ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

EFFECTS OF CROSSLINKING AND NANOSILICA ON WATERBORNE POLYURETHANE DISPERSIONS

M.Sc. THESIS

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Department of Polymer Science and Technology

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

SU BAZLI POLİÜRETAN DİSPERSİYONLARDA ÇAPRAZ BAĞLANMANIN VE NANO SİLİKANIN ETKİLERİ

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Yunus ERKAHRAMAN, a M.Sc. student of İTU Graduate School student ID 515181034, successfully defended the thesis/dissertation entitled "EFFECTS OF CROSSLINKING AND NANOSILICA ON WATERBORNE POLYURETHANE DISPERSIONS", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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ABBREVIATIONS

PU	**:** Polyurethane
VOC	**:** Volatile Organic Compounds
PUD	**:** Polyurethane Dispersion
WPU	**:** Waterborne Polyurethane
WPUD	**:** Waterborne Polyurethane Dispersion
TPU	**:** Thermoplastic Polyurethane
MDI	**:** Methylene Diphenyl Diisocyanate
HDI	**:** Hexamethylene Diisocyanate
TDI	**:** Toluen Diizosiyanat
MDA	**:** Diaminodiphenylmethane
IPDI	**:** Isophorone Diisocyanate
TDA	**:** Toluenediamine
H_{12}MDI	**:** 4,4'-Methylenedicyclohexyl Diisocyanate
HCN	**:** Hydrogen Cyanide
THF	**:** Tetrahydrofuran
TMI	**:** 3-Isopropenyl-α,α-dimethylbenzyl isocyanate
TMHDI	**:** Trimethylhexamethylene Diisocyanate
TMXDI	**:** Tetramethylxylene Diisocyanate
SS	**:** Soft Segment
HS	**:** Hard Segment
TEA	**:** Triethylamine
DMPA	**:** Dimethylol propionic acid
N-MDEA	**:** N-methyl diethanolamine
PVC	**:** Polyvinyl Chloride
DMBA	**:** Dimethylol butanoic Acid
FTIR	**:** Fourier-Transform Infrared Spectroscopy
XPS	**:** X-ray Photoelectron Spectroscopy
TEM	**:** Transmission Electron Microscopy
SEM	**:** Scanning Electron Microscope
EDX	**:** Energy-dispersive X-ray Spectroscopy

TGA : Thermal Gravimetric Analysis

AFM : Atomic Force Microscopy

DMA : Dynamic Mechanical Analysis

UV–Vis : Ultraviolet-Visible Spectrophotometry

UV : Ultraviolet

IR : Infrared

1K : One Component

2K : Two Component

PCL : Polycaprolactone

PTMG : Polytetramethylene Ether Glycol

PDMS : Polydimethylsiloxane

BDO : 1,4-Butanediol

FMA : Fluorinated Acrylate Monomer

FSPU : Si and F Modified Polyurethane

SYMBOLS

Tg	**:** Glass transition temperature
Td	**:** Degredation temperature
Tm	**:** Melting temperature
f	**:** Functionality
µm	**:** Micrometer
nm	**:** Nanometer

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EFFECTS OF CROSSLINKING AND NANOSILICA ON WATERBORNE POLYURETHANE DISPERSIONS

SUMMARY

Waterborne polyurethane dispersions (WPUDs) are versatile materials that are a type of waterborne polymer colloids, utilize water as a dispersing medium, and contain little or no organic solvent. WPUDs are increasingly replacing solventborne polyurethanes thanks to their superior properties such as very low or no volatile organic compound (VOC), low viscosity, excellent film properties, ease of use, good adhesion, high abrasion resistance, and flexibility. WPUDs are preferred in a wide range of applications and industries, including coatings, binders, adhesives, sealants, automotive, inks, biomaterials, paper, wood, footwear, textiles, and many more.

Different ways are used to improve the weak properties of WPUDs, such as poor mechanical strength, poor water and alkali resistance, relatively low heat resistance, and high raw material costs. The most common of these ways are, using crosslinkers in various structures, hybridization with polymers that contain different groups such as acrylics and silicones, and the creation of composites by adding nano or micron size inorganic fillers to the dispersion such as silica, clay, graphene oxide, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$.

Nanosilicas, which have different types such as colloidal silica, precipitated silica, fumed silica, are widely preferred for making composite materials with WPUD because of different properties such as superior hardness, low toxicity, good stability and dispersion, and low cost. The main purposes of producing WPUD/nanosilica composites using various techniques including in-situ polymerization, blending, and the sol-gel process are to develop composite materials with superior mechanical, thermal, optical, chemical, rheological, or electrical characteristics than pure WPUDs.

This study aims to obtain new waterborne PU dispersion (WPUD)/nanosilica composites by using various nano silicas and crosslinkers with different types such as isocyanate, aziridine, and waterborne PU dispersion, and investigate the effects of crosslinkers and nano silica by forming a film from these WPUD/nanosilica composites. Various tests were carried out to determine the thermal properties, crystallization behaviors, optical properties, swelling degrees of the obtained WPUD/nanosilica composite films, and it was aimed to gain the properties such as high water resistance, homogeneous distribution, and mechanical strength to the films and using them as a surface coating material in the future.

In this study, we prepared various formulations using polyether-based aliphatic waterborne polyurethane dispersion with different amounts and types of nanosilicas (hydrophobic fumed silica and aqueous silica dispersion) and different crosslinkers such as polyether modified HDI--based polyisocyanate and polyfunctional aziridine.

WPUD ratio was determined as 75% by weight, polyisocyanate ratio of 5%, and polyaziridine ratio of 2%, if present in the formulation. While fumed silica ratio ranged between 0.1 and 3% by weight aqueous silica dispersion ratio ranged between 1% and 25% by weight in the prepared formulations. WPUD/silica nanocomposites were prepared using the blending method by mechanical stirrer. Crosslinkers were added just before the tests due to the limited pot life. After pouring the prepared WPUD/silica nanocomposite dispersion into Teflon molds, cured for 4 hours at room temperature and at 50 °C for 8 hours in the oven to form films with a thickness of approximately 150μm.

Fourier transform infrared spectroscopy (FTIR) was used to examine the chemical structure of the waterborne polyurethane dispersion, silicas, and crosslinkers used in the formulations, as well as the films formed after curing, to determine the changes in the peaks with the addition of crosslinker and silica, and to compare with the pure WPUD film. Differential scanning calorimetry (DSC) was used to examine the thermal properties of the films and X-ray diffraction (XRD) was used to examine the crystallization behaviors. Scanning electron microscopy (SEM)-EDX spectrometry was used for the morphological and elemental analysis of the films. The transparency of the films was observed with an optical microscope (OM) under the same conditions. The swelling degrees of the films in water were evaluated over weight changes. Finally, the hardness values of the films were measured with the Shore D Durometer.

Characteristic polyurethane peaks were seen in the FTIR spectral analysis of the neat WPUD film. New characteristic peaks formed as a result of crosslinking reactions were determined. In addition, the presence of nano silica in the structure was determined by the appearance of characteristic Si-O-Si peaks.

According to the DSC results, it was determined that the films contained crystalline structures, and the thermal stability of the films increased with the addition of fumed silica and aqueous silica dispersion. According to XRD data, it was determined that the crystallinity increased slightly with the addition of polyisocyanate, but the crystallinity decreased significantly with the addition of polyaziridine. In addition to these, nano silica additions were also found to reduce crystallinity. Also, It was determined that the films with the lowest crystallinity were the films containing polyaziridine crosslinker and fumed silica.

In the neat WPUD film SEM images, it was observed that the surface was a rough surface consisting of nano and micron-sized polyurethane particles, and phase separations were observed on the surface. While the phase separations decreased and the surface became more uniform with the addition of polyaziridine, the phase separations increased with the addition of polyisocyanate. Also, it was observed that the surface became rougher with the addition of silica, as the silica ratio increased in the samples containing fumed silica, the silica agglomerations increased and the uniform structure did not occur. In the EDX measurements, carbon, oxygen, and nitrogen atoms were determined, and the silicon atom was also included in the structure with the addition of silica.

According to the swelling measurement results, it was found that crosslinking and the addition of a certain amount of nanosilica reduced the degree of swelling. It was

determined that the films with the lowest swelling degree were the films containing polyaziridine crosslinker and fumed silica.

As a result of the transparency tests performed with an optical microscope, it was seen that the transparency of the films decreases as the amount of silica increases. In the hardness test results, it was seen that the hardness of the films increases with the addition of a crosslinker and certain amount silica. Also, It was observed that the addition of polyaziridine increased the hardness more than the polyisocyanate.

SU BAZLI POLİÜRETAN DİSPERSİYONLARDA ÇAPRAZ BAĞLANMANIN VE NANO SİLİKANIN ETKİLERİ

ÖZET

Su bazlı poliüretan dispersiyonlar (WPUD) polimer zinciri arasına eklenen bir dispersiyon ajanı yardımı ile su içerisinde dağıtılmış poliüretan partiküllerinden oluşan ve çok az organik solvent içeren veya hiç içermeyen çok yönlü malzemelerdir. Su bazlı poliüretan dispersiyonlar, çok düşük oranda veya hiç uçucu organik bileşik içermeme, düşük viskozite, mükemmel film özellikleri, kullanım kolaylığı, yüzeye iyi yapışma, yüksek aşınma direnci ve esneklik gibi üstün özellikleri sayesinde gün geçtikçe solvent bazlı poliüretanların yerini almaktadırlar. Su bazlı poliüretan dispersiyonlar, ağaç, cam, kağıt, plastik, deri, polimerik elyaf gibi birçok farklı yüzeye uygulanabilmeleri sayesinde otomotiv, yapı, tekstil, ambalaj, mobilya, tekstil, ayakkabı vb. bir çok sektörde kaplayacı ve yapıştırıcı malzeme olarak tercih edilmektedirler.

Su bazlı poliüretan dispersiyonların solvent bazlı ürünlere göre düşük mekanik dayanım, zayıf su ve alkali direnci, düşük ısı direnci ve yüksek hammadde maliyetleri gibi dezavantajlarını iyileştirmek için farklı yöntemlere başvurulmaktadır. Bu yöntemlerden en yaygın olanları, çeşitli yapılardaki çapraz bağlayıcıların reaksiyona katılması, akrilik, silikon, alkid gibi farklı gruplara sahip polimerlerle hibridizasyon ve poliüretan matrikse silika, kil, grafen oksit, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$ gibi nano veya mikron boyutlu inorganik dolgu maddeleri eklenerek kompozitlerin oluşturulmasıdır.

Kolloidal silika, çökertilmiş silika, füme silika gibi farklı türleri bulunan nano silikalar, yüksek sertlik, düşük toksisite ve düşük maliyet gibi farklı özelliklerinden dolayı WPUD ile kompozit malzeme oluşturmak için yaygın olarak tercih edilmektedirler. WPUD/nanosilika kompozit malzeme üretmenin temel amaçları arasında daha üstün mekanik, termal, optik, reolojik veya elektriksel özelliklere sahip malzemeler geliştirmek bulunmaktadır.

Bu çalışmanın amacı, çeşitli nano silikalar ve izosiyanat, aziridin gibi farklı özelliklere sahip çapraz bağlayıcılar, ve su bazlı PU dispersiyon kullanarak yeni su bazlı PU dispersiyon (WPUD)-nanosilika kompozitleri elde etmek ve elde edilen bu WPUD-nanosilika kompozitlerinden film oluşturarak çapraz bağlayıcıların ve nano silikaların kullanımının etkilerinin incelenmesi amaçlanmıştır. Elde edilecek (WPUD)-nanosilika kompozit filmlerinin termal özellikleri, kristallenme davranışları, optik özellik, su içinde şişme derecesini belirlemek amacıyla çeşitli testler yapılarak , bu çapraz bağlayıcılar ve nano silikaların su bazlı PU dispersiyona (WPUD) etkisi incelenerek, yüksek su dayanımı, homojen dağılım, mukavemet gibi özelliklerin filmlere kazandırılarak daha iyi film oluşumunun sağlanması ve ileride yüzey kaplama malzemesi olarak kullanılabilmesi hedeflenmiştir.

