Synthesis and Characterization of Branched, Functional Polyurethane Dispersions as a Technology Platform for Self-Crosslinking Textile Coatings

by

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Synthesis and Characterization of Branched, Functional Polyurethane Dispersions as a Technology Platform for Self-crosslinking Textile Coatings

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Love many things, for therein lies the true strength, and whosoever loves much performs much, and can accomplish much, and what is done in love is done well.

Vincent Van Gogh

It's not freedom from conditions, but it is freedom to take a stand toward the conditions.

Viktor E. Franklin

Tüm bilim emekçilerine..

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Keywords: Polyurethanes, Waterborne dispersions, Branching, Functional polymers, A_2 + B_3 polymerization, Textile coatings, wrinkle recovery

ABSTRACT

Waterborne polyurethane dispersion technology has been increasingly becoming significant in the market of environmentally friendly materials for advanced coating and adhesive applications due to their high performance and zero or near zero volatile organic content (VOC) in recent decades. Although the versatile chemistry of polyurethanes enables one to design high performance coating, adhesive or elastomeric materials for a wide range of applications, current synthetic routes for linear polyurethanes have limitations in the introduction of chemical functional groups on the polymer backbone. The present study focuses on the synthesis and characterization of waterborne, branched polyurethanes with a multitude of functional end-groups via the oligomeric A_2 + B_3 methodology. While the waterborne nature of final products makes them user and environmentally friendly, the presence of functional end-groups makes them suitable coating and adhesive materials for a variety of surfaces, specifically textiles. In this thesis, one-component and self-crosslinking, or two-component, amino- or silane functional polyurethane dispersions were synthesized and examined in detail. The influence of the

degree of branching, nature of the soft segment and chemical structure of end-groups on the dispersion properties and thermo-mechanical properties of elastomeric films obtained from these dispersions was investigated systematically. Decreasing the A_2:B_3 ratio followed by silane functionalization and self-crosslinking resulted in stiffer films and coatings, due to higher crosslinking density. On the other hand, crosslinking of amino-functional PUs with water dispersible polyisocyanate compounds in a two-component waterborne system resulted in enhanced mechanical and thermal properties as a function of the degree of cross-linking controlled by the water dispersible polyisocyanate content. Upon the synthesis and characterization of branched, functional PU dispersions and films, pure wool and wool/polyester blend fabrics were coated with selected PU dispersions in an attempt to improve wrinkle recovery of fabrics. While half grade improvement was achieved with branched PU dispersions containing urea, silane and amino functionalities on pure wool surfaces, wrinkle resistance of wool/polyester blend fabrics was improved at least one grade with both self-crosslinking and two-component PU coatings due to better compatibility of polyester containing wool fabric with polyester-based PU backbone.

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ÖZET

Su bazlı poliüretan dispersiyonları, son yıllarda yüksek performansı ve sıfıra yakın uçucu organik içerik (VOC) nedeniyle ileri kaplama ve yapışkan uygulamalar için çevre dostu materyaller pazarında giderek önem kazanmaktadır. Poliüretanların çok yönlü kimyası, geniş uygulama yelpazesi için yüksek performanslı kaplama, yapışkan veya elastomerik malzemeler tasarlanmasına olanak tanısa da, lineer poliüretanlar için mevcut sentetik yollar, polimer omurgasında kimyasal fonksiyonel grupların eklenmesinde bir takım sınırlamalara sahiptir. Bu çalışma çok sayıda fonksiyonel uç grup barındıran su bazlı, dallanmış poliüretanların oligomerik $A_2 + B_3$ metodolojisi ile sentezlenmesi ve karakterize edilmesi üzerinde yoğunlaşmıştır. Nihai ürünler su bazlı olmalarından dolayı kullanıcı ve çevre dostuyken fonksiyonel uç gruplarının varlığı onları çeşitli yüzeyler, özellikle de tekstil yüzeyleri, için uygun kaplama ve yapışkan malzemeleri yapmaktadır. Bu tezde, tek bileşenli ve kendinden çapraz bağlanabilir veya iki bileşenli, amino veya silan fonksiyonelitesine sahip su bazlı poliüretanlar sentezlenmiş ve silan sistemleri ayrıntılı olarak incelenmiştir. Dallanma derecesi, yumuşak segmentin yapısı ve uç gruplarının kimyasal yapısının bu dispersiyonlardan elde edilen elastomerik filmlerin dağılım özellikleri ve termo-mekanik özellikleri üzerine, dallanma derecesi, yumuşak

segmentin yapısı ve uç gruplarının kimyasal yapısının etkileri sistematik olarak araştırılmıştır. A_2: B_3 oranının düşürülmesi, bunu takiben silan işlevselleştirmesi ve kendi çapraz bağlanması, daha yüksek çapraz bağlanma yoğunluğundan dolayı sert filmler ve kaplamalar ile sonuçlanmıştır. Öte yandan, amino-fonksiyonlu PU'ların suda çözünebilir poliizosiyanat bileşikleriyle iki bileşenli su bazlı bir sistemde çapraz bağlanması, suda çözünebilir poliizosiyanat bileşenleri tarafından kontrol edilen çapraz bağlanma derecesinin bir fonksiyonu olarak iyileştirilmiş mekanik ve termal özelliklere neden olmuştur.

Dallanmış, işlevsel PU dispersiyonlarının ve filmlerinin sentezi ve karakterizasyonu üzerine, saf yün ve yün / polyester karışımlı kumaşlar, kumaşların kırışmazlık özelliğini iyileştirmek amacıyla seçilen PU dispersiyonlarıyla kaplanmıştır. Saf yün yüzeylerinde üre, silan ve amino işlevsel grupları içeren dallı PU dispersiyonlarında yarım puan iyileşme sağlanırken, yün / polyester karışım kumaşlarının kırışıklık direnci, kendiliğinden çapraz bağlanan ve iki komponentli PU kaplamaları ile polyester içeren yün kumaşın polyester bazlı PU omurgasına uygunluğu. daha iyi olduğu için en az bir puan geliştirilmiştir.

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CHAPTER 1
GENERAL INTRODUCTION

1. Introduction

1.1. Overview

Until recent years, traditional polyurethane (PU) resin systems were most commonly synthesized in the presence of volatile organic compound (VOC) which were approximately 40 to 60% by weight. By the end of 1960s, PU dispersions (PUDs) were first prepared in low solvent or solvent-free mediums due to the environmental regulations [1]. The PU resins market especially for coating and adhesive applications was then influenced by water-borne systems because of their low toxicity by comparison conventional solvent-borne media. Consequently, aqueous PUDs have gradually grown especially in the last decades [2]. are attracting the attention of the market by increasing importance in wide-range of coating and adhesive applications, due to their superior properties including good adhesion behavior, good solvent and water resistance, abrasion resistance, outstanding flexibility, non-toxicity and eco-friendliness. Yet, PUDs demonstrate also drawbacks such as poor chemical resistance and reduced thermal and mechanical behavior if they are not cross-linked upon the application. The high reactivity of isocyanate groups toward water restricts the usage traditional water synthesis methods such as emulsion or suspension polymerization. Hence, several alternative routes have been developed for the synthesis of PUDs [2].

The synthesis of highly branched (hyperbranched) polymers (HBPU) with multitude of functional end-groups via oligomeric A_2+B_n approach was recently reported due to its wide range of application potential [3]. This technique is distinguished among other polymerization routes because several types of the A_2 or B_n monomers are commercially available or easily synthesized and one-step synthesis is possible. Therefore, the diversity of the end-group chemistry and the wide range commercially available A_2 and Bn reagents allow to easily modify the polymer structure and properties [4],[3].

This thesis focuses on the synthesis of a series of highly branched, chemically functional PUDs with tailored end-group chemistry and cross-linking behaviors using the novel

oligomeric A_2+B_3 approach. In an attempt to demonstrate that tailoring the functionality of PUDs with controlled branching enables new potential applications, newly developed functional PUDs were utilized for textile coating applications to enhance anti-wrinkling and instantaneous recovery behavior of wool fabric by the covalent attachment of the PU coating on the wool surface via the functional end-groups and formation of an elastomeric coating with good recovery on wool fabric. The PUD coating was also designed self-crosslink, or cross-link with the aid of a second component to form a barrier layer on wool surface against humidity, temperature and pressure, while retaining wool's characteristics and replacing existing solventborne coatings currently used for anti-wrinkling purposes by the textile industry.

CHAPTER 2
LITERATURE REVIEW

2. Polyurethanes

2.1 Polyurethane Chemistry

Polyurethanes (PUs) have extensive applications in a variety of industries due to their versatile properties. The chemical composition and structure of PUs has almost infinite combination of building blocks and thus property pattern, therefore end products can be varied within wide limits depending on the desired application. This feature positions PUs uniquely in the market, such that soft and elastic or rigid PU products in the form of films, foams or coatings can be seen [5],[6]. As a result, PUs can be integrated into several type products, such as paints, coatings, elastomers, insulators, foams etc. The most important types of PUs and some common examples of their uses are illustrated in Figure 1 [7].

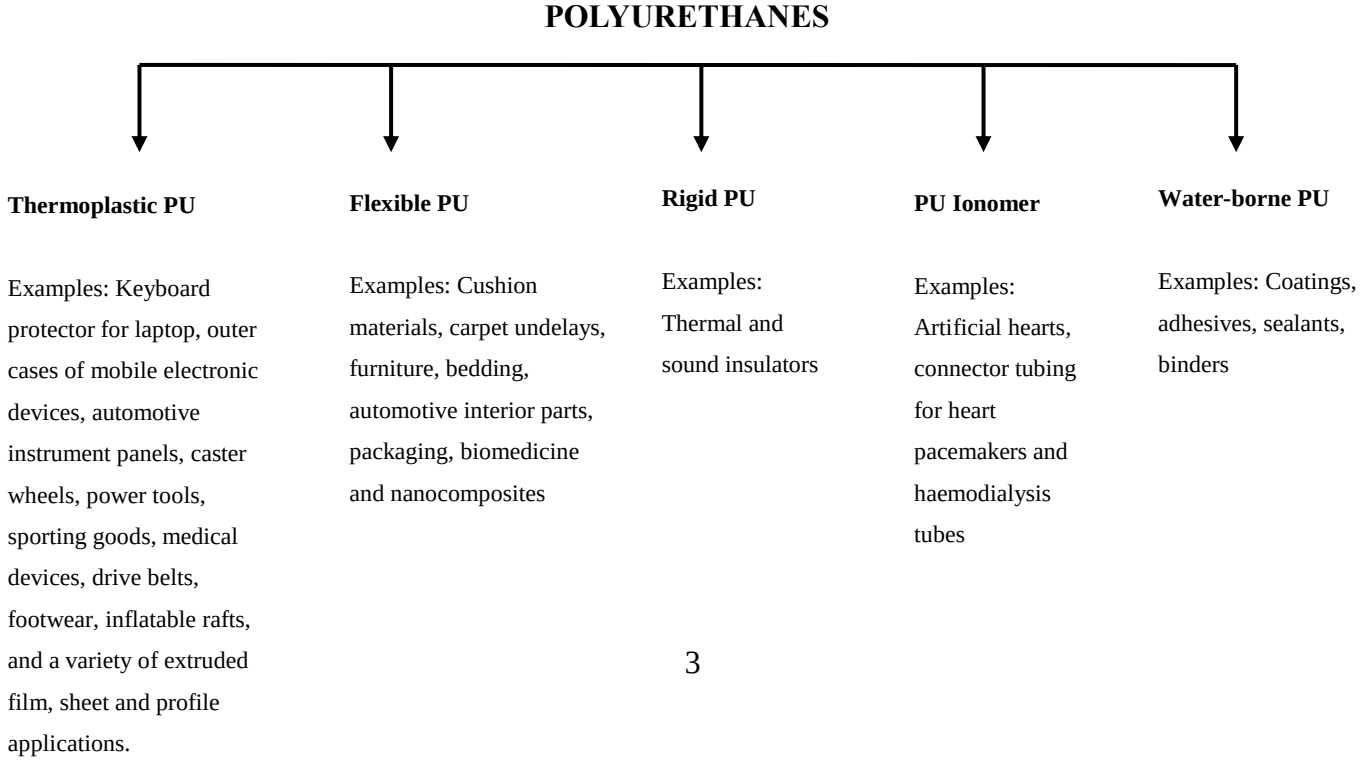


Figure 1 Important Types and Common Application Examples of Polyurethanes

The invention of PUs dates back to 1937, when the most widely used production method which is an exothermic polyaddition reaction between diisocyanate and polyester diol was achieved for the first time. This method can be achieved by two or more isocyanate groups per molecule with a polyol containing two or more reactive hydroxyl groups per molecule in the presence of suitable catalysts and additives. PUs are synthesized from the reaction between hydroxyl groups (-OH) and isocyanates (NCO). The main repeating units are called urethane groups in the PU backbone, the chain may also have other groups such as urea, ethers, esters and some aromatic compounds [7].

The general reaction for the formation urethane bonds derived from isocyanate and hydroxyl groups can be illustrated by the following formula:

Figure 2 Formation of Linear Polyurethane

In Figure 2, R represents an aliphatic, aromatic or alicyclic group attached to the isocyanate monomer and R_1 is a polyol compound which is derived from polyester or polyether. The properties of PUs generally vary depending on the structure of isocyanate and polyol components. Soft elastic PUs can be usually synthesized from polyols with flexible long chains, whereas the production of rigid PUs is achieved by a higher amount of cross-linking with short polyol chains. The long segment with low cross-linking segment provides to PUs stretching and elastic behavior, whereas tough polymers can be achieved from shorter chains with high cross-linking [7]. The functionality and the chain length of hydroxyl group and the isocyanate groups are essential for branched or cross-linked PUs, as well as some other structural changes can be effective.

Linear PUs can be obtained from the reaction between a diisocyanate (aromatic or aliphatic), diol, and a chain extender (Figure 3). The polyurethanes are considered as copolymers due to the presence of hard and soft segments which are linked by covalent type bonding. The hard segments are originated from diisocyanate-chain extender,

whereas soft segments are formed from the polyol. Hard segments are glassy or crystalline domains which gives rigidity to PUs and they are integrated into the hard domains as a physical crosslink and as filler particles within the soft segment (SS) matrix.

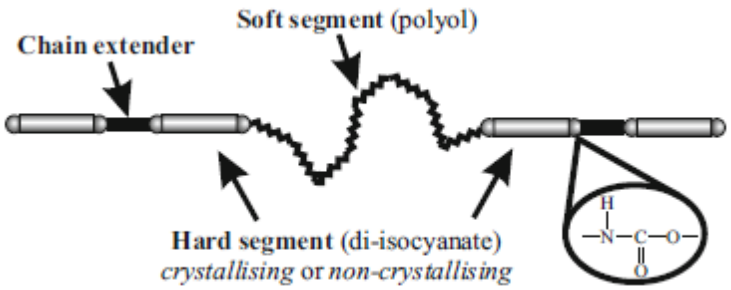


Figure 3 General Chemical Structure of Polyurethane [8]

Hard and flexible soft segments are linked to each other by the urethane groups by way of both covalent and hydrogen bonds (Figure 3). Self-association ability of the urethane groups is achieved with the help of hydrogen bonding, also they organize in either parallel or an anti-parallel form (Figure 4) [8].

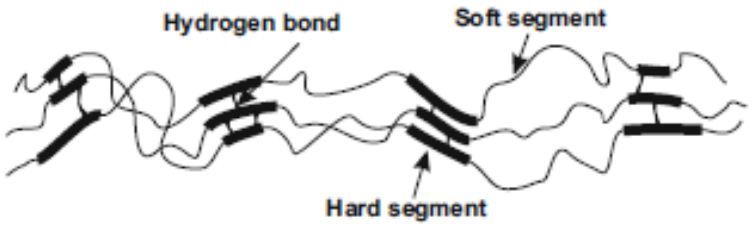


Figure 4 Illustration of Hard and Soft segments of Polyurethane [8]

Figure 5 depicts the degree of hydrogen bonding which has an important contribution to the kinetic behavior of PUs in terms of both thermal and mechanical properties. It is also important to note that these properties can be altered or enhanced by annealing techniques. The melting point and the mechanical strength of PUs are directly proportional to the degree of hydrogen bonding. Stronger bonds lead to increase in melting point which indicates a uniformity of the non-covalent polymer network. By increasing hydrogen bonds, the mechanical strength of the chain also increases that

contributes to the unique and elastomeric properties and control the hardness, modulus and tear strength. As mentioned earlier, soft segments of PUs are originated from oligomeric diols (polyester or polyether polyols) that react with diisocyanates. In contrast to the hard segments, soft segments are organized in amorphous form, and they provide flexibility and some chemical properties to the polymer network such as solvent resistivity and weatherability[8].

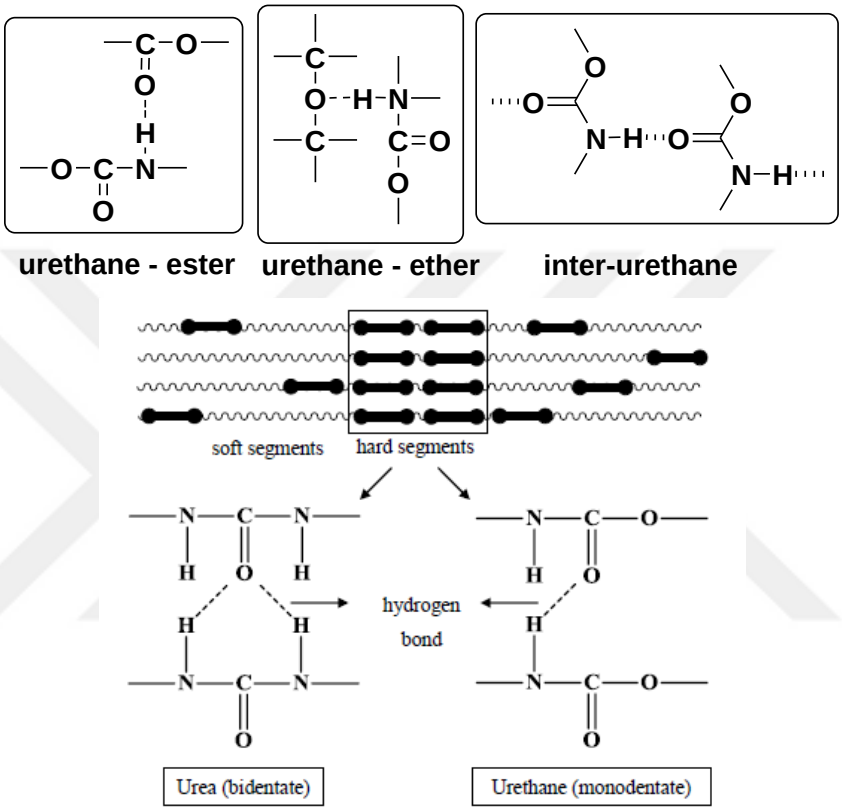


Figure 5 The Hydrogen Bonding Interaction in Polyurethane Structure [1]

2.2 Waterborne Polyurethane Dispersions

Polyurethanes have wide scale applications due to their versatile, high-performance properties. Urethane and urea groups combined with polyester or polyether type chains have unique behaviors that can present chemical, water and abrasion resistance. In addition, they can be synthesized to obtain high tensile and impact strength, along with high flexibility. Conventional solvent-based polyurethanes are gradually being restricted

due to the increasing regulations for low-pollution by the chemical industry. Owing to strict environmental regulations, solvent-based PUs are replaced with water-based systems, thereby PUDs are increasingly used in coatings, sealants, and adhesives for wood and plastics, as well as for a range of flexible substrates, such as textiles, leather, paper, and rubber [9].

The basic chemical compounds of PUDs are known from solvent-based systems which are mainly isocyanates, polyols, amines, catalysts and additives. The synthesis route of PUDs is divided into several reaction steps which begin with the polyaddition reaction of excess diisocyanates with polyols to for PU prepolymers. In next reaction, the remaining isocyanates react with short diols or amines to produce urethane or urea groups, respectively. Alternatively, the final reaction between isocyanate and water is possible, where the isocyanate group is hydrolyzed to yield amines and then urea groups in an uncontrolled manner, typically used for foam applications [10].

Several different techniques have been introduced for the controlled preparation of PUDs. The preparation of prepolymer that is the reaction of the diols (polyesters or polyethers) with diisocyanates in the presence of an internal emulsifier is the main route for all synthesis approaches. Generally, PUs are not soluble in water, besides that the hydrophilicity is an important parameter to determine the particle size distributions in PUDs. Furthermore, shelf stability is affected by polymer particle size distribution. Hence, surface modification or special treatment is required for the dispersibility and the stability of a polymer in water which can be obtained by internal or external emulsifiers [11].

Established synthesis strategies such as emulsion and suspension polymerizations cannot be used for the synthesis of PUDs due to the high reactivity of isocyanate groups towards water [12]. Therefore, alternative synthesis routes have been introduced in the literature and employed by the industry to modify polymers containing urethane and urea groups into waterborne two-phase systems. Fundamentally, there are two steps for the preparation. In the first step, a low to medium molecular weight isocyanate prepolymer from the reaction between di-or polyols and di-or polyisocyanates is prepared. The second step is the chain extension of the prepolymer and the dispersion in water in various ways by adding hydrophilic solubilizing groups during the first or second step. Successful

dispersion of small particles in continuous water system is achieved and desired without adding external surfactants [10]. Various preparation strategies can be divided into groups depending on starting components, solvents and the process sequence as listed below:

1. Prepolymer mixing process
2. Acetone process
3. Melt dispersion process
4. Ketamine-ketazine process
5. Other processes [10]

The prepolymer mixing is a conventional, most commonly used method to obtain PUDs. NCO-terminated PUs are ionically modified to mix with water for the formation of emulsion. During the prepolymer mixing, prepolymer viscosity is critical and must be reduced for the dispersion step. As a result, this method is suitable for the low viscosity prepolymers or a small amount of co-solvent is necessary. Di- or polyamines are introduced into the aqueous dispersion to carry out the chain extension reaction [10],[13]. The acetone method is a relatively more expensive strategy with two-steps procedure and allows a better control of the polymer architecture. The introduction of hydrophilic and charged groups into the polymer backbone in acetone medium is the first step of the preparation PUDs by the acetone method. By the incorporation of water into the PU/acetone mixture, the dispersion step takes a place. Waterborne dispersion of small particle size is obtained by removal of the solvent, and the stability of PUDs is achieved by the incorporation of hydrophilic groups previously into the backbone [12].

