as Mannich bases derived from phenol, phenolic resins, toluenediamine, or methylenedianiline (MDA).

In addition, blending of polyether polyols with diethanolamine, followed by reaction with TDI, also affords a urethane/urea dispersion [13]. The polymer or PHD-type polyols increase the load bearing properties and stiffness of flexible foams. Interreactive dispersion polyols are also used in RIM applications where elastomers of high modulus, low thermal coefficient of expansion, and improved paintability are needed.

2.1.4.2 Polyester polyols

Initially polyester polyols were the preferred raw materials for polyurethanes, but today the less expensive polyether polyols dominate the polyurethane market. An exception are the inexpensive aromatic polyester polyols, which have been introduced for rigid foam applications. These are obtained from residues of terephthalic acid production or by transesterification of DMT or poly(ethylene terephthalate) (PET) scrap with glycols. TBI of France is the first European company to manufacture aromatic polyester polyols directly from PET scrap bottles at lssoire with a capacity of 10 kt/a. Phthalates and terephthalates are also used. Polyester polyols are based on saturated aliphatic or aromatic carboxylic acids and diols or

mixtures of diols. The carboxylic acid of choice is adipic acid because of its favorable cost/performance ratio. For elastomers, linear polyester polyols of molecular weight of ca 2000 are preferred. Branched polyester polyols, formulated from higher functional glycols, are used for foam and coating applications.

Polyester polyol-derived polyurethanes have a lower hydrolytic stability oxidative and thermal stabilities. In addition, polyester polyols are made by the reaction of caprolactone with diols. Poly(caprolactone diols) are used in the manufacture of TPU elastomers with improved hydrolytic stability [11]. The hydrolytic stability of the poly(caprolactone diol)-derived TPUs is comparable to TPUs based on the more expensive long-chain diol adipates [58]. Polyether/polyester polyol hybrids are synthesized from low molecular weight polyester diols, which are extended with PO.

The most important chain extenders are ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, cyclohexanedimethanol, and hyroquinone dihydroxyethyl ether. Recently, 1,3-propanediol [12] and 1,2,4-butanetriol [16] have become available as new polyurethane rawmaterials. Since ethylene glycol-extended polyurethanes are prone to thermal degradation, ethylene glycol is only used as a RIM extender in thermoset polyurethane [52].

2.1.4.3 Catalysts

The most commonly used catalysts in polyurethanes are tertiary amines. As indicated earlier, there are many reactions taking place and the catalyst can be involved in any one or more of these[82]:

- The deblocking reaction, or
- the reaction of the free isocyanate with the other nucleophile, or
- an addition-elimination reaction, and/or
- side reactions.

They promote isocyanate reactions which will occur at moderate temperatures, i.e. reaction with alcohols, water, and carboxylic acids. However, the tertiary amines are not strong catalysts for the reactions of isocyanates and isocyanate derivatives at elevated temperatures [55]. Strong catalysts for these reactions are the strong bases, e.g. NaOH and NaOR.

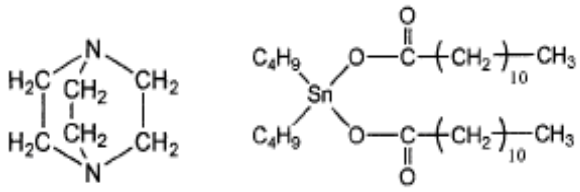
With aromatic isocyanate resins, the formation of the urethane linkage can be promoted by a number of metals in the form of organometallics and/or salts of organic acids. Tin compounds such as DBTDL and tin (II) octoate are particularly effective, having superseded the more toxic lead equivalent components.

Synergistic effects of tin and amine catalysts are of technical importance and are widely studied principally because of the differences in reactivity. Metal catalysts are usually employed in systems based on the slower reacting aliphatic isocyanate adducts[77].

Standard moisture cure catalysts used principally in adhesives are:

- Tin catalysts. Dibutyltin dilaurate (DBTDL), dibutyltin diacetate (DBTDA);
- Amines. Morpholine derivatives, tertiary amines;
- Bismuth catalysts, which are increasingly replacing mercuric catalysts.

Both blocked aromatic and aliphatic polymers use latent curatives such as ketimines and oxazolidines; however, they do have some inherent disadvantages. The use of ketimines and aldemines often produces products that have a tendency to yellow upon exposure to sunlight, and that take a longer time to achieve complete cure and retain slow evaporating ketones or aldehydes. Oxazolidine modification can also result in some yellowing and reduced chemical resistance to some acids [45].



DABCO DBTDL

Figure 2.23 : Chemical structures of DABCO and DBTDL catalysts [46]

2.2 Starch Based Biodegradable Polymers

Advances in petroleum-based fuels and polymers have benefited mankind in numerous ways. Petroleum-based plastics can be disposable and highly durable, depending on their composition and specific application. However, petroleum resources are finite, and prices are likely to continue to rise in the future.

In addition, global warming, caused in part by carbon dioxide released by the process of fossil fuel combustion, has become an increasingly important problem, and the disposal of items made of petroleum-based plastics, such as fast-food utensils, packaging containers, and trash bags, also creates an environmental problem. Petroleum-based or synthetic solvents and chemicals are also contributing to poor air quality. It is necessary to find new ways to secure sustainable world development. Renewable biomaterials that can be used for both bioenergy and bioproducts are a possible alternative to petroleum-based and synthetic products.

Agriculture offers a broad range of commodities, including forest, plant/ crop, farm, and marine animals, that have many uses. Plant-based materials have been used traditionally for food and feed and are increasingly being used in pharmaceuticals and nutraceuticals. Industrial use of agricultural commodities for fuels and consumer products began in the 1920s, but they were soon replaced by petroleum-based chemicals after World War II because of petrochemicals' low cost and durability. The three major plant-based polymers are protein, oil, and carbohydrates [81]

In nature, the availability of starch is just second to cellulose. The most important industrial sources of starch are corn, wheat, potato, tapioca and rice. In the last decade, there has been a significant reduction in the price of corn and potato starch, both in Europe and the USA. The lower price and greater availability of starch associated with its very favourable environmental profile aroused a renewed interest in development of starch-based polymers as an alternative to polymers based on petrochemicals. Starch is totally biodegradable in a variety of environments and thus permits the development of totally degradable products for specific market demands. Degradation or incineration of starch based products recycles atmospheric carbon dioxides trapped by starch-producing plants and does not increase potential global warming.

The most relevant achievements in this sector are related to thermoplastic starch polymers resulting from the processing of native starch by chemical, thermal and mechanical means, and to its complexation to other co-polymers. The resulting materials show properties ranging from the flexibility of polyethylene to the rigidity of polystyrene, and can be soluble or insoluble in water as well as insensitive to humidity. Such properties explain the leading position of starch-based materials in the biodegradable polymer field.

Starch is unique among carbohydrates because it occurs naturally as discrete granules. This is because the short-branched amylopectin chains are able to form helical structures, which crystallise. Starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The melting point of native starch is higher than the thermal decomposition temperature: hence the poor thermal stability of native starch and the need for conversion to starch-based materials with a much-improved property profile.

In nature, starch is based on crystalline beads of about 15-100 microns in diameter. Crystalline starch beads in plastics can be used as fillers or can be transformed into thermoplastic starch, which can either be processed alone or in combination with specifi c synthetic polymers. To make starch thermoplastic, its crystalline structure has to be destroyed by pressure, heat, mechanical work or use of plasticisers. Three main families of starch polymer can be used: pure starch, modifi ed starch and fermented starch polymers.

The production of starch polymers begins with the extraction of starch. Taking as an example corn; starch is extracted from the kernel by wet milling. The kernel is first softened by steeping it in a dilute acid solution, then ground coarsely to split the kernel and remove the oil-containing germ. The starch slurry is then washed in a centrifuge, dewatered and dried. Either prior, or subsequent to the drying step, the starch may be processed in a number of ways to improve its properties.

The addition of chemicals leading to alteration of the structure of starch is generally described as ‘chemical modification’. Modified starch is starch that has been treated with chemicals so that some hydroxyl groups have been replaced by for example ester or ether groups. High starch content plastics are highly hydrophilic and readily disintegrate when in contact with water. Very low levels of chemical modification can significantly improve hydrophilicity, as well as change other rheological, physical and chemical properties of starch.

Crosslinking, in which two hydroxyl groups or neighbouring starch molecules are linked chemically is also a form of chemical modification. Crosslinking inhibits granule swelling or gelatinisation and gives increased stability to acid, heat treatment and shear forces. Chemically modified starch may be used directly or palletised or otherwise dried for conversion to a final product.

Starch can also be modified by fermentation as used in the Rodenburg process. In this case the raw material is a potato waste slurry originating from the food industry. The slurry mainly consists of starch, the rest being proteins, fats and oils, inorganic components and cellulose. The slurry is held in storage silos for about two weeks to allow for stabilisation and partial fermentation. The most important fermentation process that occurs is the conversion of a small fraction of starch to lactic acid by mans of the lactic acid bacteria that are naturally present in the feedstock. The product is subsequently dried to a fi nal water content of 10% and then extruded.

Starch-based polymers have been the most studied class of biodegradable polymer for their extrusion characteristics. Extrusion processing plays a large role in establishing the polymer properties. Starch can be made thermoplastic by using technology very similar to extrusion cooking. Starch exists as granular beads of about 15-100 microns in diameter that can be compounded with another synthetic polymer as a filler. However, under special heat and shear conditions during extrusion it can be transformed into an amorphous thermoplastic by a process known as destructurising.

Starch can be destructured in the presence of more hydrophobic polymers such as aliphatic polyesters. Aliphatic polyesters with low melting points are difficult to process by conventional techniques such as film blowing and blow moulding. Films such as polycaprolactones (PCL) are tacky as extruded and have a low melt strength (over 130°C). Also, the slow crystallisation of the polymer causes the properties to change with time. Blending starch with aliphatic polyesters improves processability and biodegradability. [6-9].

Degradation of polymers can be carried out by heat, radiation or biological treatment. The radiant energy may be high energy radiation from gamma rays, ion beams, and electrons or even low-energy radiation from ultraviolet light. Chemical degradation results from treatment with chemicals such as acis and alkalis. Biodegradation of polymers results from the use of microorganisms and enzymes. [66]

2.2.1 Starch

Starch is a highly hydrophilic polymer that consists of anhydroglucose units linked by α-D-1,4-glycosidic bonds [4]. There are two distinct structural molecular classes, namely, linear amylose and highly branched amylopectin. Linear amylose is linked

by α-l,4-bonds and branched amylopectin is linked by α-1,6-bonds. The molecular structure of an amylopectin is illustrated in Figure 2.24; the molecular structure of amylose is similar to the linear portion of the amylopectin structure. The structure of monosaccharide D-glucose can be either in an open-chain or a ring form [70]. The ring form is highly thermodynamically stable and has a structure similar to that of sugar in solution. The aldehyde group at carbon number 1 is highly reactive, making it a reducing sugar.

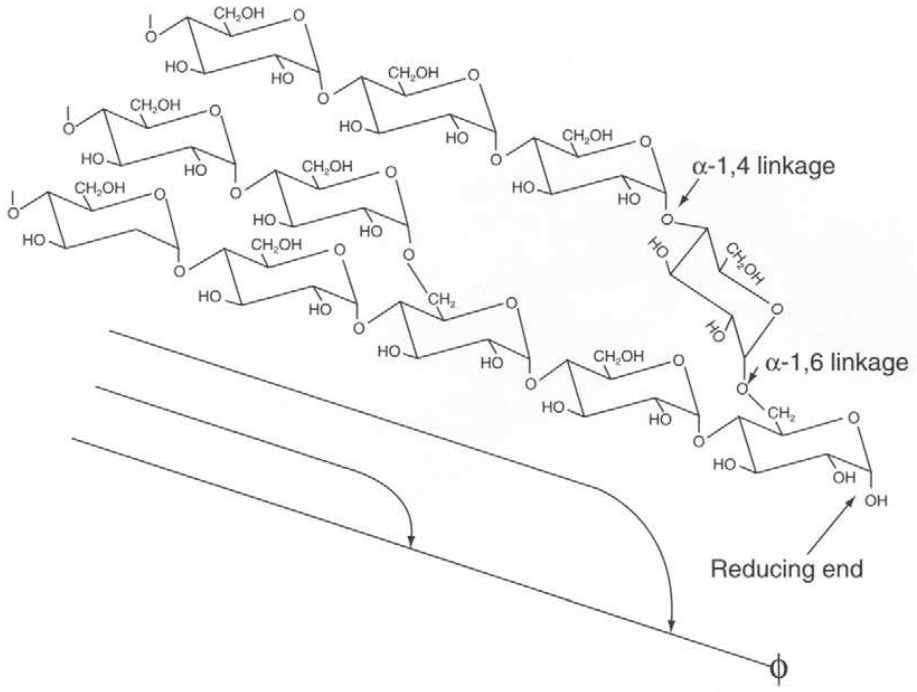


Figure 2.24 : General molecular structure of starch

Natural starch exists in a granular form. The granular shape and size are different in different plants (Figure 2.25). Corn starch granules are mainly spherical (Figure 2.25A), wheat starch has both spherical and disk-shaped granules (Figure 2.25B), and potato starch has a smooth granular surface and is mainly oval (Figure 2.25C).