Bu çalışmada, polieter bazlı alifatik su bazlı poliüretan dispersiyon (WPUD)-kompozitleri hazırlanırken hidrofobik füme silika ve sulu silika dispersiyonu olmak üzere iki farklı nano silika ve iki farklı kimyasal yapıya sahip polieter ile modifiye edilmiş hekzametilen diizosiyanat (HDI) ve çok fonksiyonlu poliaziridin çapraz bağlayıcı kullanılarak çeşitli formülasyonlar hazırlanarak deneyler yapılmıştır. WPUD oranı ağırlıkça %75, eğer formülasyonda var ise poliizosiyanat oranı %5 ve poliaziridin oranı %2 olarak alınmıştır. Hazırlanan formülasyonlarda füme silika oranı ağırlıkça %0,1 ile %3 arasında alınırken sulu silika dispersiyonu oranı ağırlıkça %1 ile %25 arasında farklı değerler alınarak deneyler yapılmıştır. WPUD/silika nanokompozitleri direkt karıştırma (blending) methoduyla mekanik mikser kullanılarak hazırlanmıştır. Çapraz bağlayıcılar ise kısıtlı kap ömründen dolayı testlerden hemen önce eklenerek kısa süreli bir karıştırmaya tabi tutulmuştur. Hazırlanan WPUD/silika dispersiyonunun teflon kalıplara dökülmesinin ardından 4 saat oda sıcaklığında ve 50 °C de 8 saat fırında kürlenerek yaklaşık 150µm kalınlığında filmler elde edilmiştir.

Formülasyonlarda kullanılan su bazlı poliüretan dispersiyonun, silikaların ve çapraz bağlayıcıların ve ayrıca kürleme sonrası oluşan filmlerin kimyasal yapısını incelemek, çapraz bağlayıcı ve silika ilavesiyle piklerde oluşan değişimleri belirlemek için ve saf WPUD film ile karşılaştırma yapmak amacıyla Fourier dönüşümlü kızıl ötesi spektroskopisi (FTIR) kullanılmıştır. Filmlerin termal özelliklerini incelemek için diferansiyel taramalı kalorimetri (DSC), kristallenme davranışları incelemek için X-ışını kırılımı (XRD) kullanılmıştır. Filmlerin morfolojik ve elementel analizi için taramalı elektron mikroskobu (SEM)-EDX spektrometresi kullanılmıştır. Filmlerin şeffaflığı aynı koşullar altında optik mikroskop (OM) yardımı ile gözlemlenmiştir. Filmlerin su içinde şişme dereceleri ağırlık değişimleri üzerinden değerlendirilmeye tabi tutulmuştur. Son olarak Shore D Durometre ile filmlerin sertlik değerleri ölçülmüştür.

Saf WPUD filminin FTIR spektral analizinde karakteristik poliüretan pikleri görülmektedir. Çapraz bağlanma reaksiyonları sonucu oluşan yeni karakteristik pikler de görülmektedir. Ayrıca yapıda nano silikaların varlığı karakteristik Si-O-Si piklerinin görülmesiyle tespit edilmiştir.

DSC sonuçlarına göre, filmlerin kristal yapılar içerdiği, filmlerin termal dayanımının füme silika ve sulu silika dispersiyonu ilavesiyle arttığı tespit edilmiştir. XRD verilerine göre poliizosiyanat ilavesi ile kristalinitenin fazla değişmediği çok az miktarda arttığı fakat poliaziridin ilavesiyle kristalinitenin kayda değer miktarda azaldığı tespit edilmiştir. Bunlara ek olarak, nano silika ilavelerinin de kristaliniteyi azalttığı tespit edilmiştir. En düşük kristaliniteye sahip filmlerin poliaziridin çapraz bağlı füme silika içeren filmler olduğu belirlenmiştir.

SEM görüntülerinde saf WPUD filminin nano ve mikron boyutlu poliüretan parçacıklardan oluşan pürüzlü yüzeyi ve yüzeydeki faz ayrımları gözlemlenmiştir. Poliaziridin ilavesiyle faz ayrımlarının azaldığı ve yüzeyin daha uniform bir hal aldığı görülmekte iken poliizosiyanat ilavesiyle faz ayrımlarının arttığı gözlemlenmiştir. Silika ilavesiyle yüzeyin daha pürüzlü hale geldiği gözlemlenirken füme silika içeren numunelerde silika oranı arttıkça silika aglemerasyonlarının arttığı ve uniform yapının oluşmadığı görülmüştür. EDX ölçümlerinde karbon, oksijen ve azot atomları tespit edilirken silika ilavesiyle silisyumun da yapıya katıldığı tespit edilmiştir.

Şişme testleri sonucunda çapraz bağlayıcı ve belirli bir miktara kadar silika ilavesiyle şişme derecesinin azaldığı tespit edilmiştir. En düşük şişme derecesine sahip olan filmlerin poliaziridin çapraz bağlı füme silika içeren filmler olduğu belirlenmiştir.

Optik mikroskop ile yapılan şeffaflık testleri sonucunda silika miktarı arttıkça filmlerin şeffaflığının azaldığı görülmektedir. Sertlik testi sonuçlarında çapraz bağlayıcı ve belirli miktara kadar silika ilavesiyle filmlerin sertliklerinin arttığı görülmektedir. Poliaziridin ilavesinin poliizosiyanata göre sertliği daha fazla arttırdığı gözlemlenmiştir.

1. INTRODUCTION

The first polyurethanes were invented by Otto Bayer and his co-workers at the laboratories of I.G. Farben at Leverkusen Germany in 1937. First attempts stay focussed on PU products made from aliphatic diisocyanate and diamine forming polyurea, till the exciting feature of PU obtained from an aliphatic diisocyanate and glycol, were carried out [1]. The initial commercial application of PU as a millable elastomer, adhesive, and coating started in 1945–1947. After these, flexible and rigid polyurethane foams took their place among commercial products, respectively [2]. Polyurethanes are formed by the chemical reaction of di or polyisocyanates and diols or polyols under appropriate conditions. These reactions usually take place in the presence of different additives. For example, chain extenders, catalysts, blowing agents, emulsifiers, stabilizers [1].

The chemical composition of polyurethanes differs greatly depending on the variety of polyol and di-or poly-isocyanate used in the synthesis. The several unique chemical structures that are feasible for polyurethane make it a versatile polymer. One of the characteristics that make polyurethanes specific and flexible is the bonding of hydrogen between polymer chains. Hydrogen bonding between neighboring polymer chains forms a simulated crosslinking that creates a major development within the physical/mechanical characteristics of the polymer [3, 4].

Polyurethanes are a very special polymer group that has been developed in many new types since the 1940s and is used in many areas today. These types can be listed as rigid polyurethane foams, flexible polyurethane foams, thermoplastic polyurethanes, polyurethane ionomers, coatings, adhesives, sealants, elastomers, binders, and waterborne polyurethane dispersions. PUs have recently been used in many different applications, such as building and construction applications, automotive applications, coating applications, marine applications, medical applications, appliances, flooring and packaging applications, apparel applications [3].

In the past, high performance and appearance were the most effective in determining the resin in polyurethane coatings. Nowadays, there has been a new trend towards reducing the use of volatile organic compounds (VOC) by considering environmental impacts. As a result, this trend was continued and legal regulations were made regarding the restriction of the use of VOC, and some regulations were made in this direction widely all over the world, especially in Germany and America. Waterborne polyurethane dispersions (WPUD) are quickly increasing part of the PU coating industry due to environmental effects regulations [5].

Today, WPUDs have a wide range of applications, such as paints, inks, adhesives, papers, constructions, consumer goods [6]. WPUDs have many advantages in terms of application as well as being environmentally friendly, including excellent adhesion to many substrates, chemical resistance, high viscosity, good film properties, solvent resistance, abrasion resistance, and elasticity [3].

Nanoparticles are materials that have a very important effect on improving the properties of polymers and modifying polymers. The properties of nanoparticles such as size, shape, structure, surface conditions have an important place in their effects on composites [7]. With the growing interest in nanomaterials, many different nanoparticles such as SiO_2, TiO_2, ZnO, $BaSO_4$, Al_2O_3, Fe_2O_3, $CaCO_3$, and CeO_2 were used to develop composites with polyurethanes to enhance the PUs poor properties [8, 9]. Nanosilicas are combined with a variety of polymers, including polyurethanes, to form nanocomposite materials. The key advantages of nanosilica for composites include the reinforcing of polymeric films, improved scratch and abrasion resistance, improved thermal and insulation properties, and increased resistance to UV radiation [10].

2. POLYURETHANE

2.1 Polyurethane Chemistry

Polyurethanes are polymers formed by urethane groups formed as a result of the reaction of polyisocyanate-derived isocyanate and polyol-derived hydroxyl groups (Figure 2.2) [6]. In addition, a polyurethane structure may contain different groups other than urethane groups such as ester, ether, urea, and amide groups [11]. Figure 2.1 shows the synthesis of urethane from alcohol and isocyanate reaction.

If needed, suitable additives and catalysts may be added for polyurethane synthesis. Additives that can be added into the synthesis contain pigments, crosslinkers, chain extenders, surfactants, fillers [3].

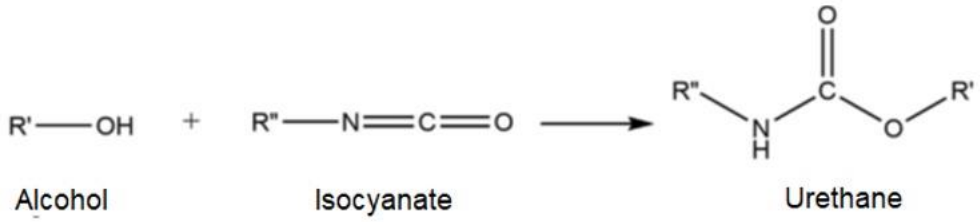


Figure 2.1 : Synthesis of urethane from alcohol and isocyanate reaction [11].

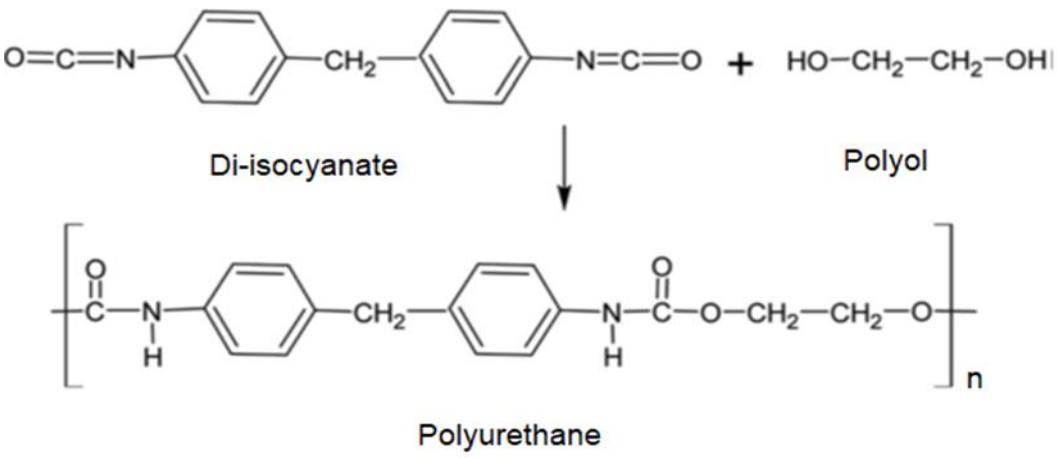


Figure 2.2 : Main reaction for the synthesis of polyurethane [3].

Various types of polyurethanes occur according to the raw materials selected at the beginning, such as foam, rigid, TPU, etc. In addition to these, factors such as crosslinker type and density, branching, chain length, molecular weight also create polyurethane structural diversity [4]. Polyurethanes are polymers with a wide variety of structures. PUs can be very hard or very soft depending on their structure [11].

PUs are block copolymers with varying hard and soft segments in their structure (Figure 2.3) [4]. Soft and hard segments impart various special properties to polyurethanes. Soft and hard segments originate from different molecules and bonds. Soft segments (SS) are usually caused by polyols, and the reaction of isocyanates and crosslinkers is effective in the formation of hard segments (HS). Soft segments provide polyurethane elastomeric properties, while hard segments provide mechanical properties [1].

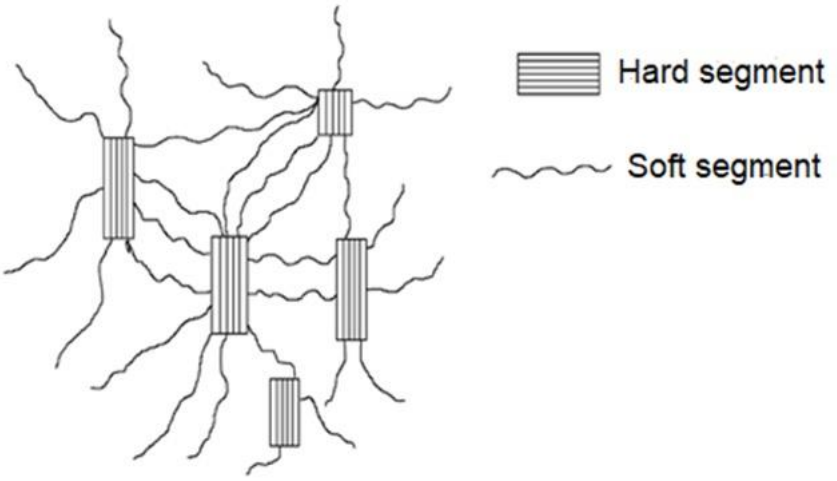


Figure 2.3 : Schematic illustration of two-phase morphology of polyurethane [4].