PUDs are eco-friendly polymers due to its drying stage which enables to obtain PU coatings or adhesives just by the evaporation of water, without the release of any volatile organic content. Compared to their solvent analogs, water-borne systems can provide the following advantages: viscosity and flow behaviors independent of molecular weight, non-toxicity, good adhesion, flexibility and high strength at low temperature, which allow PUDs to be applied in different areas ranging from coatings and adhesives to films and membranes. Apart from its wide application areas, PUDs also have several drawbacks due to its poor surface behaviors, low chemical and water resistance and deficiency in mechanical strength and thermal stability if applied as a one-component, non-crosslinked

coating. [14]. Similarly, several characteristics of PU coatings from PUDs such as mechanical strength, chemical and solvent resistance may be inadequate for high-performance applications utilization when compared to solvent-based systems. Water-based mediums with low number of crosslinks exhibit improvements, however they do not have the same degree as solvent systems. To improve the mechanical strength, chemical and solvent resistance properties of PUDs higher crosslinking density must be achieved. However, highly crosslinked PUDs cannot be prepared easily in a single pack owing to problems of high viscosity prepolymers or limited coalescence of formulated dispersions. As a result, one component waterborne polyurethane systems are deficient in chemical resistance to compared to crosslinked two-pack solvent-based polymer dispersions. Two-component polyurethane coatings, also called two-package coatings, are composed of two resin packages mixed immediately prior to application. One package mostly includes a resin with reactive chemical groups, for instance hydroxyls of amines; the other packages have a polyisocyanate a resin capable of reacting with the chemical compounds. The key point that two-component PU coating have is the rapid curing reaction once the two resins are mixed. In the case of a two-component waterborne system, both components are expected to be pre-dispersed in water or water dispersible during the application, yet two-components coating formulations have limited pot-life during the application. There are several methods for imparting crosslinking ability to one-component coatings via the post-crosslinking during film formation. Among them, PU chains possessing both blocked isocyanate and hydroxyl groups in the form of waterborne dispersion or solventborne solution are commonly employed. However, such designs have limited applicability due to high temperature requirements for de-blocking reactions during drying and film-formation stages. On the other hand, alternative post-crosslinking that can occur during or shortly after film formation through a chemical reaction is always desirable and therefore there exists a need for alternative synthesis approaches to develop one-component, self-crosslinking PUDs. [15].

2.2.1 Silane Functional Waterborne Polyurethane Dispersions

2.2.1.1 Basics of Silane Chemistry

In the periodic table, carbon and silicon belong to same group which can conveniently bond to four other atoms in their most stable state. However, silicon-based chemicals offer important physical and chemical properties compared to analogous carbon-based chemicals. Silicon is capable of participating in unique and useful chemical reactions due to its more electropositive properties that carbon, and it does not form stable double bonds. Silicon-based chemicals fundamentally have monomeric and polymeric materials [16],[17].

Silanes are called as monomeric silicons. A silane and carbon-based chemical structures are shown in Figure 6 to understand differences and similarities in physical and chemical behaviors between silicon- and carbon-based materials. A silane that is composed of at least one carbon silicon bond (CH_3-Si-) pattern is called as an organosilane that is a very stable and non-polar bond, also gives rise to low surface energy, hydrophobic effects. Similar effects can be achieved from carbon-based chemicals, although these effects are improved with silanes. The silicon hydride (-Si-H) is a very reactive structure which reacts with water to produce reactive silanol (-Si-OH) components and will add across carbon-carbon double bonds to obtain new carbon-silicon-based chemicals. Stable methyl or ethyl ether species can be achieved by the methoxy or ethoxy group on the carbon compound by attaching to silicon yields a very reactive and hydrolysable methoxysilane or ethoxysilane structure. The aminopropyl part of the organofunctional groups will behave chemically the same in the organosilicon substituent as it does in the carbon-based component. The effects of silicon on the chemistry of the organofunctional group will be defined from the distance of the amine or other organofunctional group from silicon. The organofunctional silane reactivity will be like organic analogs in carbon chemistry, if the organic spacer groups are a propylene linkage. Vinyl silanes (-Si-CH=CH_2) and silicon hydrides (-Si-H) are useful reactive silane groups in silicon chemistry, although the reactive compound is bonded directly to the silicon atom [18].

Chlorosilanes, silylamines (silazanes), alkoxysilanes and acyloxysilanes are obtained from the attachment of chlorine, nitrogen, methoxy, ethoxy or acetoxy directly to silicon, respectively. These molecules are very reactive and have special inorganic reactivity properties which will react readily with water, even moisture adsorbed on a substrate, to form silanol groups. These silanols then attach to other silanols to produce siloxane bond (-Si-O-Si) which is a very stable bond. In Figure 7, reaction steps of alkoxysilanes were clearly illustrated. In the beginning, hydrolysis of the alkoxy groups occur. First and second alkoxy groups are then hydrolyzed and go through condensation to oligomers in the second step. The hydrogen attached to a silanol is more electrophilic and much more reactive than the hydrogen of a carbinol compound due to the larger and more electropositive structure of silicon that results in a high dipole moment for the silanol chemicals and extended hydrogen bonding. Self-condensation can be triggered or controlled by using fresh solutions, alcoholic solvents, dilution, and selection of pH ranges. In addition, silane groups can react with polymer and mineral compounds, forming durable covalent bonds across the interface. Due to the hydrolysis process, stress relaxation can be provided at the organic/inorganic domain which support the improvement in adhesion and durability properties of material [19],[20],[21]

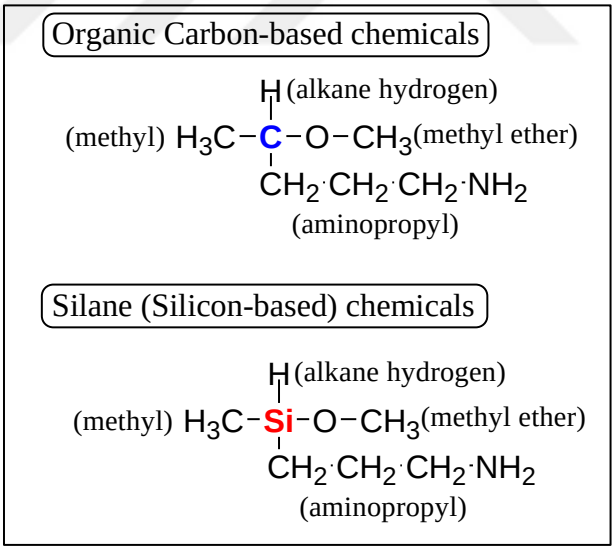


Figure 6 Carbon vs. Silicon Chemistry

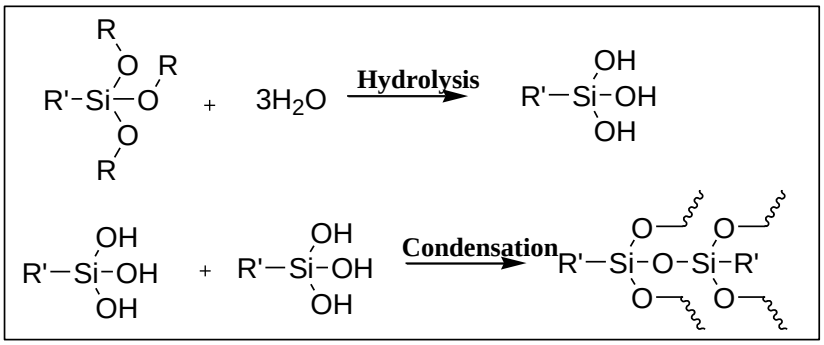


Figure 7 Hydrolysis and condensation mechanism of silane group

2.2.1.2 Typical Silane Applications

The chemical pattern of silanes provides a wide range of applications area due to its unique chemical structure, which allows them to attach to both organic and inorganic substrates. In adhesives and sealants industry, sophisticated and expensive processes for instance screwing, welding or riveting were replaced with silanes that are generally called coupling agents. Due to self-curable behavior of silane groups when exposed to moisture and heat, they have become the most popular material in adhesive and sealants industry. Silanes provide wet and dry adhesion, superior mechanical properties, higher storage stability, resistance to heat, moisture, atmospheric factors and solvents and ease of processing to the materials in several areas such as construction, transportation and marine. Silanes can be used to crosslink polymers such as acylates, polyethers, polyurethanes, and polyesters, and achieve enchantments in tear resistance, elongation at the break, abrasion resistance through the formation of an interpenetrating network. In high performance coatings, metal treatment and resin systems, silane has an again significant role generally as an adhesion promoter that behave as the binding agent between organic resins and inorganic surfaces. Hydrophobic dispersing agent is another role of silane groups which occur by the attachment of hydrophobic organic groups to silicon and impart that same hydrophobic behavior to a hydrophilic inorganic surface. They are used as durable hydrophobic agents in construction, bridge and deck applications. Silanes are used as moisture scavengers to convert water molecules to alcohol molecules in the presence of moisture thanks to the hydrolysis mechanism of the

three alkoxy groups on silanes. Organotrialkoxysilanes are often used in sealants and other moisture-sensitive formulations as water scavengers. Silanes also are used in a variety of applications such as composites, electronics, filler and pigments, pharmaceuticals, photovoltaics, plastics and thermoplastics, thermosets etc. [18],[22],[23].

2.2.1.3 Silane Functional Waterborne Polyurethane Dispersions

In the literature, different crosslinking mechanisms have been studied for waterborne coatings, including UV-crosslinking, heat activation, and two-component systems which have their own drawbacks. UV-cross linkable and heat-activated strategies must have either UV source or a heat source, thereby these needs limit their application area in industry. In addition to that, a two-component system has a short pot-life after mixing. In recent publications, Subramani and his co-workers reported a study on the synthesis and characterization of waterborne, crosslinkable silylated linear PUDs (SPUs) with improved chemical resistance, mechanical and thermal properties. NCO-terminated hydrophilic PU prepolymer was synthesized and terminated by incorporation of 3-aminopropyl trimethoxysilane (APTMS). Compared to standard PUs, SPUs exhibit fast ambient moisture curing, good adhesion to several substrates, enhanced weatherability and light resistance [24]. In 2007, Subramani et al. described the preparation of waterborne dispersions of externally chain extended PU/urea mixtures terminated by hydrolysable trialkoxysilane groups and containing anionic solubilizing groups. This study presented an effective route to synthesize one-package aqueous SPUs with excellent storage stability more than 12 months with superior properties [25]. H. Sardon et al. synthesized room temperature self-curable hybrid waterborne PUs that is illustrated in Figure 8 by using acetone process, employing (3-aminopropyl) triethoxysilane (APTES) at different concentrations. This study is one of the first reports that investigates the effect of curing agent on particle morphology by transmission electron microscopy (TEM) and surface properties (ζ-potential). In the research, PUs could cure at room temperature due to the condensation of silanol groups during the drying process, giving rise to a covalently linked organic/inorganic hybrid film. NMR, FT-IR and gel content

measurements were reported after curing the PUs at room temperature and revealed that crosslinking occurred during the drying process, not during polymerization [2]. The research of Sardon and co-workers focused on thermal and mechanical properties of room temperature self-curable hybrid PU films from dispersions. Two series of isophorone diisocyanate (IPDI) based PUs were studied; polyester and polyether as soft segments. APTES was incorporated at different ratios into the PU chains. According to DSC and DMTA experiments, relative crystallinity of polyester based PUs were decreasing by the addition of APTES. Moreover, APTES content had a great effect on mechanical properties of polyether based PUs whereas polyester based PUs showed the opposite behavior. As a result, the properties and crosslinking behavior of the segmented PUs can be modified with the APTES content [26]. Park et al. used PUDs as an attractive option in marine coatings to protect the surface from marine biofouling. In their study, N-[3-(trimethoxysily)propyl]-ethylenediamine (TMSIP-EDA) was used as a chain extender and crosslinker. The TMSIP-EDA amine group reacted with NCO group of the prepolymer and the methoxy group induced branching with Si-O-Si via a hydrolysis and condensation reaction in water dispersion [27], and Li et al. synthesized PUDs by using α,ω-aminopropyl polydimethylsiloxane (APDMS) mixed with soft segments for moisture permeable textile coating [28].

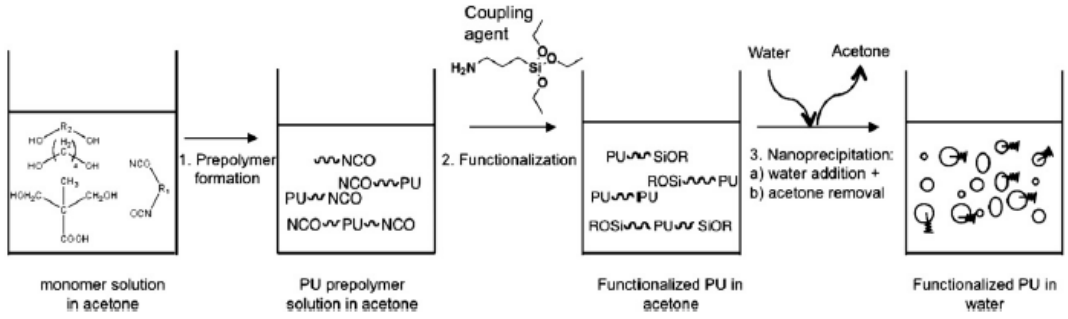


Figure 8 Scheme illustrating the different steps involved in the preparation of waterborne silanized polyurethane dispersion [2]

As can be seen from prior art in the literature, silane functionalization of PUs are limited to low molar mass linear chains with two end-groups. In this thesis, we report the

synthesis of branched PUs with increased number of end-groups functionalized with silane groups in the form of waterborne dispersion for the first time in the literature as a new family of self-crosslinking coating material.

2.3 Highly Branched Polymers

2.3.1 Background

To start with, the branching is a general and important phenomenon that can be observed in nature from living to nonliving things such as Crab Nebula, forked lightning, river basins, trees, nerves, veins, snow crystals, nervures, and proteoglycan from light-years to kilometers and to microscale and nanoscales (Figure 10). This phenomenon provides faster and more efficient transfer, dissipation, and distribution of energy and/or material [29].

On the other hand, in polymer chemistry, the definition of hyperbranched polymers begins with DuPont researchers, Kim and Webster, reporting the synthesis of random branch-on-branch structured macromolecules by single-step polycondensation of AB_2-type monomers in the late 1980s. However, highly branched polymers' history is quite long and complex as summarized in Figure 9. Flory et al. described the concepts of "degree of branching" and "highly branched materials" by the calculation of molecular weight (MW) distribution of three-dimensional polymers up to the state of gelation. Highly branched polymers have gained important attention by the theoretical report of Flory in 1952 which explains the preparation of highly branched polymers without gelation by polycondensation of AB_x monomers where $x \geq 2$ [29].

Year	Case	Lead Authors
Before 1900	Tartaric acid + glycerol	Berzelius
1901	Glycerol + phthalic anhydride	Smith
1909	Phenolic + formaldehyde	Baekeland
1929–1939	Glycerol + phthalic anhydride	Kienle
1941	Molecular size distribution in theory	Flory
1952	AB_n polymerization in theory	Flory
1982	$AB_2 + AB$ copolymerization	Kricheldorf
1987–1991	AB_2 homopolymerization	Kim/Webster Odian/Tomalia Fréchet/Hawker

Figure 9 History of Hyperbranched Polymers [29]

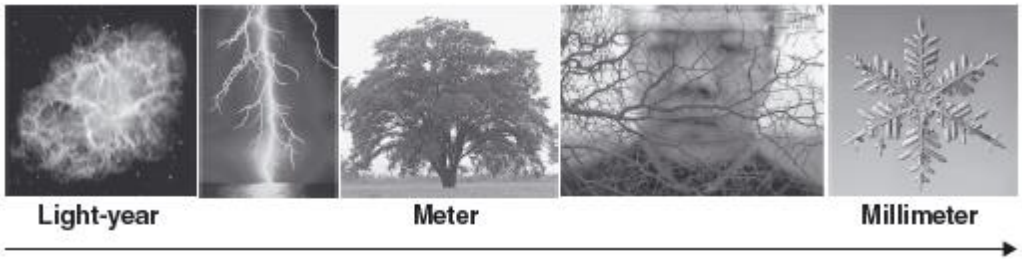


Figure 10 Selected branching patterns (from left to right Crab Nebula, fork lightening, tree, vascular network, snow crystal) [29]

Highly branched polymers include several different systems for instance dendritic, hyperbranched, or multibranched, and they offer unique properties. Highly branched polymers are known as high functionality polymeric materials and they are achieved by the presence of branch points or the presence of more than two end-groups. Branched systems bring enhanced characteristics to material when compared with their linear analogues, and the presence of increased number of functional end-groups provide numerous possible modification for various applications. However, highly branched polymers have important drawbacks including broad molecular weight distributions and irregular branching. Highly branched systems mostly exhibit inferior mechanical

behaviors when compared to their linear analogues due to shorter segment lengths than the critical molecular weight for entanglement (M_c), which is the minimum molecular weight at which a polymer chain entangles, measured by the molecular weight dependence of viscosity. Numerous studies are available in the literature that introduce methodologies for the synthesis and characterization of a wide range of highly branched and dendritic macromolecules using condensation, addition, and ring-opening polymerization [4],[30],[31].

2.3.2 Branching in Step-Growth Polymerization

The step-growth polymerization of AB_x (where $x \geq 2$) involves the reaction between the functional groups of A and B monomers which occurs arbitrarily. This strategy obeys normal step-growth polymerization characteristics as fundamental advantages whereas gelation, undesirable side-reaction can be called as drawbacks of the process. This step-growth polycondensation strategy had been used widely in the preparation of a scope range of highly branched systems [32]. However, limited availability or tedious lengthy synthesis of AB_2 monomers has limited wide use of this strategy since it was first reported.

2.3.2.1 Introduction to A_2+B_3 Approach

A_2 and B_3 polymerization, also named as A_2+B_3 polymerization, is a novel approach that has drawn a great deal of attention in the last decades to prepare highly branched polymers (Figure 11). Several types of difunctional (A_2) and trifunctional monomers (B_3) are commercially available, or much less effort is required to synthesize symmetrical A_2 and B_3 monomers compared to AB_n monomers. Several important variables are present including the ratio of functionalities, solvent and reagent purity and the reaction time and temperature that affect the success of A_2+B_3 method.

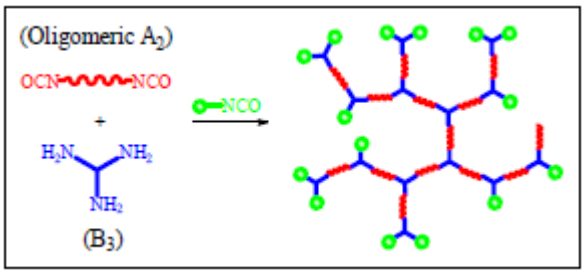


Figure 11 Oligomeric A_2 + B_3 approach to hyperbranched, segmented polymers [33]

To generate highly branched polymers, the reaction occurs between two monomers; one with two "A" and the other with three "B" functional groups in the A_2+B_3 approach (Figure 11). There are three fundamental assumptions for A_2+B_3 strategy: (1) an equal reactivity of all A or B groups at any given stage of the reaction with no side reactions; (2) the reaction is restricted to the condensation of A and B groups and (3) there is no intramolecular cyclisation and chain termination in the process [33]. According to historical perspective, in the 19th century, Berzelius prepared highly branched resins by the reaction between tartaric acid (A_2B_2 monomer) and glycerol (B_3 monomer). Later, Watson and Smith introduced the reaction between phthalic anhydride (latent A_2) and glycerol (B_3 monomer) in Figure 9. In fact, in 1940s Flory [34] described the topic of "degree of branching" and "highly branched materials" by using probability theory to calculate molecular weight (MW) distribution of linear polymers. Afterwards, studies continued to determine the MW distribution also for branching systems in the state of gelation. On the other hand, highly branched polyesters were synthesized by Kirchedorf et al., by the copolymerization of AB and AB_2 type monomers in 1982. The name of "highly branched polymers" originated from Kim and Webster due to their dissolvable highly branched polyphenylene in 1988. Spindler and Fréchet [35] introduced the first production of highly branched polyurethanes by using blocked isocyanate chemistry in AB_2 polymerization. The first two pioneering studies that demonstrated the preparation of highly branched polymers via A_2 + B_3 approach was reported in 1999. Kakimoto et al. [36] described the synthesis of highly branched aromatic polyamides which were derived from commercially available aromatic diamines (A_2) and trimesic acid (B_3). In addition, Fréchet et al. [37] introduced the preparation of highly branched polyether epoxies via

proton-transfer polymerization from 1,2,7,8-diepoxyoctane (A_2) and 1,1,1-tris(hydroxymethyl)ethane (B_3) using various molar ratios of A_2 and B_3. Stopping the reactions immediately prior to gelation resulted in soluble, network-like products with reasonable molar mass and high degrees of branching, which resembled highly branched polymers. After that, Kumar and Ramakrishnan [38],[39] synthesized wholly aromatic highly branched polymers with urethane linkages by the polymerization of 3,5-dihydroxy benzozyl azide. This synthesis reported an important result, which was the fact that T_g of highly branched polymer without the oxyethylene spacer (x=0) was 106°C and when the length of spacer increased to x=2 T_g decreased to 13°C. Moreover, the same research group prepared highly branched polymers with urea linkages by the utilization of the polycondensation of 3,5-diamonobenzoylazide monomers. The first preparation of highly branched polymers with urea and urethane linkages by the synthesize of commercially available A_2 and CB_n (n=2 or higher) was achieved by Gao and Yan [40]. Eventually, Bruchmann and Schrepp [41] reported a one-step strategy for the synthesize of highly branched poly(urethane urea)s, using commercially available A_2 and B_3 monomers, where A_2 monomer was a diisocyanate (isophorone diisocyanate or toluene diisocyanate) and the B_3 monomer was an aminoalkanediol [42],[33]. Yet, none of these polyurethanes showed typical properties of linear, segmented structures due to the nature of A_2 and B_3 monomers used. In 1952, Flory demonstrated his theoretical strategy for polycondensation of BA_x (where $x \geq 2$) monomers (A+B→AB), that gives highly branched or hyperbranched polymers (HBPs). According to Flory, gel-free highly branched polymers can be achieved by the polycondensation of two-or more A functional groups and one B functional group. Similarly, the synthesis of a highly branched polymer from the polycondensation of A_2 and B_3 monomers was dependent on the molar ratio of A_2:B_3 ratio and functional group conversion [34]. The theory of gelation was described statistically for the formation of cross-linked infinite networks obtained from various combinations of multifunctional monomers that produce a three-dimensional network at a certain monomer conversion for a given stoichiometric ratio of functional groups. For that reason, gel point identification of A_2+B_n polymerizations is crucial to produce highly branched polymers in gel-free state. It is well established that polycondensation reactions with multifunctional groups may be organized in an infinite molecular weight polymer

network, or gel, at high monomer conversion. The gel point begins to occur at a critical point of monomer conversion during polymerization, and it is dependent on the functionality and the concentration of the multifunctional (f>2) branching agent. In the statistical theory of nonlinear step-growth polymerization, for instance A_2 + B_3 approach, a branching coefficient, *α*, is described as the probability that a given functional group of branch unit (B_3) is attached to another branch unit. Generally, *α* can be determined from the ratio of the "A" and "B" functional groups and the extent of reaction at a given time. In the case of an A_2 + B_n polymerization, α can be calculated by using following equations:

$$\alpha_C = \frac{1}{(f-1)}$$

Equation 1

$$\alpha = \frac{rp_A^2\rho}{1 - rp_A^2(1-\rho)}$$

Equation 2

Where (α) is the probability of branching, (α_c) defines the gel point, (f) is the functionality of branched units, (p_A and p_B) are the fraction of A and B type monomers that have reacted, (ρ) is the ratio of A groups on branch units to all A groups in the reaction mixture, and (r) is the ratio of the A groups to that of B groups. Flory demonstrated that gel formation is impossible when $\alpha < \alpha_c$, but may occur when $\alpha > \alpha_c$ [30].