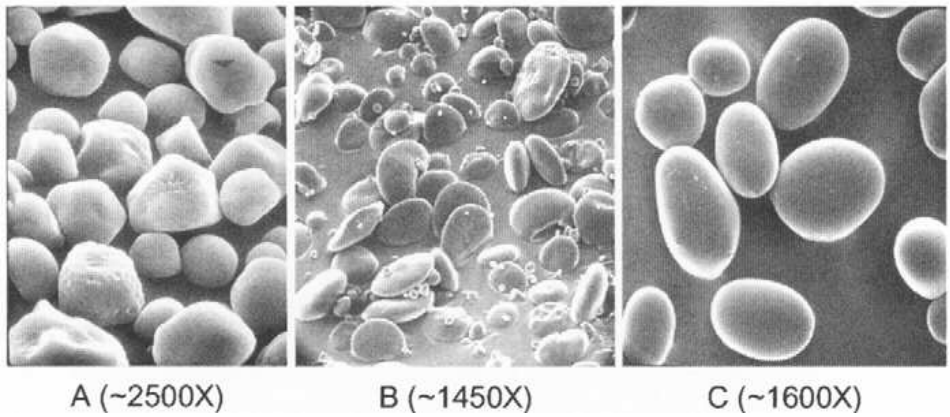


Figure 2.25 : Granular shape of various starches: (A) corn, (B) wheat and (C) potato

The disk-shaped wheat starch granule has an average diameter of 25 μm, and the spherical-shaped granule has a smaller diameter of less than 10 μm (Figure 2.26) [61].

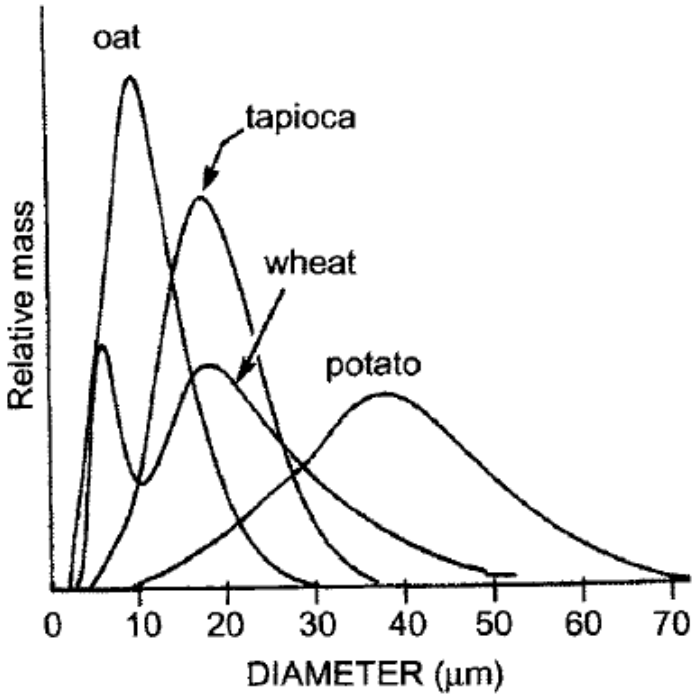


Figure 2.26 : Starch granule size distributions [41]

A cornstarch granule has an average diameter of 10.3-11.5 μm [17], whereas potato starch has a larger granule size with an average diameter of about 40 μm [61]. Starch consists of amorphous and crystalline phases (Figure 2.27).

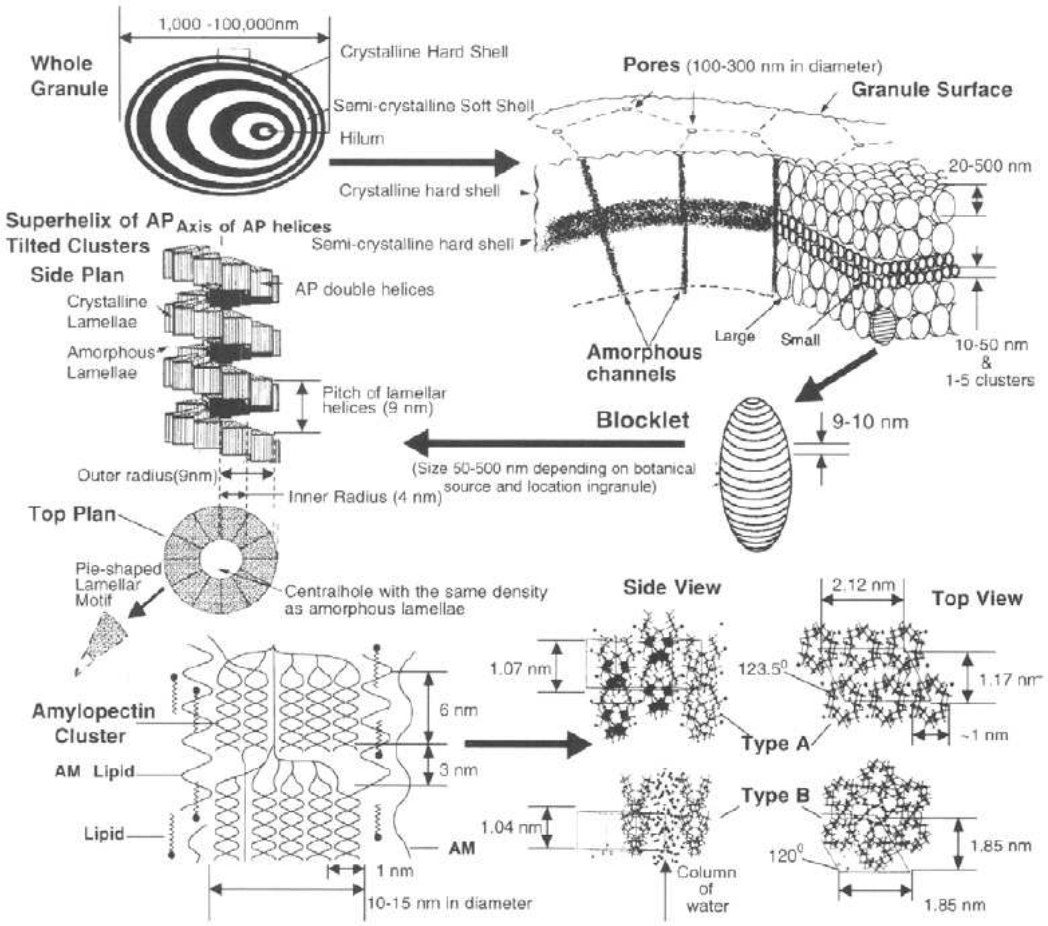


Figure 2.27 : Overview of starch granule structure

As illustrated in Figure 2.27, following the arrow direction, the crystalline hard shell layers alternate with a semicrystalline soft shell. The amorphous channels are braided in the crystalline hard shell. The crystalline hard shell consists of many blocklets with a superhelix amylopectin (AP) structure that alternately spirals between crystalline and amorphous lamellae. The amylopectin, amylose, lipids, and amylose-lipid are entangled into a complex structure in a form dictated by biological information, starch postmodification, and processing conditions. On heating, starch undergoes various phase changes from glassy to rubbery, to gelatinized, and to a melted crystal. A typical fully gelatinized starch melt presents a smooth, entangled, and mushy structure (Figure 2.27).

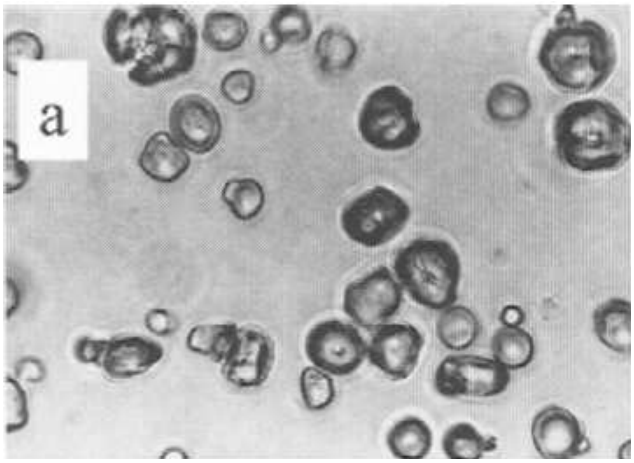


Figure 2.28 : Optical microscopy of (a) raw cornstarch [29]

2.2.2 Starch modified with polyurethanes

The nature of brittleness caused by the relatively high glass transition temperature (*Tg*) and lack of a sub-*Tg* main-chain relaxation (β-transition) limits the use of starch in plastics. Moreover, the brittleness increases with time due to free volume relaxation and retrogation. To overcome the inherent problems with starch, Kweaon and co-workers sythesized starch-g-polycaprolactone copolymers by a reaction of a diisocyanate-terminated polycaprolactone-based prepolymer (NCO-PCL) with corn starch at a weight ratio of starch to NCO-PCL of 2:1 as shown in Figure 2.29. On grafting of NCO-PCL (35-38 wt%) prepared with TDI or 4,4-diphenylmethane diisocyanate MDI onto starch, the *Tg* values of both copolymers were 238°C. However when TDI was replaced by hexamethylene diisocyanate (HDI), the *Tg* of the material was found to be around 195°C. On grafting NCO-PCL (PCL-1250), the degradation temperature (*Td*) changed depending on the type of isocyanate used. The starch-*g*-PCL copolymers prepared with the MDI intermediate were most stable, to the point of thermal degradation when compared with those from TDI and HDI. Barikani and Mohammadi (2007) found that the *Tg* values of the starch-*g*-PCL copolymers decreased with increasing percentage of the urethane prepolymer and depended on the crosslinking effect of prepolymer prepolymer between two chains of starch and strong hydrogen bonding between molecules, which affected chain mobility of starch-modified urethane in different ways. Hydrophobicity of the starch grafted with a PCL-based urethane prepolymer increased with increasing amount of urethane prepolymer. According to the authors, this modified starch could be used as

filler in biodegradable starch-based polyurethane due to better dispersion and compatibility [77].

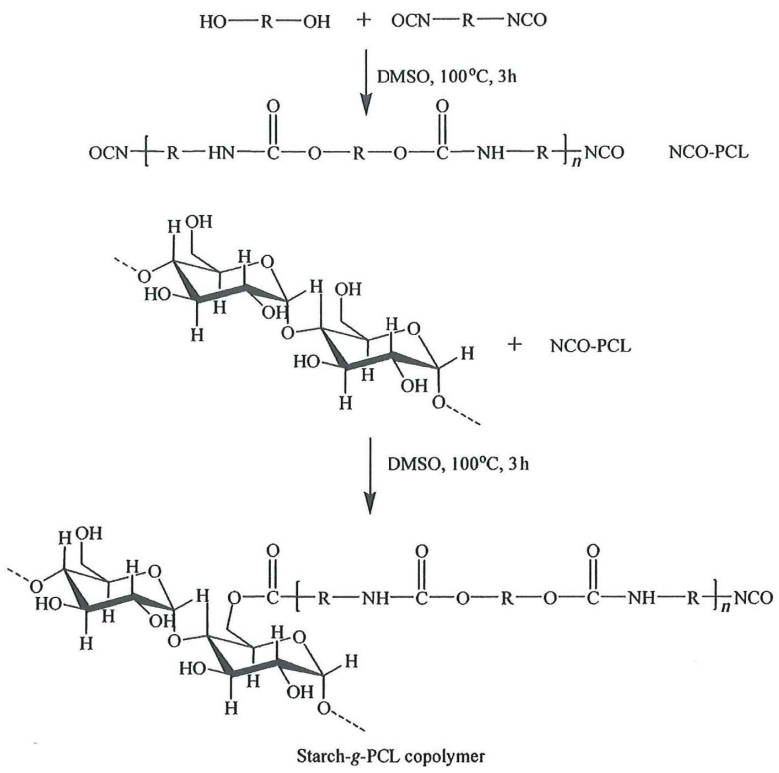


Figure 2.29 : Reaction of starch –PCL copolymer

2.2.3 Degradation of specialty polymers

Degradability refers to the stability of the polymers in a given environment. Any or all of the following degradation mechanisms may be operative in the degradation process;

- Biodegradation is promoted by enzymes and may be either aerobic or anaerobic. Operative in all environments, burial, surface exposure, waterways..etc. and may lead to complete removal from the environment.
- Photodegradation is promoted by irradiation, e.g. sunlight, and is restricted to surface environment exposure. It rarely leads to complete removal, though fragments reduced may biodegrade.
- Chemical degradation is promoted by chemical reaction through additives in the plastics, e.g. metals, functional groups and is operative under all conditions. Fragments produced may biodegrade. [66]

3. EXPERIMENTAL PART

3.1 Materials

In starch-polyurethane (SPU) film synthesis, Desmodur BL 3175 SN (from Bayer Chemicals), Dibutyl Tin Dilaurate (DBTDL), commercial corn starch and commercial wheat starch were used.

Desmodur BL 3175 SN (free NCO content < % 0.2, blocked NCO content approximately 11.1%) is a type of phenol-blocked aliphatic polyisocyanate based on hexamethylene diisocyanate (HDI).Using aliphatic polyisocyanates provides to polyurethane coatings; no yellowing, chemical resistance and exceptional gloss retention[69].

Dibutyl Tin Dilaurate (DBTDL) is a organometallic tin compound that is added to allow the reaction to take place at a rapid rate and a lower temperatures.

3.2 Equipments

3.2.1 Infrared analysis (IR)

Infared analysis were performed on Thermo Scientific Nicolet IS10 FT-IR spectrometer.

3.2.2 Thermogravimetrical analysis (TGA)

Thermal gravimetrical analysis were performed on a TA TGA Q50 instrument at a heating rate 20 °C/min.

3.2.3 Contact angle meter

The contact angle of cured SPU films was measured by KSV CAM 100 instrument.

3.2.4 Tensile loading machine

Zwick Z010 Universal Tensile Tester was used to determine properties such as modulus, elongation at break and strength.

3.2.5 Scanning electron microscopy (SEM)

The bulk morphology of FPU films was observed by Scanning Electron Microscopy (SEM LEO 1530VP).

3.3 Preparation of formulations

Different film formulations including blocked polyisocyanate, solvent, dibutyl tin dilaurate and two different starch containing compounds were developed. Formulation compositions are shown in Table 3.1.