2.2 Raw Materials

Raw materials obtained from many different sources are used in the synthesis of polyurethanes. Raw materials are divided into three main groups, polyisocyanates, polyols, and additives. Additives include blowing agents, catalysts, surfactants, chain extenders and crosslinkers, flame retardants, fillers [8, 11].

The main sources of polyisocyanates and polyols are petroleum, coal, salt, air, and renewable natural materials. Figure 2.4 shows the participation of polyether polyols and some types of polyisocyanates from PU raw material sources.

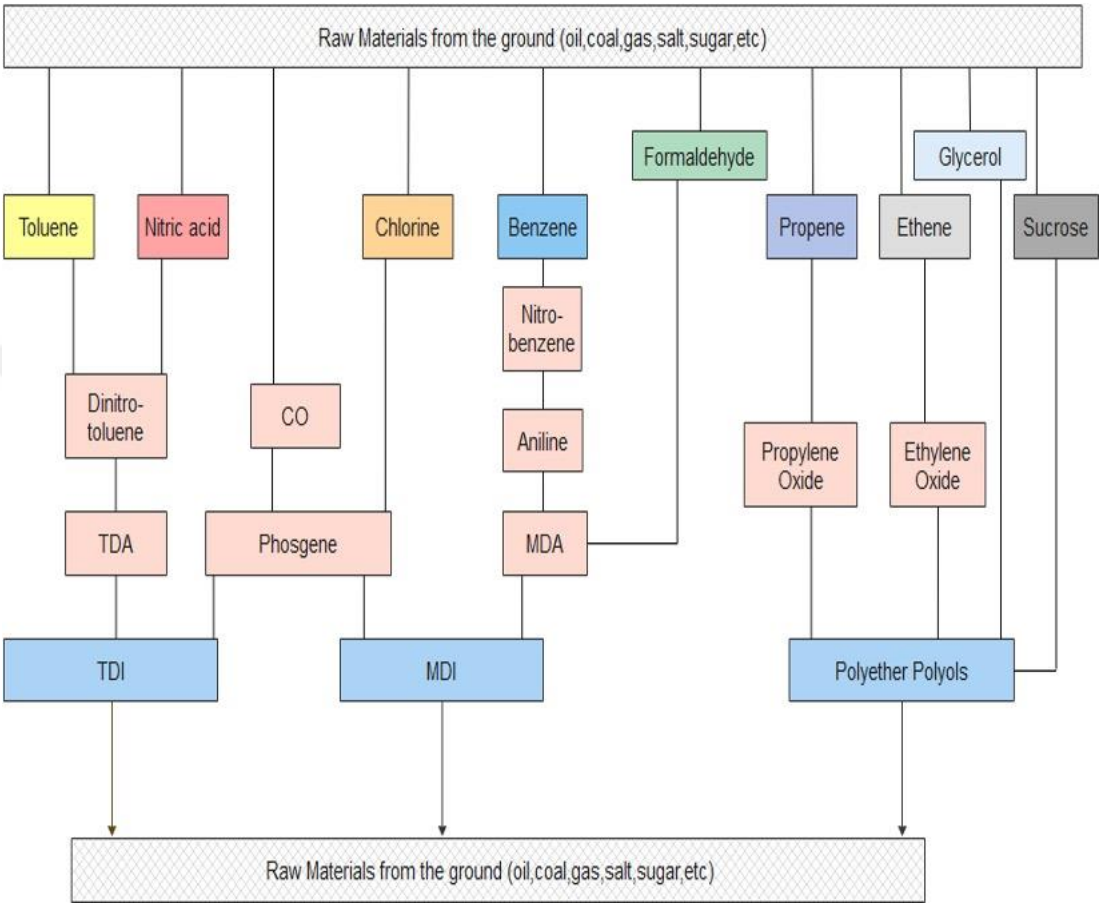


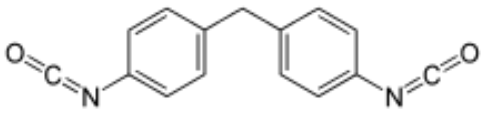
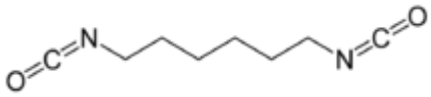
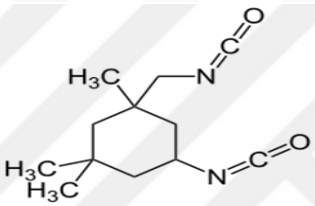
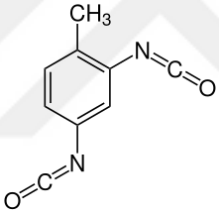
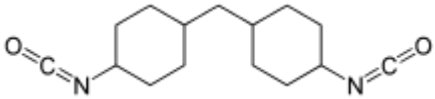
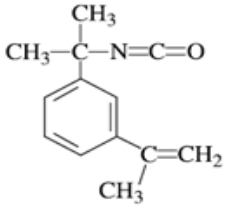
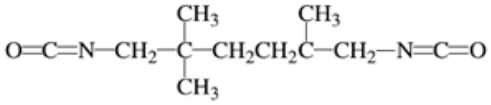
Figure 2.4 : The "family tree" of PU raw materials [11].

2.2.1 Isocyanates

Difunctional or polyfunctional isocyanates are the main raw materials required for the synthesis of polyurethanes [13]. These isocyanates are molecules with at least two or more NCO groups in their structures. Isocyanates are highly reactive compounds, create a variety of chemically different products in conjunction with – OH and – NH functional groups [14]. Isocyanates can be aliphatic, cycloaliphatic, polycyclic, or aromatic in nature [1]. Aromatic isocyanates are consumed much more than other isocyanate types [12]. Among the isocyanates, the most commonly used are MDI, TDI, and aliphatic diisocyanates. In the selection of isocyanates, besides the properties such as reactivity and price, it is effective in the desired properties in the end product such

as color and transparency. The structures of some commonly used isocyanates are shown in Table 2.1 [3].

Table 2.1 : Structures of some important isocyanates.

Code	Types	Structure
MDI	Aromatic	
HDI	Aliphatic	
IPDI	Aliphatic	
TDI	Aromatic	
H_{12}MDI	Aliphatic	
TMI	Aliphatic	
TMHDI	Aliphatic	

2.2.1.1 Reactions of isocyanates

Reactions of isocyanates are divided into two main groups: active hydrogen donors and nonactive hydrogen reactions, respectively. The most important of these categories is the category in which it constitutes active hydrogens donors [4].

Isocyanates are very reactive molecules. The nucleophilic addition reactions made with chemicals containing active hydrogen are the most known [13]. Isocyanates perform these reactions by forming different products with different compounds. For example, urethane with hydroxyl compounds, urea with amines, and amine with water [14]. The general active hydrogen reaction is shown in Figure 2.5 below.

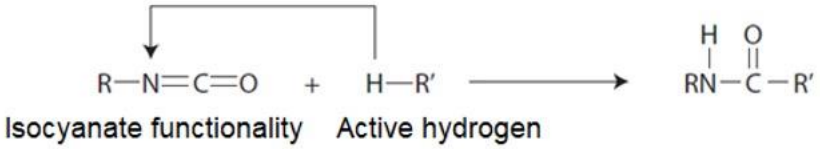


Figure 2.5 : The reaction of isocyanates with active hydrogen compounds [4].

Some important reactions of isocyanates are as follows:

1. Reaction of isocyanates with OH including groups;

Isocyanate alcohol reactions take place at ambient temperature and generally no catalysts are used (Figure 2.6) [14]. The reactivity of alcohols in urethane formation reactions with isocyanates varies according to their structure. The most reactive of these are primary alcohols, followed by secondary and tertiary alcohols, respectively [4].

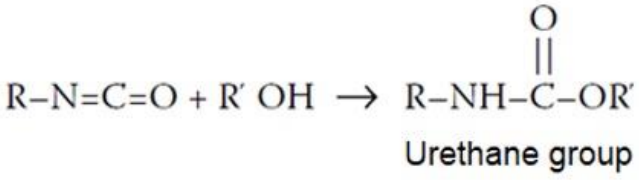


Figure 2.6 : The reaction of alcohol with an isocyanate to form urethane group [14].

2. Reaction of isocyanates with NH including groups;

Isocyanates react with primary and secondary amines to form urea or substituted urea (Figure 2.7) [13]. These reactions are faster and more severe than alcohol reactions [4, 15].

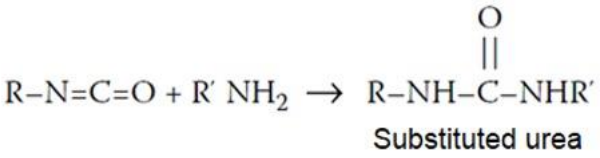


Figure 2.7 : The reaction of amine with an isocyanate to form urea [13].

3. Reaction of isocyanates with urea and urethane groups;

Urethane and urea groups formed as a result of the reaction of isocyanates with groups containing OH and NH containing acidic protons in their structures. These urethane and urea compounds can react with isocyanates respectively to form allophanate and biuret (Figure 2.8) [13, 15].

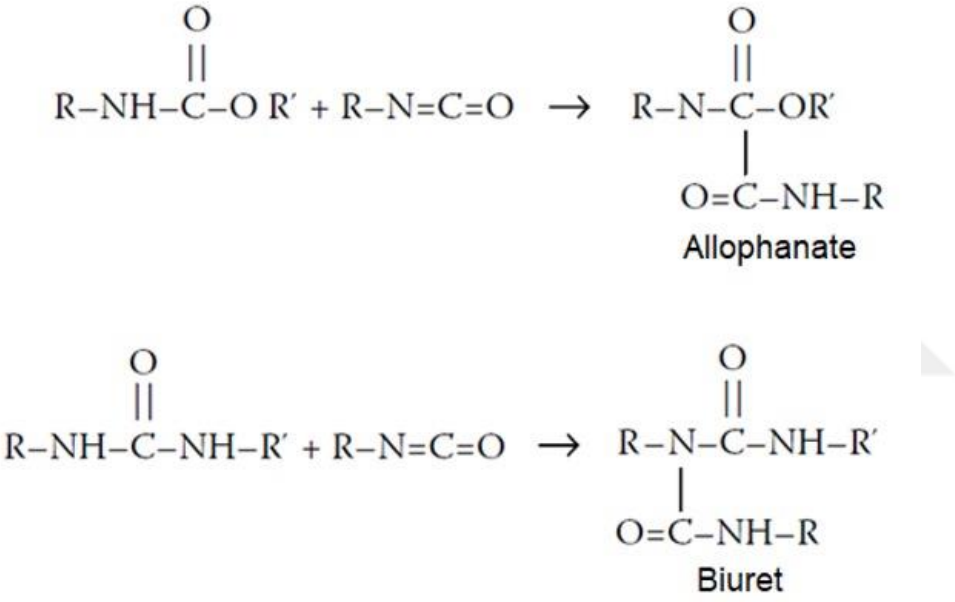


Figure 2.8 : Formation of allophanate and biuret by reaction of urethane and urea with an isocyanate.

Reaction of isocyanates with water;

Isocyanates react violently and rapidly with water to initially form unstable carbamic acid, which decomposes and generates amines. In these reactions, carbon dioxide gas also occurs (Figure 2.9). Amine is more reactive than water and readily reacts with another isocyanate to form urea [13].

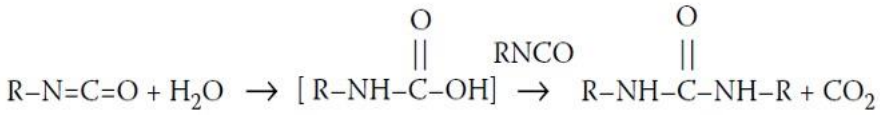


Figure 2.9 : Reaction of isocyanates with water.