To determine the gel point of an A_2 + B_3 system, when A_2 and B_3 monomers are fed into the reaction mixture with equimolar amounts, where f = 3, it can be calculated that α_c = 1/2 and r = 2/3. In our present study, all our B groups are on branching units (B_3) ρ = 1. Supposing that $\alpha = \alpha_c$ at the gel state:

$$\alpha = \alpha_C = rp_A^2 = \frac{p_B^2}{r}$$

Equation 3

If the values $\alpha_c = 1/2$ and r = 2/3 were substituted in Equation 2.3, $P_A =$ 0.866 and $P_B =$ 0.577 are found. In an $A_2 + B_3$ system with A_2:B_3 ratio of 1:1, the gelation will occur when 57.7% of the B_3 monomer or 86.6% of the A_2 monomer has reacted [30]. From Equation 3, the maximum α value is equal to one, which refers a fully crosslinked system. The value of α can also be associated to the degree of branching of a material, that increases as a function of monomer conversion. In Figure 12, the relationship between P_A and α in the case of r = 1 and 1.5 are shown clearly. B_3 is a branching unit, therefore α_c is equal to 0.5 from Equation 2.1. If r is equals to 1 or 1.5, the value of α is over 0.5 at high conversion of A function as can be deduced from dashed lines. In addition, the weight fractions of sol-gel are proportional to α in the $\alpha c<\alpha<1$ regime. Calculation of the critical conversion of A and B groups (P_{Ac} and P_{Bc}) at the gel point for various r values, based on Equation 1 and Equation 2 are significant in an $A_2 + B_3$ systems. In other words, although infinite network formation which is defined as gel formation is not allowed statistically in the case of polymerization of AB_x monomers, it is critical in $A_2 + B_3$ systems [36].

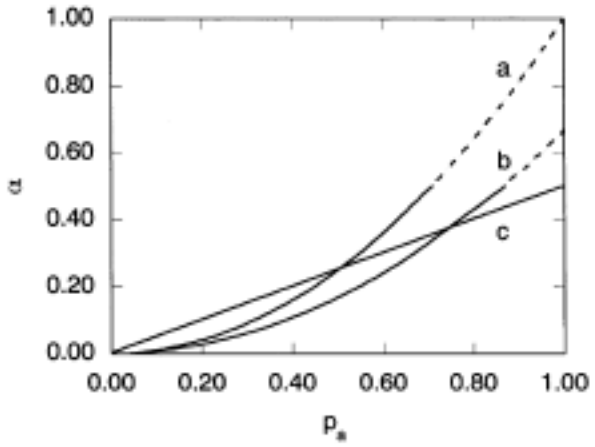


Figure 12 Relationship Between p_a and α for the Polymerization of A_2+ B_3 Monomers ([*B*]/[*A*]=1.0 (a); 1.5 (b); AB_2 Monomers (c)) [30]

For point a;

r = [B]: [A] = 1.0 ([A_2]: [B_3] = 1.5) $p_a = 0.71$, $p_b = 0.71$

For point b;

r = [B]: [A] = 1.5 ([A_2]: [B_3] = 1.0) $p_a = 0.87$, $p_b = 0.58$

Table 1 summarizes the critical conversion of A and B groups for different A to B ratios. As the molar ratio of A to B functional groups is increased, the gel point is reached sooner, at lower monomer conversion, and gelation might become more difficult to avoid [30].

A_2:B_3	r=A: B	p_{Ac}	p_{Bc}
0.75:1.00	0.50	1.00	0.500
0.90:1.00	0.60	0.913	0.548
1.00:1.00	0.67	0.866	0.577
1.25:1.00	0.83	0.775	0.645
1.50:1.00	1.00	0.707	0.707
2.00:1.00	1.33	0.612	0.816
3.00:1.00	2.00	0.500	1.000

Table 1 Calculation of gel point in A_2 + B_3 polymerization (α_c=0.5) for various monomer ratios using Equation 1 and Equation 3

2.2.3.2 Highly Branched, Segmented Polyurethanes

Unal et. al. [4] synthesized highly branched, segmented polyureas and poly(urethane urea)s via oligomeric A_2+B_3 approach which showed mechanical properties comparable to their linear analogues. In this study, an isocyanate end-capped polyether (PPO or PTMO) was synthesized and used as an oligomeric monomer and reacted with a B_3 triamine monomer. This novel method can be extended from elastomers to engineering thermoplastics by using a large number of telechelic oligomers (A_2) including poly(dimethylsiloxane) (PDMS) or poly (ethylene glycol) and trifunctional monomer (B_3) mixtures shown in Figure 13 and Figure 14, respectively.

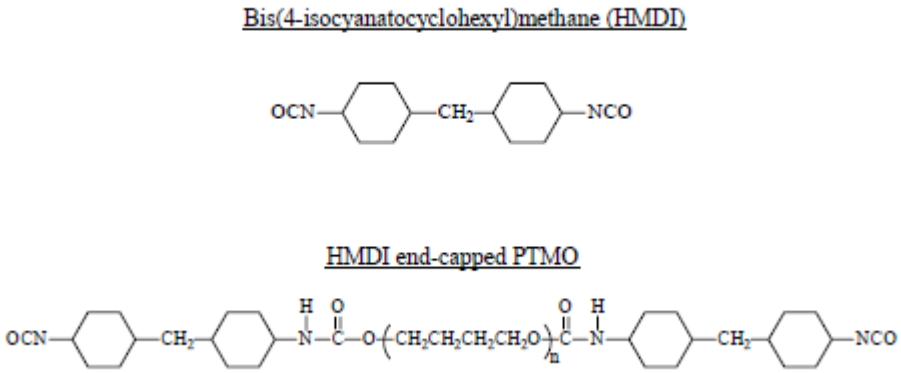


Figure 13 Chemical structures of monomeric and oligomeric A_2 reagents [4]

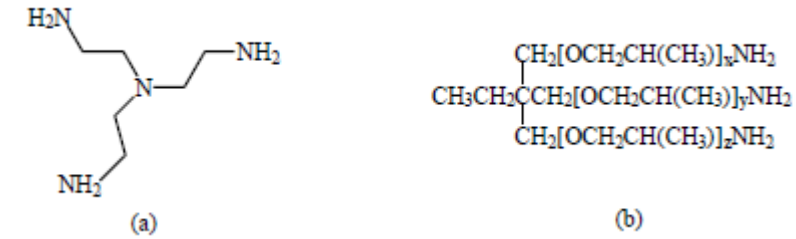


Figure 14 Chemical structures of triamines used: (a) tris(2-aminoethyl) amine (TRIS), (b) poly(oxyalkylene)triamine (ATA), where x + y + z = 5.3 and M_W = 440 g/mol [4]

Table 2 shows the chemical compositions of polyurethanes and their linear analogues synthesized via oligomeric A_2 + B_3 approach. In Figure 15, stress-strain curves and test results were demonstrated for both linear and highly branched PUs. The linear PU showed strong elastomer behavior due to its 35 wt% hard segment values in Table 2. The uncapped PU elastomer based on ATA trimer (PTMO2-ATA*) displayed weak modulus and tensile strength, however it still shows excellent recovery following up to 1100% elongation. PTMO2-ATA had enhanced tensile properties due to urea endcapping. Similar to the uncapped homologue (PTMO-ATA*), PTMO2-ATA also displays excellent recovery following high elongation.

Table 2 Chemical compositions of segmented, hyperbranched poly (urethane urea) s and a homologous linear TPUU (PTMO2-MDAP) (* = no CHI end-capping) [4]

sample	HMDI (g)	soft segment		triamine		CHI (g)	HS (%)
		M_n (g/mol)	amount (g)	type	amount (g)		
PTMO2-ATA*	17.70	2000	67.50	ATA	14.85	--	33
PTMO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO3-ATA	11.45	3500	76.25	ATA	9.60	2.70	24
PPO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO2-TRIS	18.80	2000	71.55	TRIS	5.20	4.45	28
PTMO2-MDAP*	26.90	2000	65.00	MDAP	8.10	--	35

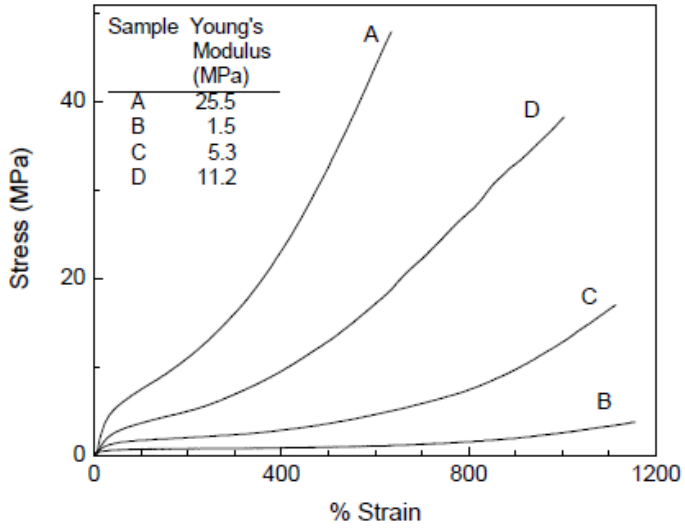


Figure 15 Comparison of the stress-strain behavior of hyperbranched, segmented poly(urethane urea) elastomers and a homologous linear TPUU: (A) PTMO2-MDAP*, (B) PTMO2-ATA*, (C) PTMO2-ATA and (D) PTMO2-TRIS (* = no CHI end-capping) [4]

As a result, the oligomeric A_2+B_3 approach has drawn the attention due to the ability to control the distance between branched points by controlling the length of the A_2 oligomer,

which has enabled the synthesis of branched, functional segmented PUs with entanglement ability and enhanced mechanical properties compared to short A_2+B_3 polymerization products.

2.4 Wool Surface and Chemistry

2.4.1 Introduction

The considerable quantities of fibers obtained from animals, for instance wool from sheep, are used commercially in the textile industry. Wool is one of the ancient textile materials which survived to the present time. Despite the biodegradability of natural fibers, it is unknown when wool was first used as a textile product. According to archaeological findings, wool may be the first fiber used for making cloth, which may have been wool felt. A large number of wool types depend on various breeds of sheep production that are classified according to fiber length and diameter. In general, coarse wools are used in interior textiles, such as carpets and upholstery, and fine wools are used in the production of fabrics [43].

2.4.2 Structure and Composition of the Wool Fiber

From the breeding of sheep, raw wool contains up to 70% impurities such as wool grease, residuals from perspiration (suint), dirt, and vegetable matters. To look particularly into the wool grease, it is composed of a mixture of fatty acids and esters; and suint consists of potassium salts of fatty acids, plus phosphate, sulfate, and nitrogenous compounds. During the scouring process grease, suint, and dirt are eliminated from the wool. In worsted step, vegetable matter is removed by carding and combing, whereas on the woolen system it is removed by carbonizing with sulfuric acid. Wool is a member of a group materials known as α-keratin, due to α-helical shape (Figure 17-a). Various examples can be given for α-helical conformation such as horns and beaks. Keratins have been classified as hard and soft according to their composition. A characteristic of hard keratins such as wool, hair, horns, and claws is a higher concentration of Sulphur (in

excess of 3%) that is found in soft keratins for instance in skin. The Sulphur in keratins is fundamentally present in the form of the amino acid cystine.

Wool is composed of a complex mixture of approximately 170 different proteins which have a wide range scale of higher molecular mass from below 10,000 Da to greater than 50,000 Da. The basic structural units of proteins are amino acids, also wool contains 20 amino acids shown in Table 3, which have the general formula $NH_2CH(R)COOH$, where (R) is the side segment of amino acid. Proteins are poly-condensation products of different amino acids are attached together to form polypeptide chain, shown in the following figure:

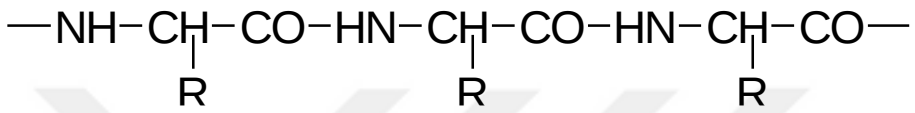
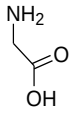
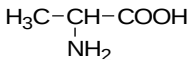
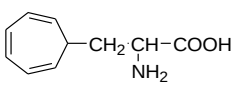
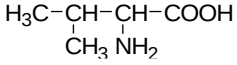
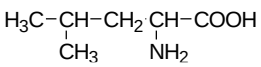
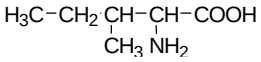
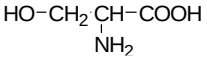
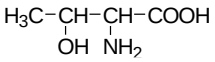
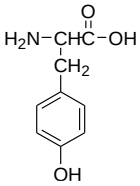
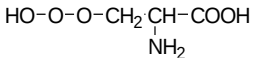
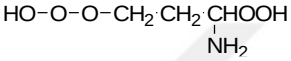
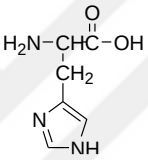
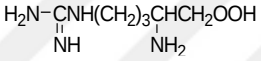
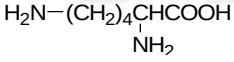
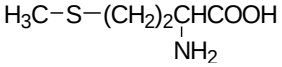
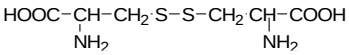
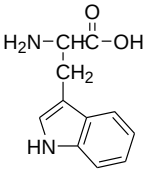
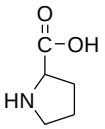


Figure 16 Formation of Polypeptide Chain

The side chains present in the amino acid residues of polypeptides can be aliphatic, aromatic, or other cyclic groups. They vary in size and chemical behavior and play an important role in both the physical and chemical properties of wool.

Table 3 Structure and Amount of Major Amino-Acids in Wool

		mol %		
Amino-acid	**Structure**	**[44]**	**[45]**	**Nature of Side Chain**
Glycine		8.6	8.2	Hydrocarbon
Alanine		5.3	5.4	Hydrocarbon
Phenylalanine		2.9	2.8	Hydrocarbon
Valine		5.5	5.7	Hydrocarbon
Leucine		7.7	7.7	Hydrocarbon

Isoleucine		3.1	3.1	Hydrocarbon
Serine		10.3	10.5	Polar
Threonine		6.5	6.3	Polar
Tyrosine		4.0	3.7	Polar
Aspartic Acid		6.4	6.6	Acidic
Glutamic Acid		11.9	11.9	Acidic
Histidine		0.9	0.8	Basic
Arginine		6.8	6.9	Basic
Lysine		3.1	2.8	Basic
Methionine		0.5	0.4	Sulphur-containing
Cystine		10.5	10	Sulphur-containing
Tryptophan				Heterocyclic
Proline		5.9	7.2	Heterocyclic

Glycine, alanine, phenylalanine, valine, leucine, and isoleucine have non-polar (hydrocarbon) side chains, so their chemical reactivity is lower than those that have the polar side chains of serine, threonine, and tyrosine. Acidic and basic groups have the most influence on the chemical reactivity of wool. Wool fibers consist basic amino and acidic carboxyl groups equally in the side chains. These groups are responsible for the ability of wool to combine with large number of acids and alkalis. Moreover, they are significant for dyeing process due to their interactions with anionic wool dyes. Therefore, wool has a net positive charge below pH4 and a net negative charge above pH8. In the range pH4-8, both types of group are fully ionized and the net charge carried by the fiber is zero (the fiber is in the isoelectric state).

The reactivity potential of wool fiber with a wide range of chemicals is much higher than other textile fibers. Reactive groups can be listed as three main types: peptide bonds, the side chains of some of the amino acids, and disulfide crosslinks. Thus, this property of wool brings new possibility into many industrial processes, for instance, in the areas of shrink proofing, dyeing, flame resistance, and finishing.

Various types of covalent crosslinks and noncovalent interactions are the links that is holding together the individual polypeptide chains in wool (Figure 17-b) The disulfide bond of cystine is the most important covalent link containing most of the sulfur groups in wool. Disulfide bridges can be obtained between either separate polypeptide chains or different parts of the same segment. The disulfide linkages mostly account for stabilizing wool fiber, particularly in the wet state.

Non-covalent interactions also contribute to the stabilization of wool which are hydrogen bonds between amide groups and other hydrogen donating and accepting groups: ionic interactions (salt linkages) between ionized carboxyl and amino groups: and hydrophobic interactions between the nonpolar groups of alanine, phenylalanine, valine, leucine, and isoleucine. These hydrogen bonds and ionic interactions have significant effect on the physical properties of dry wool, however they are easily disturbed when wool absorbs water. Besides hydrogen bonds and salt linkages, hydrophobic interactions are not easily broken by water, thus they have an important role in mechanical properties of wool even at high water content.

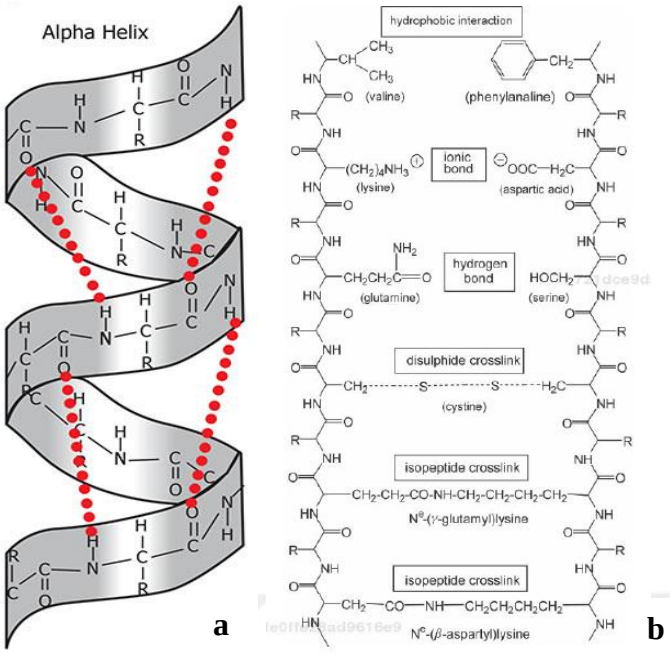


Figure 17 a) α-helix Structure of Wool b) Covalent Crosslinks and Noncovalent Interactions

Wool contains regions that differ from each other in physical and chemical composition. The complex morphological structure of fine wool fiber is illustrated in Figure 18.

Except for the other parts of wool fiber, the most important structure that makes wool unique among other fibers is referred as cuticle cells or scales. These scales are responsible for wool's ability to be felt under moisture and for wettability and tactile properties. Cuticle cells overlap both along and around the circuit of each fiber like tiles on a roof, can be observed in the scanning electron microscope (Figure 19). [43],[46],[47],[48],[49].

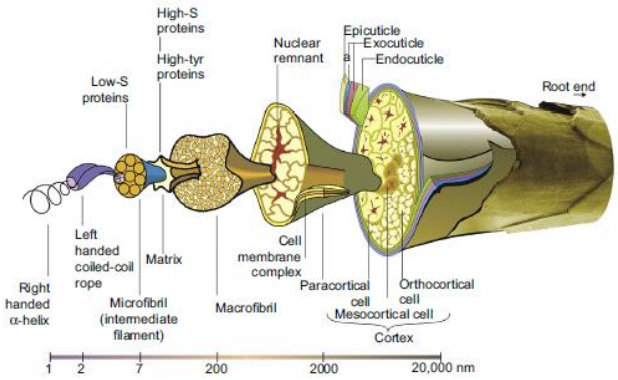


Figure 18 Structure of Wool Fiber [43]

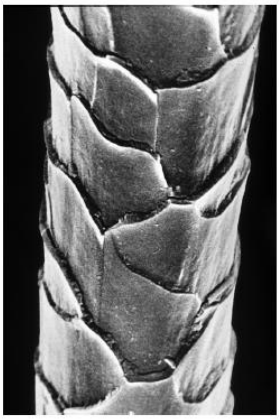


Figure 19 Scanning Electron Microscopy Image of Pure Wool Fiber [43]

2.5 Wool Fiber Properties

2.5.1 Wrinkling and Wrinkle Recovery

Hydrogen bonds and disulfide bridges in a wool fabric can be deformed by moisture, temperature and pressure during long meetings, long hour travels and the wrinkling of wool fabric become permanent with constant posture of body due to the breaking and re-arrangement of these bonds.

Wool has superior wrinkle recovery ability among most of other textile fibers. Some of the proteins in the intermediate filaments are helical and crystalline, and these give wool elasticity, resilience, and good wrinkle recovery. The wrinkle recovery properties of wool are controlled by the tensile and thermal behavior. Wrinkle recovery is highly dependent on the T_g values of conditions: recovery is poorer when wrinkles are introduced under

conditions above T_g and when recovery is obtained below T_g. In hot and humid environments where local wetting and wrinkle introduction occur simultaneously, poor wrinkle recovery of wool is still inevitable [49].

Wrinkle recovery is a time-dependent behavior, therefore if deformation time is short enough, recovery of most wrinkles will be observed rapidly. Unlike the short deformation times, wool fiber will lose some of the elastic recoverability due to stress relaxation or creep, for this reason if strong smoothing forces are not applied later, the wrinkle may never recover completely [50]. Wool's advantage over other fibers is that introduction of wrinkles during wear are easily removed by hanging a garment overnight in a humid environment. As a result, fiber matrix will be relaxed, and recovery of elastic helical proteins will be occurred [49]. However, instantaneous recovery of wrinkles in wool fabric is still highly desired by manufacturers and customers.

2.5.2 Prior Art on the Wrinkle Recovery of Wool Fabric

A wide range of studies can be found on the wrinkle recovery of wool fiber in the literature. Enhancements in the wrinkle recovery of wool fabric can be accomplished by a variety of chemical treatments and by annealing process.

Whitfiel and co-workers [51] studied several reactive urethane elastomer applications on wool surface. The polymer is introduced to the wool in an organic solvent and crosslinked by diamine separately in aqueous medium. During machine laundering, the treated wool showed better resistance to felting shrinkage with little or no alteration in the textile properties of the wool. De Boos et al. [52] reported a study on resorcinol-formaldehyde resin treatment with annealing and de-annealing processes, and their proposal was that annealed wool can be stabilized by chemical crosslinking, if cross-linking occurred faster than annealing, the wool would become stabilized in the un-annealed state. When resin treatments were applied in combination with annealing to achieve better wrinkle-recovery behavior, the effects of the resin and annealing were additive. Combination of resin treatments and annealing (before or after treatment) process showed better wrinkle-recovery than untreated wool, because the de-annealing processes were blocked by the higher cross-linked systems. Alternatively, the resin formed under annealing conditions

may have been more effective in improving wrinkle-recovery than resin formed under non-annealing conditions, independently of any annealing effects.