Table 3.1: General formulation compositions

Blocked Polyisocyanate	HDI based Aliphatic Blocked Polyisocyanate (Desmodur®)
Catalyst	Dibutyl Tin Dilaurate (DBTDL)
Solvent	DMSO
Starch Compound	Wheat Starch, Corn Starch

To improve the surface properties of polyurethane film, three different starch-containing compounds were added to formulations at different ratios; 4/5, 5/6, 6/7, 9/10. The name and ratios of these starch containing compounds in the formulations are shown in Table 3.2 and Table 3.3.

Table 3.2: The name and percent of starch-containing compounds in CSPU's

Sample Name	Starch-Containing Compound	Ratios in Bulk
CSPU- 1	Corn Starch	4/5
CSPU- 2	Corn Starch	5/6
CSPU- 3	Corn Starch	6/7
CSPU-4	Corn Starch	9/10

Table 3.3: The name and percent of starch-containing compounds in WSPU's

Sample Name	Starch-Containing Compound	Ratios in Bulk
WSPU- 1	Wheat Starch	4/5
WSPU- 2	Wheat Starch	5/6
WSPU- 3	Wheat Starch	6/7
WSPU-4	Wheat Starch	9/10

3.3.1 Preparation of blocked-polyisocyanate

The blocked polyisocyanate was dissolved in solvent with a mechanical stirrer, as desired content (10ml solvent for 1g Desmodur®) in flask at 45°C for 15 minutes then in room temperature for 1 hour.

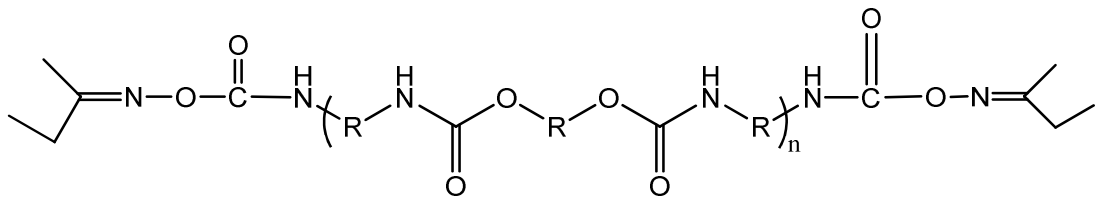
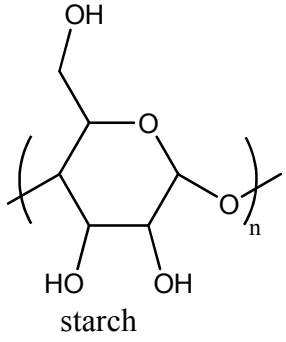


Figure 3.1 : Blocked polyisocyanate

3.3.2 Preparation of starch solution

For the starch composition, corn and wheat starch were dried in a vacuum oven at 90°C for 15 hours before preparation of the solution.

To prepare the starch solution, required amount of starch (10ml solvent for 1g starch) is added to three-neck 100ml round bottom flask equipped with mechanical stirrer, condenser and thermometer. The corn starch mixture was heated to 50°C for at least 12 hours while stirring. The wheat starch mixture was heated to 50°C for at least 15 hours while stirring. Forming of a clear solution shows complete dissolving of starch.



starch

Figure 3.2 : Starch

3.4 Synthesis

3.4.1 CSPU-1 and WSPU-1 synthesis

The reaction was placed in 100 ml round-bottom, three-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and Dean–Stark trap. The flask was placed in oil bath and set at 85°C. 4g starch containing solution was added to flask. 1g blocked-polyisocyanate containing solution was added to Dean-Stark trap. The reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture. The prepolymer solution was slowly added to starch solution through Dean–Stark trap the system was heated to 85°C, while stirring for 30 min. The mixture was then stirred for 3 hours at the same temperature. The reaction mixture was cooled to room temperature. The product was clear, yellow, viscous liquid.

3.4.2 CSPU-2 and WSPU-2 synthesis

The reaction was placed in 100 ml round-bottom, three-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and Dean–Stark trap. The flask was placed in oil bath and set at 85°C. 5g starch containing solution was added to flask. 1g blocked-polyisocyanate containing solution was added to Dean-Stark trap. The reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture. The prepolymer solution was slowly added to starch solution through Dean–Stark trap the system was heated to 85°C, while stirring for 30 min. The mixture was then stirred for 3 hours at the same temperature. The reaction mixture was cooled to room temperature. The product was clear, yellow, viscous liquid.

3.4.3 CSPU-3 and WSPU-3 synthesis

The reaction was placed in 250 ml round-bottom, three-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and Dean–Stark trap. The flask was placed in oil bath and set at 85°C. 6g starch containing solution was added to flask. 1g blocked-polyisocyanate containing solution was added to Dean-Stark trap. The reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture. The prepolymer solution

was slowly added to starch solution through Dean–Stark trap the system was heated to 85°C, while stirring for 30 min. The mixture was then stirred for 3 hours at the same temperature. The reaction mixture was cooled to room temperature. The product was clear, yellow, viscous liquid.

3.4.4 CSPU-4 and WSPU-4 synthesis

The reaction was placed in 250 ml round-bottom, three-necked flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and Dean–Stark trap. The flask was placed in oil bath and set at 85°C. 9g starch containing solution was added to flask. 1g blocked-polyisocyanate containing solution was added to Dean-Stark trap. The reaction was carried out in a constant temperature oil bath, with a steady flow of dry nitrogen passing continuously over the mixture. The prepolymer solution was slowly added to starch solution through Dean–Stark trap the system was heated to 85°C, while stirring for 30 min. The mixture was then stirred for 3 hours at the same temperature. The reaction mixture was cooled to room temperature. The product was clear, yellow, viscous liquid.

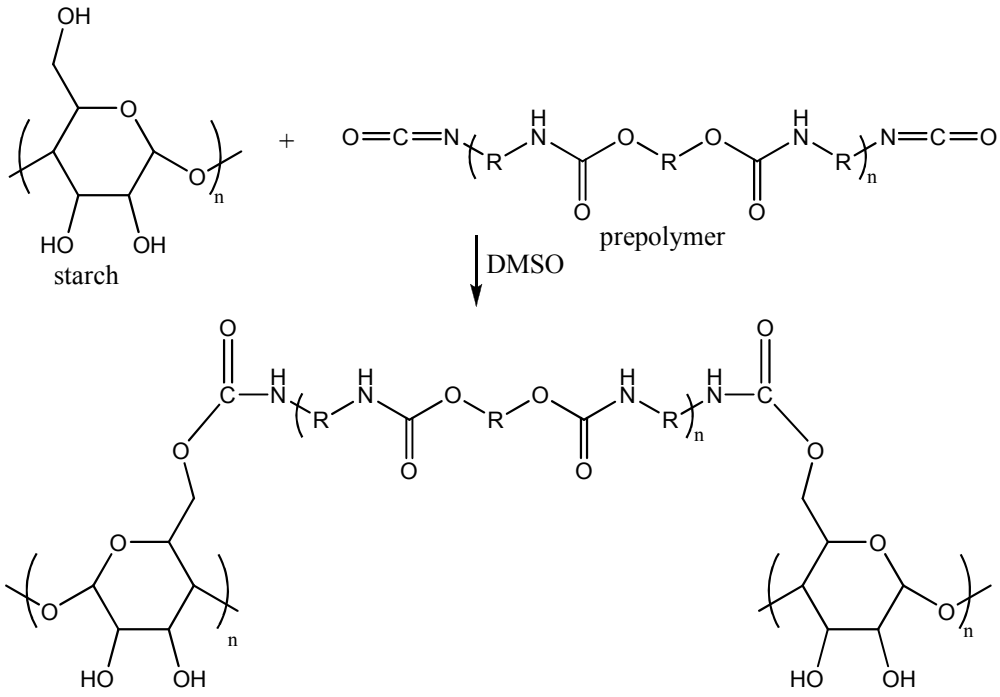


Figure 3.3 : Starch-modified polyurethane film synthesis

3.5 Preparation of free film

The formulated solutions were cast onto glass substrate 10cm x 10cm to obtain free films. The glass substrates were silanated with %5 chloro trimethyl silane containing solution before use to provide cured film peeled off easily. Solution was applied onto the glass substrate as a layer about 4mm.

For thermal curing of samples, a typical oven was used. Formulation were polymerized at 145°C for 20 minutes then 90°C for 10 minutes. The films were waited during one day.

3.6 Analysis

Following tests; Infrared Analysis (IR), Thermal Gravimetric Analysis (TGA), Contact angle measurement, Tensile tests, Solvent Resistance, Gel Content and SEM were performed to monitor thermal, morphological and film properties of CSPU and WSPU films.

3.6.1 Infrared analysis

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies.

IR absorption positions are generally presented as either wavenumbers ($\tilde{\nu}$) or wavelengths (λ). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. The wavenumber unit (cm^{-1}, reciprocal centimeter) is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast,

wavelengths are inversely proportional to frequencies and their associated energy. At present, the recommended unit of wavelength is μm (micrometers), but μ (micron) is used in some older literature[66]. The results are given in the Figure 4.4 – Figure 4.13.

3.6.2 Thermal gravimetric analysis

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere [84]. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking [69].

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 5–10 mg were placed in the sample pan and heated from 25°C to 600°C under N_2 (flow rate: 40 mL/min) at an applied heating rate of 20°C /min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The results are given in Table 4.1 and 4.2.

3.6.3 Contact angle measurement

The determination of solid-vapor γ_{SV} and solid-liquid γ_{SL} interfacial tensions is of importance in a wide range of problems in pure and applied science. Because of the difficulties involved in measuring directly the surface tension involving a solid phase, indirect approaches are called for: Several independent approaches have been used to estimate solid surface tensions, including direct force measurements; contact angles; capillary penetration into columns of particle powder; sedimentation of particles; solidification front interaction with particles; film flotation; gradient theory; Lifshitz theory of van der Waals forces; and theory of molecular interactions. Among these methods, contact angle measurements are believed to be the simplest [34].

Contact angle measurement is easily performed by establishing the tangent (angle) of a liquid drop with a solid surface at the base. The attractiveness of using contact angles θ to estimate the solid-vapor and solid-liquid interfacial tensions is due to the relative ease with which contact angles can be measured on suitably prepared solid surfaces. It will become apparent later that this seeming simplicity is, however, very misleading.

The possibility of estimating solid surface tensions from contact angles relies on a rellation which has been recognized by Young [79] in 1805. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions : solid-vapor, γ_{SV}, solid-liquid, γ_{SL} , and liquid-vapor, γ_{LV} (Fig.3.4.). This equilibrium relation is known as Young's equation:

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV}, - \gamma_{SL}$$

where θ is the Young contact angle, i.e. a contact angle which can be inserted into Young's equation. It will become apparent later that the experimentally accessible contact angles may or may not be equal to $\theta_{Y.}$

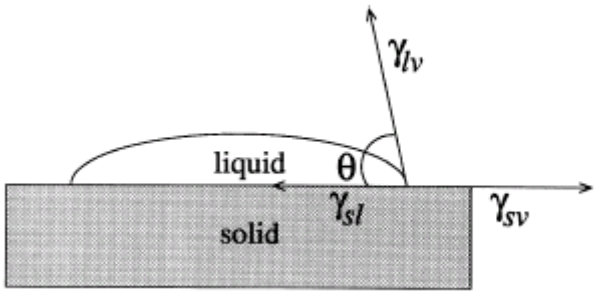


Figure 3.9 : Scheme of a sessile-drop contact angle system

Contact angle is a well-known technique for investigating and controlling adhesion, surface treatments and cleaning, and polymer film modification. The wetting of solid substrates is a basic feature of many natural and industrial processes and contact angle is a simple, rapid, and sensitive method of characterizing the wettability of a solid surface[34].

The wettability of the film surfaces was measured using a contact angle KSV CAM100 system at ambient temperature. The equilibrium contact angles of 5µL water droplets were measured by the sessile drop method. The contact angles were

measured as follows: a 5µL water droplet was placed on the sample using a syringe, and contact angle was recorded.

The water contact angle of FPU films prepared in our experiments are listed in Table 4.3.

3.6.4 Gel content measurement

A cured film sample (m_1) was accurately weighted, and then added to the Soxhlet extractor with acetone as extraction agent for 6 h. The cured film was dried until its weight was constant (m_2). Gel content of the cured film was calculated by equation,

Gel content(%) = $(m_2/m_1) \times 100\%$

Where m_1 is the weight of the cured film sample; m_2 is the residual weight of the cured film sample.[makale referans]. The results are shown on the Table 4.6.

3.6.5 Solvent resistance

The Solvent resistance of the films after curing were immersed in various solvents (m_1, 0.005-0.03g g/10 ml) for one day. The cured film was dried until its weight was constant. After drying, the films were reweighted (m_2) and calculated weight loss.

Weight loss (%) = $(m_1-m_2)/m_1 \times 100$

Solvents used in this test and results are shown in the Table 4.4 and Table 4.5.

3.6.6 Tensile test

Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, proportional limit, reduction in area, tensile strength, yield point, yield strength and other tensile properties.

The main product of a tensile test is a load versus elongation curve which is then converted into a stress versus strain curve. Since both the engineering stress and the engineering strain are obtained by dividing the load and elongation by constant values (specimen geometry information), the load-elongation curve will have the same shape as the engineering stress-strain curve. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain

curve. A typical engineering stress-strain curve is shown below. If the true stress, based on the actual cross-sectional area of the specimen, is used, it is found that the stress-strain curve increases continuously up to fracture.

The linear-elastic region of the curve indicates that no plastic deformation has occurred. In this region , when the stress is reduced, the material will return to its original shape. In this linear region, the line obeys the relationship defined as Hooke's Law where the ratio of stress to strain is a constant.