2.2.1.2 Types of isocyanates

a)Aromatic isocyanates

Aromatic isocyanates are much more reactive than aliphatic isocyanates [16]. MDI and TDI are the most widely used and important aromatic isocyanates in the polyurethane industry. Toluene diisocyanate (TDI) is derived from toluene. In industry, TDI can only be used as the 2.4 isomers or as a mixture of 2.4 and 2.6 isomers. Usually, TDIs are colorless liquids with low viscosity at ambient temperature [16, 17]. Another monomer, MDI, is colorless and crystalline at ambient temperature. MDI is available in substances that are liquids whether they consist of mixtures of isomers and homologues [18]. They have much less vapor pressure and are less toxic than TDI [17]. Structures of TDI, MDI, and its isomers are given in Figure 2.10 and Figure 2.11, respectively.

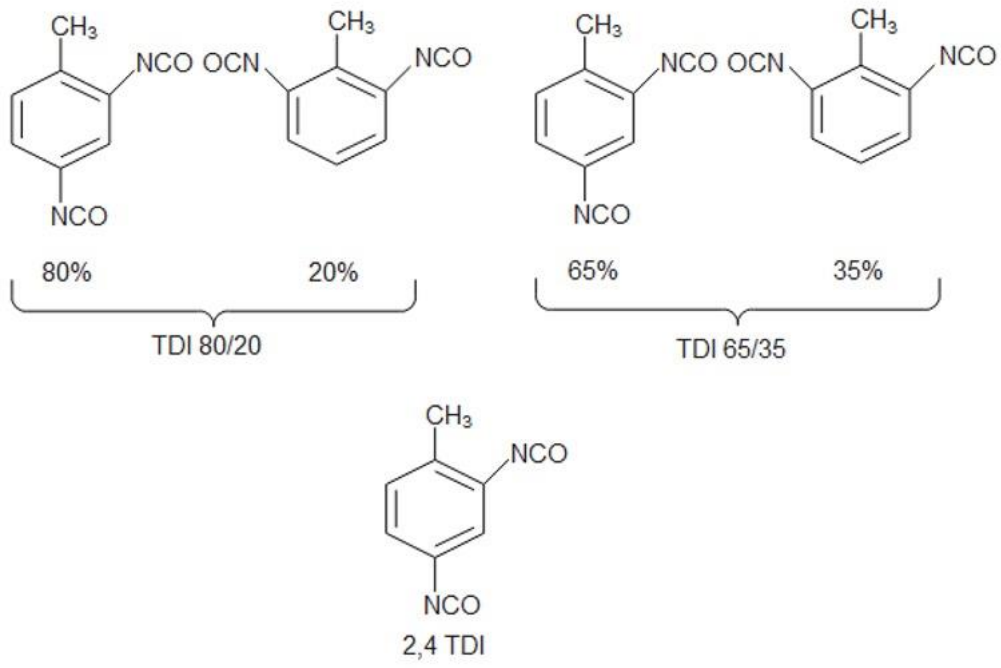


Figure 2.10 : The chemical structures of commercial TDI [19].

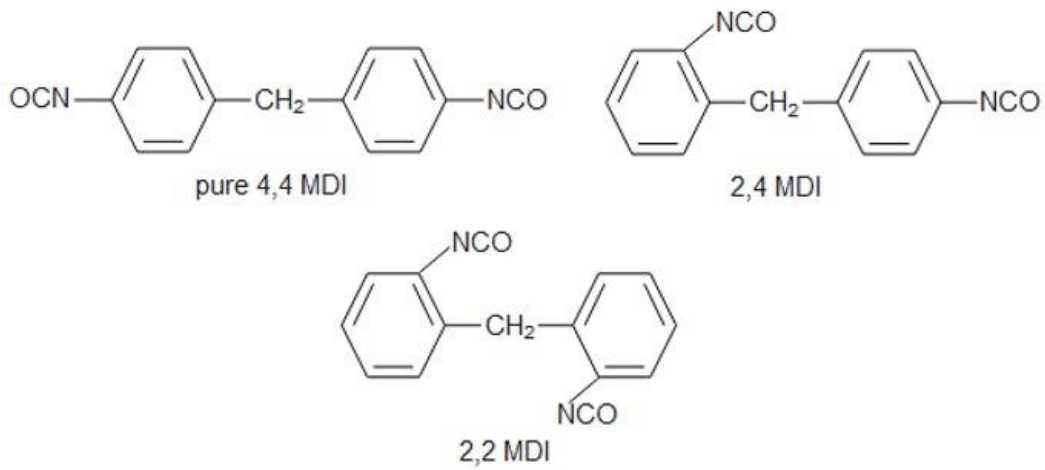


Figure 2.11 : The chemical structures of pure MDI [19].

b) Aliphatic Isocyanates

The most commonly used aliphatic isocyanates include hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and dicyclohexylmethane 4,4t-diisocyanate (H_{12}-MDI) [16]. Aliphatic isocyanates are generally colorless and less reactive than aromatic isocyanates [20]. HDI is the most widely used aliphatic isocyanate. HDI is manufactured from the phosgenation of hexane diamine and phosgene [12]. IPDI formation is based on isophorone and HCN reaction, less toxic than other isocyanates and is an aliphatic isocyanate compound generally used in light stable coatings [4]. The formation of H_{12}MDI is based on the reaction of hydrogenated MDA and phosgene. Known for its low volatility, H_{12}MDI is preferred in the coating industry [15].

2.2.2 Polyols

Polyols are one of the most important raw materials in polyurethane production and they are the raw materials used in polyurethane applications in the most volumes. Generally, the role of polyols in the polyurethane structure is to provide softness and elasticity [12]. Polyol compounds are alcohols, containing multiple hydroxyl groups in their structure. These hydroxyl groups play an active role in determining the characterization by an inversely proportional relationship with molecular weight [11]. In general, polyols are considered in two groups structurally:

The first group includes low molecular weight polyols and generally polyols in this group are used as chain extenders or crosslinkers in polyurethane production. Commonly used low molecular weight polyols include propylene glycol, ethylene glycol, dipropylene glycol, diethylene glycol, 1,4 butanediol, triethanolamine, glycerol [19].

Another group of polyols is the low molecular weight polymers known as oligo-polyols. Oligo-polyols involve terminal hydroxyl groups and they are characterized by molecular weight distribution and average molecular weight. The general formula of oligo- polyols are shown in Figure 2.12 below.

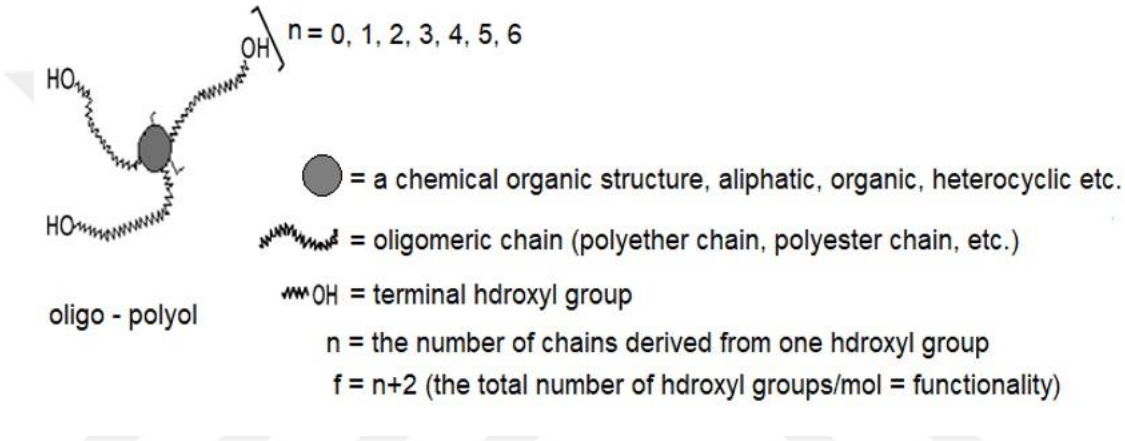


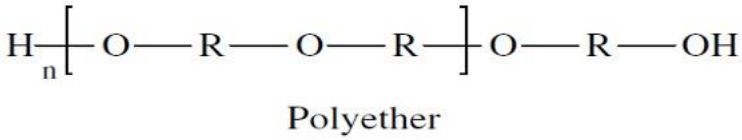
Figure 2.12 : The general formula of oligo- polyols for polyurethanes [19].

2.2.2.1 Types of polyols

The two main groups of polyols are polyether polyols and polyester polyols. In addition to these groups, there are also polyol types such as polyacrylate, polycarbonate, polybutadiene, graft, and polycaprolactone [11]. Table 2.2 shows the advantages and disadvantages of different types of polyols.

2.2.2.2 Polyether polyols

Polyether polyols are produced by the addition of ethylene oxide and/or propylene oxide to a polyhydroxy molecule with the alkali catalyzed polymerization technique [11]. THF is another important compound to polyether polyol synthesis except for ethylene oxide and propylene oxide [12]. Polyethers can have different molecular weights, functionalities, and branchings, which can vary depending on the functionality of the starting alcohols and ratios of ethylene or propylene oxide to starting alcohol (Figure 2.13) [18].

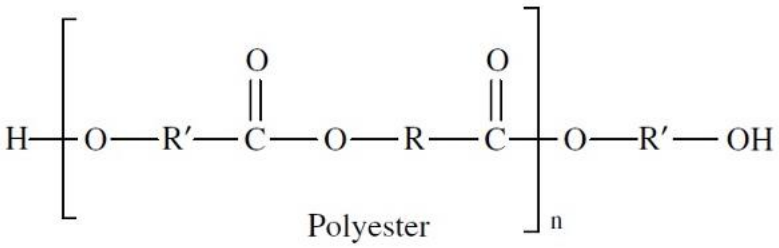


Polyether

Figure 2.13 : Structure of polyether.

2.2.2.3 Polyester polyols

Polyesters are polyols manufactured by condensation of multifunctional polyhydroxy and polyacid monomers that contain various high molecular weight substances in their structure (Figure 2.14) [16]. Polyesters are the group with the highest volume in polyol production after polyethers. For polyurethane production, polyester polyols are divided into two groups as aliphatic and aromatic polyesters [11]. The synthesis methods of these two groups are different and they are generally preferred in different applications due to their special properties, for example, low molecular weight aromatic polyesters are mostly used in rigid foams, while aliphatic polyesters are preferred in polyurethane coatings and adhesives [3, 11].

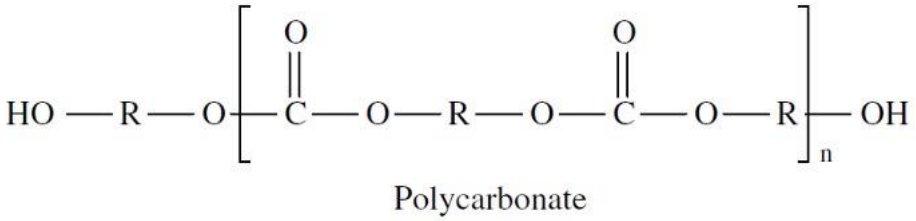


Polyester

Figure 2.14 : Structure of polyester.

2.2.2.4 Other polyols

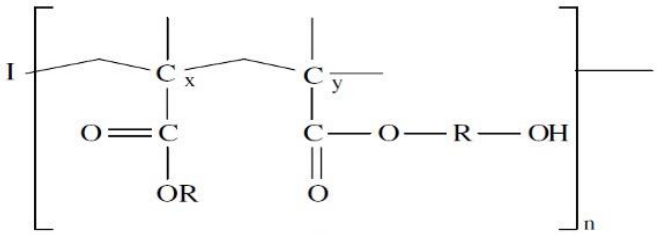
Polycarbonate polyols: Polycarbonate polyols are used in polyurethane coatings and adhesives that require high performance. Their prices are much higher than other polyols. Polycarbonate polyols have aliphatic carbonic ester groups in their structure (Figure 2.15) [12].



Polycarbonate

Figure 2.15 : Structure of polycarbonate.

Polyacrylate Polyols: The polyacrylate polyols include copolymers of acrylic and/or methacrylic acid esters, ethyl acrylate, butyl acrylate, and methyl methacrylate which contain hydroxyl groups (Figure 2.16). Acrylic polyols are used in two-component coating systems. In addition, acrylic polyols find application in wood coatings and anticorrosion finishes [17].



Acrylic

Figure 2.16 : Structure of acrylic.

Polycaprolactone polyols: Poly (e-caprolactone) (PCL) produce generally by ring opening polymerization of e-caprolactone in the existence of metal alkoxides (Figure 2.17). The superior properties of polycaprolactones are flexibility, weather resistance, and low viscosity, thanks to these properties, they are used in 2K polyurethane coatings [21].