Leeder [53] investigated the recovery behavior of wool by crosslinking with difunctional reagents or with large amounts of polyfunctional polymers, by stabilization with reactive metal salts, and by incorporation of bulky additives which excluded H_2O from the wool structure at high humidity. Treatment with ninhydrin, benzoquinone, tannic acid, formaldehyde, glyoxal, potassium dichromate, or formaldehyde-pyrogallol copolymers increased wrinkle recovery, however formic acid decreased recovery property.

Moon and Kang [54] described a method that explains the effect of treatments with epoxide or silicone polymers, and their mixture which applied in a simple pad-dry-cure process. Each treatment contributed to the wrinkle-recovery of wool fiber by a different mechanisms. The epoxide serviced by alternating the viscoelastic properties of wool fibers and provided higher resilience, whereas silicone polymers acted mostly by reducing the frictional component of wrinkling with the thin film formation on the fiber surface. Chapman [55] explained that the polymer provides elastic connections between fibers in order to enhance the wrinkle-recovery of wool fabric.

Shishoo and colleagues [56] investigated three treatments: a) reacting wool fabric with crosslinking agent Fixapret CPN (dihydroxydimethylol ethylene urea), b) annealing i.e., heating wool fabrics at high temperature and high humidity for longer time, c) applying Synthappret LKF (an isocyanate-terminated polyurethane prepolymer) on wool surfaces. They achieved significant improvement in the wrinkle recovery of wool fabrics after heating wool at 45±1°C and 80±1% RH for at least 48 hr. Further wrinkle-recovery improvement can be a combination of annealing and Fixapret CPN or Synthappret LKF applications. Jones [57] published an article based on application of elastomeric polymers on wool surface in order to improve wrinkle recovery behavior. The most effective groups of polymers were poly(dimethylsiloxanes) and soft polyurethanes, particularly those based on poly(oxypropylene) polyols and hexamethylene di-isocyanate. A room-temperature-curing poly(dimethylsiioxane) utilizing an aminofunctional alkoxysilane cross-linking agent (Dow Corning as DC109) was applied on the wool surface, and better adhesion was observed between wool surface and chemical. The percent wrinkle-recovery value increased by increasing the polymer (DC109 or Synthappret LKF) added

on. In the same study, the flexural rigidity of the treated fabric was also reported, and like wrinkle-recovery, the flexural rigidity increased with polymer added on, however increase in flexural rigidity produced by the silicone elastomer was much less than that produced by the polyurethane. Moreover, polyurethanes showed weaker effect on wrinkle-recovery after washing, and especially dry-cleaning. Pitmann et al. [58] reported the effect of urea on wrinkle recovery of wool fibers. They found that urea can improve wrinkle recovery, raising it up to 20-25%. However, the improvement started after 7% deposition of urea on wool surface. Most improvement occurred between 7% and 10% uptake, and further additions of urea caused unacceptable handle and stiffness properties. Moreover, the urea treatment imparted stability to dry-cleaning. On the other hand, they also studied the effect of glycerol and ethylene glycol which are hydrophilic components, and they found that these compounds did not show any contribution to wrinkle recovery of wool fiber. De Boos [59] examined the effect of polyurethane elastomers in wrinkle recovery of wool fiber. Wool fabrics were treated with urethane, and their stiffness were reduced by deactivation of pre-polymer and by mixing high molecular weight polyols with urethane prepolymer prior to its application on the wool surface. This reduction was achieved without affecting the improved wrinkle-recovery. No important decrease in the wrinkle-recovery of treated fabrics occurred until 40% of the isocyanate groups had been reduced. The additives had no contributions to washing or dry-cleaning properties of the wrinkle-recovery effect induced by the polyurethane. In addition, the application of the majority of these polymers on wool surface was achieved with organic solvents, which is a huge restriction due to today's regulations.

In this thesis, silane functional, waterborne polyurethanes were specifically designed to have self-crosslinking ability with adhesion to polar surfaces and high elastic recovery in an attempt to provide a novel, environmentally friendly solution to enhance the wrinkle recovery of wool fabric.

CHAPTER 3

3. Experimental

3.1 Materials

Hexamethylene diisocyanate (HDI), polyol of ethylene glycol/adipic acid/butane diol (M_n=2000, Desmophen 1652), polyol of neopentyl glycol/adipic acid (M_n=2000, Desmophen 107-55) were purchased from Covestro (previously Bayer MaterialScience AG). Diethylenetriamine (DETA), acetone (99.5%), cyclohexyl isocyanate (CHI) were purchased from Aldrich Chemical Corporation. 3- isocyanatopropyltriethoxysilane (A-Link 25, IPTES) was kindly donated by Momentive Performance Materials. Sodium 2-[(2-aminoethyl) amino] ethanesulphonate (Vestamin A-95, AEAS) was kindly donated by Evonik Industries. All materials were used as received.

3.2 Synthesis Waterborne, Branched, Functional Polyurethane Dispersions (HBPUDs)

In this study, HBPUDs were synthesized via oligomeric A_2 + B_3 approach which was described in CHAPTER 2, the synthesis route contains mainly five steps: a) preparation of the polyurethane pre-polymer, b) emulsification, c) branching, d) functionalization and e) dispersion and distillation.

Synthesis of a series of functionalized HBPUDs was conducted in 500mL & 1L four-necked, round-bottomed flaks equipped with a mechanical stirrer, thermocouple, reflux condenser, and addition funnel. The reaction temperature was controlled by a temperature controller attached to the thermocouple and heating mantle.

a) Preparation of the polyurethane pre-polymer

A pre-calculated amount of polyester polyol was charged into the dried 500mL four-necked round-bottomed that was equipped with an overhead stirrer, reflux condenser and thermocouple that was connected to a heating mantle to control the reaction temperature. The polyol was dewatered by applying vacuum (~2 mbar) for 15 min, at 75 – 85 °C. Upon the removal of vacuum, the temperature was set to 60 °C, HDI was slowly added into the reaction flask, and the reaction was stirred for 3h at 80°C. The synthesis of NCO-

terminated prepolymer was monitored by FT-IR spectroscopy based on a decrease in the NCO (isocyanate) signal at 2260 cm^{-1}, and appearance of urethane carbonyl (C=O) peaks at 1711 cm^{-1}. NCO content of the reaction mixture during the prepolymer process was monitored by the back-titration method (ASTM D2572-97) and the completion of the reaction was verified when measured NCO content was equal to or below the theoretical NCO value. Upon the completion of the prepolymer reaction, the reaction temperature was set to 60 °C and the NCO-terminated PU prepolymer was dissolved in acetone to obtain a prepolymer concentration of 35-40 wt% at 48 °C.

b) Emulsification step

Following the prepolymer synthesis, 15% aqueous solution of the pre-calculated amount of the ionic monomer, AEAS was fed into the reaction mixture at 48 °C to form the anionic A_2 oligomer.

c) Functionalization Step

End-group Functionalization & Self-crosslinking mechanisms

Upon the completion of the branching step by slow addition of the ionic A_2 oligomer into B_3 monomer solution, amino-functional, branched, waterborne PUDs were obtained.
In order to obtain urea functionalized PUDs, a pre-calculated amount of CHI compound was added dropwise into the reaction mixture immediately after the branching step at 48°C.
In order to obtain silane functional PUDs, a pre-calculated amount of IPTES compound was added dropwise into the reaction mixture immediately after the branching step at 48°C.

d) Dispersion and distillation step

Fourier transform infrared spectroscopy (FT-IR) was used to monitor all reaction steps of polymerization, to identify specific peaks of polyurethane dispersion. It is awaited to be completely disappeared or negligible of NCO stretching vibration band (~2260 cm^{-1}) for water addition (distillation) step. During the distillation period, distilled water was slowly

added at high stirring rate into the reaction mixture to disperse PU chains while cooling the mixture to 42°C. Finally, acetone was removed from the reaction mixture by vacuum distillation and complete removal of acetone was ensured at 42°C, 50 mbar. If needed, solids content was adjusted to 30-35% and then the final product, waterborne polyurethane dispersion was collected by filtering through a 50-micron filtration media.

3.3 Characterization

Particle size and distribution of PUDs were determined using ZetaSizer, Malvern Instruments provided with laser diffraction and polarized light of three wavelengths detectors. Approximately 0.1 mL of PU dispersion was diluted with distilled water to an adequate concentration in the cell and measured at room temperature. Refractive index of PU and water was 1.50 and 1.30, respectively.

Polymerization reaction step was monitored using a Nicolet IS10 Fourier Transform Infrared Spectrometer equipped with an ATR system and ASTM D2572-97 titration method.

Tensile stress test of PU films was performed on a universal testing machine Zwick Roell Z100 UTM, with a load cell of 200 N, a crosshead speed of 25 mm/min and grip to grip separation was 22mm, and dog-bone shaped samples were prepared according to ASTM D1708-10 standard test method. Three to five specimens were measured, and their average stress-strain values with standard deviations were reported.

Permanent set deformation (%) results were carried out using a universal testing machine Zwick Roell Z100 UTM, with a load cell of 200 N, a crosshead speed of 25 mm/min and grip to grip separation of 22mm with dog-bone shaped samples prepared according to ASTM D1708-10 standard test method. The samples were stretched to 25%, 50% and 125% of their initial length, and then allowed to retract to zero elongation. The deformation test was repeated 9 cycles without any holding time for viscoelastic relaxation of the specimen. Three to five samples were performed, and their average stress to permanent deformation results were reported.

Thermogravimetric analysis of PU films was performed on Mettler Thermogravimetric Analyzer (TGA). Samples were heated from 30°C to 600°C with 10K/min heating rate under 50 mL/min nitrogen atmosphere.

Thermo-mechanical analyses of PU films were studied using dynamic mechanical analyzer (DMA, Mettler) with tensile mode at a heating rate 3K/min and frequency of 1 Hz in a temperature range between -75 to 150°C. The specimen size was 10mm length and 0.5 width with varying thicknesses.

Differential scanning calorimetry measurements were done using TA Q2000 DSC instrument. Samples were first heated up to 150°C at a heating rate 10°C per minute and cooled down to -120°C at the same heating rate per minute.

Gel content (%) tests were carried out by using Soxhlet extraction to calculate crosslinking degree of PU films. Toluene was selected as the extraction solvent. For extraction measurements, dried polymer (G_1) and thimble (G) were precisely weighed, the polymer was put into thimble and extracted with toluene for 24 hours. The polymer containing thimble was weighed again (G_2) after drying. To calculate the crosslinking degree (%) of PU film the following equation was applied;

$$\text{Crosslinking degree} = \text{Gel content (\%)} = [(G_2\text{-}G)/G_1] * 100$$

Scanning Electron Microscopy (SUPRA 35VP, LEO, Germany) was utilized to analyze the coated wool fabric surfaces. Samples were previously coated with gold.

Wrinkle recovery of wool fabric was analyzed according to AATCC 128 (M&S) test standard by our partner company YünSA. Fabric was cut in 28*15cm (warp and weft respectively) dimensions (Figure 20-a), and it is engaged to the plates (Figure 20-b). 3500-gram weight was applied on fabric for 20 minutes (Figure 20-c). Lastly, fabric was taken to the grading board for comparison with reference fabrics right after the test, reported as before and after 24 hours, reported as after (Figure 20-d, e). Grading scale is starting from 1 (the worst) to 5 (the best).

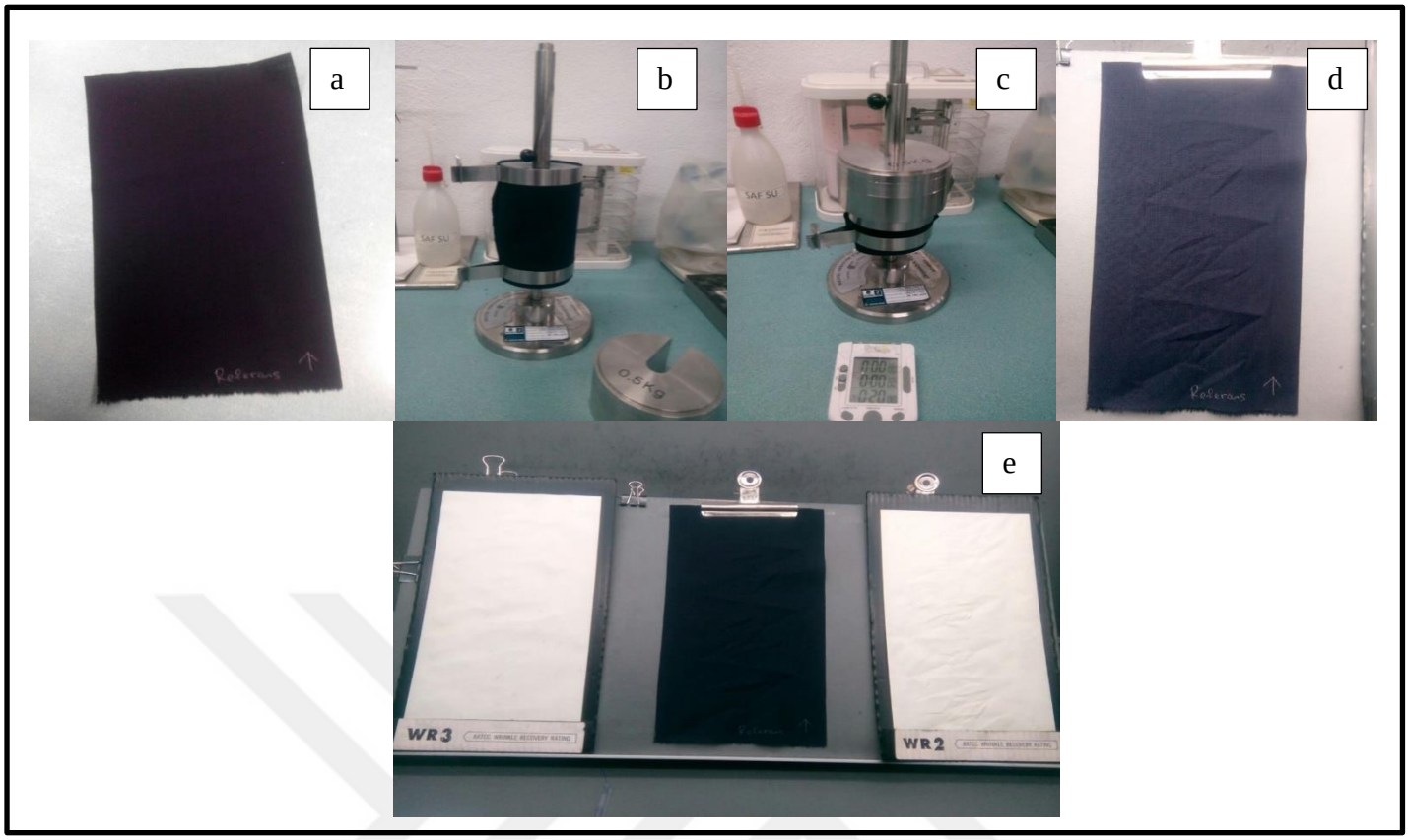


Figure 20 a) Fabric Dimensions (28*15cm), b) Fabric was Engaged to the Plates, c) 3500-gram Weight was Applied on Fabric for 20 minutes d) Fabric was Hanged on Grading Board e) Fabric was Compared to References

CHAPTER 4

4. Results and Discussion

4.1 Synthesis of Functional, Branched Waterborne Polyurethane Dispersions (PUDs)

This thesis focuses on the development of novel synthetic methodologies for chemically functional, branched PUs in the form of waterborne dispersions for textile coating applications. For this purpose, step growth polymerization which termed as A_2+B_n ($n>2$) strategy was applied to obtain waterborne, highly branched PUDs (HBPUDs). By using this strategy, highly branched polyurethanes with multitude functional groups were designed and obtained as demonstrated in Figure 21. Following the typical PU prepolymer synthesis with an NCO: OH ratio varying between 1.80-2.00 in our syntheses, the prepolymer was dissolved in acetone and then an ionic group was incorporated into the prepolymer backbone in the emulsification step. During the emulsification step, the ionic monomer was dissolved in water/acetone mixture during the addition into the PU chain to avoid formation of imine as a result of the reaction between amine and acetone as shown in Figure 22. In this study, AEAS was used as the ionic diamine monomer during the synthesis of PUDs, which possesses two amino-and a sodium sulfonate ionic group per molecule as depicted in Figure 23. AEAS acted as a chain extender due to the presence of excess isocyanate end-groups of PU prepolymer with respect to amine groups of the ionic monomer and as a result, ionic groups were attached along polymer chains of branched, functional, waterborne polyurethane dispersions in order to act as internal emulsifying agent. It is important to construct the PU backbone with ionic compounds to achieve enough hydrophilicity for water dispersibility, yet, once dried, corresponding films or coatings need to be hydrophobic and water resistant for a wide range industrial application. Therefore, the content of ionic compound in the polyurethane chain is a most critical parameter to control the particle size and distribution of PUDs and achieve a good balance of hydrophilicity/hydrophobicity. In this study, the SO_3 content was kept between 1.50 and 1.90 wt% with respect to the polymer backbone for optimum water dispersibility based on previous studies [60].

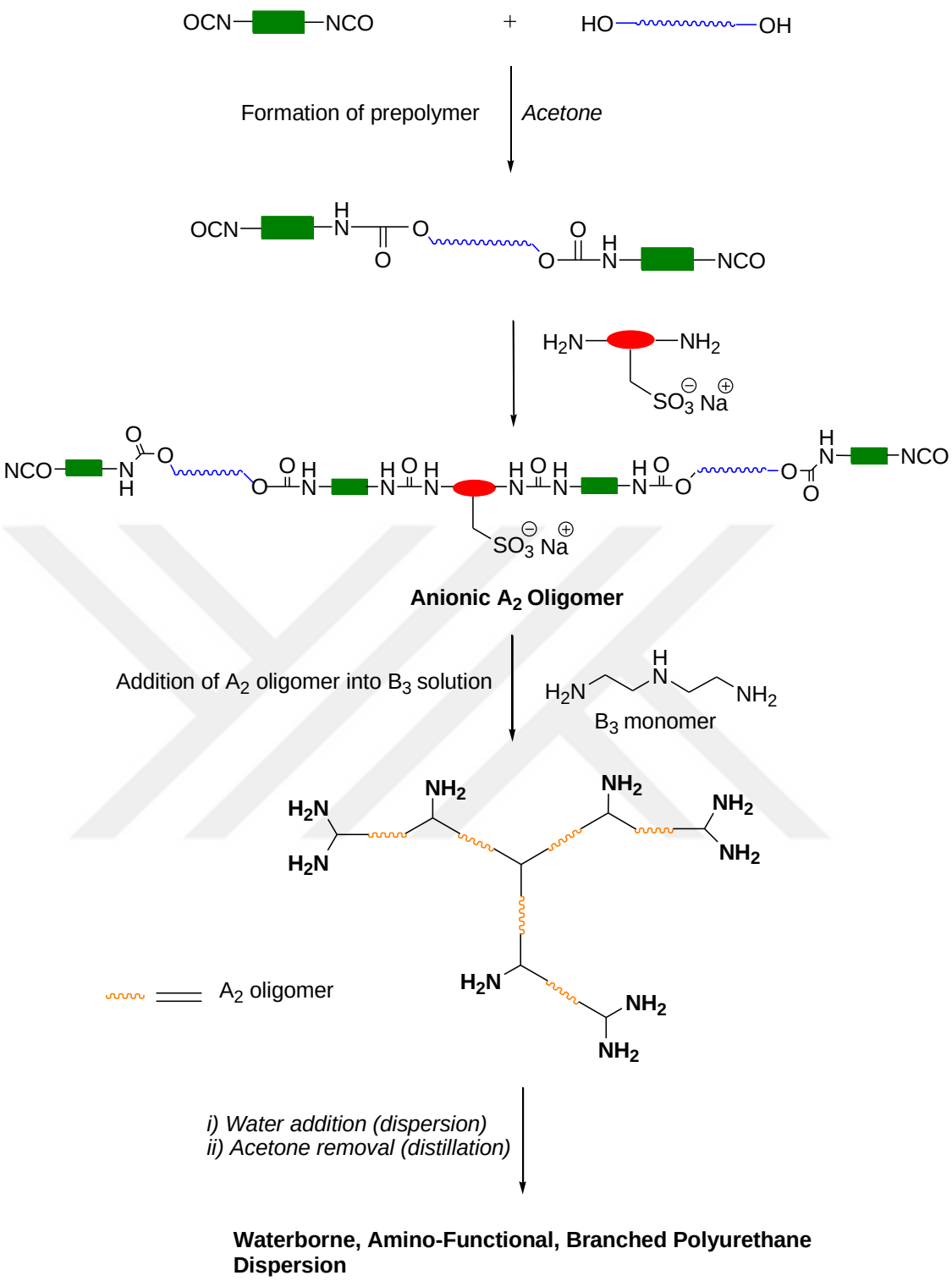


Figure 21 Synthesis of Waterborne, Amino-Functional, Branched PUDs via oligomeric A_2+B_3 approach

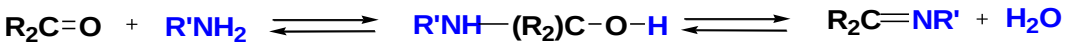
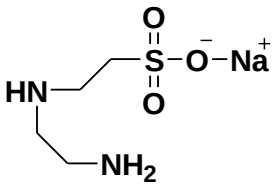


Figure 22 Formation of Imine Compound



Sodium 2-[(2-aminoethyl)amino)ethanesulphonate

Figure 23 Chemical Structure of Ionic Compound

In our study, highly branched, functional and waterborne PUDs were prepared via the oligomeric A_2+B_n (n>2) methodology where B_n was used as a branching agent, so called tri-functional amine (B_3), and reacted with A_2 type oligomers made of NCO-terminated polyester polyols. Then, branched PU polymers were synthesized without any gelation by controlling the ratio of the A_2: B_n molecules (thus A: B groups), which was critical, as marked in Table 1 previously. B_3 solution is prepared by charging distilled water, acetone and tri-functional branching agent, diethylenetriamine (DETA, Figure 24), into 1L dried, four-necked round-bottomed flask equipped with mechanical stirrer, reflux condenser, and thermocouple that was connected to a heating mantle in order to control the temperature. Following the synthesis of the ionic A_2 oligomer, a pre-calculated amount based on the desired A_2:B_3 ratio was transferred into an addition funnel and slowly added into the B_3 monomer (DETA) solution dropwise. Water was again used to prepare the B_3 solution to avoid imine formation with acetone upon the A_2 oligomer addition. During this period, the temperature was kept constant at 48°C.