The slope of the line in this region where stress is proportional to strain and is called the modulus of elasticity or Young's modulus. The modulus of elasticity (E) defines the properties of a material as it undergoes stress, deforms, and then returns to its original shape after the stress is removed. It is a measure of the stiffness of a given material. To compute the modulus of elastic , simply divide the stress by the strain in the material. Since strain is unitless, the modulus will have the same units as the stress, such as kpi or MPa. The modulus of elasticity applies specifically to the situation of a component being stretched with a tensile force. This modulus is of interest when it is necessary to compute how much a rod or wire stretches under a tensile load.

Axial strain is always accompanied by lateral strains of opposite sign in the two directions mutually perpendicular to the axial strain. Strains that result from an increase in length are designated as positive (+) and those that result in a decrease in length are designated as negative (-). Poisson's ratio is defined as the negative of the ratio of the lateral strain to the axial strain for a uniaxial stress state.

Poisson's ratio is sometimes also defined as the ratio of the absolute values of lateral and axial strain. This ratio, like strain, is unitless since both strains are unitless. For stresses within the elastic range, this ratio is approximately constant. For a perfectly isotropic elastic material, Poisson's Ratio is 0.25, but for most materials the value lies in the range of 0.28 to 0.33. Generally for steels, Poisson’s ratio will have a value of approximately 0.3. This means that if there is one inch per inch of deformation in the direction that stress is applied, there will be 0.3 inches per inch of deformation perpendicular to the direction that force is applied. Only two of the elastic constants are independent so if two constants are known, the third can be calculated. In this study, tensile tests were applied to 35mm x 5 mm dimensions SPU free films. The results are shown in Table 4.7 and Table 4.8.

3.6.7 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition.

Morphologic properties of FPU films was observed in SEM analysis and SEM micrographs of fluorinated and non-fluorinated FPU films are shown in Figure 4.17.

4. RESULTS AND DISCUSSION

In this thesis, starch modified polyurethane free-film materials were prepared. Formulations consist of blocked polyisocyanate, corn and wheat starch, solvent and catalyst. All film formulations are coated on glass substrates and cured thermally. Corn and wheat starch containing films obtained in different starch ratios. Samples were subjected to further tests.

4.1 Infrared Analysis

Basically two different types of starch, 4 different starch-containing compounds were used to prepare SPU; Corn starch and wheat starch based films. To determine the functional groups in films, these films were analyzed with IR spectra. FT-IR spectrum of Block Polyurethane is shown in Figure 4.1, also the IR spectrum of corn starch (Figure 4.2) and wheat starch (Figure 4.3) is seen.

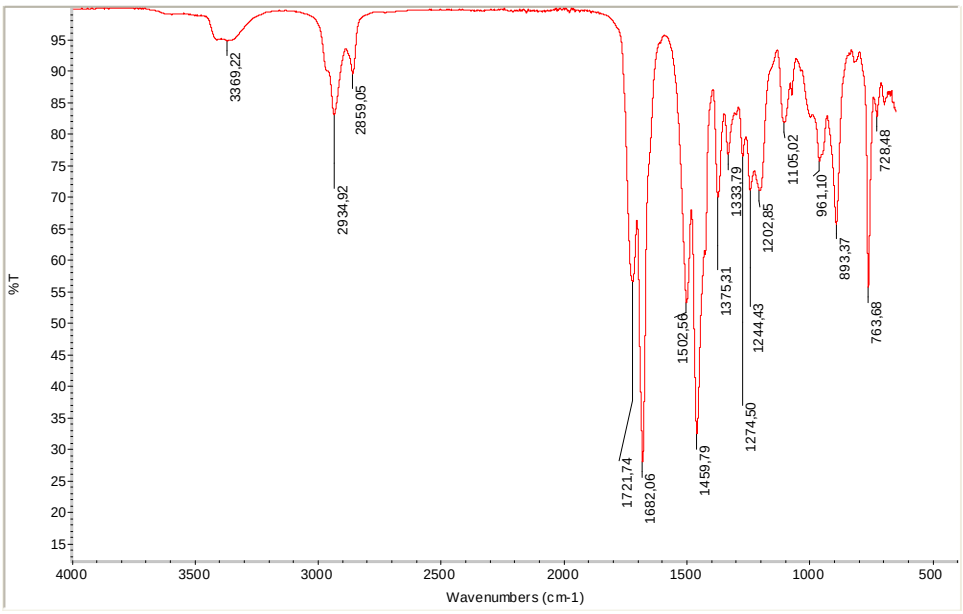


Figure 4.1 : IR spectra of block-polyurethane

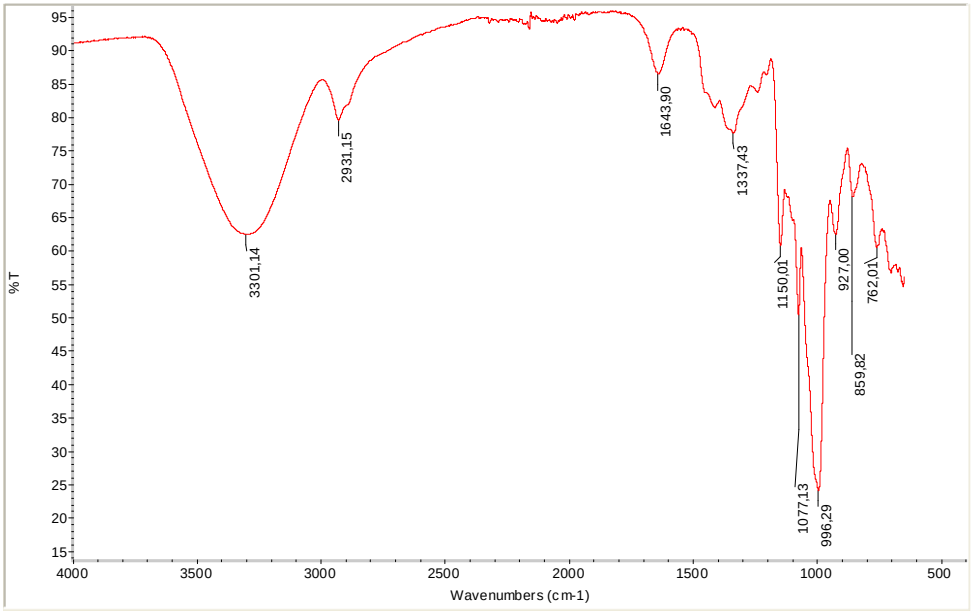


Figure 4.2 : IR spectra of corn-starch

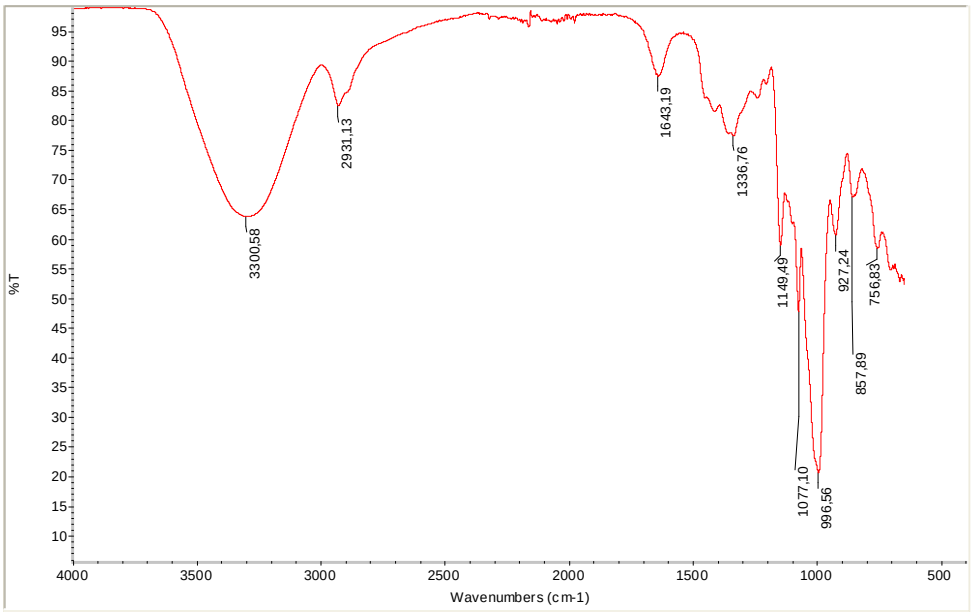


Figure 4.3 : IR spectra of wheat starch

In spectrum of corn and wheat starch (Figure 4.2 and Figure 4.3), -O-H stretching at 3300 cm^{-1}, -C-H stretching at 2930 cm^{-1}, C-C-O stretching at 1643 cm^{-1} and 857-859 cm^{-1} were observed. The C-O-C stretch of starch content seen at 1080 cm^{-1}.

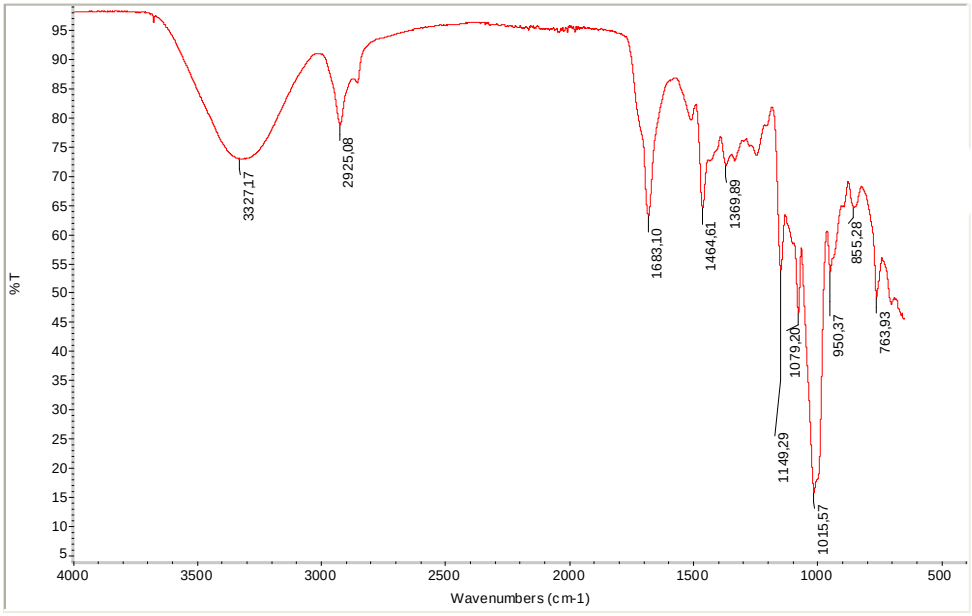


Figure 4.4 : IR spectra of CSPU-1

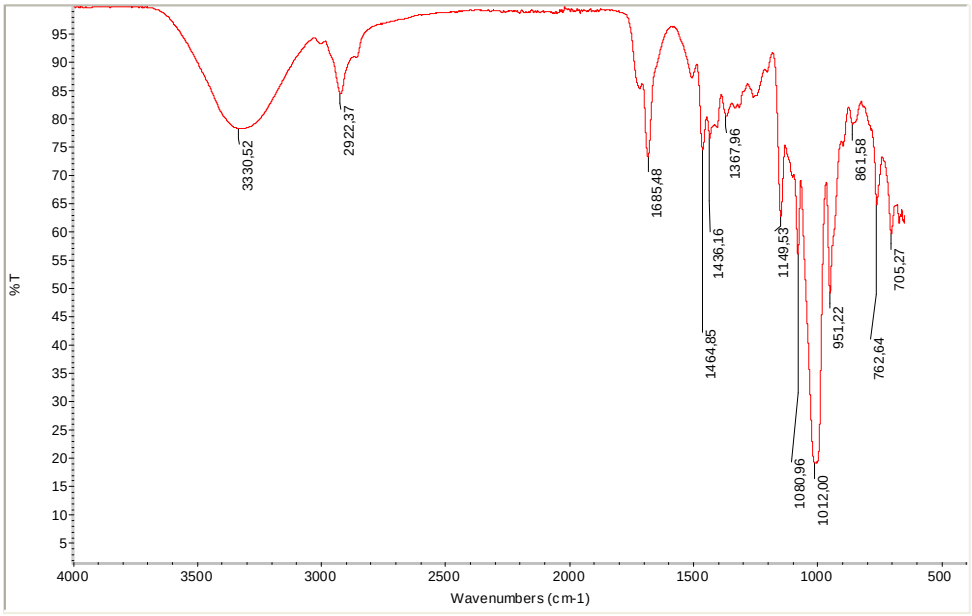


Figure 4.5 : IR spectra of CSPU-2

In Figure 4.4 and 4.5, IR spectra of films CSPU-1 and CSPU-2 are seen.