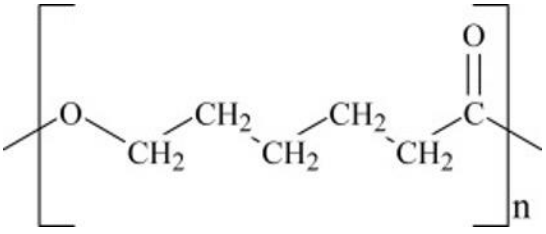


Figure 2.17 : Structure of polycapralactone.

Table 2.2 : Advantages and disadvantages of different polyols from different sources [12].

Polyol Backbone	Advantages	Disadvantages
Polyether polyols based on propylene oxide and ethylene oxide	Hydrolytic stability, cost, viscosity, flexibility	Oxidative stability, modulus/strength, thermal instability,
Aliphatic polyester polyol	Oxidative stability, modulus/strength	Viscosity, hydrolytic stability
Aromatic polyester polyol	Flame retardance, modulus/stiffness	Viscosity, low flexibility
Polyether polyols based on tetrahydrofuran	Hydrolytic stability, modulus/strength	Oxidative stability, viscosity, cost
Polycarbonate polyols	Hydrolytic stability, oxidative stability, modulus/strength	Viscosity, cost
Acrylic polyols	Hydrolytic stability, oxidative stability, hardness	Viscosity,low flexibility,cost
Polybutadiene polyols	Low temperature flexibility, solvent resistance	Viscosity, cost
Polycaprolactone polyols	Low viscosity, weather resistance, flexibility	Low-temperature resistance, hydrolysis

2.2.3 Additives

For polyurethane production, additives are needed besides polyols and isocyanates. These additives may have different functions, such as changing the reaction conditions, modifying the final product. Additives include many groups such as crosslinking agents/chain extenders, catalysts, surfactants, blowing agents, flame retardants, colorants. Some of the additives are used directly in the polyurethane synthesis reaction, while some are used externally in the formulation. [1, 11] Table 2.3 shows the additives used in PU production and the reasons for their use.

Table 2.3 : Components of polyurethanes and reasons for their inclusion [3].

Additives	Reasons for use
Isocyanate	Responsible for the PU reactivity and curing properties
Polyols	Contributes flexible long segments, which produces soft elastic polymers
Catalysts	To speed up the reaction between the isocyanate and polyols and to allow reaction at a lower reaction temperature
Plasticizers	To reduce material hardness
Pigments	To produce colored PU materials, especially for aesthetic purposes
Crosslinkers/chain extenders	For structural modification of the PU molecule and to offer mechanical support that will enhance the material properties
Blowing agents /surfactants	To aid the production of PU foams, to help control the formation of bubbles during synthesis, and to control the foam cell structure
Fillers	To minimize cost and to improve the material properties, such as stiffness and tensile strength
Flame retardants	To reduce material flammability
Smoke retardants	To reduce the rate of a possible smoke generation when the material is burnt

2.2.3.1 Chain extenders and crosslinkers

In fact, chain extenders and crosslinkers are compounds used for the same purpose, the property that makes these compounds different from each other is their functionalities. Difunctional ones are known as chain extenders, while those with three or more functionalities are known as crosslinkers. Crosslinkers (f = 3 or more) and chain extenders (f = 2) are low molecular weight diols/triols and diamine compounds that react with the NCO group [4, 13].

Di- and polyhydric alcohols are used as OH crosslinking agents/chain extenders. Aromatic diamines, whose NH_2 groups react much more slowly with NCO because of the steric hindrance caused by are used broadly as NH_2 crosslinking agents/chain extenders [11]. Alcohols form urethane structures and amines create urea structures. Network densities of polyurethanes are controlled by means of crosslinkers or chain extenders [13]. Crosslinkers and chain extenders are useful for changes in the

morphological structure of polyurethanes. They are mostly used in PU adhesives, elastomers, and fibers [11]. Table 2.4 shows the common chain extenders/crosslinker structures and properties.

Table 2.4 : Structure and properties of common chain extenders/crosslinkers used in urethane chemistry [12].

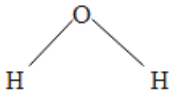
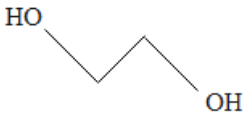
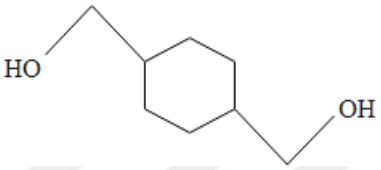
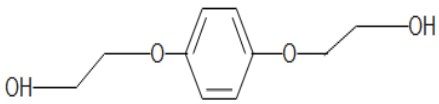
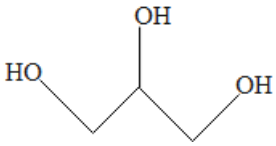
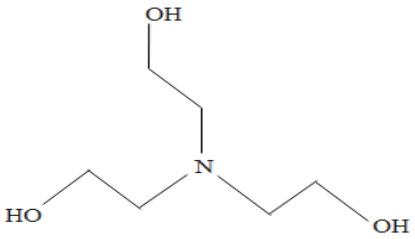
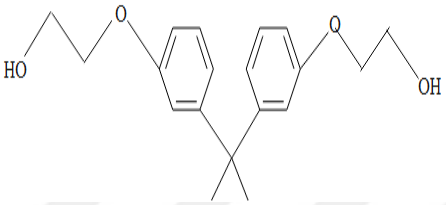
Chain extender-Crosslinker	Structure	Mol wt g/mol	Eqv.wt g/eq	OH/NH number
Water		18	9	6233
Ethylene glycol		62	31	1808
Cyclohexane dimethanol		144	72	779
Hydroquinone bis(2 hydroxy ethyl) ether		198	99	567
Glycerine		92	31	1828
1,6-Hexane diamine		116	58	967

Table 2.4 (continued) : Structure and properties of common chain extenders/ crosslinker used in urethane chemistry [12].

Chain extender-Crosslinker	Structure	Mol wt g/mol	Eqv.wt g/eq	OH/NH number
Triethanolamine		149	50	1122
Bisphenol A bis(2-hydroxylethyl) ether		316	155	355

2.3 Waterborne Polyurethane Dispersions

Innovative technologies have been produced for the development of more eco-friendly and less hazardous to health coatings to meet the rising demands of customers. There have been many coating solutions established to meet these demands and conventional solvent-borne requirements, coatings are now being replaced with environmentally friendly coatings. One of these coating solutions is WPU dispersions. WPUDs have some superior properties over traditional solvent-borne polyurethanes. These features include low viscosity, extremely low VOC content, less odor, easy application, better gloss, and greater chemical resistance [22, 23].

Aqueous polyurethane dispersions, which first appeared in the 1960s, rapidly found a place in the market and began to be used as commercial products in the 1970s [24]. WPU dispersions are colloidal systems containing nano and micron-sized polyurethane particles in an aqueous medium. These polyurethane particles have a special backbone that can be dispersed in an aqueous medium [25].

WPUDs, which are versatile and environmentally friendly materials, have found a wide range of applications when they combine their environmental properties with their extraordinary performance properties such as toughness, abrasion resistance, hardness, flexibility, chemical resistance, and adhesion [26]. PUDs are used as an

adhesive, coating, or ink on many surfaces such as plastic film, leather, textile, wood, and paper [27].

WPUDs can be lower than solvent-borne polyurethanes in terms of features such as mechanical strength, exterior durability, water resistance. Crosslinking is one of the most important and common methods used to improve these properties. In general, crosslinkers react with polymer chains to form chemically crosslinked polymers, which maximize the thermal and mechanical properties of the final products. Although there are many crosslinker groups, the most commonly used among them are carbodiimides, polyaziridines, and isocyanates. Crosslinking in WPUs can take place as one-component (1K) or two-component (2K). These two crosslinking systems have advantages, in the 2K crosslinking system, there are problems such as the need to add the second component to the product just before application, limited pot-life, and transportation. For these reasons, the 1K crosslinking system is more advantageous in production and application and is used more in practice [28, 29].

Waterborne PUDs involve the dispersion of polyurethane in aqueous systems. Their properties are thus strongly dependent on the structure of polyurethanes, in particular, the existence of the soft segments (SS) and hard segments (HS) [30]. The components that make up the soft segment in PUDs are generally polyols or in other words, macrodiols with a molecular weight ranging from 500 to 5000 g / mol. Commonly used polyols can be given as examples of polyether, polyester, and polycarbonate polyols [31].

In PUDs, the parts that generally form the hard segments (HS) are the structures formed by diols, isocyanates, or various crosslinkers [32]. The most important criterion for the selection of isocyanates is the reactivity with water. Therefore, aliphatic isocyanates with lower reactivity and ensure greater control of reactions such as isophorone diisocyanate (IPDI), 4,4-dicyclomethane diisocyanate (H_{12}MDI), and 1,6-hexamethylene diisocyanate (HDI) may prefer [24].

2.3.1 Synthesis methods of polyurethane dispersions

There are diverse processes for the synthesis of aqueous polyurethane dispersions, the first step in all of these processes is the reaction of diols-polyols and diisocyanates-polyisocyanates to form a prepolymer in the presence of an emulsifier. Emulsifiers are hydrophilic materials that, provide the dispersion and stabilization of polyurethane in

water. The emulsifier can be a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a nonionic group poly(ethylene oxide). WPU dispersions can be three types that non-ionic, cationic, and anionic depending upon the type of hydrophilic segments present in the PU backbone [33, 34]. The schematic representation of particle formation in nonionic and ionic waterborne polyurethane/urea dispersions is shown in Figure 2.20.

Anionic PUs constitute the group that is still most used commercially today. The PU anionomers generally contain sulfonates and carboxylates. Subsequently, the acid group is neutralized with a base, usually triethylamine (TEA), to give a group of hydrophilic carboxylate. The type of neutralizing agent used here is one of the factors affecting the properties of the dispersion. Dimethylol propionic acid (DMPA) is the most preferred potential ionic center, the key advantage of DMPA is the steric hindrance of the COOH group, which prohibits it from reacting with the isocyanate groups (Figure 2.18) [24, 34]

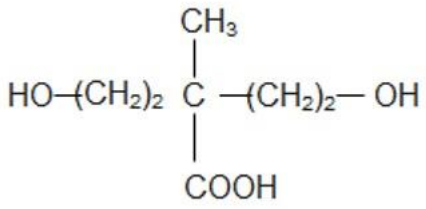


Figure 2.18 : Structure of Dimethylol propionic acid (DMPA).

Cationic PUs is one of the types of waterborne polyurethanes in which the cationic group is integrated into the polymer backbone to make chains water dispersible. Cationic aqueous PUs are commonly used for adhesives, membranes, man-made leathers, and coagulants. The physical characteristics of cationic PUs depend on both hard and soft segments as well as chain extender and dispersion center. The soft segment gives the film fine elasticity, flexibility, and durability, while the hard segment gives the properties of tensile strength and hardness. One of the most common monomers for synthesizing cationic PUs is N-methyl diethanolamine (N-MDEA) (Figure 2.19).

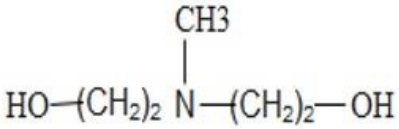


Figure 2.19 : Structure of N-methyl diethanolamine (NMDEA).

Nonionic dispersions of PUs have significant benefits over ionic dispersions such as stability against electrolytes, pH change, freezing, and strong shear forces. Conversely, nonionomer dispersion is unreliable for heating due to a reduction in polyether solubility in water at a rising temperature [35].

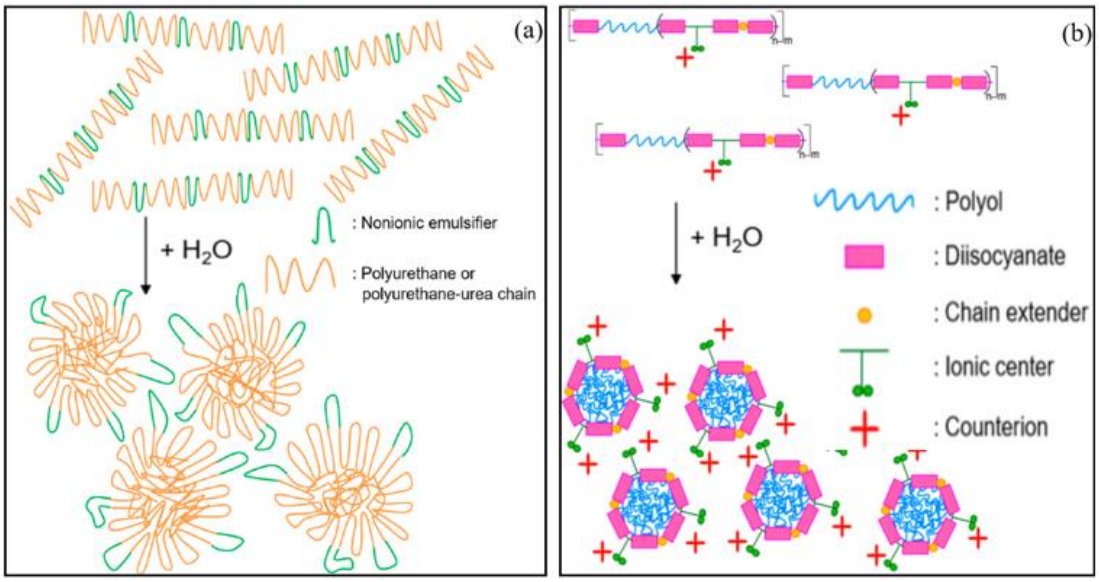


Figure 2.20 : Schematic representation of particle's formation in (a) nonionic, (b) ionic waterborne polyurethane/urea dispersions [36] .