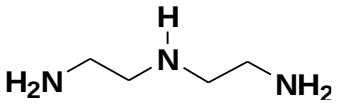


Figure 24 Chemical Structure of Tri-functional Branching Agent, Diethylenetriamine (DETA)

Upon completion of A_2 addition into B_3 solution, by following dispersion and distillation steps amino-functional HBPUDs were obtained. To achieve better mechanical properties for corresponding coatings as well as better adhesion to surface and chemical resistance, end-group functionalization and crosslinking strategies were critically developed for designed HBPUDs. Starting from HBPU-amine, amino-functional HBPU, which was initially obtained, firstly, end-group termination with mono functional isocyanate compound, CHI (Figure 25-a) was achieved immediately after the addition of A_2 oligomer into B_3, to form HBPU-urea. Secondly, amino-end-groups were reacted with 3-isocyanatopropylethoxysilane (IPTES, Figure 25-b) to form silane terminated PUs, HBPU-silane. End-group functionalization strategies developed and used throughout this study were summarized in Figure 26. Following the dispersion and distillation steps, corresponding dispersions were obtained. As discussed earlier, once they are exposed to moisture and heat triethoxysilane end-groups were expected to undergo hydrolysis and condensation reactions. Thus, a self-crosslinking mechanism was envisioned for HBPUD-silane samples during the film formation stage to yield crosslinked PU films or coatings as depicted Figure 27. Alternatively, HBPUD-amine samples were mixed water dispersible polyisocyanates (schematically depicted in Figure 25-c) prior to the coating application or film casting to produce crosslinked thermoset PU films by a two-component system (Figure 28).

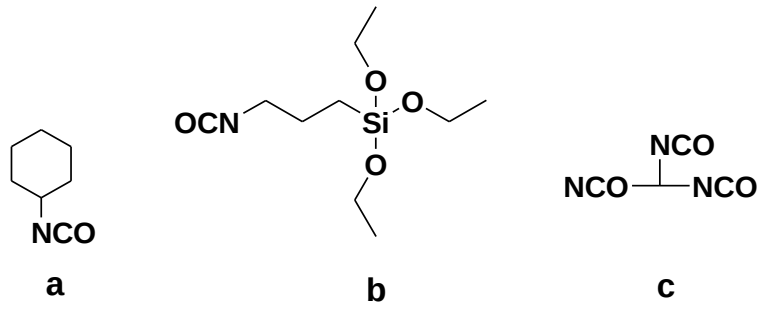


Figure 25 a) Cyclohexyl isocyanate (CHI) b) 3-isocyanatopropylethoxysilane (IPTES) c) Water-dispersible Polyisocyanate

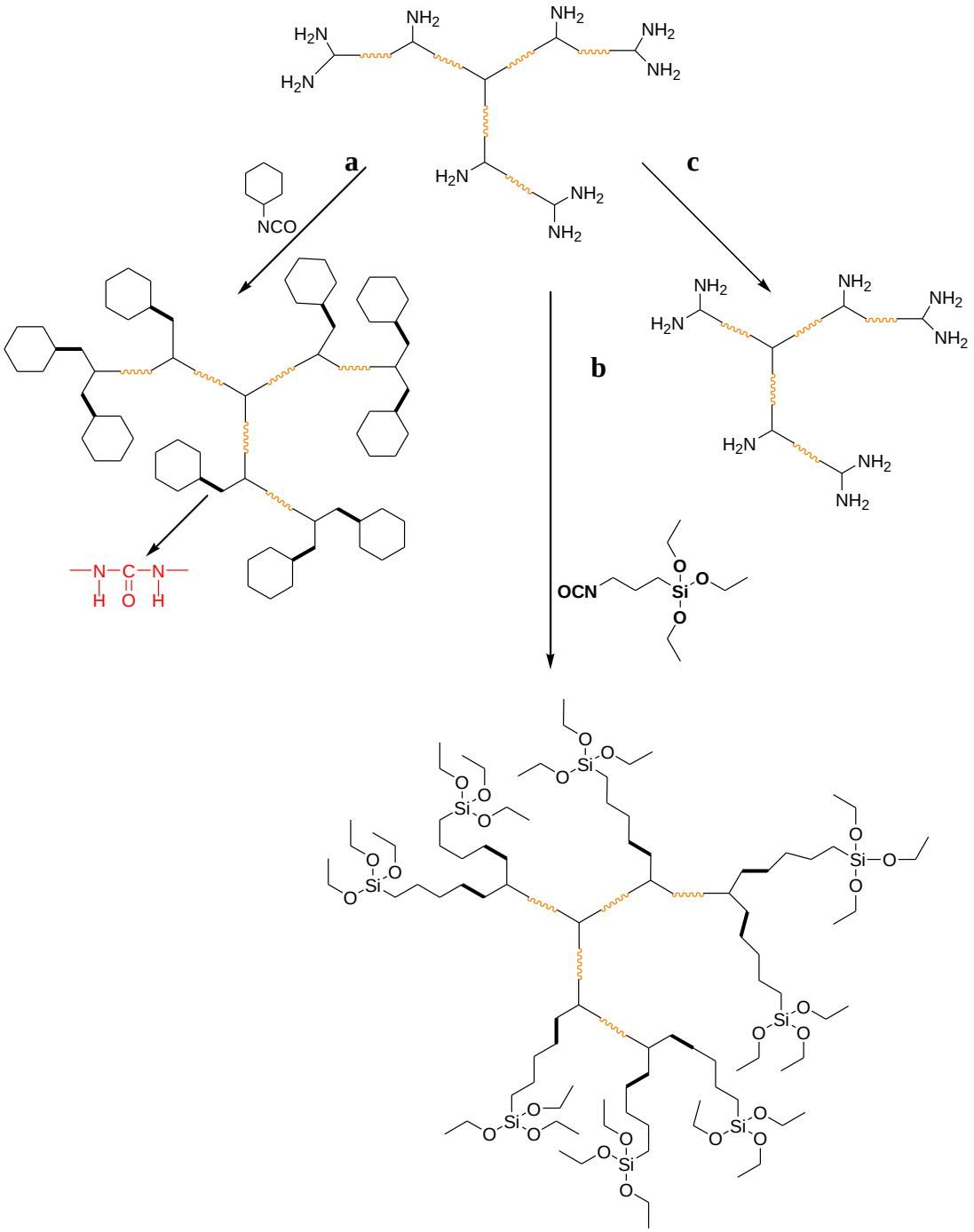


Figure 26 End-group Functionalization Strategies to obtain (a) Non-crosslinking HBPU-urea, (b) Self-crosslinking HBPU-silane, (c) HBPU-amine suitable for two component crosslink

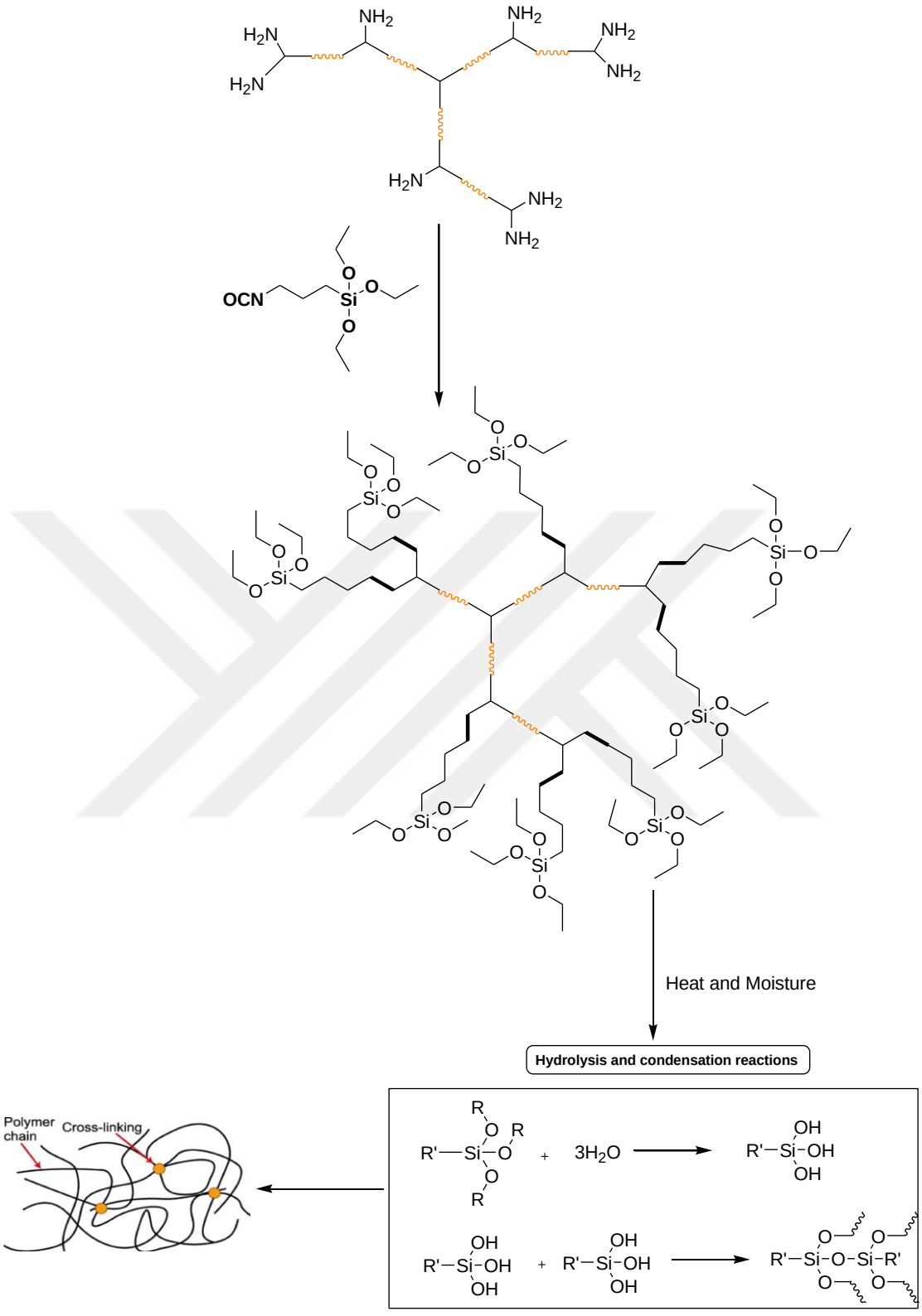


Figure 27 Self-Crosslinking Mechanism of HBPU-silane

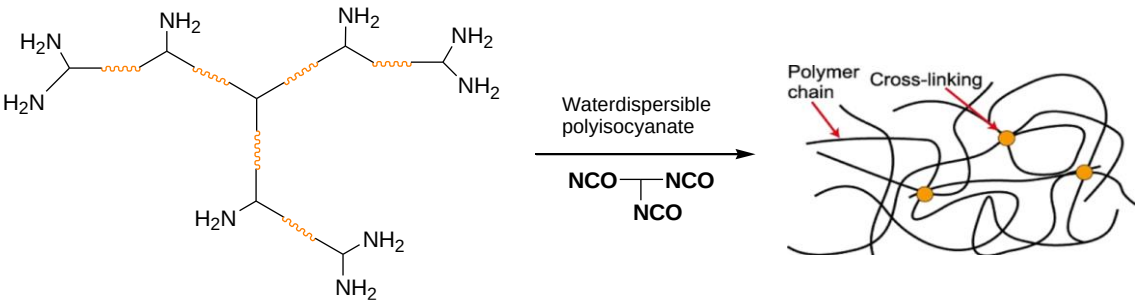


Figure 28 Crosslinking Mechanism of HBPU-amine with Water dispersible Polyisocyanates in a Two-component System

To achieve gel-free and homogeneous PU dispersions, the order and rate of monomer addition were significant parameters. In general, a slow addition of A_2 into B_n monomer in dilute solution avoids premature gelation. Determination of the gel point is critical to achieve a good balance of molecular weight/thermo-mechanical properties and branching/functionality. Therefore, functional, branched, PUDs were prepared in this thesis based on the slow addition of oligomeric A_2 into B_3 monomer. In a conventional polymerization strategy used for the synthesis of step-growth polymers, all reactants are charged into the reactor at once in the beginning of the reaction. However, isocyanates are highly reactive and they are sensitive to moisture either from solvents or humidity. Determination of optimum reaction time for A_2 + B_3 polymerization was critical to avoid reaction between isocyanate and water, which was used as a co-solvent for ionic monomer addition in small amounts to prevent amin-acetone reaction to form imine. For this purpose, the change in the NCO concent of the A_2 oligomer in acetone and water mixture at 5:1 ratio was examined at two temperatures, room temperature and 48 °C. As shown in to Figure 29, the undesired isocyanate consumption (NCO%) due to possible reaction with water present in the A_2 oligomer and B_3 monomer solution was minimized with less than 5% loss for up to 10-15 minutes, which is adequate for desired A_2+B_3 polymerization reaction. It is clearly seen in Figure 30 that no precipitation due to excess urea formation as a result of the isocyanate-water reaction takes place in the A_2 oligomer solution for up to 60 minutes.

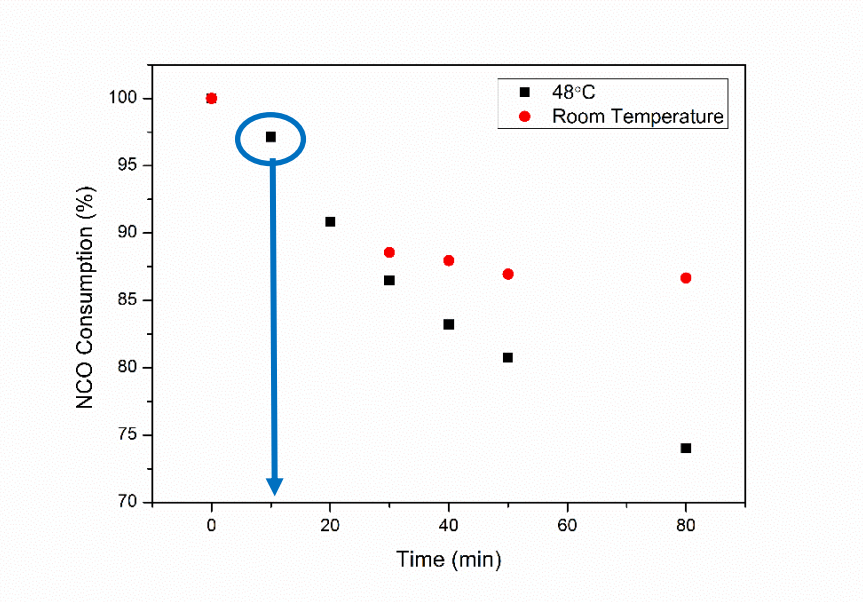


Figure 29 Change in the NCO Content of the A_2 Oligomer in Acetone:Water=5:1

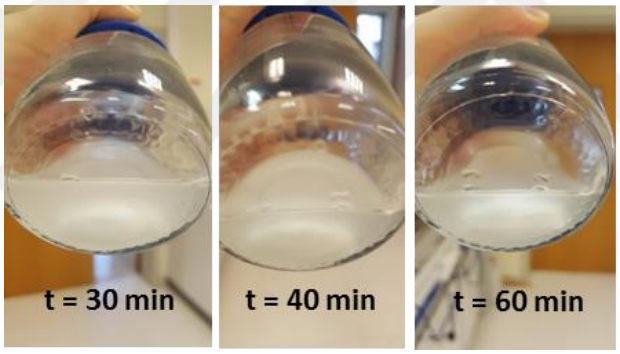


Figure 30 No Precipitation was Observed in the A_2 Oligomer Solution

In the oligomeric A_2+B_3 approach performed in this study, to synthesize NCO-terminated prepolymer prior to reacting with ionic compound AEAS in acetone, the temperature was maintained at 80°C. The whole reaction was monitored and followed by FT-IR spectroscopy (Figure 31) due to complete disappearance of isocyanate peaks at 2260 cm^{-1} and appearance of urea peaks at 1655 cm^{-1}. In this synthesis, acetone used in waterborne PU preparation to dissolve the PU polymer and assist in the emulsification step, which was then easily removed from the polymer/water mixture under vacuum upon the completion of the polymerization and dispersion.

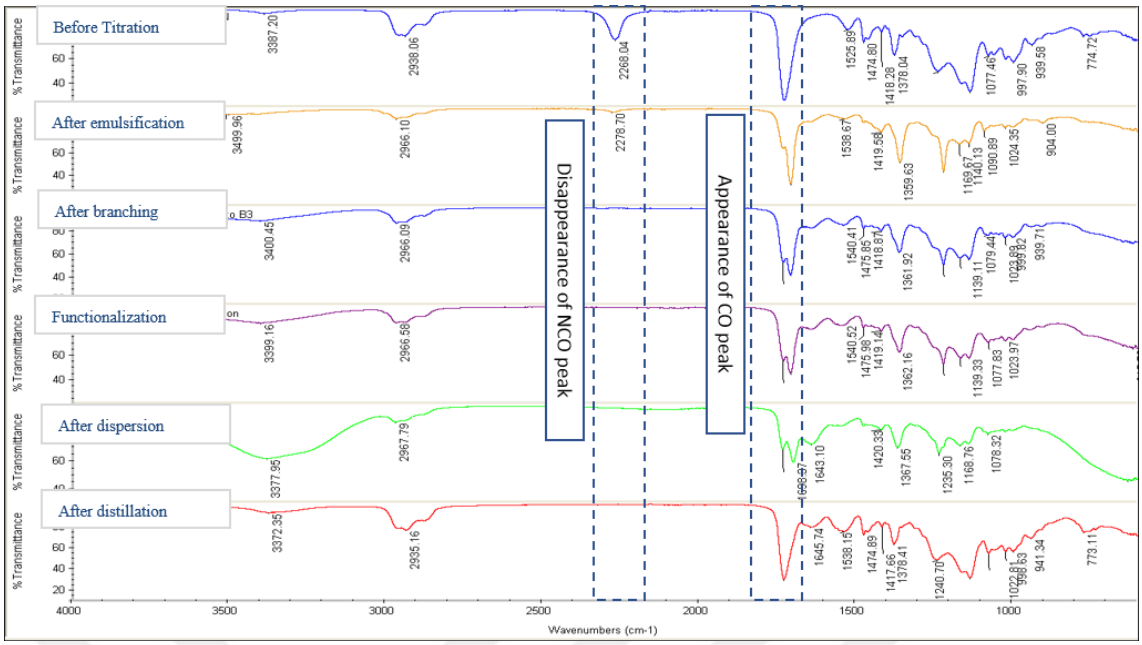


Figure 31 HBPU-silane (A_2:B_3=0.85) Polymerization Followed by FT-IR Spectroscopy

In the oligomeric A_2+B_3 polymerization approach, three structural parameters that have a pronounced effect on final PUDs and their corresponding PU films were studied in this thesis: A_2:B_3 ratio, polyol type and end-group type.

4.1.1 The effect of A_2:B_3 ratio on PUDs and their PU films

Although general pattern of the synthesis approach was clearly demonstrated Figure 21 and discussed above in detail, gel point determination as a function of A_2 oligomer addition is a critical point to achieve a good balance of thermo-mechanical properties and functionality in A_2 + B_3 polymerization. In addition, premature gelation issues are expected to be avoided by working below the critical A_2:B_3 ratio. Firstly, the principles of A_2 + B_n approach was recalled in order to obtain highly branched polymers with multitude of functional end groups and controlled distance between branch points as discussed in Chapter 2 in detail. In the theory of Flory, in the beginning of the reaction all monomers were charged into the mixture, and assuming no side reactions, the critical monomer conversions can be calculated by using Equation 1 and Equation 3 at gel state. Although these equations are based on the assumption that all monomers were charged at

the same time, it was presumed that they would be applicable to the slow addition of A_2 into B_3 due to fast reaction between isocyanate and amine groups. In our study, tri-functional monomer was used as a branching agent (B_3), and in the presence of B_3 α_c that is the probability of branching for gelation becomes 0.50 for an A_2+B_n polymerization as calculated from Equation 3. In our A_2 + B_3 system, the gelation was expected to occur occur when 57.7% of the B_3 monomer or 86.6% of the A_2 oligomer has reacted, which can be presumed that when 86.6% of the A_2 oligomer is added into B_3 monomer [30]. In Figure 32, the gel point determination was clearly illustrated for our case. By increasing A_2 amount into B_3 from the line left to right, branching increases with an increasing viscosity. Gel point was visually detected by a sudden increase in viscosity during A_2 addition into B_3 and confirmed by insoluble species in the reaction mixture. At this point, the critical A_2 oligomer amount to reach the gel point was determined by calculating the the amount of A_2 oligomer added into B_3 from a pre-weighed solution into the addition flask, which occurred nearly at 87% A_2 addition. Upon reaching the gel point, as pictured in Figure 32, the product is useless for coating applications. On the other hand, a more controlled topology during the polymerization is provided from slow addition of A_2 onto B_n. By using this method, the formation of side reactions and the risk of gelation during the reaction will be also limited, because the stoichiometric balance of reactants will be controlled throughout the polymerization. To achieve gel-free polymer, A:B ratio should be much more lower than the critical value shown in Table 1. When A: B ratio close to that of the critical ratio, slow addition of A_2 into B_n even in dilute solution might be necessary to control topology and to avoid undesired gelation.

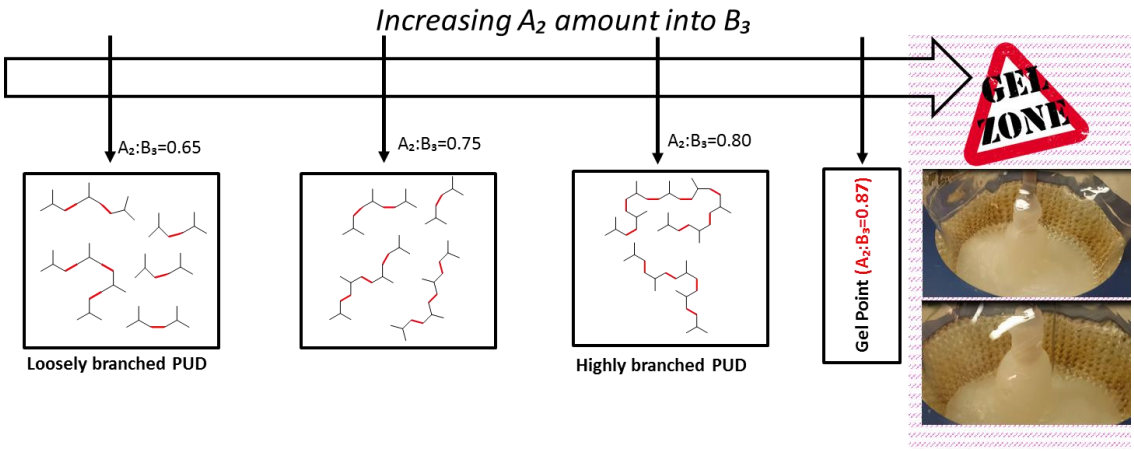


Figure 32 Illustration of the Gel Point Determination

It is important to note that, molecular weight has a critical effect on mechanical properties of PUDs films. We first investigated effect of A_2:B_3 ratio on mechanical behavior of HBPU-urea films. HBPUD-urea samples were synthesized via A_2+B_3 approach with three different A_2:B_3 ratios and end-group functionalization was achieved with cyclohexylisocyanate (CHI) as previously shown in Figure 25. According to Figure 33, neither of films showed elastomeric behavior, however, increasing A_2:B_3 from 0.80 to 0.86 resulted in slightly increased tensile strength at break with similar Young's Modulus values as summarized in Table 4. It should be noted that HBPU-urea films with the ratios of A_2:B_3 = 0.80 and 0.83 respectively, did not break at any point even up to 2000% elongation. These results clearly show that an effective crosslinking mechanism is necessary for such HBPUDs to be useful in coating applications.