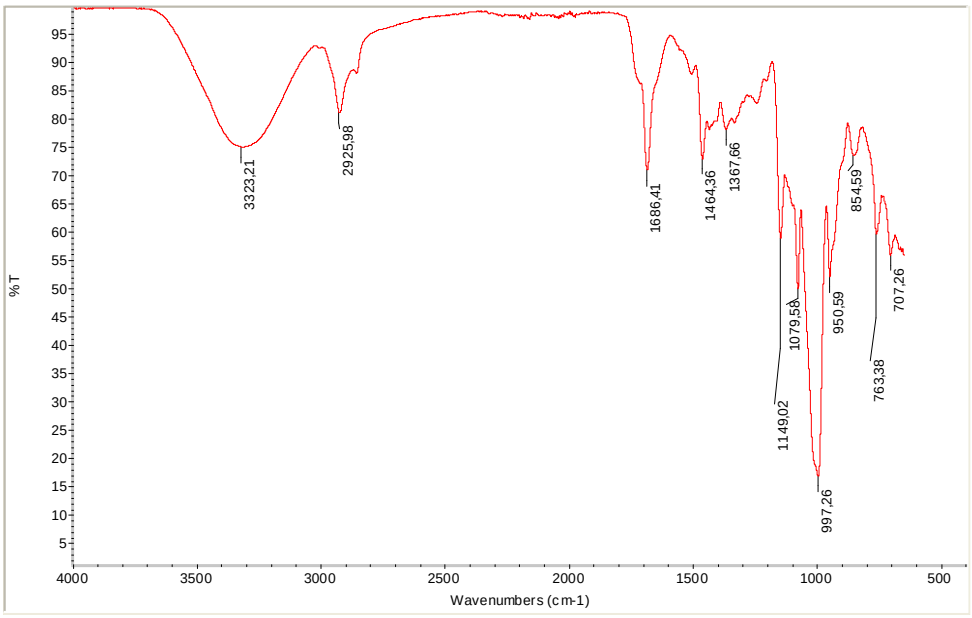


Figure 4.6 : IR spectra of CSPU-3

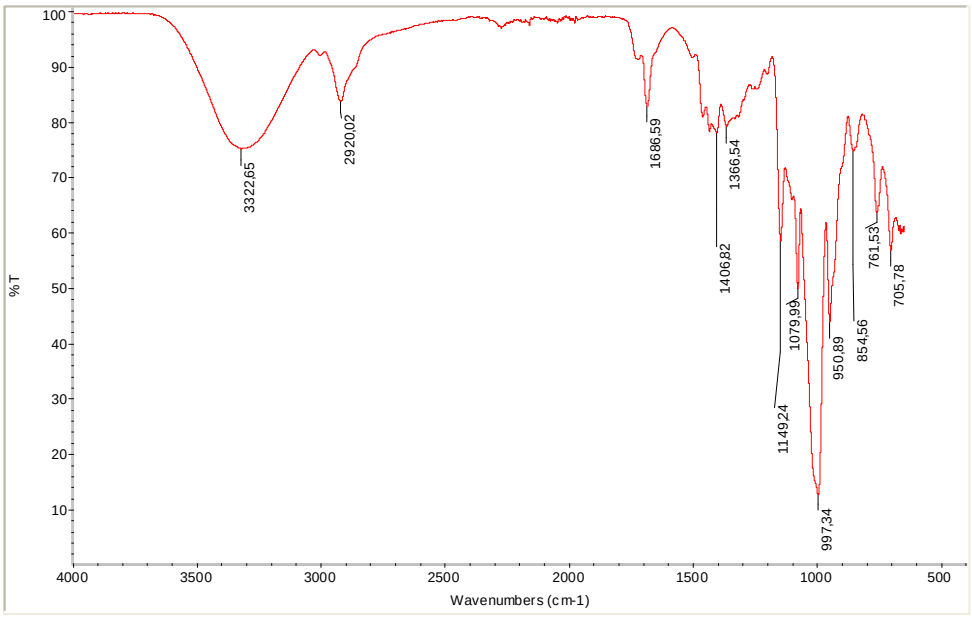


Figure 4.7 : IR spectra of CSPU-4

The IR Spectra showed medium peak of -O-H stretching of SPU's between 3322 and 3327 cm^{-1}. The polyurethane –C-H stretching peak was seen at 1463 cm^{-1}. Due to the reaction rate the peak was decrased while the starch content of the films were increased, also the peak was disappeared in CSPU-4. The peak at 1683 cm^{-1} was due with the reaction between -NCO groups of prepolymer and starch -OH groups, as the reaction rate increases, the increase in the peak was seen.

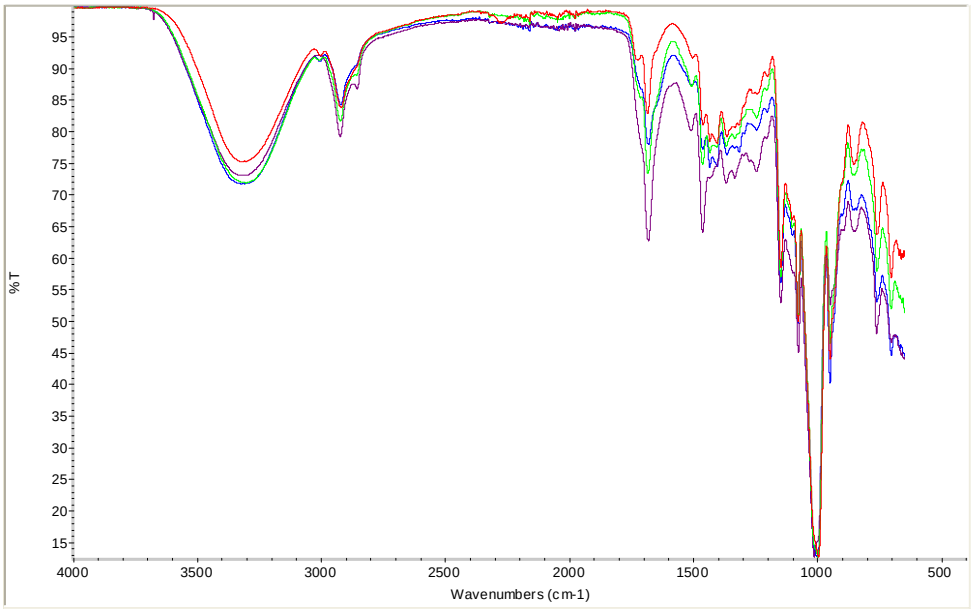


Figure 4.8 : IR spectra of CSPU's

In Figure 4.8 the IR Spectra of all samples of CSPU's are seen. The purple spectra shows the CSPU-1, green spectra shows CSPU-2, blue spectra shows CSPU-3 and red spectra shows CSPU-4.

As the characteristic infrared spectrum of native starch is shown in Figure 4.2, its prominent broad peak is around 3300 cm^{-1} associated with the hydroxyl groups. After the reaction, intensity of the -OH band was shifted to lower frequencies. The presence of stretching 2920 cm^{-1}, characteristic of the C-H stretching of methylene groups associated with urethane, was shown in CSPU's. Also, the polyurethane –C-H stretching peak at 1463 cm^{-1} changed due to the reaction rate. The rate was decrased while the starch content of the films are increased. The characteristic peaks of polyurethane and starch was observed at 850 cm^{-1} and 1680 cm^{-1}. These differences clearly confirmed that the reaction between at least some of the corn starch -OH functions and the -NCO groups of urethane had taken place.

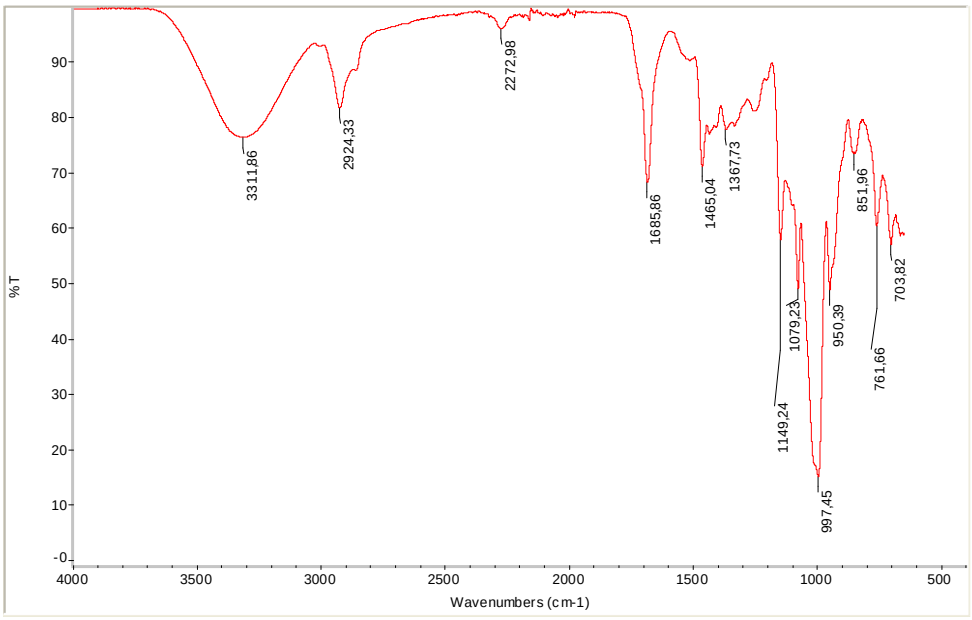


Figure 4.9 : IR spectra of WSPU-1

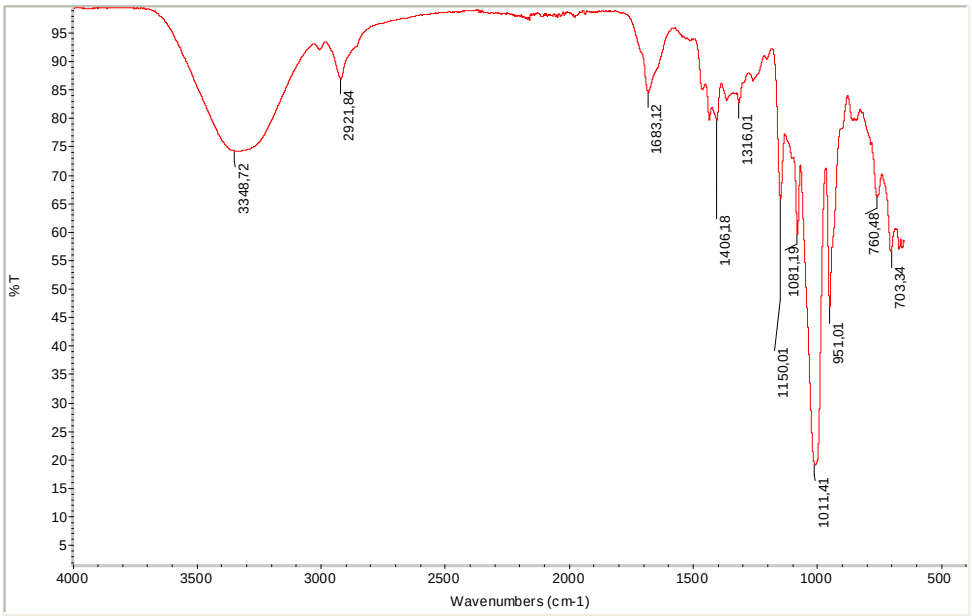


Figure 4.10 : IR spectra of WSPU-2

In Figure 4.9 and Figure 4.10 IR Spectra of WSPU-1 and WSPU-2 is seen. The specific SPU peaks are also seen in the spectra of WSPU's.

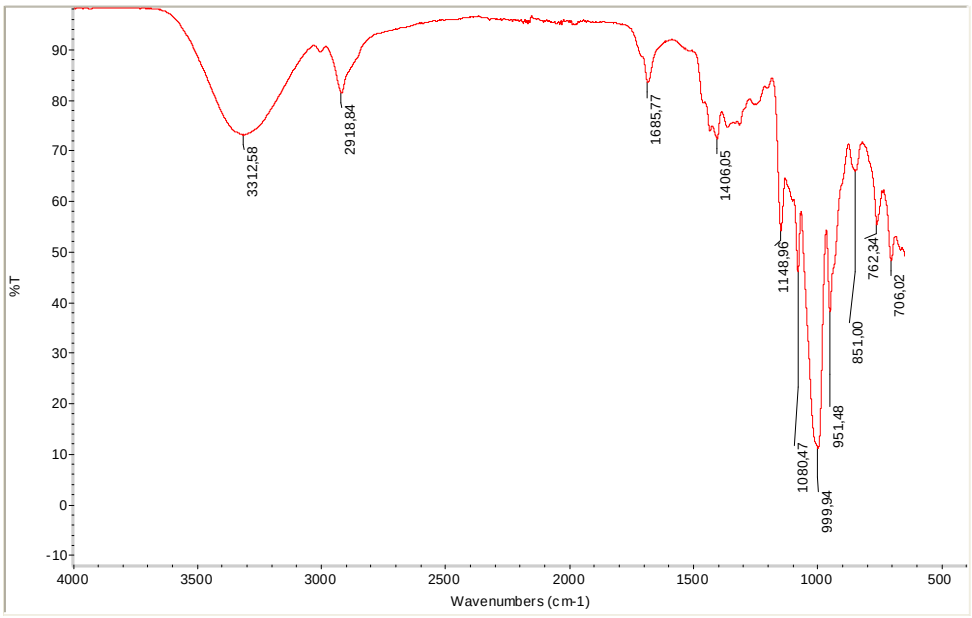


Figure 4.11 : IR spectra of WSPU-3

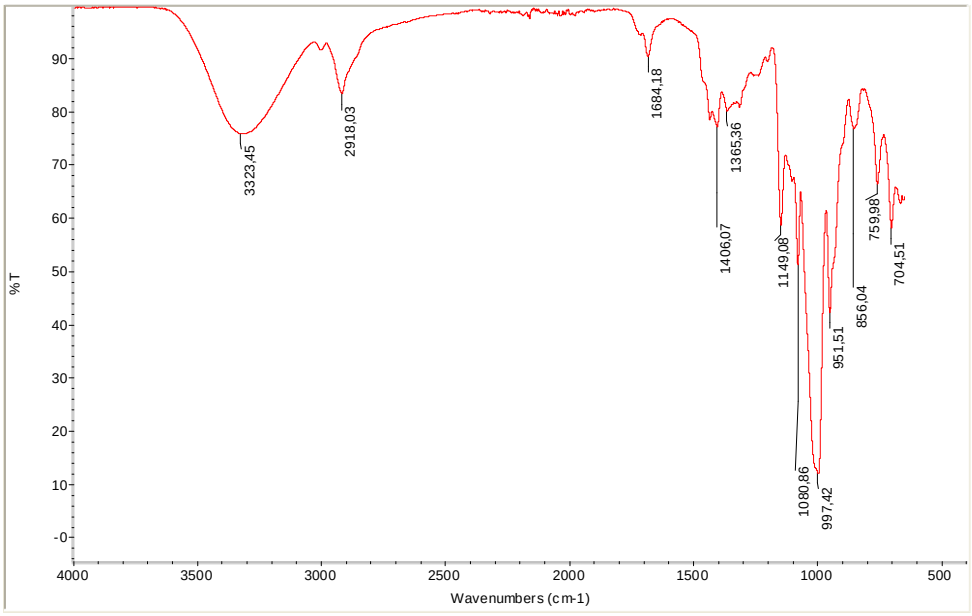


Figure 4.12 : IR spectra of WSPU-4

The polyurethane –C-H stretching peak between 1406 cm^{-1} was decrased while the starch content of the films were increased due to the reaction rate also in WSPU's but the intensity of the peaks are lower than CSPU's. It was considered that the reaction rate in WSPU's was lower than CSPU's generally. The peak at 1680 cm^{-1} was due to the reaction between -NCO groups of prepolymer and starch -OH groups, as the

reaction rate increases, the increase in peak was seen also in WSPU's. The IR Spectra show medium peak also in WSPU's of -O-H stretching 3300 cm^{-1}.