2.3.1.1 Prepolymer mixing process

The prepolymer mixing method is an increasingly important method with the contribution of being a method that can synthesize polyurethane with little or no solvent. The hydrophilically modified NCO-terminated PU prepolymer and water are mixed to form an emulsion, usually by adding a small amount of water-miscible cosolvent. In the prepolymer method, the viscosity value is very important and must be low, otherwise, the dispersion will be very difficult, a very small amount of solvent can be used to reduce the viscosity value [26, 37]. By adding di-or poly-functional chain extenders to the aqueous dispersion, the chain extension step is completed, this step happens in the heterogeneous phase. To successfully perform the prepolymer

mixing method, the dispersing step must be performed in a short time at a temperature below the critical point where the NCO groups start to react with water. Prepolymers, consisting of cycloaliphatic diisocyanate, are most widely used typically due to their low water reactivity [24]. The typical steps of the pre-polymer mixing method have been illustrated in Figure 2. 21.

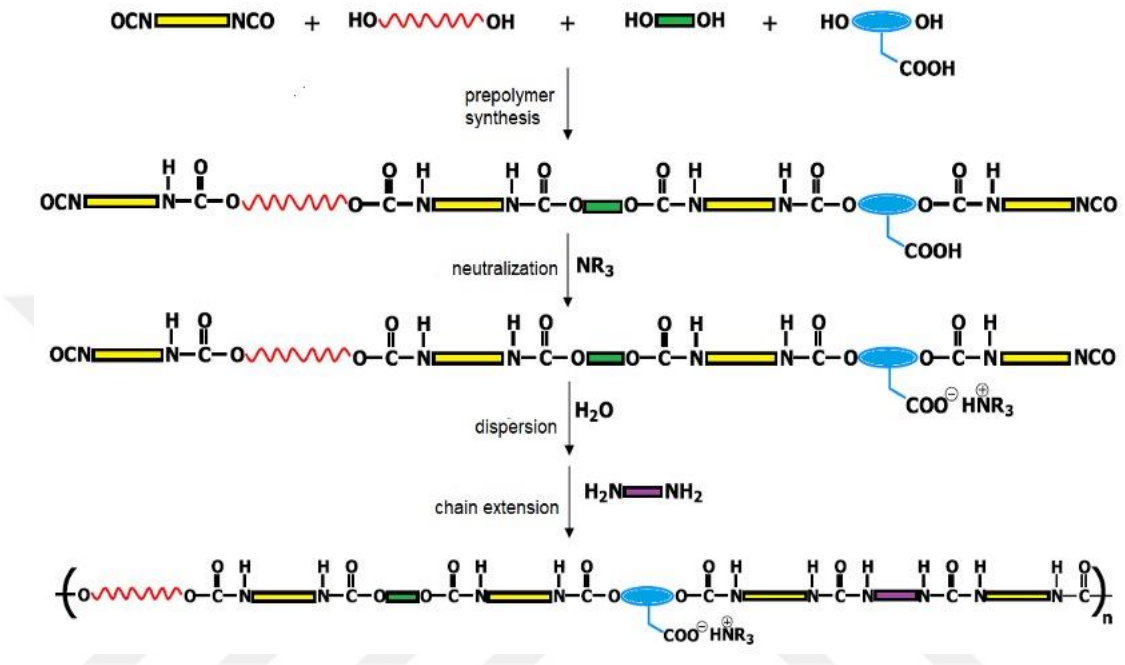


Figure 2.21 : Prepolymer mixing method for the synthesis of WPU dispersions [38].

2.3.1.2 Acetone process

The acetone process is the most preferred method among PU dispersion synthesis methods after the prepolymer mixing method. The acetone process has the important advantage of ending the polymerization in acetone before water is added [39]. The acetone process occurs in two steps. In the initial step, PU is synthesized in an acetone medium and at the same time, potentially charged groups are integrated into the polymer backbone. In a second step, water is added to the mixture of PU-acetone. Lastly, low-boiling acetone is easily distilled from the medium, so the end product contains little or no VOCs. Polar solvents such as tetrahydrofuran or methyl ethyl ketone may be used as an alternative to acetone. Advantages of the acetone process include a broad variety of structural and emulsion variations, solvent-free quality end products, good reproducibility, and good viscosity adjustment. In addition to the advantages of the acetone process, there are also negative aspects such as the production of linear polyurethanes that can only be soluble in acetone, the use of too

much acetone and the economical costs of this acetone distillation, and low reactor efficiency due to the use of high amounts of solvent [24, 40]. The typical steps of the acetone process have been illustrated in Figure 2.22.

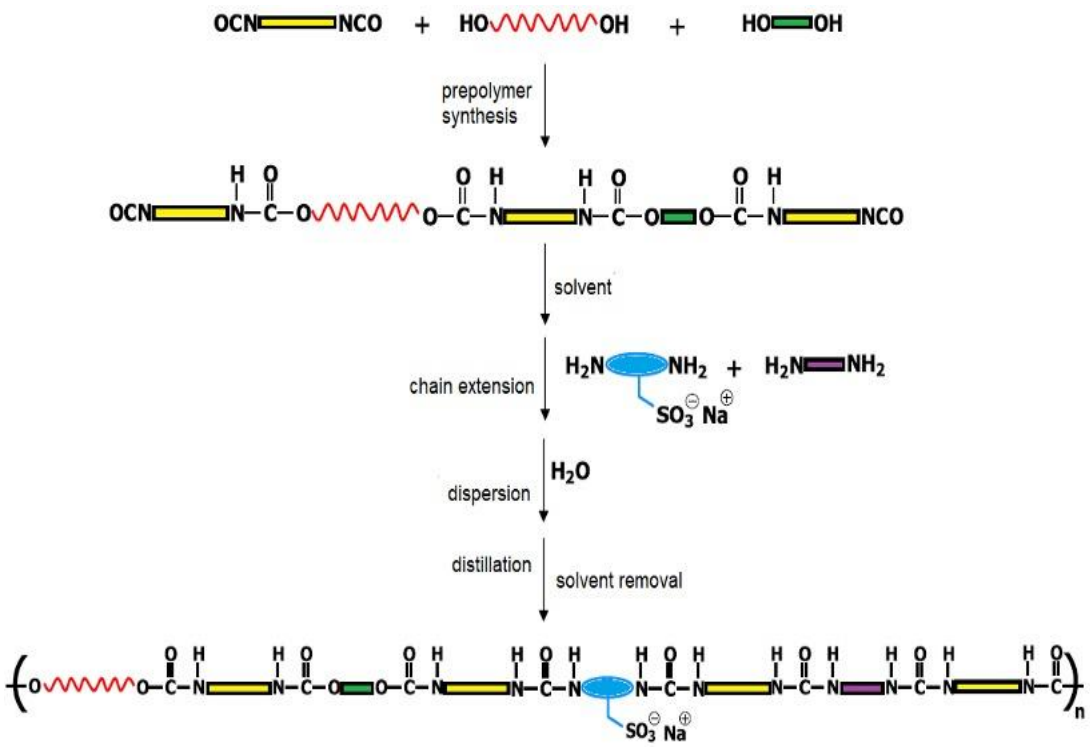


Figure 2.22 : Acetone method for the synthesis of WPUDs [38].

2.3.1.3 Melt dispersion and ketamine/ketazine processes

The melt dispersion process is the solvent-free method used in waterborne polyurethane synthesis. In the Melt dispersion process, isocyanate-terminated prepolymers react with urea or ammonium to form biuret groups. This prepolymer is then spread in water and reacted with formaldehyde. The final step is the reaction of condensation and the formation of polyurethane or urea [33].

The process of ketamine-ketazine can be viewed as a variation of the prepolymer mixing method. During this process, the isocyanate prepolymer is mixed with a blocked amine (ketamine) or hydrazine (ketazine) and dispersed within the aqueous medium. The amino function is released concurrently with hydrolysis and chain extension. Unlike the prepolymer method, the released amine is already uniformly distributed among the dispersed particles [34].

2.3.2 Applications of waterborne polyurethane dispersions

Waterborne polyurethane dispersions have many applications in different industries today, primarily because they are environmentally friendly, non-toxic, and non-flammable. In many industrial applications, WPUDs are valuable, such as coatings, adhesives, ink binders, glass fibers, paper sizing, synthetic leathers, biomaterials, membranes, packaging films, and waterproof textiles [33].

WPUDs are examined in types such as one component, two component, UV-curable, or hyperbranched and are preferred in different applications according to these properties. While 1K WPU dispersions are preferred for applications such as wood coatings or synthetic leather surface coatings, 2K WPU dispersions are preferred for hard coatings on glass and polycarbonate or high performance coatings. On the other hand, UV-curable WPU dispersions are used in weathering resistance coatings, heat resistance coatings, hyperbranched ones are preferred in high performance coatings [41].

Vanesa García et al. synthesized various WPUDs derived from polycarbonate of hexanediol using the acetone method and applied these different WPUDs as a coating on stainless steel plates. Diverse hard segments contained in the WPUDs were obtained by varying (NCO/OH) molar ratios. Raising the NCO/OH ratio reduced the mean particle size, raised the polydispersity, and reduced the Brookfield viscosity of the waterborne polyurethane dispersions. Moreover, the greater NCO/OH ratio the higher the urea and urethane hard segment content, higher the glass transition temperature value, and higher the elastic modulus of the polyurethane. Also, NCO/OH ratio affected the adhesion of the polyurethanes, and the adhesion of the PU coatings was very high [42].

Erica Scrinzi et al. interpreted the aesthetic durability of WPU coatings when applied on wood for use in interior applications. The WPUs in this study are commercial products produced by ICA to be used in the wood coating. These polyurethanes were applied to the wood surface and melamine surface as a base coat and a top coat to evaluate in different tests. The aesthetic properties of the samples were measured by measuring their color and gloss properties. UV radiation exposure was applied for weathering. Taber and falling abrasive tests were preferred for abrasion and erosion tests, respectively. Environmental scanning electron microscopy was used to observe

surface morphology. As a result, the initial surface roughness and gloss properties of transparent and pigmented coatings were determined and their mar resistances were compared [43].

Sam Cha Song et al. used environmentally friendly WPU dispersions instead of solvent-borne polyurethanes in this work and evaluated the results of several different properties by applying a surface coating on PVC. In this project, different commercial polyol products such as polyether diol, polyester diol, caprolactone diol, polycarbonate diol were used to synthesize polyurethanes. Isophorone diisocyanate (IPDI) was used as isocyanate. To introduce a hydrophilic ionic group, dimethylol butanoic acid (DMBA) was used. Mono-terminated reactive silicone was included in the synthesis.

Functional group peaks of the synthesized polyurethanes were analyzed by FT-IR. Polyurethanes contact angles and surface energies and particle sizes were measured. The mechanical and viscoelastic properties of cured films were analyzed by using a universal testing machine (VFD-M, DST) and dynamic mechanical analyzer (DMA) respectively. Lastly, adhesion was measured by ASTM D 3359. Considering the basic results of the measurements, it was observed that WPUDs containing polycarbonate polyol formed relatively high tensile strengths, when DMBA content increased, particle size and adhesion decreased and tensile strength increased. Besides, contact angle and tensile strength improved as the content of reactive silicone increased, while surface energy and elongation decreased due to reactive silicone hydrophobicity [44].