Table 4 Summary of the Properties of HBPUD-urea Samples and Their Films

Sample #	HBPU-urea A_2:B_3=0.80	HBPU-urea A_2:B_3=0.83	HBPU-urea A_2:B_3=0.86
Hard Segment, %wt	23	23	23
NCO/OH ratio	2	2	2
Ionic Content, %	1.81	1.81	1.81
Solids, %(w/w)	32	32	32
Z-Average (d.nm)	425	259	432
A_2:B_3	0.80	0.83	0.86
Tensile Strength at break, Mpa	0.2±0.004*	0.5±0.01*	0.85±0.03
Strain %	2168.98 ± 0.11	2168.98 ± 0.11	1688.54 ± 26.45
Young Modulus, MPa	1.49±0.16	2.05±0.15	2.36±0.21
Polyol: AA/NPG, Diisocyanate: HDI			

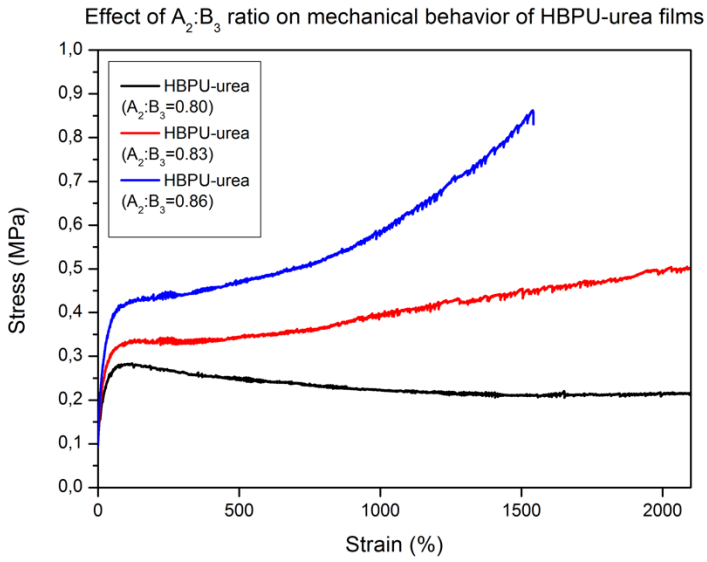


Figure 33 Mechanical characterization of HBPU-urea films with different A_2:B_3 ratios

The effect of A_2: B_3 ratio was also found to be more critical in HBPU-silane films obtained from HBPUD-silanes with 0.75 and 0.85 A_2: B_3 ratios as summarized in. As shown in Figure 34, if A_2: B_3 ratio decreased 0.85 to 0.75, corresponding self-crosslinked coatings were stiffer and less flexible, which was due to lower initial molar mass of branched PU, resulting in higher degree of crosslinking and stiffer PU network, which was confirmed by higher Young's modulus of HBPU-silane at A_2:B_3=0.75 in Table 5. Both HBPU-silane films showed very high gel contents, which confirmed that the hydrolysis and condensation stages of of silane groups successfully occurred to obtain self-crosslinked films and coatings as discussed in Figure 27.

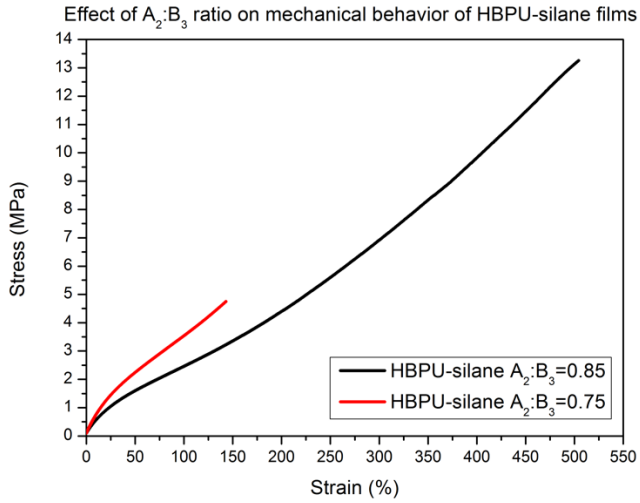


Figure 34 Mechanical Characterization of HBPU-silane Films with Different A_2:B_3 Ratios

Table 5 Summary for the Properties of HBPU-silane PUDs and Their PUDs Films

Sample #	HBPU-Silane A_2:B_3=0.85	HBPU-Silane A_2:B_3=0.75
Hard Segment, %wt	25	26
NCO/OH ratio	2	2
Ionic Content, %	1.75	1.75
Solids, %(w/w)	31	31
Z-Average (d.nm)	154	246
Gel Content %	89	91
A_2:B_3	**0.85**	**0.75**
Tensile Strength at break, MPa	12.02±1.74	4.09±0.91
Strain at break, %	460.73±61.63	117.10±36.40
Young's Modulus, MPa	6.26±0.37	8.53±0.40
Polyol: AA/NPG , Diisocyanate: HDI		

When HBPU-urea and HBPU-silane samples at different A_2:B_3 ratios are compared, it is clear that hydrolysis and condensation reactions of silane end-groups provide better mechanical properties to end-product due to the high crosslinking degree, and final mechanical properties are clearly affected by the A_2:B_3 ratio.

4.1.2 The effect of polyol structure and length on HBPUDs and their films

The chemical structure and length of the soft segment in PUs have a critical role in determining the micro-phase morphology including hard and soft segments in the final product. In general, as summarized by Yilgor et al. [61] in various studies, the soft segment molecular weight in relation with critical entanglement molecular weight (M_c) is critical. For example, in the case of poly(propylene glycol) (PPG), by keeping hard segment content of copolymers at constant value, PU samples with soft segments having number average molecular weights greater than M_c usually show higher tensile strength and lower hysteresis than those having soft segment molecular weight below M_e. Another significant report by Yilgor et. al. [62], studies the mechanical hysteresis and set behavior

of silicone-urea copolymers with similar hard segment contents but different molecular weight of soft segments using polydimethysiloxane (PDMS-3K, PDMS-11K, and PDMS-32K). As a result, when PDMS molecular weight increased, hysteresis and instantaneous set values decreased accordingly.

In this study, polyester-based polyols at were used due to. In this study, it was critical to retain other wool fabric characteristics such as color, touch, rubbing fastness, oil and water repellency, chemical resistance (dry cleaning). The effect of soft segment structure was studied with two polyols, polyester polyol of adipic acid/neopentyl glycol (AA/NPG) and polyester of adipic acid/ethylene glycol/diethylene glycol/butanediol (AA/DEG/BD/EG) due their known use in PUs for textile applications. The polyol length was kept constant at Mw of 2000 g/mol and their effect on the final properties of PUDs and their PUDs films was investigated as summarized in Table 6 and in Figure 35.

Table 6 Properties of PUDs and Their Films with Different Polyol Types Incorporated to the Soft Segment

Sample #	**HBPU-silane**	**HBPU-silane**
Polyol Type	**Adipic acid/Neopentyl glycol**	**Adipic acid/Diethylene glycol/Butane diol/Ethylene glycol**
Hard Segment, % wt	25	25
NCO/OH ratio	2	2
Ionic Content, %	1.75	1.70
Solids, % (w/w)	31	28
Z-Average (d.nm)	154	183
A_2:B_3	0.85	0.85
Tensile Strength at break, MPa	12.02 ±1.74	12.15 ±1.44
Strain, %	460.73 ±61.63	341.59 ±17.49
Young's Modulus, MPa	6.86 ±0.37	5.15±0.84

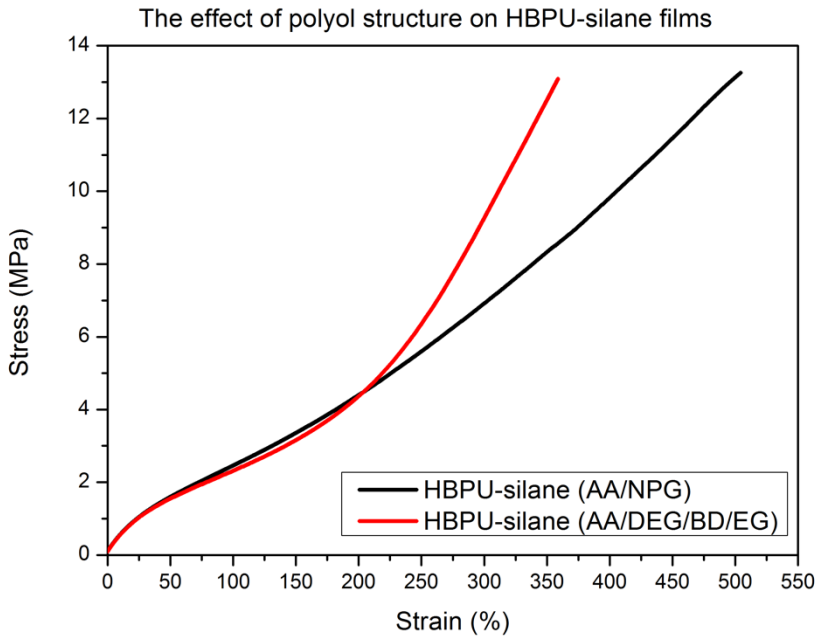


Figure 35 Mechanical Characterization of HBPU-silane Films with Polyol Structures

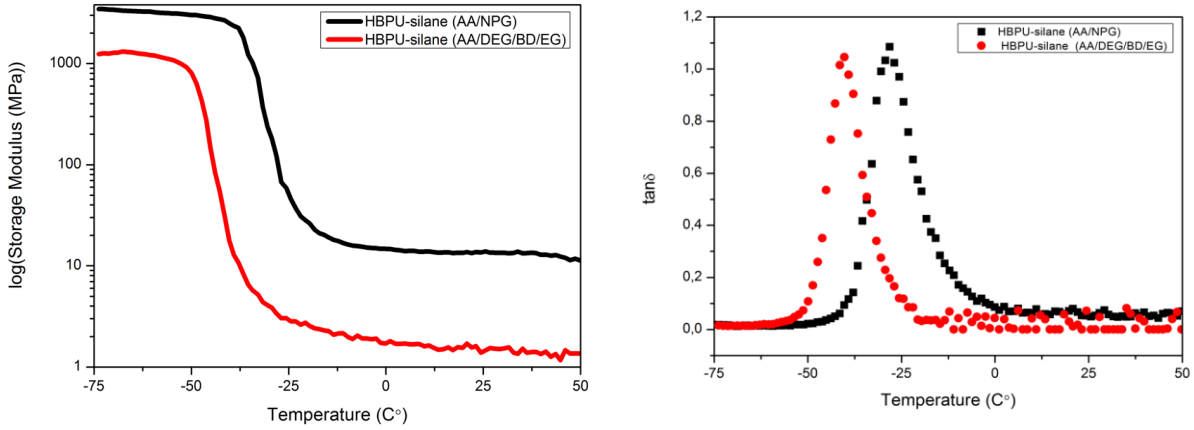


Figure 36 Thermo-mechanical Characterization of HBPU-silane Films with Polyol Structures

The chemical nature of the soft segment is known to be a key parameter for the elastic behavior of the PU films by determining the chain mobility and the elastic property. Figure 36 demonstrates the comparative DMA behavior of HBPU-silane films with different soft segment structures. and same hard segment contents. As expected, AA/NPG

based polyester polyol containing PU films resulted in slightly higher modulus values under DMA, due to the more rigid nature of AA/NPG compared to AA/DEG/BD/EG based system. AA/NPG polyester polyol based PUs showed slightly higher T_g compared to AA/DEG/BD/EG. However, stress-strain tests showed that AA/DEG/BD/EG polyol might undergo a strain-induced crystallization behavior upon elongation as shown in Figure 35. Both polyester polyols were found to be useful in this study based on these mechanical and thermo-mechanical properties.

4.1.3 The effect of functional end-group type on HBPUDs and their films

The synthesis route for HBPUD-amine products was described earlier and summarized in Figure 21 in detail. It is important to note that corresponding HBPU-amine films alone were useless due to their poor mechanical and chemical properties. Therefore, to achieve better mechanical properties as well as better adhesion to surface and chemical resistance, end-group functionalization and self-crosslinking strategies were developed. Various end-group functionalization starting from HBPU-amine were done as summarized Figure 26. First, end-group termination with mono functional isocyanate compound, CHI, to form HBPU-urea as a reference polyurethane was performed. Secondly, reaction of amino-end-groups with IPTES compound was performed to obtain silane end-groups, which can undergo hydrolysis and condensation reactions and yield self-crosslinked PU films or coatings (Figure 27). Lastly, HBPU-amine samples were mixed and crosslinked with water dispersible polyisocyanates in a two-component system, yielding crosslinked PUs (Figure 28).

As summarized in Table 7 and Table 8, a dispersion sample of each functionalized PU polymer was synthesized, while keeping all other parameters such as the A_2:B_3 and NCO:OH ratios constant. After each functionalization reaction, HBPUDs were characterized for particle size, pH and viscosity properties. HBPUD-urea dispersions resulted in the highest particle size and viscosity values, which was presumed to be due to hydrogen bonding urea end-groups. In addition, HBPUD-amine dispersions have the highest pH value because of the higher basicity of amine groups. Once amino-functional

HBPUDs were functionalized with silane groups, viscosity of dispersions slightly increased primarily due to increased urea content. (Table 8 and Figure 37).

Table 7 Properties of PUDs and Their Films with Different End-Group Functionalizations

Sample #	HBPU-Urea	HBPU-Amine	HBPU-Silane
Hard Segment, %wt	23	21	25
NCO/OH ratio	2	2	2
Ionic Content, (SO_3%)	1.80	1.85	1.80
Solids, %(w/w)	34	32	32
Gel content, %	0	0	91
A_2:B_3	0.85	0.85	0.85
Tensile Strength at break, MPa	0.01±0.005	0.0±0.37	12.02±1.74
Strain at break, %	*	788.02±35.7	460.73±61.63
Young's Modulus, MPa	1.17±0.20	1.02±0.18	6.26±0.37

Table 8 Physical Properties of HBPU Dispersions

Dispersion Sample	Viscosity (Cps)*	pH	Stability	Gel Content (%)
HBPU-urea	570	9.54	Stable	-
HBPU-amine	24	9.80	Stable	-
HBPU-silane	162	9.31	Stable	91

* Measured at 30%solids

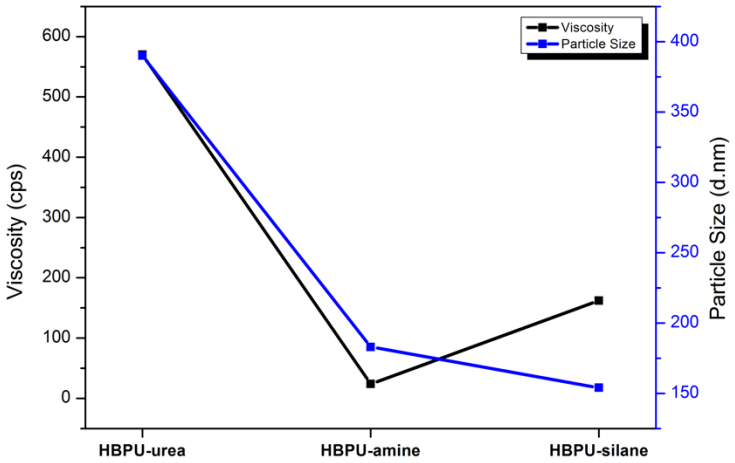


Figure 37 Viscosity vs Particle Size of HBPU-silane, HBPU-amine and HBPU-urea Dispersions

Gel content measurements give an indication of the crosslinking degree of HBPU films. As shown in Table 8, HBPU-silane films showed 93% gel content, which clearly confirmed the proposed self-crosslinking approach for PU films. As expected, HBPU-amine and HBPU-urea samples did not have any gel content.

The shelf life of HBPUD was affected by various factors which are pH, solid content, viscosity and particle size of the media. In addition, HBPUD-silane samples are prone to crosslinking on the shelf due to premature hydrolysis and condensation of silane groups in the waterborne dispersion. The HBPUDs stored at ambient medium (25°C) for 8 months were visually checked and they were all stable without any precipitation, including the HBPUD-silane sample. Moreover, pH values of dispersions were still in the basic range as reported in Table 9.

Table 9 pH values of HBPU Dispersions after 8 months

Dispersion Sample	**pH (after 8 months)**
HBPUD-urea	7.60
HBPUD-amine	8.67
HBPUD-silane	8.37

In order to confirm the successful incorporation of silane groups on polymer chain-ends, and successful hydrolysis and condensation reaction of these silane groups during the PU film formation, FT-IR analyses were performed on dispersion samples and thermoset PU films to identify silane bonds in polyurethane chains. HBPUDs-silane are usually composed of polyurethane backbone with condensable terminal groups which can undergo crosslinking mechanisms while water evaporation and film formation. These reactions led to form a stable siloxane linked network. In Figure 38, HBPU-amine and HBPU-silane films were monitored by FT-IR spectroscopy. Characteristic isocyanate (NCO) peaks were disappeared (around 2260 cm^{-1}), so all isocyanate groups were consumed at the end of reaction. The band of 1670 cm^{-1} refers to the strong carbonyl (C=O) stretching vibrations of urethane and urea groups of both HBPU-amine and HBPU-silane films. When FT-IR spectra were analyzed between 600 to 1300 cm^{-1}, Si-O stretching around 1050cm^{-1} and Si-C vibrations around 750cm^{-1} could be seen only for the HBPU-silane film as shown in Figure 39.

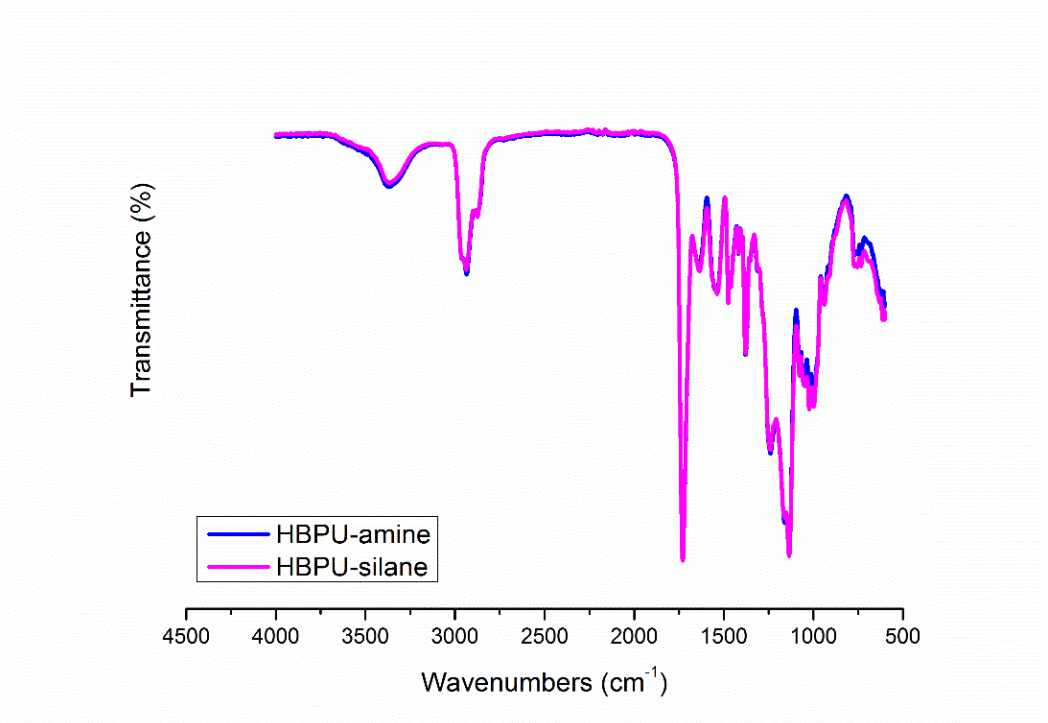


Figure 38 FT-IR Spectra of HBPU-amine and HBPU-silane films

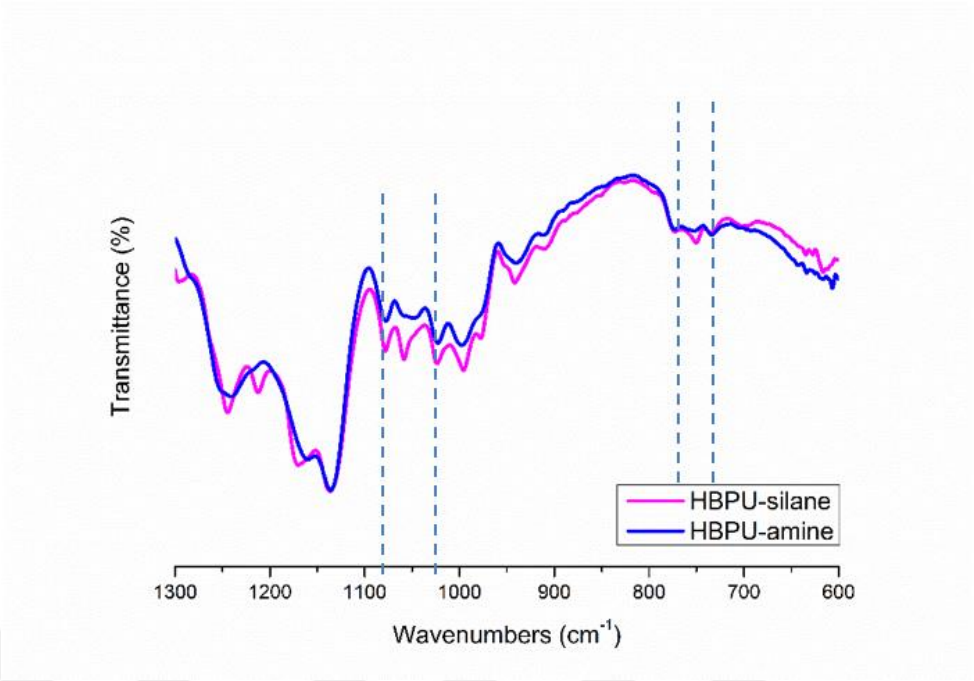


Figure 39 Short FT-IR Range of HBPU to identify silane bonds

Thermal analyses of HBPU-urea and HBPU-silane films were carried out by TGA and DSC tests. TGA analysis did not show any significant difference in the thermal stability of HBPU-urea and HBPU-silane films as shown in Figure 40. According to DSC result in Figure 41, pure AA/NPG based polyester polyol's T_g was around -49 ºC and upon its incorporation into the PU backbone, soft segment T_g was found to be significantly increased up to around -35 ºC and further crosslinking of the HBPU-silane sample did not have any effect on the soft segment T_g as the values were similar for both HBPU-urea and HBPU-silane films.