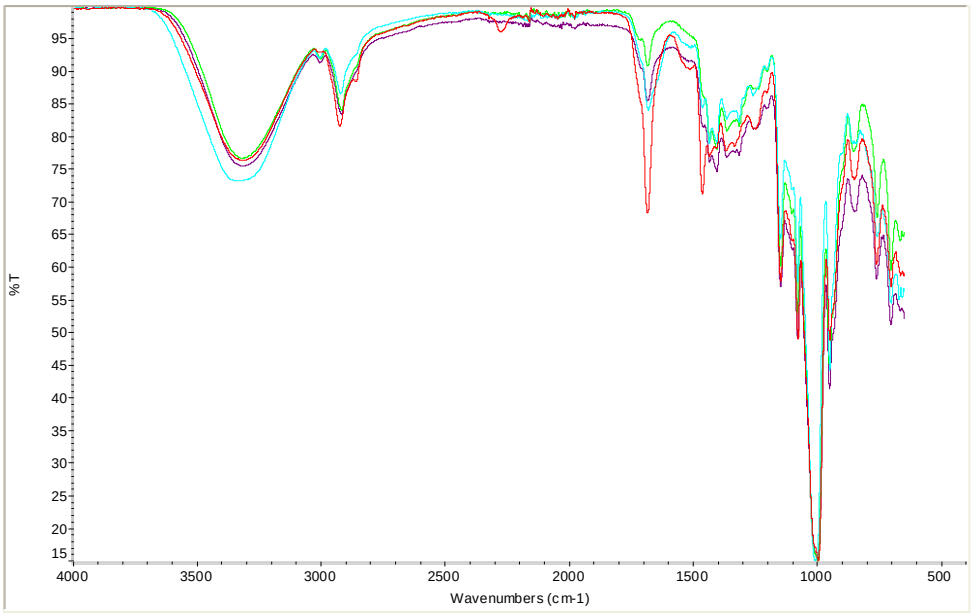


Figure 4.13 : IR spectra of WSPU's

In Figure 4.13 the IR Spectra of all samples of WSPU's are seen. The red spectra shows the WSPU-1, purple spectra shows WSPU-2, blue spectra shows WSPU-3 and green spectra shows WSPU-4.

As the characteristic infrared spectrum of native wheat starch is shown in Figure 4.3, its prominent broad peak was around 3300 cm^{-1} associated with the hydroxyl groups also in wheat starch. After the reaction, intensity of the -OH band was shifted to lower frequencies. The presence of stretching 2920 cm^{-1}, characteristic of the C-H stretching of methylene groups associated with urethane, was shown in WSPU's. Also, the polyurethane –C-H stretching peak at 1400 cm^{-1} due to the reaction rate. The reaction rate was decrased while the starch content of the films were increased. The characteristic peaks of polyurethane and wheat starch was also observed at 850 cm^{-1} and 1680 cm^{-1}. However, in IR spectra of WSPU-1, the peak of isocyanates at 2200 cm^{-1} was seen, which shows us that some of isocyanate groups did not react with –OH groups.

These differences clearly confirmed that the reaction between at least some of the wheat starch -OH functions and the -NCO groups of urethane had taken place.

4.2 Thermal Gravimetric Analysis

Thermogravimetry involves the continuous recording of mass versus temperature or time as a sample is heated in a furnace with a controlled environment. The principal applications of TGA in polymers are (*1*) determination of the thermal stability of polymers, (*2*) compositional analysis, and (*3*) identification of polymers from their decomposition pattern. Also, TGA curves are used to determine the kinetics of thermal decomposition of polymers and the kinetics of cure where weight loss accompanies the cure reaction [20].

TGA was carried out in a nitrogen atmosphere with heating rate of 20°C/ min., films are heated to 800°C for analysing thermal stabilities of the SPU's. Figure 4.8 and 4.9 are showed TGA curves for free films of different starch content.

The thermogravimetric behaviour of the native starch showed in Figure 4.14, after moisture loss up to 100°C, a degradation started at 310°C with an ended at 349°C and overall mass loss of 93% at 600°C. Polyurethane started degrating at 209°C and showed 97% weight loss at 600°C.

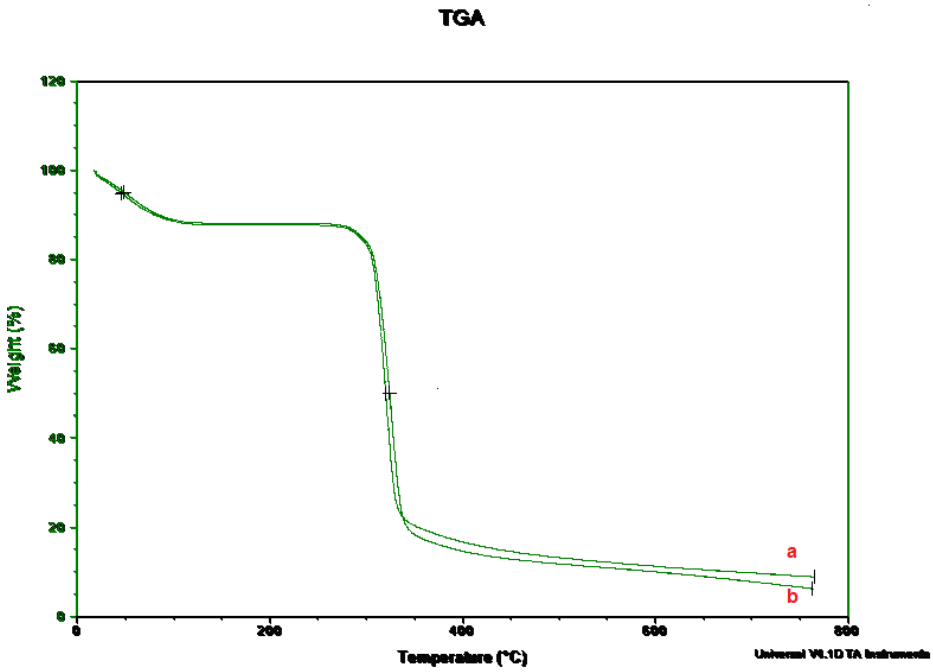


Figure 4.14 : TGA thermogram of native a.wheat starch b.corn starch

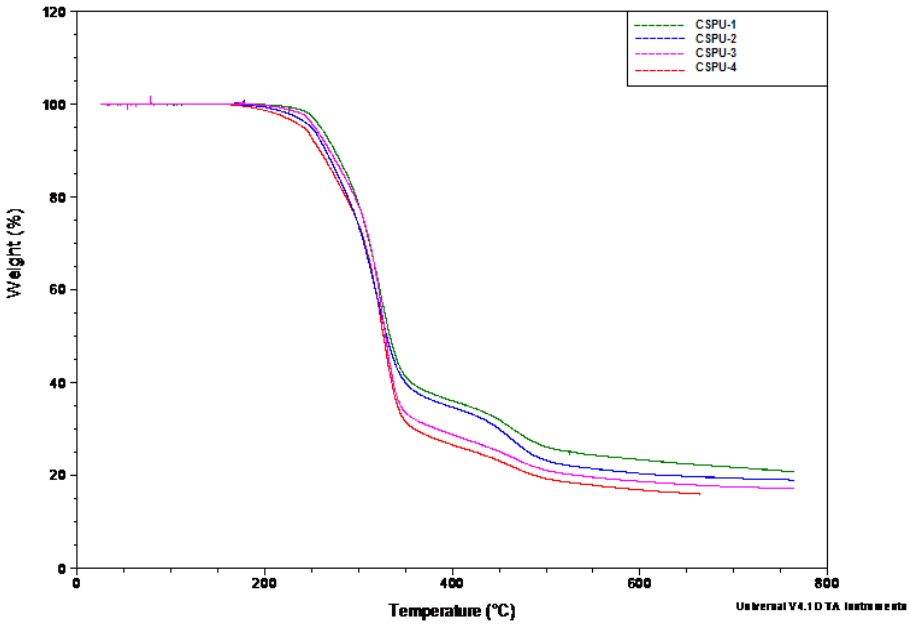


Figure 4.15 : TGA thermogram free films prepared with corn starch

The TGA analysis of the samples prepared with corn starch films (CSPU-1, CSPU-2, CSPU-3, CSPU-4) are seen in Figure 4.15. TG tracing of sample CSPU-1, its thermal degradation begun around 215°C and ended at 350°C, in sample CSPU-2, its thermal degradation begun around 213°C and ended at 348°C. TG tracing of sample CSPU-3, its thermal degradation begun around 210°C and ended at 347°C, in TG tracing of sample CSPU-4, its thermal degradation begun around 200°C and ended at 343°C.

The TGA analysis of the samples prepared with wheat starch films (WSPU-1, WSPU-2, WSPU-3, WSPU-4) are seen in Figure 4.16. TG tracing of sample WSPU-1, its thermal degradation begun around 198°C and ended at 350°C also tracing of sample WSPU-2, its thermal degradation begun around 197°C and ended at 348°C. TG tracing of sample WSPU-3, its thermal degradation begun around 197°C and ended at 346°C and TG tracing of sample WSPU-4, its thermal degradation begun around 198°C and ended at 345°C.

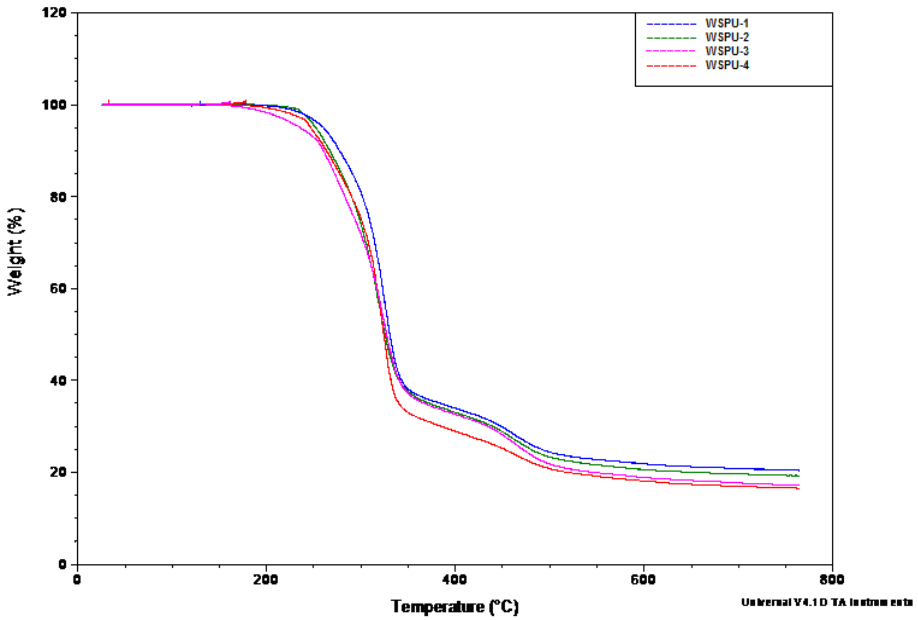


Figure 4.16 : TGA thermogram free films prepared with wheat starch

The thermorams of CSPU's and WSPU's exhibited two stage weight loss steps. The weight loss in first stage was attributed to the loss of volatile products like dehydration and weight loss in second stage was attributed to formation of carbonaceous residue. The temperature at which sample started to loose its weight was reduced from 215°C to 200°C in corn starch 198°C to 194°C in wheat starch while the starch content was increased. Also the first stage weight loss temperatures were lower than reference non-starched polyurethane film [27]. Thermal stability of the samples are decreasing while starch content is increasing. Starch occurs in the form of granules which consists of highly branched amylopectin and and linear amylose molecules. The highly branched nature of amylopectin does not form compact packing. As starch content increases, the weight loss temperature gets reduced. The weight loss temperature in 50% was also decreased from 333°C to 326°C in corn and 330°C to 323°C in wheat with the increase in starch composition, The weight loss temperature in 50% are also lower than reference non-starched polyurethane film [89]. This was because the branched structure makes material poor stabile against heat. Thermogravimetric analyses showed that with the increase in the polyurethane content, final weight shifted to higher values. The delay in degradation caused by crosslink density of the polyurethane. Also, the As it is seen in Figure 4.14 the differences in residues between starch contents, is accordingly with native starch content of the films. WSPU's have higher residue content than CSPU's.