Fangfang Yu et al. worked on obtaining a highly waterproof material by crosslinking siloxane WPUs and fluorinated acrylates. The NCO-terminated prepolymer was obtained by reaction of Isophorone diisocyanate (IPDI), Poly (tetramethylene oxide glycol) (PTMG, Mn = 2000 g mol − 1), and polyether-modified polydimethylsiloxane (PDMS, Mn = 3100). Following the addition of DMPA as an emulsifier, chain extenders hydroxyethyl methylacrylate (HEMA) and 1,4-butanediol (BDO) were also added to the system. After obtaining the vinyl-terminated PU prepolymer, the neutralization agent TEA and fluorinated acrylate monomer (FMA) were added to the system. After the necessary processes, with different percentages of FMA containing Si and F modified PUs (FSPU) were obtained as the final product. Trimethylolpropane-tris- (β-N-aziridinyl) propionate (XR-100) was added to the prepared WPUs as a crosslinking agent to form a crosslinked film.

For the characterization of crosslinked films and WPUs, measurements were carried out with many devices such as FTIR, XPS, TEM, SEM, TGA. As a result of all these studies, it was observed that XR-100 used as a crosslinking agent increased hardness, viscosity, tensile strength, and solvent resistance. Particle size, elongation at break, thermal stability, and contact angle increased with the increase of FMA content, on the other hand, the tensile strength, modulus, and optical transmittance significantly decreased. It has also been found the convenient ratio of the hydrophobic segment and crosslinking agent can remarkably improve the mechanical, thermodynamic, and surface properties of hybrid materials [45].

Jianjun Li et al. synthesized low gloss WPUs and applied WPUs on leather to adjust the gloss. For the synthesis of low gloss waterborne polyurethane, IPDI, PTMG (1000 g/mol), and DMPA were reacted with the presence of a bismuth acid catalyst. TEA was added to neutralize DMPA. Following that, sulfonic acid sodium salt and hydrazine hydrate were added, and the reaction was completed. UV–vis. spectrophotometer FTIR, AFM, and SEM devices were used for the characterization of WPU films. The amounts of NCO/OH, DMPA, sulfonic acid sodium salt, and hydrazine hydrate were changed and their effects on the WPU film were observed. As a result, it was proved by FTIR that low gloss WPU was successfully synthesized. SEM and AFM results showed that the WPU film surface was a rough surface composed of many micro-spherical granules and provided the low gloss effect. Also, It was observed that more microsphere and better stability could be created by changing the amount of NCO/OH, DMPA, sulfonic acid sodium salt, and hydrazine hydrate [46]. Figure 2.23 shows the matt surface forming mechanism.

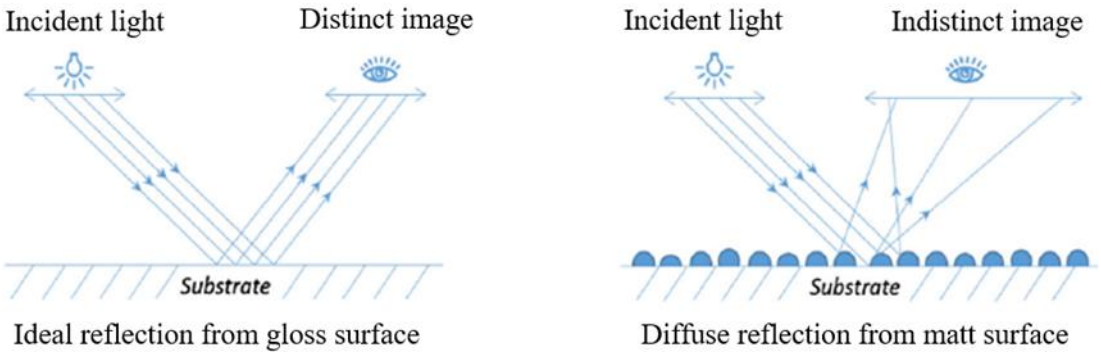


Figure 2.23 : The matt surface forming mechanism [47].

2.3.3 WPUD/silica nanocomposites

WPUs have become highly preferred materials for adhesive and coating applications on different surfaces with their unmatched properties such as elasticity, abrasion resistance, flexibility, versatility, and excellent film-forming properties. However, WPU films inferior in terms of drying rate, mechanical strength, stiffness, and water resistance when compared to solvent borne polyurethane films. Inorganic fillers such as silica, ZnO, TiO2, Fe2O3, SiO2, clay, cellulose nano-crystals are widely used in reinforcing WPUs films. Especially, nanosized fillers incorporated into a WPU matrix are an important tool for improving the properties of WPU films [48, 49].

Generally, four main ways are used in the preparation of organic-inorganic nanocomposites: Sol-gel process (the addition of inorganic precursor into the organic polymer), the integration of inorganic particles into a polymerizable monomer mixture, usage of a mixture of monomers and inorganic precursors - all matrices are subsequently formed in situ, blending method (the mixing of inorganic particles with a final organic polymer). The uses of these four ways are available in practice, and they have advantages and limits according to their intended use [50, 51].

Among the nanosized fillers, silica is widely used due to its specialties such as excellent stability, high hardness, and low price in organic-inorganic nanocomposites. Silica particles are divided into 3 groups as fumed silica, precipitated silica, and colloidal silica. Fumed silica and precipitated silica are available in powder form. Colloidal silica exists perfectly round shape of particles, homogenously dispersed in alcohol or water [50, 52].

The blending method is the simplest and most commonly used technique for preparing polymer/silica nanocomposite. This method is classified as melt blending and solution blending. Melt blending is the most preferred method due to its benefits such as effective processability, efficiency, low cost, and environmental containment. In the melt blending process, the polymer and silica are sheared in the melt at a temperature equal to or greater than the polymer's melting point. The product exfoliates and disperses to the required extent under the proper conditions. Solution blending is a liquid-state powder processing method that achieves a high degree of molecular mixing and is commonly used in material preparation and processing [53, 54].

In-situ polymerization and the sol-gel process are other important silica/polymer nanocomposite preparation methods. The sol-gel process is a synthesis way that contains the preparation of a sol, successive gelation, and solvent separation. The key benefits of the sol-gel process are high purity homogeneous product manufacturing and processing at low temperature and pressure [53,55]. In general, the in situ polymerization process consists of three continuous stages. The nanoscale additives are first pretreated with surface modifiers, and then the modified additives are dispersed in monomer (s). Following this, bulk or solution polymerization occurs. The nanocomposites are then produced in situ during the polymerization process. Using the in situ polymerization process has a number of benefits. These benefits include ease of use, process speed, and improved finished product efficiency. Figure 2.24 shows the general approaches to preparing polymer/silica nanocomposites.

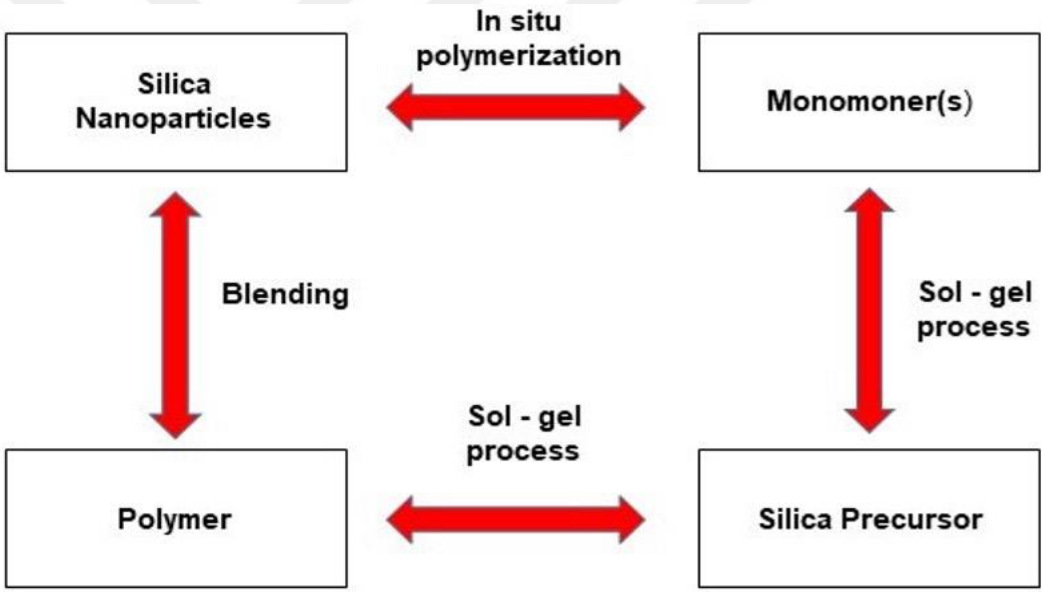


Figure 2.24 : General approaches to prepare polymer/silica nanocomposites [54].

Yongchun Chen et al. have studied the structure and properties of PU / nanosilica composites. In this study, nanosilica particles were directly incorporated into polyester polyol resins utilizing in situ polymerization and blending methods, then cured by isophorone diisocyanate (IPDI) to obtain nanocomposite film. The silica sol was prepared according to Stober's method by changing the ammonia content while holding the other components unchanged. Two methods were used to incorporate the nanosilica particles in polyester polyol resin: one method was in situ polymerization, in which silica sol was mixed with the monomers first, followed by condensation

polymerization using the same techniques and parameters as for pure polyester polyol resin preparation. The other method was the blending method in which the silica sol was mixed with polyol resin directly at 160 ° C for 0.5 hours vigorously.

FTIR, TGA, TEM, DMA, Ultraviolet-visible spectra (UV – vis) devices were used in the characterization of silica powders and films. Besides these, tensile properties, abrasion resistance, and macrohardness measurements were also performed. According to the measurement results, the in situ polymerization method shows higher values than the blending method. Also, the size of the silica particles is a very important factor and in this study, the 28 nm (which have the most hydroxyl value at their surfaces) silica particles have the highest values in Tg, tensile properties, macrohardness, abrasion resistance, and UV absorbance measurements. Based on these results, polyester-based polyurethane coatings with better mechanical properties and UV shielding properties compared to corresponding pure organic coatings could be produced using in situ polymerization or even a blending method [56].

Magdalena Serkisa et al. formed organic-inorganic nanocomposite films consisting of WPU dispersion and colloidal silica. The solution blending method was used to prepare nanocomposites. The organic part of the nanocomposite was PUD with an approximate molecular weight of 2770 g mol $^{-1}$, which was synthesized as a result of the reaction of polycarbonate macrodiol, HDI, and DMPA. The inorganic part was composed of colloidal silica with a molecular weight of 60.08 g mol $^{-1}$ and a specific surface area of 140 m2 g $^{-1}$. PU / silica nanocomposites were prepared by mixing with a magnetic stirrer at 700 rpm for 1.5 hours at room temperature. Then, the prepared composites were cast on Teflon plates and cured at room temperature for 5 days, then at 50 ° C for 20 hours. Nanocomposites samples containing from 5 to 60 wt% of the nanosilica were prepared, calculated on the dry weights of silica and polyurethane.

In this study, it has been studied to determine and compare the mechanical, thermal, surface, and swelling properties of PU/silica nanocomposite films. Nanocomposites with up to 10 wt% silica have polymer-like morphology and better mechanical properties than pure polymer form, smoother surfaces, and lower swelling in water. In cases where the silica ratio was 32 wt % and above, ceramic-like properties appeared, and hard and brittle films were seen. Ultimately, the best properties(mechanical, thermal, swelling, and surface) for coating on different substrates have been achieved with films containing up to 10% nanosilica by weight [50].

In another study, Mohammad Mehdi Jalili et al. investigated the separate effects of hydrophilic and hydrophobic nanosilicas on 2-pack polyurethane clear coatings. Acrylic polyol and aliphatic polyisocyanate have been used in the study to synthesize PU. Untreated hydrophilic silica with an average particle size of 40 nm and hydrophobic silica with an average particle size of 15 nm (treated with dimethyldichlorosilane) were selected for nanocomposite preparation with PU. Many measurements were made to compare PU dispersions and films containing different amounts of silica with the reference pure PU without silica.

As a result, coatings that include hydrophobic nanosilica showed better improvements in mechanical and physical properties. In addition, morphological research with TEM confirmed that hydrophobic nanosilicas dispersed thoroughly with the PU matrix. Lubricating behavior and lower mechanical properties of the hydrophilic nanosilica have been also observed [57].

3. EXPERIMENTAL

3.1 Materials

NeoRez® R-1010 (DSM)

It was used as it received. Neorez R-1010 is a polyether based aliphatic waterborne polyurethane dispersion.

Product specifications

Delivery form : approx. 32% solids in water.

Chemistry : WB urethane

Viscosity (Brookfield 25 °C): 400- 1000 mPa.s

Appearance: Milky white liquid

pH : 8

MFFT : <5 °C

Applications : Overprint lacquers on paper, automotive interior coatings, film coatings on various substrates.