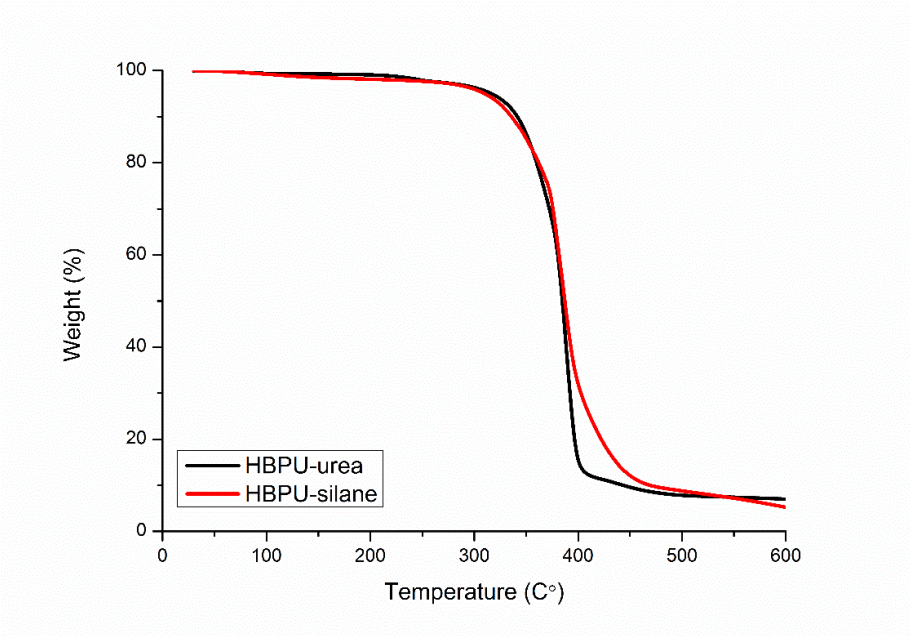


Figure 40 TGA analyses of HBPU-silane and HBPU-urea films

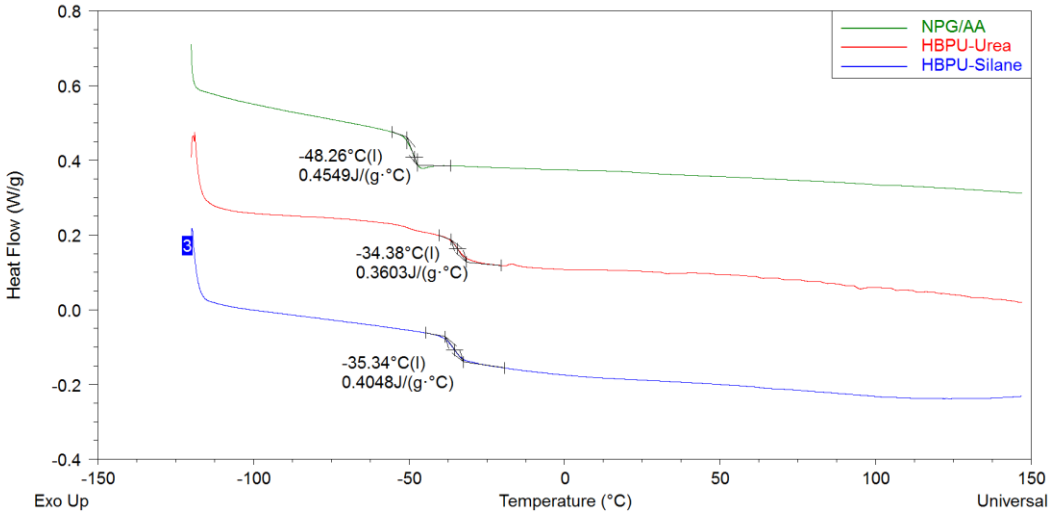


Figure 41 DSC curves of HBPU-silane, HBPU-urea films and soft segment polyol

Mechanical properties of HBPU-amine, HBPU-urea and HBPU-silane films were compared by stress-strain tests as shown in Figure 42. The stress-strain behavior of HBPU-amine and HBPU-urea shows that these samples could not make useful coatings alone as they showed very low tensile strength values. However, stress-strain behavior of

PU films dramatically change upon silane functionalization, due to the envisioned crosslinking effect that occurs during the drying and film formation stages of HBPU-silane samples. Physical recovery behavior of corresponding coatings and films was also critical for the desired anti-wrinkling effect. As shown in Figure 43, PU films from silane terminated crosslinked polymers showed significantly lower permanent set values, as low as 5% in the 9th cycle of 25% elongation compared to the urea terminated non-crosslinked PU films.

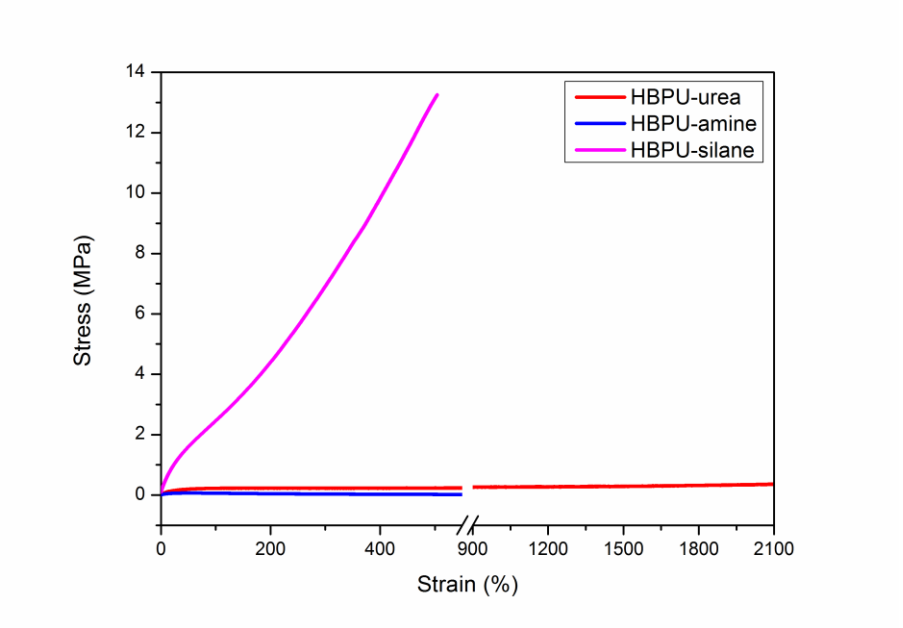


Figure 42 Mechanical characterization of HBPU-amine, HBPU-urea and HBPU-silane films

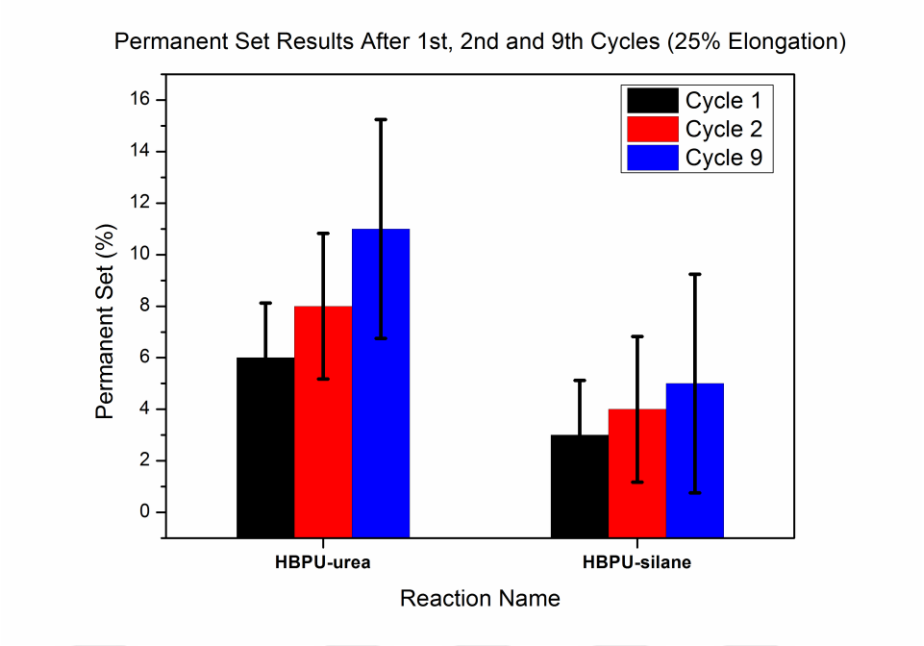


Figure 43 Permanent set test results of HBPU-urea and HBPU-silane films

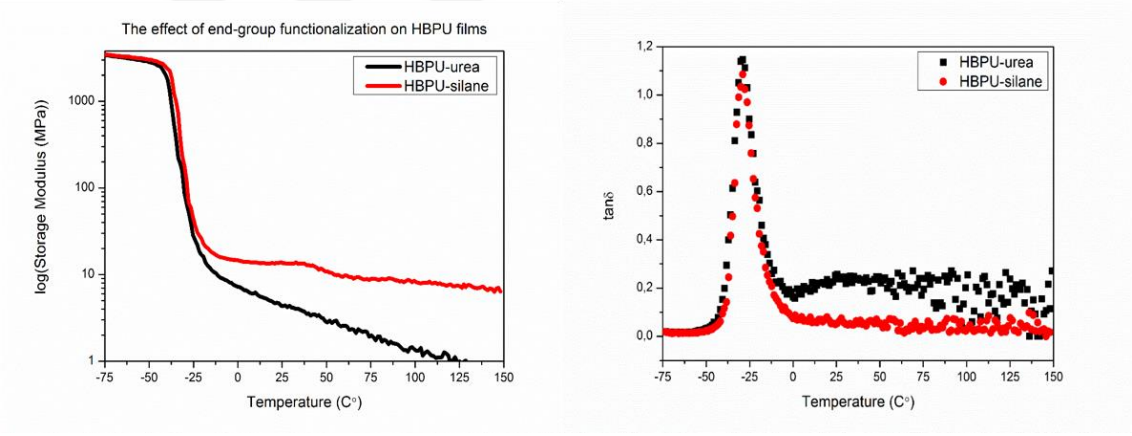


Figure 44 Thermo-mechanical characterization of HBPU-silane and HBPU-amine films

The comparison of the thermo-mechanical behavior of HBPU-urea and HBPU-silane films also clearly showed effect of silane functionalization and post-crosslinking as shown in DMA results in Figure 44 with similar soft segment T_gs, yet a longer rubbery plateau and higher storage modulus for the HBPU-silane film.

Another key crosslinking strategy that was developed and used in this study was the two-component system based on novel HBPU-amine dispersions. For this purpose, a commercially available waterdispersible polyisocyanate with a functionality of >2 was

used as the second component and mixed into HBPU-amine immediately before the film making or coating process. The effect of the polyisocyanate crosslinker amount on the mechanical and thermal properties of corresponding thermoset films was investigated by mixing various amounts of polyisocyanate (1 to 9.5 wt%) into the HBPU-amine dispersion. The degree of crosslinking was expected to increase with increasing amount of the polyisocyanate compound and as shown in Figure 45, thermoset PU films showed higher stress value with lower elongation, and they became stiffer with increasing crosslinker amount. The physical recovery behavior of PU films was also enhanced with increasing degree of crosslinking as shown in Figure 46, with permanent set values as low as 5% in the 9th cycle after 25% elongation in each cycle.

Interestingly, the interesting degree of crosslinking resulted in slight enhancement of the thermal stability of PU films as shown in TGA curces in Figure 47.

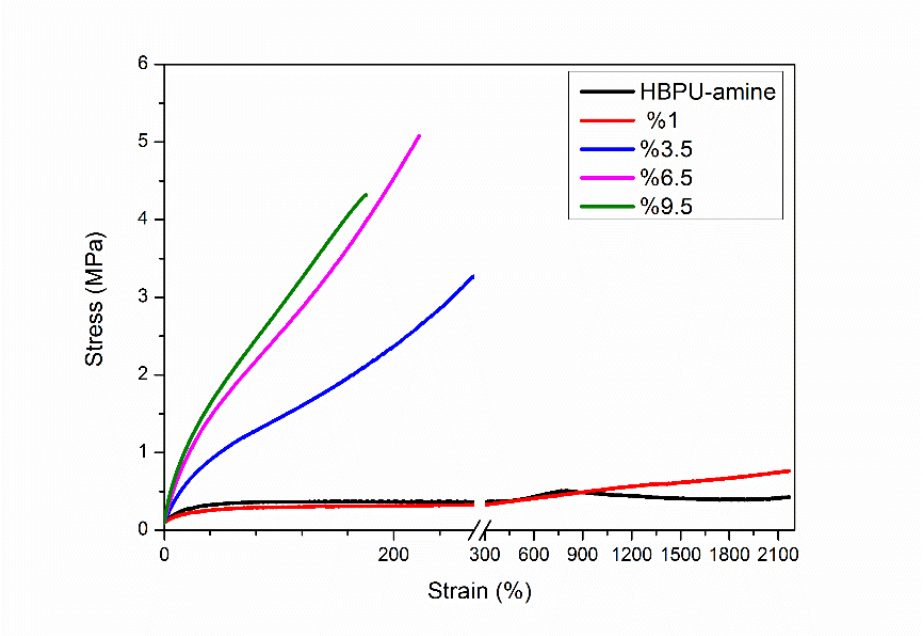


Figure 45 Stress-strain curves of HBPU-amine and its crosslinked PU films with various levels of polyisocyanate

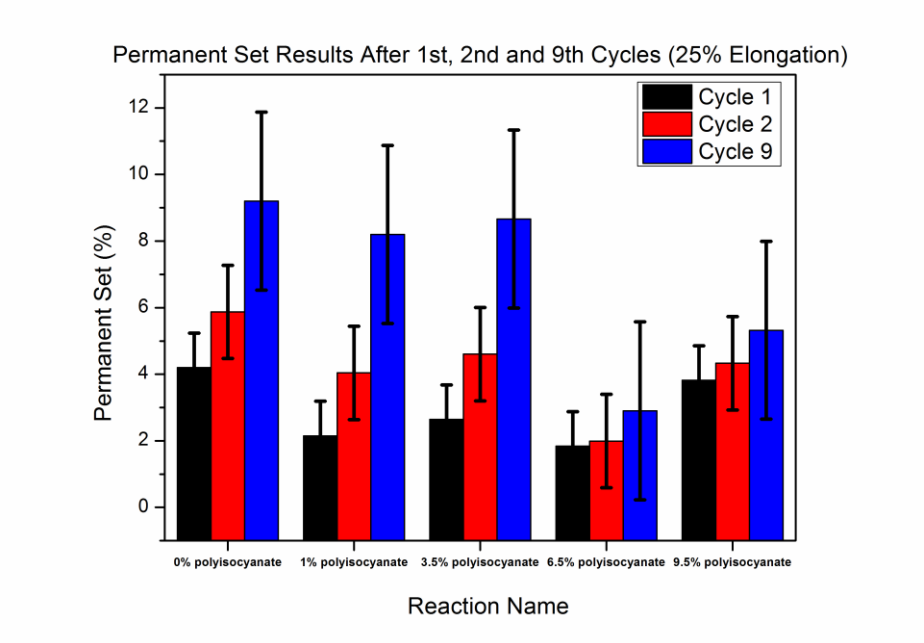


Figure 46 Permanent Set test results of HBPU-amine and its crosslinked PU films with various levels of polyisocayanate

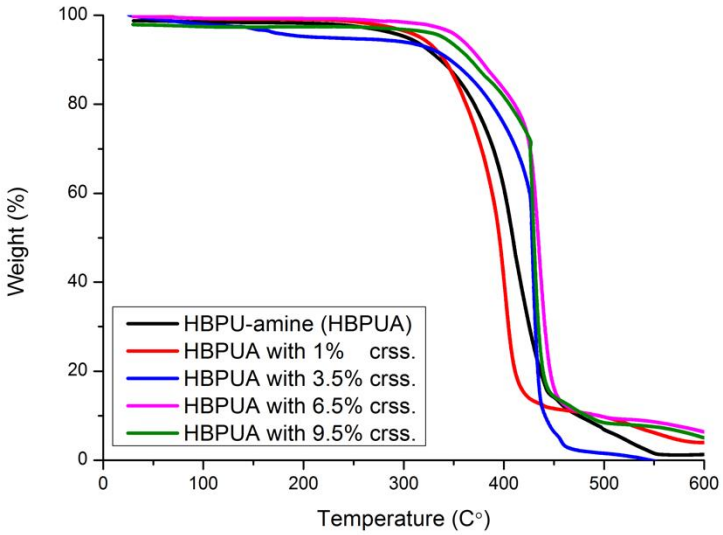
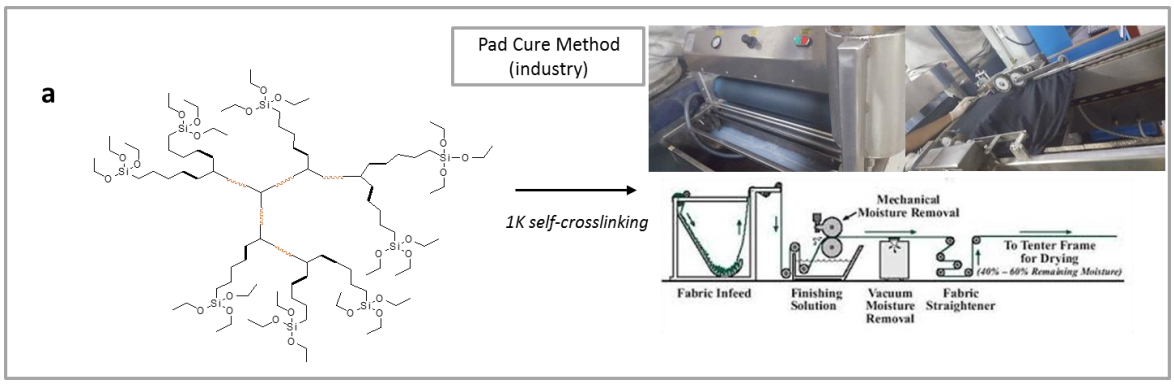


Figure 47 Thermo-gravimetric analyses of HBPU-amine and its crosslinked HBPU films with various levels of polyisocyanate

4.2 Application of HBPUDs on Wool Fabric

Following the extensive study on the synthesis and characterization of HBPU dispersions and their corresponding films, which demonstrated the development of novel self-crosslinking (HBPU-silane) or a two-component crosslinking (HBPU-amine + polyisocyanate) coatings with tunable mechanical and thermos-mechanical properties, selected dispersions were applied HBPU on wool fabric to improve wrinkling properties. Three different application procedures was utilized as shown in Figure 48: (a) Direct application of HBPU-silane or HBPU-urea dispersion on wool fabric at different concentrations, (b) Application of HBPU-silane dispersions on wool in the presence of a small amount of polyisocyanate crosslinker, (c) Application of the two-component HBPU-amine+polyisocyanate system. These coating applications were either done using the pilot pad cure line at YünSA facilities, or by mimicking the pad cure method in laboratory scale. In addition to the waterdispersible polyisocyanate, a commercially available, blocked waterborne polyisocyanate was utilized due to the limited pot life of polyisocyanate containing dispersions. Contrary to regular polyisocyanates, blocked polyisocyanates only de-block and act as crosslinkers at elevated temperatures, above 100 ºC, and thus give stable coating formulations.



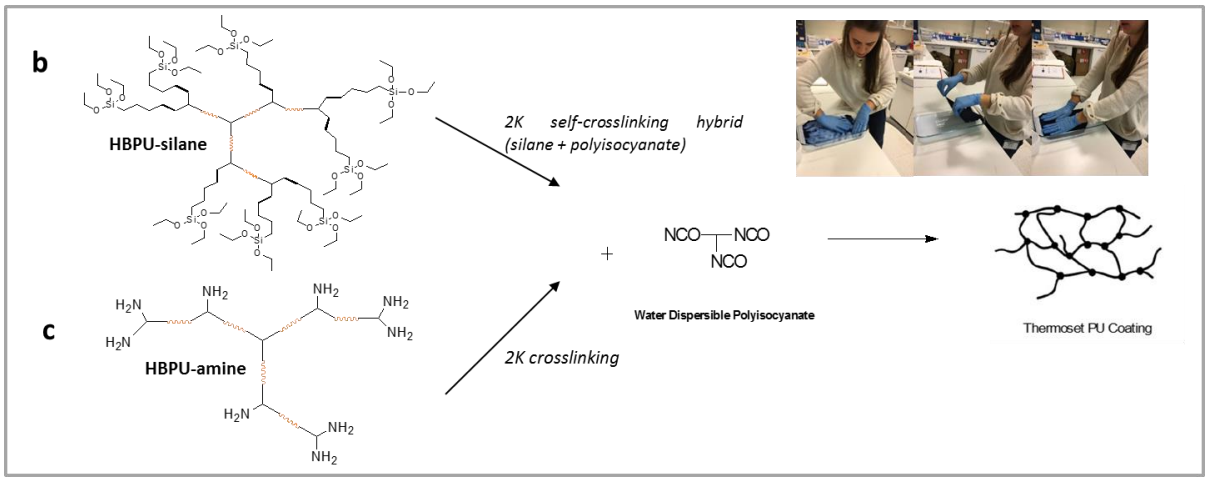


Figure 48 Application of HBPUDs on wool fabric by pad cure method in both pilot and laboratory scale

Initially, HBPU-amine with 1 wt% polyisocyanate crosslinker (with respect to solid HBPU-amine), HBPU-urea by itself and HBPU-silane by itself and in the presence of 5 wt% blocked polyisocyanate (with respect to solid HBPU-silane) were applied on wool fabric by the pad cure method in the laboratory and then the wrinkle recovery of each sample was tested by YünSA with a grading from 1 to 5 for fabric samples immediately after applying a constant weight (reported as “before”) and 24 hours later (reported as “after”). As summarized in Table 10, a half grade improvement was achieved for both HBPU-amine and HBPU-silane dispersions. Although this was a visible enhancement by evaluators, at least one grade improvement was targeted.

Table 10 Wrinkle recovery results of application of HBPUDs on wool fabric

	Wrinkle Recovery	
	Reference Fabric (100% wool)	HBPU-Amine + 1% polyisocyanate
Before	2	2/3
After	4	4
	Wrinkle Recovery	
	Reference Fabric (100% wool)	HBPU-urea (0.1% solid content)
Before	2/3	2/3
After	4	4/5
	Wrinkle Recovery	
	Reference Fabric (100% wool)	HBPU-silane + 5% blocked isocyanate
Before	2	2/3
After	4/5	4

In order to better assess the coating quality depending on the application or the dispersion concentration, wool surfaces were analyzed by SEM after coating at various dispersion concentrations using route (a) or (b). As shown in Figure 49, the PU coating was not clear on the surface of wool fabric at when HBPU-silane was applied at 0.1 wt% concentration. Upon increasing the PUD concentration from 0.1 to 1.0 wt%, the presence of a more uniform PU coating was more evident. Interestingly, when various levels of water dispersible polyisocyanate from 1 to 6 wt% with respect to the solid polymer was mixed into the HBPU-silane sample and applied at 1 wt% dispersion concentration, the coating on wool fibers became visible and uniform with increasing crosslinker, which is a sign of better adhesion of the coating on the wool surface. However, none of these samples showed any significant enhancement of the wrinkle recovery for the wool fabric.