Table 4.1 : TGA analysis values of corn starch containing films

TGA analysis			
Film	%5 weight loss temperature(^{0}C)	%50 weight loss temperature(^{0}C)	Residue (%)
CSPU-1	259,74	333,40	19,83
CSPU-2	249, 95	329,90	18,05
CSPU-3	243, 23	328,69	17,17
CSPU-4	241,27	326,50	16,02
Non-Starched	275,87	379,00	3,89

Table 4.2 : TGA analysis values of wheat starch containing films

TGA analysis			
Film	%5 weight loss temperature(^{0}C)	%50 weight loss temperature(^{0}C)	Residue (%)
WSPU-1	260,14	330,58	20,46
WSPU-2	252,14	325,41	19,18
WSPU-3	246,82	324,13	17,15
WSPU-4	235,89	323,18	16,51
Non-Starched	275,87	379,00	3,89

4.3 Contact Angle Measurement

The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured in free films on glass with eight different starch-polyurethane films which were cured. For each measurement one drops of water was tested on the surfaces and results are tabelated in Table 4.3.

Table 4.3 : Contact angle results

Water Contact Angle			
CSPU-1	85	WSPU-1	85
CSPU-2	86	WSPU-2	86
CSPU-3	87	WSPU-3	87
CSPU-4	89	WSPU-4	88
Non-Starched	82	Non-Starched	82

As it is seen from the Table 4.3, the water uptake of the blends decreases with increasing starch content. In reference non-starched polyurethane film sample's contact angle degree was lower than all starch contented films [27]. This behavior was because of strong hydrogen bonding interaction between PU and starch.

4.4 Solvent Resistance

This test was appiled according to section 3.6.5. the solvents and the results were listed in tables.

Table 4.4 : Solvent resistance of CSPU films

Film	CSPU-1	CSPU-2	CSPU-3	CSPU-4
Solvents	Weightloss (%)	Weightloss (%)	Weightloss (%)	Weightloss (%)
Xylene	16	17	20	26
Methanol	19	21	24	29
Chloroform	2	4	7	10
%10 CH3COOH	15	19	24	29
%10HCl	20	24	26	32
%10NaOH	3	5	6	8

Table 4.5 : Solvent resistance of WSPU films

Film	WSPU-1	WSPU-2	WSPU-3	WSPU-4
Solvents	Weightloss (%)	Weightloss (%)	Weightloss (%)	Weightloss (%)
Xylene	18	21	23	27
Methanol	23	24	27	34
Chloroform	6	8	11	15
%10 CH3COOH	21	24	29	35
%10HCl	24	27	30	35
%10NaOH	4	5	7	9

According to the results in Table 4.4 and Table 4.5 , weightloss can be seen in all cured films. Due to the increasing starch content of the film, weight loss in all solvents is increasing. In corn starch contented species CSPU's, weight loss can be clearly seen accordingly with the increasing starch ratio. Althought the starch content of the films is the same in CSPU and WSPU film, weightloss is increased in the wheat starch contented films.

4.5 Gel Content

This test was applied to measure polymerization degree of system. This procedure was proceeded mentioned in section 3.5.10. Gel content values are listed in Table 4.6.

Table 4.6 : Gel content of cured films

Gel Content (wt%)		Gel Content (wt%)	
CSPU-1	99,56	WSPU-1	98,54
CSPU-2	99,42	WSPU-2	97,10
CSPU-3	97,32	WSPU-3	96,30
CSPU-4	93,68	WSPU-4	92,97

The results shows us that the unreacted parts of the cured material in CSPU-1 and CSPU-2 are under 1% , CSPU-3 is under 3% and CSPU-4 is nearly 6%. The unreacted part of the cured films are increasing while starch content of the films were also increasing. In WSPU films, it can be seen than the unreacted parts were higher in all starch contented species when it was compared to CSPU's. Because of steric hinderance of starch benzene groups and bulky structure of starch, polymerization of chains was getting harder. Because of high polymerization degree in CSPU-1 and CSPU-2, high gel content value can be seen.

4.6 Tensile Test

The mechanical specification of free films, prepared at 35x5x2 mm dimensions, made clearly with measurement of stress-strain values. Stress-strain values for SPU films are given in Table 4.7 and Table 4.8.

Table 4.7 : Stress-strain analysis of CSPU films

	E-Modulus (N/mm^2)	Elongation at break (%)	Tensile Strength (Mpa)
CSPU-1	0,46	85	0,67
CSPU-2	0,51	110	0,52
CSPU-3	0,57	155	0,37
CSPU-4	0,70	162	0,30

Table 4.8 : Stress-strain analysis of WSPU films

	E-Modulus (N/mm^2)	Elongation at break (%)	Tensile Strength (Mpa)
WSPU-1	0,42	72	0,51
WSPU-2	0,45	87	0,42
WSPU-3	0,51	115	0,34
WSPU-4	0,65	132	0,28

The application area of the polymeric film very dependent on tensile properties, particularly modulus, tensile strength and elongation at break point. These properties are also related to the crosslinking density in polymeric film as well as to the chemical structure of the formulation. Polymeric film prepared from unmodified polyurethane film exhibited higher modulus and tensile strength. The higher strength and modulus is due to the fact that there is a greater amount of crosslink density and rigidity of the polyurethane chain as well. As it is seen from results of CSPU and WSPU species, the tensile strength and modulus decrease as the starch ratio is increased for CSPU-2, CSPU-3 and CSPU-4 modulus and tensile strength has decreased when it is compared to CSPU-1 while the elongation increases. The starch addition is caused polyurethane chain to be longer, mobility of anhydride increases the probability of reactive moieties combining, so that it makes the chain more flexible. Also, available hydroxyl groups to form hydrogen bonding has been reduced, this could weaken interaction of the starch molecules and increase their mobility. In the table, The reason is that wheat starch used in the film long chains cause the elongation to increase but also it makes the structure chains weaker than the corn starched species.

The very similar results can be seen in WSPU films. The decrease in E-Modulus and tensile strength and also increase in elongation is seen while the starch content of the films is increasing. However, the lower E-Modulus and tensile strength values in similar starch contented CSPU and WSPU films is the reason of increased steric hindrance of wheat starch films which are higher than corn starch films.

4.7 Scanning Electron Microscopy(SEM) Analysis

Scanning Electron Microscopy (SEM) was used to understand bulk morphology of starch grafted polyurethane.

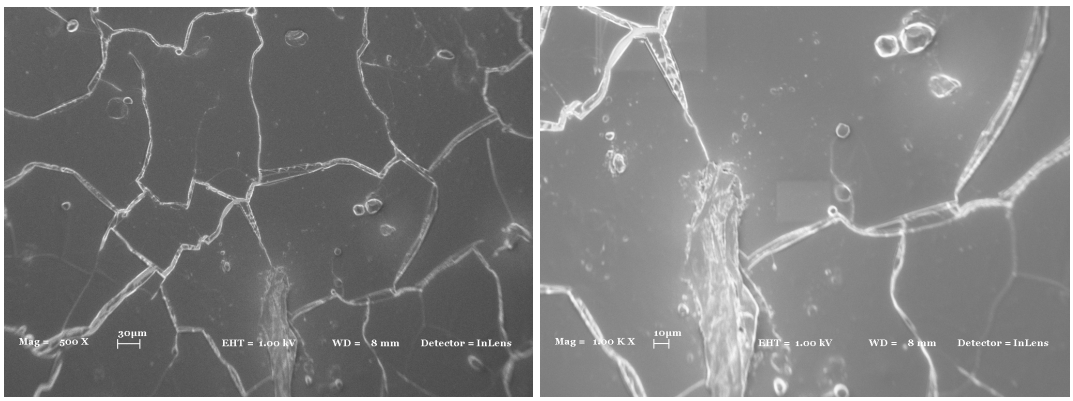


Figure 4.17 : SEM of CSPU-2 (A) (m = 500X), (B) (m = 1000X)

The SEM microraph of CPU-2 shows the crystalline and amorphous phases in the structure. Also starch can be seen as a granule in SEM.

4.8 Degradation of Films

4.8.1 Degradation of films by sunlight

The sample film CSPU-2 was exposed to sunlight for a month.

Figure 4.18 : Film CSPU-2 after the sunlight exposure

The IR Spectra of the film CSPU-2 shows us that the –O-H stretching (3330 cm-1) of SPU films shifted to lower frequencies with the decomposition of the film. The analysis of the film showed a slight decrease in the wavelength 2924 cm-1 indicating the C-H bonds. Also the characteristic peak at 1680 cm-1 which was shown due to the reaction between –NCO groups of prepolymer and –OH groups of starch, has sharp decrease. The peak shown at 1460 cm-1 was the stretching of –C-H in polyurethane, which was increasing due to the rate of reaction, was also decreasing with the exposure of sunlight. The characteristic peak of polyurethane which was shown at 850 cm-1, is also decrasing due to the degradation of film. The decrease in the specific peaks of the SPU film 1680 cm-1 and 3330 cm-1 were the proof of degradation.

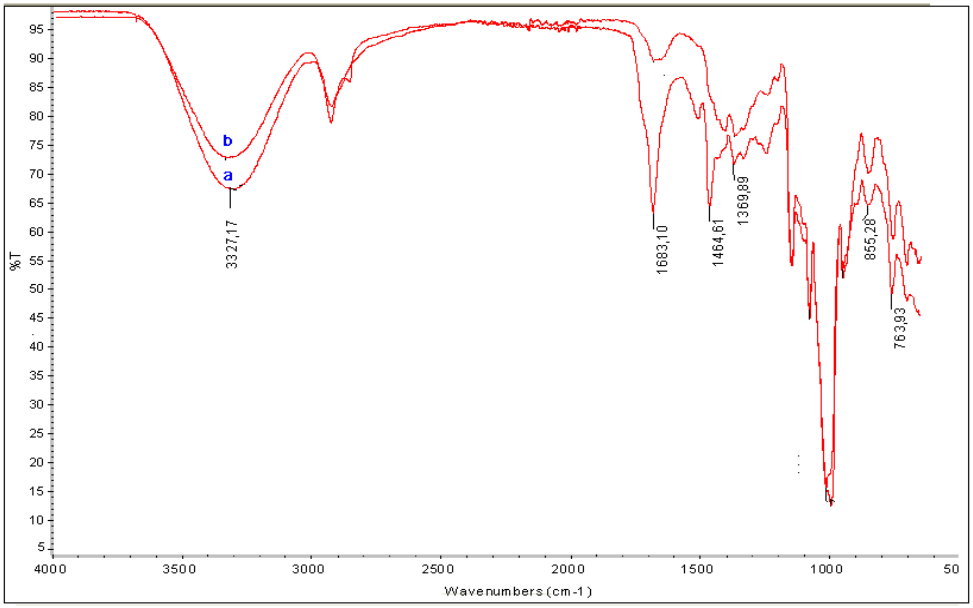


Figure 4.19 : a. IR Spectra of CSPU-2, b.After exposure to sunlight for a month

4.8.2 Degradation of films by UV light

The sample film CSPU-2 was exposed to UV lamp (3000 W) for 45 minutes, 90 minutes, 135 minutes, 180 minutes.

Figure 4.20 : Film CSPU-2 after the UV light exposure

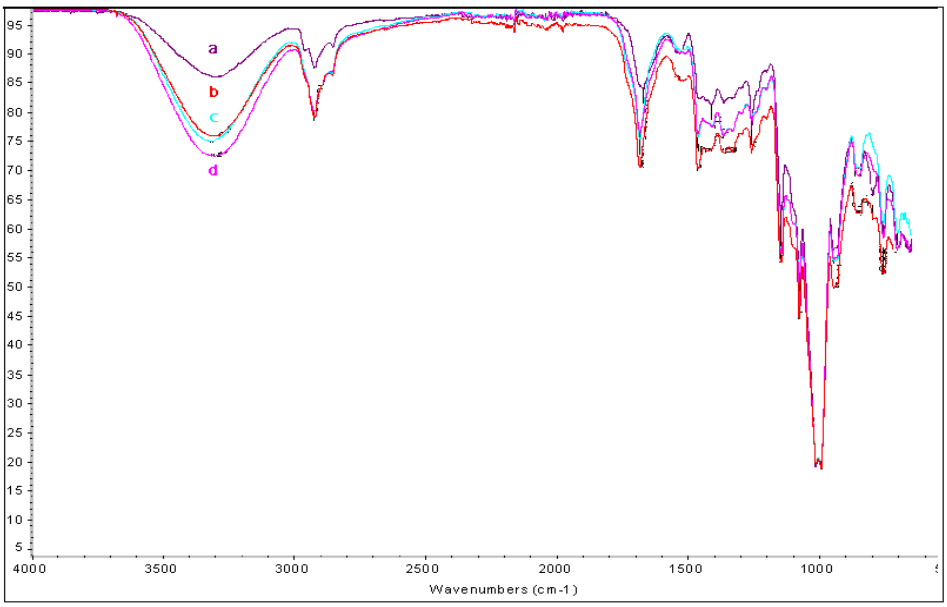


Figure 4.21 : Degradation of CSPU-2 in a.180 min. b.135 min. c.90 min d. 45 min.

The similar results as the sunlight exposure was seen in the UV lamp (3000W) exposure. The decrease in the specific peaks which are shown at 3330 cm-1 –O-H stretching of CSPU, peak at 2924 cm-1 indicating the cleavage of C-H bonds, in wavelength 1680 cm-1 reaction of prepolymer –NCO groups and starch –OH groups, the stretching of –C-H in polyurethane at 1460 cm-1 and characteristic peak of polyurethane at 850 cm-1 are decreasing because of the degradation occuring in the film. However, the difference in the IR Spectra occurs in the wavelength between 1400 cm-1 and 1600 cm-1. The formation of C=C bond at the region 1400 cm-1 and 1600 cm-1 and the slight increase in the peak was seen because of the polyurethane degradation especially for 180 min. exposure time and 135 min. exposure time.

5. CONCLUSIONS

Eight different starch grafted polyurethane film formulations based on blocked polyisocyanates were prepared. For modification of the polyurethane film by two different starches, four different components were used. One of these chemicals, named Desmodur® BL 3175 SN, is a special type of HDI based aliphatic blocked polyisocyanate . Commercially used native corn starch and wheat starch were used as a grafting agent. Also Dibutyl Tin Dilaurate (DBTDL) was used as catalyst and DMSO as a solvent. All formulations were applied on glass substrates and cured with temperatures in 145°C. As a second step, obtained free films were tested for their chemical, thermal and morphological properties.

The ratios of the samples were chosen to obtain optimum feature of free films, the films that have lower starch content did not contain desired film properties, also higher starch content has very low resistance.

FT-IR was used to characterize the structure of the films. The thermal properties were elucidated by thermogravimetric analysis (TGA), the surface hydrophobicity was evaluated by contact angle measurement.

FT-IR analysis showed us that the specific peaks of the starch grafted films were decreased with the increasing starch content. The reaction rate consist of the active groups of blocked polyisocyanate and starch was decreased with increasing the starch content.

Also with the increasing incorporation of the groups of starch and polyisocyanate, thermal stability of the films was increased with decreased starch content. But the weight loss temperatures of the samples were still lower than reference non-starched film.

Contact angle values of the films showed us the hydrogen bonding of the polyisosyanate and starch groups make modified films hydrophobic when it was compared to reference non-starched polyurethane film.

Gel content test helps to measure the percentage of unreacted monomers and oligomers. In analysis results, high starch content reduces polymerization, so the values became low.

Moreover, solvent resistance test showed the low chemical stability of materials against alkalis and acids, the results were also the proof of the degredability of the films.

At lower modification ratios, which has lower starch content the films yielded lower flexibility, but also higher strength which was seen from the stress-strain values.

Because of the results that were obtained, optimum ratio of the starch content was determined as 1/5 mass ratio of polyurethane/ starch.

Finally, the degradability of the films are measured in CSPU-2 by the FT-IR analysis of degradated sample under sunlight and UV-lamp. The degradation of the samples can be seen in the IR Spectrums. The specific peaks which were regarding to starch-grafted films decreased with exposure to sunlight and UV-lamp, the specific degradation peak of polyurethane was also seen in the spectra.

REFERENCES

[1] **Backus, J. K.**, 1977: *Polyurethanes*, Chap. 17 , Wiley-Interscience, New York.

[2] **Backus, J.K.,** 1988: *Encyclopedia of Polymer Science and Engineering*, Vol.13, Wiley-Interscience, New York.

[3] **Barikani, M. and Mohammadi, M., 2007:** *Synthesis and characterization of starch-modified polyurethane*, Carbohydrate Polymers, Volume 68, 773-780

[4] **BASF**, 1992: Eur. Pat. 566925.

[5] **BASF,** 1983: DE 3314790.

[6] **Bastioli, C.,** 2003: Handbook of Biodegradable Polymers, Rapra Technology Ltd, 5.

[7] **Bastioli, C.,** 2003: Handbook of Biodegradable Polymers, Rapra Technology Ltd, 11-13.

[8] **Bastioli, C.,** 2003: Handbook of Biodegradable Polymers, Rapra Technology Ltd, 20-22.

[9] **Bastioli, C.,** 2003: Handbook of Biodegradable Polymers, Rapra Technology Ltd, 257-260.

[10] **Bayer O.**, 1947: Angew. Chem. A 59, 257.

[11] **Bonk, H.W.,** 1971: *J. Elastom. Plast.* **3**, 157.

[12] *Chem. Eng. News*, 1995, 10.

[13] **Dietrich, M.,** 1985: U.S. Pat. 4761434.

[14] **Dusek, K.,** 1987: Makromol. Chem. Suppl., 17, 481.

[15] **Eckert, H., and Forster B.,** 1987: *Angew. Chem.*, 922

[16] **Eggersdorfer, M.,** 1989: Eur. Pat. 297444.

[17] **Eliasson, A. C**., 1996: Gudmundsson, M. In *Carbohydrates in Food,* Eliasson, A. C., Ed.; Marcel Dekker, New York, pp. 431-503.

[18] **Erner W.E. and Odinak A.,** 1968: U.S. Pat. 3384653

[19] **Findeisen, K., Wagner, K., Schafer, W. and Hennig, H.J.,** U.S. Pat. 4,088,665

[20] **Flynn, J.H.,** "Thermal Analysis" in EPSE Second Ed., *Sci. Thermal Research & Data Analysis*, 690-723.

[21] **Gaonkar, S.,** 1990: *Macromolecules* **23**, 3533.

[22] **Goldschmidt, A., Streitberger, H.J.,** BASF Handbook on Basics of Coating Technology,BASF Coatings AG, Münster, Germany (2003)

[23] **Griffin, G.R., Willwerth, L.J.,** 1962: The thermal dissociation of blocked toluene diisocyanates, *Ind Eng Chem Prod Res Dev***, 1**, 265-268.

[24] **Hentschel, W.,** 1884: *Ber. Dtsch. Chem. Ges*.**17**, 1284.

[25] **Holtschmidt, H. and Oertel, G.,** 1962: *Angew. Chem. Int. Ed.* **1**, 617 .

[26] **Huang, Y., Chu, G., Nieh, M., Jones, F.N.,** 1995: *J. Coat. Technol.* ,**67**, 842.

[27] **İşcanı, B.,** 2009: Preparation of Fluorine Contaning Polyurethane Coating Materials.

[28] **Kawamura, C. and Umezawa, K.,** 2010: US7838592 B2,

[29] **Ke, T. and Sun, X.,** 2002: Thermal and Mechanical Properties of Poly(Lactic Acids)/Starch/MDI Blending with Triethyl Citrate, *J. Appl. Polym. Sci.*, 88(13), 2947-2955.

[30] **Knolker, H.J., Braxmeier, T. and Schlechtingen G.,** 1995: *Angew. Chem. Int. Ed.* **34**, 2497.

[31] **Kordomenos, P.I., Dervan A.H. and Kresta J.,** 1982: *J. Coat. Technol.* **54**, 43.

[32] **Kothandaraman, H., Sultan Nasar, A., Kamal Lakshmi, R.,** 1994: Synthesis and thermal dissociation of phenol- and naphthol-blocked diisocyanates, *J Appl Polym Sci***, 53**, 31-38.

[33] **Kurita, K., Matsumura, T. and Iwakura J**., 1976: *J. Org. Chem*. **41**, 2070.

[34] **Kwok, D.Y., Neumann, A. W.,** 1999: Contact angle measurement and contact angle interpretation, *Adv. in Coll.and Interf. Sci.,* **81**, 167-249.

[35] **Laas H.J., Halpaap, R. and Pedain, J.,** 1994: *J. Prakt. Chem.* **336**, 185.

[36] **Liebersohn, A.and Kohn D.H.,** 1979: *J. Appl. Polym. Sci.* **23**, 3445.

[37] **Lin, J.J., Speranza, G.P., Cuscurida, M.,** 1997: *Ind. Eng. Chem. Res*., **36**, 4231.

[38] **Maclaren J.A.,** 1971: *Chem. Ind. (London)* 395.

[39] **Madorsky, S.L.,** 1964: *Thermal Decomposition of Organic Polymers*, Wiley-Interscience, New York.

[40] **Maier, G.,** 1996: *Angew. Chem. Int. Ed.* **35**, 1696.

[41] **Moon, M.H. and Gidings, J.C,** *J. Food Sci*. 1993, 58, 1166.

[42] **Mormann, W. and Leukel, G.,** 1989: *J. Polym. Sci. A* **27**, 4341.

[43] **Mormann, W. and Brahm, M.,** 1991: *Macromolecules* **24**, 1096.

[44] **Mormann, W. and Brahm, M.,** 1993: *Polymer* **34**, 187.

[45] **Mowrer, N. R., Rojas, J. L.,** 1998: *US Patent* No. 5,760,155 (to Ameron International Corporation), June 2.

[46] **Ni, H., Nash, H.A., Worden, J.G., Soucek, M.D.,** 2002: Effect of Catalysts on the Reaction of an Aliphatic Isocyanate and Water, *J.Polym.Sci.,* **40**, 1677-1688.

[47] **Occhiello, E. and M. Corti**, 2003: *Polyurethanes*, Wiley, New York.

[48] **Odian, G.,** 2004: *Principles of Polymerization*, Wiley, New York.

[49]**Ohkubo T. and Okada R.,** 1993: in *Proceedings Polyurethane World Congress*, Vancouver, Canada, 527.

[50] **Peerlings, H.W., and Meijer A.W.**, 1999: *Tetrahedron Lett*. **40**, 1021.

[51] **Philips, L.N., Parker, D.B.V.,** 1964: Polyurethane Chemistry, Technology and Properties,Iliffe,London.

[52] **Randall, D.,** 2002*: The Polyurethanes Book*, Wiley-Interscience, New York.

[53] **Rochery, M., Vroman, I., and Lam, T.M.,** 2000: *Liebigs Ann. Chem.* **37**, 259.

[54] **Sankar, G., Nasar, A.S.,** 2008 : Effect of Isocyanate Structure on Deblocking and Cure-Reaction of N-methylaniline- Blocked Diisocyanates and Polyisocyanates, *European Polymer Journal*, **8**, 11-25.

[55] **Saunders, J. H.,** 1959: The Reactions of Isocyanates and Isocyanates Derivatives at Elevated Temperatures, *Rubber Chem.and Tech*., **32**,337-345.

[56] **Sayigh, A.A.R., and H. Ulrich**, 1970: U.S. Pat. 3492331.

[57] **Schnabel W.J. and Kober E.,** 1969: *J. Org. Chem*. **34**, 1162.

[58] **Schollenberger, C.S. and Stewart, F.D.,** 1971: *Advances in Urethane Science and Technology*, Vol.**1**, Technomics, Stamford, Conn., p. 65.

[59] **Segura, D.M., Nurse, A.M., Phelps, R., Segura, A.,** 2005: H*andbook of Adhesives and Sealants,***1**,101-162.

[60] **Shawl, E.T., Zajazek J.G. and Kessling H.S.,** 1991: Eur. Pat. Appl. EP 408277.

[61] **Shi, Y.; Seib,** 1988: *Is Wheat Unique*, Pomeranz, Y., Ed.; American Association of Cereal Chemists, St. Paul, MN.

[62] **Silverstein, R.M., Webster, F.X. and Kiemle, D.,** 1981: *Spectrometric Identification of Organic Compounds***,** 4th edition. New York: John Wiley & Sons, 166.

[63] **Singh, B., Chang, L.W. and Forgioni**, 1984: P.S., U.S. Pat. 4439616.

[64] **Smith, C.P., Reisch, J.W. and O'Connor, J.M.,** 1992: *J. Elast. Plast.* **24**, 306.

[65] **Spitler, K.G. and Lindsey, J.J.,** 1982: *J. Cell. Plast.* **17**, 43.

[66] **Swift, G.,** 1990: Degradability of Commodity Plastics and Specialty Polymers, ACS Publications.

[67] **Szycher, M.,** 1999: *Szycher's Handbook of Polyurethanes*, CRC Press, **4,** 4.1-4.15.

[68] **Tassela, X., Barbryb, D., Tighzerta, L**., 2000: A New Blocking Agent of Isocyanates, *European Polymer Journal*, **36**, 1745-1751.

[69] **Thermal Analysis of Polymers**, *Encyclopedia of Polymer Sceince and Technology*, 2005.

[70] **Thomas, D. J., Atwell,** 1973: *Starches,* American Association of Cereal Chemists, St. Paul, MN; 1999. *Coproducts,* Fishman *et al.,* Eds., ACS Symposium Series 575.

[71] **Ulrich, H.,** 1997: *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., Vol. **24**, John Wiley & Sons, Inc., New York, pp. 695–726.

[72] **Ulrich**, **H.,** 1996: *The Chemistry and Technology of Isocyanates,* John Wiley & Sons, Inc., Chichester.

[73] **Ulrich, H., Tilley J.N. and Sayigh A.R.,** 1964: *J. Org. Chem*. **29**, 2401, 3334.

[74] **Url-1** <*http://www. pcimag.com*>, Troubleshooting Metal Catalyzed Urethane Systems.

[75] **Url-2** <*http://www.specialchem4coating.com* >, Aliphatic Polyisocyanates.

[76] **Yamamoto, R.,** 1981: Eur. Pat. 23649.

[77] **Young, T.,** An Essay on the Cohesion of Fluids, *Philosophical Transactions of the Royal Society of London*, **95,** 65-87 (1805)

[78] **Yu, L.,** 2009: *Biodegradable Polymer Blends and Composites from Renewable Resources,* Wiley-Interscience, **4**, 94-95.

[79] **Young, T.,** 1805: An Essay on the Cohesion of Fluids, *Philosophical Transactions of the Royal Society of London,* **95,** 65-87.

[80] **Waldmann, T.E. and McGhee W.D.,** 1994:*J. Chem. Soc., Chem. Comm.,* 957

[81] **Whistler, R. L., BeMiller, J. N.,** 1997: *Carbohydrate Chemistry for Food Scientists,* American Association of Cereal Chemists, St. Paul, MN.

[82] **Wicks, D.A., Wicks, Jr. Z.W.**, 1999: Blocked isocyanates III: Part A. Mechanisms and chemistry,*Organic Coatings*,**36,** 148-172.

[83] **Wicks, D.A., Wicks, Jr. Z.W.,** 2001: Multistep chemistry in thin films; the challenges of blocked isocyanates, *Organic Coatings,* 43, 131–140.

[84] **Zengel, H.**, 1980: Brit. Pat. 2031907.

CURRICULUM VITAE

Candidate's full name: Pınar MUTLU

Place and date of birth: Karamürsel 23/04/1985

Permanent Address: Kartaltepe Mah. Pembe Ay Sok. 34-13 Bakırköy/ İstanbul

Universities and Colleges attended: Istanbul Technical University