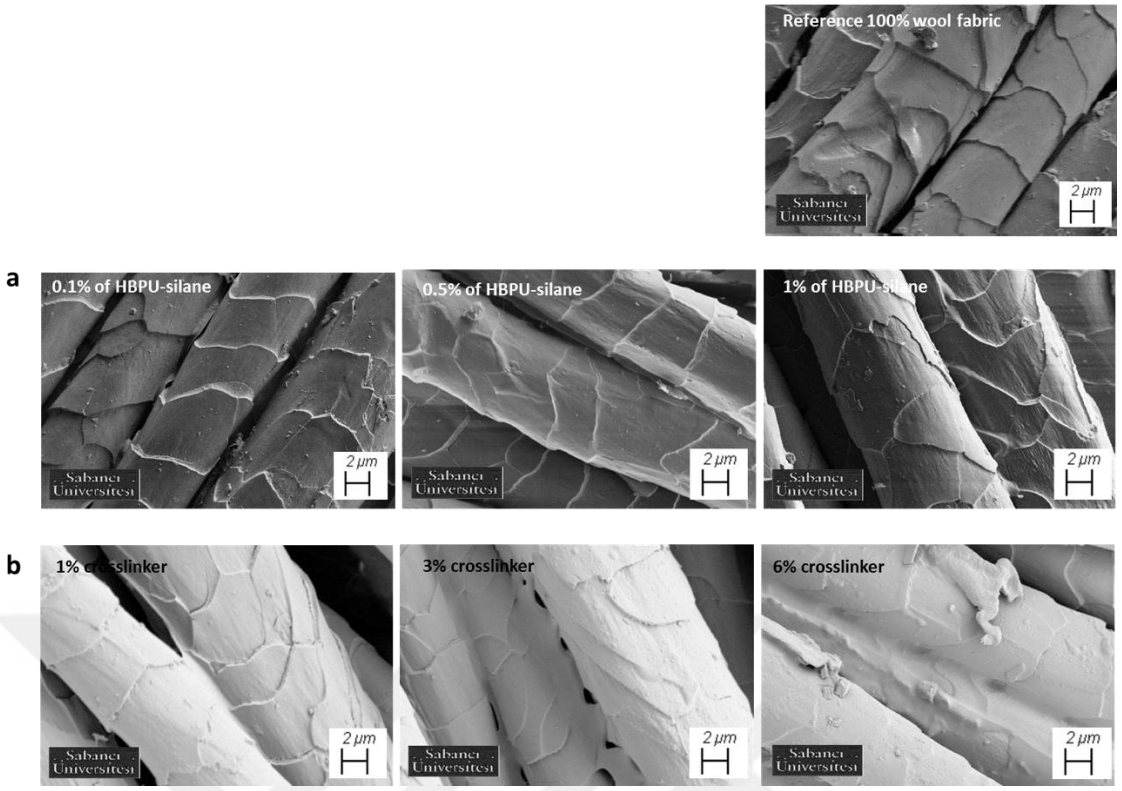


Figure 49 Scanning Electron Microscopy Analysis of HBPU Coated Wool Surfaces

As an alternative approach to enhance the degree of crosslinking and alter adhesion mechanisms, new HBPUD samples with partial silane (50%) and partial amine (50%) functional end-groups (HBPUD-amine&silane) were synthesized in order to apply on wool in the presence of polyisocyanate or triethoxysilane crosslinkers as depicted in Figure 25. The newly developed HBPUD-amine&silane was expected to result in altered adhesion to wool surface through the reaction of silane end-groups with the wool surface (residual -OH or –SH groups) and through the crosslinking or bridging role of the polyisocyanate compounds between amino-end-groups and the wool surface, forming an interpenetrating network.

During the application of HBPU-amine dispersions as well as the newly synthesized HBPUD-amine&silane with various levels of polyisocyanate crosslinker (0 to 6 wt%), a 45/55 wool/polyester blend fabric was used in addition to the pure wool fabric for the pad cure method at 10 wt% dispersion concentrations at YünSA facilities and wrinkle

recovery characterization was performed as a function of time after the removal of the weight.

Although the anti-wrinkling behavior of pure wool was not enhanced with HBPU-amine and HBPU-silane & amine, both of these coatings clearly imparted anti-wrinkling behavior to wool/polyester blend fabric with at least one grade improvement in three different post-treatment conditions as summarized in Table 11, Table 12, Table 13, Table 14, Table 15, and Table 16. It is known that polyester is the only common type of fiber that provides higher wrinkle recovery than wool. In addition, polyester does not absorb moisture and its recovery behaviors are not affected while under hot and moisture conditions [63]. In the case of HBPU coated polyester/wool fabric, in addition to advantages above, it can be presumed that the presence of polyester fibers in the wool fabric clearly enhanced the interaction of polyester-based HBPU coatings, resulting in better physical recovery compared to the uncoated polyester/wool fabric.

Table 11 Wrinkle Recovery Analysis of Wool/Polyester Blend Fabric with and without HB-PU Partial Amine and Partial Silane Coating with normal conditions of treatment (1 bar or 0,8 bar pressure, 110 °C temperature, 4 minutes)

	WRINKLE RECOVERY RESULTS				
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine & Silane (0% polyisocyanate)	HBPU- Amine & Silane (1% polyisocyanate)	HBPU- Amine & Silane (3% polyisocyanate)	HBPU- Amine & Silane (6% polyisocyanate)
0 minute	2	2/3	2/3	2/3	2/3
15 minutes	2/3	3	3	3	3
45 minutes	3	3	3	3/4	3
2 hours	3	4	4	4	4
6 hours	3/4	4/5	4/5	4/5	4/5
24 hours	4/5	5	5	5	5

Table 12 Wrinkle Recovery Analysis of 100% Wool Fabric with and without HB-PU Amine Coating with normal conditions of treatment (1 bar or 0,8 bar pressure, 110 °C temperature, 4 minutes)

	WRINKLE RECOVERY RESULTS			
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine (3% polyisocyanate)	HBPU- Amine (6% polyisocyanate)	HBPU- Amine (9% polyisocyanate)
0 minute	2	2/3	2	2/3
15 minutes	2/3	3	2/3	3
45 minutes	3	3	3	3/4
2 hours	3	4	3/4	4
6 hours	3/4	4/5	4	4/5
24 hours	4/5	5	5	5

Table 13 Wrinkle Recovery Analysis of Wool/Polyester Blend Fabric with and without HB-PU Partial Amine and Partial Silane Coating without Post-Treatment

	WRINKLE RECOVERY RESULTS				
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine & Silane (0% polyisocyanate)	HBPU- Amine & Silane (1% polyisocyanate)	HBPU- Amine & Silane (3% polyisocyanate)	HBPU- Amine & Silane (6% polyisocyanate)
0 minute	2	2	2	2	2
15 minutes	2/3	2/3	2/3	2/3	2/3
45 minutes	2/3	2/3	2/3	2/3	2/3
2 hours	3	3	3	3	2/3
6 hours	4	4	3/4	3/4	2/3
24 hours	4/5	4	3/4	4	3

Table 14 Wrinkle Recovery Analysis of Wool/Polyester Blend Fabric with and without HB-PU Amine Coating without Post-Treatment

	WRINKLE RECOVERY RESULTS			
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine (3% polyisocyanate)	HBPU- Amine (6% polyisocyanate)	HBPU- Amine (9% polyisocyanate)
0 minute	2	2	2	2
15 minutes	2/3	2/3	2	2/3
45 minutes	3	3	2/3	2/3
2 hours	3	3	3	3
6 hours	3/4	3/4	3	3/4
24 hours	4/5	3/4	3/4	4

Table 15 Wrinkle Recovery Analysis of Wool/Polyester Blend with and without HB-PU Partial Amine and Partial Silane Coating with mild environmental conditions (0,8 bar pressure, 110°C temperature, 12 minutes)

	WRINKLE RECOVERY RESULTS				
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine & Silane (0% polyisocyanate)	HBPU- Amine & Silane (1% polyisocyanate)	HBPU- Amine & Silane (3% polyisocyanate)	HBPU- Amine & Silane (6% polyisocyanate)
0 minute	2	2/3	2/3	2/3	2/3
15 minutes	2/3	2/3	3	2/3	3
45 minutes	3	3	3/4	3	3/4
2 hours	3	4	4/5	4	4
6 hours	3/4	4/5	4/5	4/5	4/5
24 hours	4/5	5	5	5	5

Table 16 Wrinkle Recovery Analysis of Wool/Polyester Blend with and without HB-PU Amine Coating with mild environmental conditions (0,8 bar pressure, 110°C temperature, 12 minutes)

	WRINKLE RECOVERY RESULTS			
Time	Reference Fabric (Wool/Polyester Blend)	HBPU- Amine (3% polyisocyanate)	HBPU- Amine (6% polyisocyanate)	HBPU- Amine (9% polyisocyanate)
0 minute	2	2/3	2/3	2/3
15 minutes	2/3	3	3	3
45 minutes	3	3/4	3/4	3/4
2 hours	3	4	4	4
6 hours	3/4	4/5	4/5	4/5
24 hours	4/5	5	5	5

CHAPTER 5

5. Conclusions

Novel branched, functional and waterborne polyurethane dispersions were designed and synthesized via the oligomeric A_2+B_3 polymerization approach. To obtain highly branched polyurethane dispersions with a multitude of chemically functional end-groups in balance with enhanced mechanical properties the degree of branching was controlled by A_2:B_3 ratio, while end-group functionalizations were realized with amine, urea, silane, or amine&silane groups. Amino-functional branched polyurethane dispersions were demonstrated to be new raw materials for two-component waterborne coating systems when used in combination with a waterdispersible polyisocyanate compound. On the other hand, newly developed silane functional branched polyurethane dispersions were reported for the first time as a self-crosslinking coating, which offers unique advantages of both one-component and two-component systems for instance the ease of use and improved mechanical properties, respectively, in waterborne coating and adhesives applications. For this purpose, amino-functional branched polyurethanes were reacted with 3-isocyanatopropyltriethoxysilane prior to the dispersion and distillation steps in a feasible way. The dispersion stability of final products was confirmed by dynamic light scattering (DLS), solution viscosimetry and pH measurements. As expected, coatings obtained from silane functional HBPUs self-crosslinked by hydrolysis, and condensation of ethoxysilane end-groups during drying and film formation processes, resulting in improved mechanical properties compared to amino- or urea-functionalized analogues. The crosslinked structure, enhanced mechanical properties and thermal properties of resulted coatings were confirmed by soxhlet extraction, stress-strain tests, hysteresis tests and dynamic mechanical analysis (DMA). In order to demonstrate their usefulness, these branched, functional, and waterborne polyurethanes were applied on 100% wool and 45/55 wool/polyester blend fabric in order to enhance the anti-wrinkling property. Although very low degrees of anti-wrinkling improvements were achieved with pure wool fabric, when wool/polyester blend fabric surface was coated with functional waterborne polyurethane dispersions with varying degrees of crosslinking, a significant

degree of improvement was achieved in wrinkle recovery presumably due to better interaction between polyester-based polyurethane coating and polyester containing wool fabric.

In conclusion, this thesis reports a novel roadmap summarized below to improve wrinkle resistence of wool fabric by synthesizing waterborne, branched, and chemically functional polyurethane dispersions to obtain self-crosslinking or two-component crosslinking coatings and applying them on wool fabric for the first time in the literature. These new generation functional polyurethanes have a great potential as waterborne textile coating with tunable degrees of branching and crosslinking for desired final properties. The usefulness of these newly developed dispersions as textile coatings was demonstrated as coatings on wool and wool/polyester blend surfaces, which resulted in improvement of the wrinkle recovery.

THESIS ROAD MAP

BIBLIOGRAPHY

1. Szycher, M., *Szycher's handbook of polyurethanes*. 2012: CRC press.
2. Sardon, H., et al., *Synthesis of room temperature self-curable waterborne hybrid polyurethanes functionalized with (3-aminopropyl) triethoxysilane (APTES).* Polymer, 2010. **51**(22): p. 5051-5057.
3. Chen, H. and J. Kong, *Hyperbranched polymers from A 2+ B 3 Strategy: recent advances in description and control of fine topology.* Polymer Chemistry, 2016. **7**(22): p. 3643-3663.
4. Unal, S., et al., *A new generation of highly branched polymers: hyperbranched, segmented poly (urethane urea) elastomers.* Macromolecules, 2004. **37**(19): p. 7081-7084.
5. Clemitson, I., *Castable polyurethane elastomers*. 2015: CRC Press.
6. Dieterich, D., *Aqueous emulsions, dispersions and solutions of polyurethanes; synthesis and properties.* Progress in Organic Coatings, 1981. **9**(3): p. 281-340.
7. Akindoyo, J.O., et al., *Polyurethane types, synthesis and applications–a review.* RSC Advances, 2016. **6**(115): p. 114453-114482.
8. Prisacariu, C., *Polyurethane elastomers: from morphology to mechanical aspects*. 2011: Springer Science & Business Media.
9. Park, J., S. Bae, and B. Kim, *Hyperbranched waterborne polyurethanes.* Polymer bulletin, 2013. **70**(3): p. 859-869.
10. Noble, K.-L., *Waterborne polyurethanes.* Progress in organic coatings, 1997. **32**(1): p. 131-136.
11. Chattopadhyay, D.K. and K. Raju, *Structural engineering of polyurethane coatings for high performance applications.* Progress in polymer science, 2007. **32**(3): p. 352-418.
12. Sardon, H., et al., *Waterborne polyurethane dispersions obtained by the acetone process: A study of colloidal features.* Journal of applied polymer science, 2011. **120**(4): p. 2054-2062.
13. Kim, B., *Aqueous polyurethane dispersions.* Colloid & Polymer Science, 1996. **274**(7): p. 599-611.
14. Coogan, R.G., *Post-crosslinking of water-borne urethanes.* Progress in Organic coatings, 1997. **32**(1): p. 51-63.
15. Lai, X., Y. Shen, and L. Wang, *Preparation and properties of self-crosslinkable polyurethane/silane hybrid emulsion.* Journal of Polymer Research, 2011. **18**(6): p. 2425-2433.
16. Leyden, D.E. and W.T. Collins, *Silylated surfaces*. Vol. 7. 1980: CRC Press.
17. Plueddemann, E.P., *Chemistry of silane coupling agents*, in *Silane coupling agents*. 1991, Springer. p. 31-54.

18. https://www.xiameter.com/en/ExploreSilicones/Documents/Silane%20Chemistry-1a-95-718-01-F2.pdf.
19. Witucki, G.L., *A silane primer: chemistry and applications of alkoxy silanes.* Journal of coatings technology, 1993. **65**: p. 57-57.
20. Osterholtz, F. and E. Pohl, *Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes: a review.* Journal of Adhesion Science and Technology, 1992. **6**(1): p. 127-149.
21. Brinker, C., *Hydrolysis and condensation of silicates: effects on structure.* Journal of Non-Crystalline Solids, 1988. **100**(1-3): p. 31-50.
22. http://www.dynasylan.com.
23. http://www.dowcorning.com/.
24. Subramani, S., et al., *Synthesis and characterization of water-borne crosslinked silylated polyurethane dispersions.* Journal of applied polymer science, 2005. **98**(2): p. 620-631.
25. Subramani, S., et al., *Synthesis and properties of room temperature curable trimethoxysilane-terminated polyurethane and their dispersions.* Polymers for Advanced Technologies, 2007. **18**(8): p. 601-609.
26. Sardon, H., et al., *Thermal and mechanical behaviour of self-curable waterborne hybrid polyurethanes functionalized with (3-aminopropyl) triethoxysilane (APTES).* Journal of Polymer Research, 2012. **19**(9): p. 9956.
27. Rahman, M.M., H.-H. Chun, and H. Park, *Preparation and properties of waterborne polyurethane-silane: A promising antifouling coating.* Macromolecular Research, 2011. **19**(1): p. 8-13.
28. Lei, H., et al., *Preparation and properties of waterborne siloxane-containing polyurethane for moisture permeable textile coating.* e-Polymers, 2011. **11**(1): p. 750-759.
29. Yan, D., C. Gao, and H. Frey, *Hyperbranched polymers: synthesis, properties, and applications*. Vol. 8. 2011: John Wiley & Sons.
30. Unal, S., *Synthesis and characterization of branched macromolecules for high performance elastomers, fibers, and films*. 2005, Virginia Tech.
31. McKee, M.G., et al., *Branched polyesters: recent advances in synthesis and performance.* Progress in Polymer Science, 2005. **30**(5): p. 507-539.
32. Yates, C. and W. Hayes, *Synthesis and applications of hyperbranched polymers.* European Polymer Journal, 2004. **40**(7): p. 1257-1281.
33. Gurunathan, T., S. Mohanty, and S.K. Nayak, *Hyperbranched Polymers for Coating Applications: A Review.* Polymer-Plastics Technology and Engineering, 2016. **55**(1): p. 92-117.
34. Flory, P.J., *Principles of polymer chemistry*. 1953: Cornell University Press.
35. Spindler, R. and J.M. Frechet, *Synthesis and characterization of hyperbranched polyurethanes prepared from blocked isocyanate monomers by step-growth polymerization.* Macromolecules, 1993. **26**(18): p. 4809-4813.
36. Jikei, M. and M.-a. Kakimoto, *Hyperbranched polymers: a promising new class of materials.* Progress in Polymer Science, 2001. **26**(8): p. 1233-1285.

37. Emrick, T., H.-T. Chang, and J.M. Frechet, *An A2+ B3 approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents.* Macromolecules, 1999. **32**(19): p. 6380-6382.
38. Kumar, A. and S. Ramakrishnan, *A novel one-pot synthesis of hyperbranched polyurethanes.* Journal of the Chemical Society, Chemical Communications, 1993(18): p. 1453-1454.
39. Kumar, A. and S. Ramakrishnan, *Hyperbranched polyurethanes with varying spacer segments between the branching points.* Journal of Polymer Science Part A: Polymer Chemistry, 1996. **34**(5): p. 839-848.
40. Gao, C. and D. Yan, *"A2+ CB n" Approach to Hyperbranched Polymers with Alternating Ureido and Urethano Units.* Macromolecules, 2003. **36**(3): p. 613-620.
41. Bruchmann, B. and W. Schrepp, *The AA*+ B* B2 approach A simple and convenient synthetic strategy towards hyperbranched polyurea-urethanes.* e-Polymers, 2003. **3**(1): p. 191-200.
42. Sheth, J.P., et al., *A comparative study of the structure–property behavior of highly branched segmented poly (urethane urea) copolymers and their linear analogs.* Polymer, 2005. **46**(23): p. 10180-10190.
43. Rippon, J.A., *The structure of wool.* 2013.
44. Bradbury, J., G. Chapman, and N. King, *The chemical composition of wool II. Analysis of the major histological components produced by ultrasonic disintegration.* Australian journal of biological sciences, 1965. **18**(2): p. 353-364.
45. Leeder, J.D. and R.C. Marshall, *Readily-extracted proteins from merino wool.* Textile Research Journal, 1982. **52**(4): p. 245-249.
46. Robbins, C.R., *Chemical composition of different hair types*, in *Chemical and physical behavior of human hair*. 2012, Springer. p. 105-176.
47. Mizell, M.H.L.R., *ELASTICITY OF WOOL AS RELATED TO ITS CHEMICAL STRUCTURE.* 1942.
48. Rogers, G., *Electron microscopy of wool.* Journal of ultrastructure research, 1959. **2**(3): p. 309-330.
49. Hearle, J.W., *High-performance fibres*. 2001: Elsevier.
50. Menefee, E., et al., *Water Transport and Wrinkle Recovery of Wool.* Textile Research Journal, 1982. **52**(1): p. 86-92.
51. Whitfield, R., D. Remy, and A. Pittman, *Reactive Polymer Finishes for Wool: Part IV: Phase Boundary Limited Cross-Linking of Reactive Polyesters and Polyethers to Yield Polyurethanes.* Textile Research Journal, 1967. **37**(8): p. 655-660.
52. De Boos, A., J. Leeder, and I. Watt, *5—THE WRINKLING BEHAVIOUR OF WOOL FABRICS: THE TREATMENT OF ANNEALED WOOL WITH RESORCINOL–FORMALDEHYDE POLYMERS.* Journal of the Textile Institute, 1975. **66**(1): p. 28-34.
53. Leeder, J., *Wrinkling Behavior of Wool Fabrics: Changes Induced By Chemical Modification.* Textile Chemist & Colorist, 1971. **3**(8).
54. Moon, S.J. and T.J. Kang, *Effects of epoxide and silicone polymers on the mechanical and performance properties of wool fabric.* Textile Research Journal, 2000. **70**(12): p. 1063-1069.

55. Chapman, B., *7—THE RÔLE OF EXTERNAL POLYMERS IN IMPROVING THE WRINKLE-RECOVERY OF WOOL FABRICS.* Journal of the Textile Institute, 1976. **67**(2): p. 43-49.
56. Shishoo, R., E.-M. Holst-Wallin, and M. Cednäs, *Studies of Wrinkling Properties of Wool Fabrics Part I: Treatments to Improve Wrinkle Recovery of Wool Fabrics.* Textile Research Journal, 1974. **44**(1): p. 30-34.
57. Jones, F., *The Effect of Elastomeric Polymers on the Flexural Rigidity and Wrinkle-Recovery of Wool.* 1975.
58. Pittman, A., J. Morgan, and C. Pardo, *Effect of Urea on Wrinkle Recovery Properties of Wool.* Textile Research Journal, 1981. **51**(5): p. 365-366.
59. De Boos, A., *6—WOOL–POLYMER SYSTEMS: THE WRINKLE-RECOVERY AND HANDLE OF WOOL FABRICS TREATED WITH POLYURETHANE ELASTOMERS.* Journal of the Textile Institute, 1976. **67**(2): p. 37-42.
60. Doğan, N.A., *SYNTHESIS and CHARACTERIZATION of NOVEL WATERBORNE POLYURETHANE DISPERSIONS.*
61. Ertem, S.P., et al., *Effect of soft segment molecular weight on tensile properties of poly (propylene oxide) based polyurethaneureas.* Polymer, 2012. **53**(21): p. 4614-4622.
62. Yilgor, I., et al., *Influence of soft segment molecular weight on the mechanical hysteresis and set behavior of silicone-urea copolymers with low hard segment contents.* Polymer, 2011. **52**(2): p. 266-274.
63. Johnson, N.A. and I. Russell, *Advances in wool technology*. 2008: Elsevier.