Bayhydur® ultra 3100 (Covestro)

It was used as it received. Bayhydur® ultra 3100 is a polyether modified hydrophilic aliphatic polyisocyanate crosslinker based on hexamethylene diisocyanate (HDI) (Figure 3.1).

Product specifications

Delivery form : 100% non volatile content

Chemistry : polyisocyanate

NCO content : 17.4%

Monomeric HDI : < 0.10

Equivalent weight : approx. 241

Functionality : approx. 3.1

Appearance: Transparent liquid

Viscosity at 25 °C : approx. 2500 mPa.s

Applications : Crosslinker for coating materials or adhesives for industrial and trade applications.

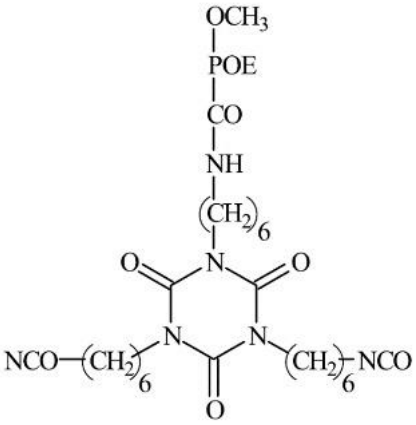


Figure 3.1 : Structure of Bayhydur® ultra 3100 [58].

Crosslinker® CX-100 (DSM)

Crosslinker CX-100 is a 100% active polyfunctional aziridine liquid crosslinker (Figure 3.2). It was diluted 1:1 with water before the use.

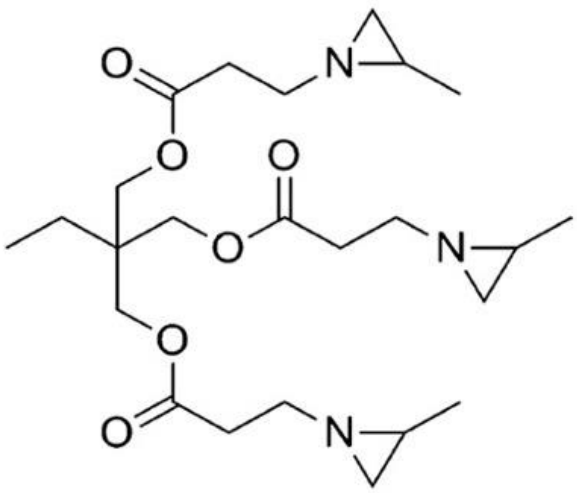


Figure 3.2 : The structural formula of CX-100 [59].

Product specifications

Delivery form : 100 % solid

Chemistry : Trimethylolpropane tris(2-methyl-1-aziridinepropionate)

Equivalent weight : approx. 166

Viscosity (Brookfield 25 °C): 100- 300 mPa.s

Appearance: Clear yellowish liquid

pH : 10.5

Applications : Crosslinker for acrylic emulsions and urethane dispersions.

Nanobyk – 3620 (BYK Chemie GmbH)

It was used as it received. Nanobyk – 3620 is a surface-treated nanosilica dispersion in water.

Product specifications

Delivery form : 30% solids in water.

Particle size D50 : < 100 nm

Viscosity (20 °C) : 11 mPa·s

pH : 10

Appearance: Yellowish liquid

Applications : Wood and furniture coatings, industrial coatings, architectural coatings, 2 K polyurethane coatings.

AEROSIL® R 972 (Evonik)

It was used as it received. AEROSIL® R 972 is a fumed silica after-treated with DDS (dimethyldichlorosilane) [60]. Figure 3.3 shows the surface groups of Aerosil R 972. Figure 3.4 shows the schematic of silica surface functionalization by dimethyldichlorosilane (DDS).

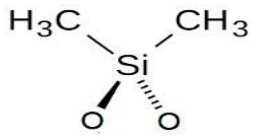


Figure 3.3 : AEROSIL® R 972 surface groups.

Product specifications

Delivery form : Powder

Chemistry : Hydrophobic fumed silica

Mean particle diameter : 15 nm

Specific surface area (BET) : 90 - 130 m^2/g

pH (in 4% dispersion) : 4.5

Appearance: White powder

Applications : General industrial coatings, printing inks, and powder coatings.

Ammonia solution (25%)

It was used as it received.

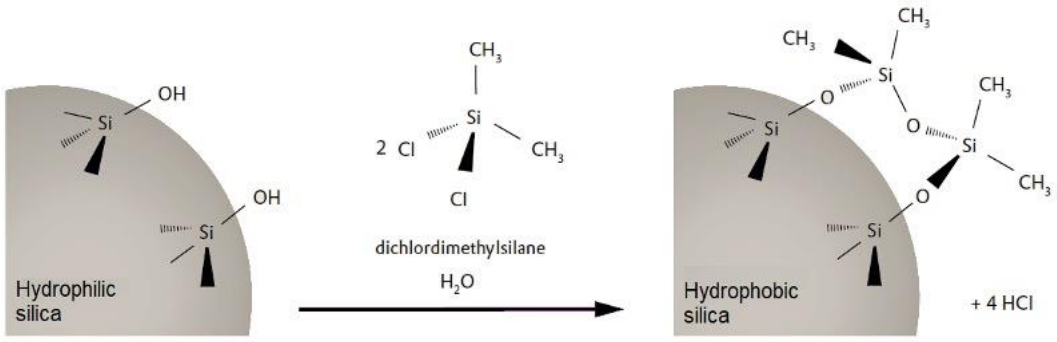


Figure 3.4 : Schematic of silica surface functionalization by DDS.

3.2 Preparation of Waterborne Polyurethane Dispersions

For the preparation of neat WPUD and crosslinker containing dispersions, Neorez R-1010, Bayhydur 3100, CX-100, ammonia, and distilled water were used. To prepare neat WPUD, Neorez R-1010, ammonia, and water were added to a beaker at the percentages given in Table 3.1 and mixed for totaly 15 minutes at room temperature with a mechanical stirrer at 250 rpm. To prepare dispersions containing crosslinker,

after preparation of neat WPUD, Bayhydur 3100 or CX-100 was added the beaker just before the application because of the limited pot life of the crosslinkers and mixed under the same conditions for an additional 15 minutes. CX-100 was diluted 1:1 with water before added to the dispersion, whereas Bayhydur 3100 was added directly.

Table 3.1 : Sample designation and composition of WPU dispersions**.**

Sample code	Neorez R-1010	Water	Ammonia	CX-100 (2%)	Bayhydur 3100 (5%)
WPUD	75	24.80	0.2	-	-
BWPUD	75	24.80	0.2	-	+
CWPUD	75	24.80	0.2	+	-

All values in the tables show the wt% of components.

3.3 Preparation of WPUD/Silica Dispersions

For the prepare, Aerosil R 972 containing dispersions, Neorez R-1010, ammonia, Aerosil R 972, and water were added to a beaker at the percentages given in Table 3.2 and mixed for totally 8 hours at room temperature with a mechanical stirrer at 1000 rpm. Aerosil R 972 amount ranged between 0.1 and 3% by weight (Figure 3.5). Addition of Aerosil R 972 above 3% caused high viscosity and proper mixing could not be achieved.

Table 3.2 : Sample designation and composition of WPUD/fumed silica nanocomposites**.**

Sample code	Neorez 1010	Aerosil R-972	Water	Ammonia	CX-100 (2%)	Bayhydur 3100 (5%)
APU-1	75	0.1	24.70	0.2	CAPU-1	BAPU-1
APU-2	75	0.2	24.60	0.2	CAPU-2	BAPU-2
APU-3	75	0.3	24.50	0.2	CAPU-3	BAPU-3
APU-4	75	0.5	24.30	0.2	CAPU-4	BAPU-4
APU-5	75	0.75	24.05	0.2	CAPU-5	BAPU-5
APU-6	75	1	23.80	0.2	CAPU-6	BAPU-6
APU-7	75	2	22.80	0.2	CAPU-7	BAPU-7
APU-8	75	3	21.80	0.2	CAPU-8	BAPU-8

All values in the tables show the wt% of components.

For the prepare Nanobyk- 3620 containing dispersions, Neorez R-1010, ammonia, water, and Nanobyk- 3620 were added to a beaker at the percentages given in Table 3.3 and mixed for totally 2 hours at room temperature with a mechanical stirrer at 1000 rpm. Nanobyk- 3620 amount ranged between 1% and 25% by weight (Figure 3.5). Addition of Nanobyk- 3620 above this amount caused high viscosity and proper

mixing could not be achieved. All the prepared WPUD/silica dispersions were kept at room temperature for 18 hours to minimize the bubbles formed during mixing. After these steps, if a crosslinker is to be used in the WPUD/Silica dispersions, 5% by weight of Bayhydur 3100 or 2% by weight of CX-100 was added and mixed with a mechanical stirrer at 250 rpm for 20 minutes at room temperature.

Table 3.3 : Sample designation and composition of WPUD/aqueous silica dispersion nanocomposites.

Sample code	Neorez 1010	Nanobyk 3620	Water	Ammonia	CX-100 (2%)	Bayhydur 3100 (5%)
NPU-1	75	1	23.80	0.2	CNPU-1	BNPU-1
NPU-2	75	3	21.80	0.2	CNPU-2	BNPU-2
NPU-3	75	5	19.80	0.2	CNPU-3	BNPU-3
NPU-4	75	10	14.80	0.2	CNPU-4	BNPU-4
NPU-5	75	15	9.80	0.2	CNPU-5	BNPU-5
NPU-6	75	20	4.80	0.2	CNPU-6	BNPU-6
NPU-7	75	25	0	0.2	CNPU-7	BNPU-7

All values in the tables show the wt% of components.

3.3.1 Preparation of films

For the film formation, prepared dispersions were poured into polytetrafluoroethylene (Teflon) molds in dimensions (50 mm, 25 mm, 1 mm) and (25 mm, 10 mm, 1 mm). The samples were dried at room temperature for 4 hours and then in the oven at 50 °C for 8 hours. The film thickness (~150 μm) was controlled by the amount of mixture used per unit area of the Teflon mold.

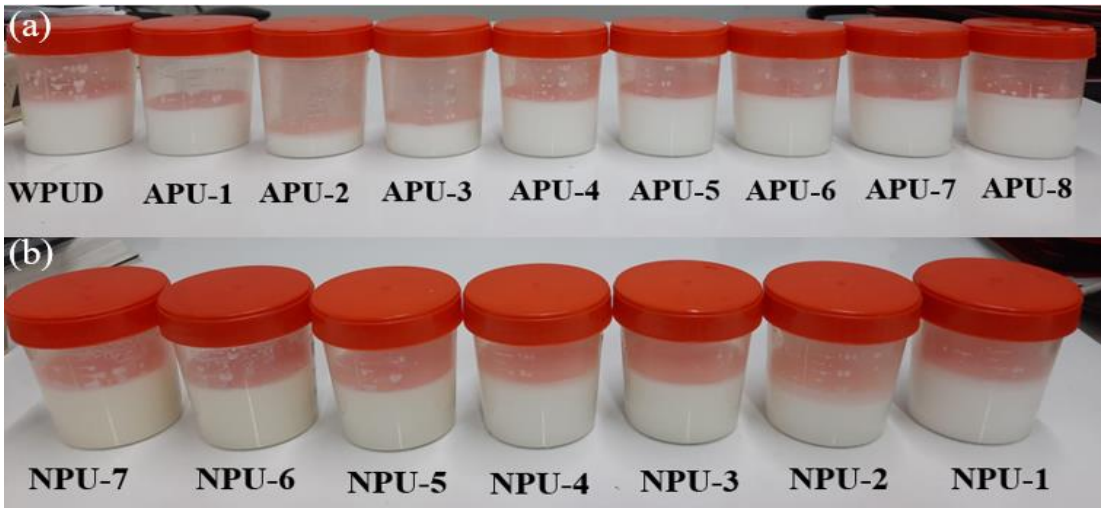


Figure 3.5 : Pictures of neat WPUD and (a) Aerosil R 972 containing dispersions, (b) Nanobyk- 3620 containing dispersions.

3.4 Crosslinking Mechanism of WPUD with Polyfunctional Aziridine and Polyisocyanate

The crosslinking reaction between polyfunctional aziridine and the carboxylic group of waterborne polyurethane dispersion can proceed at a reasonable rate at ambient conditions, and no heat or catalyst is required to complete the curing process (Figure 3.6). The multiaziridine rings of crosslinker CX-100 can react rapidly with carboxylate groups in WPUD to create secondary amine and ester groups, resulting in a more crosslinked structure [61- 63]. In general, new functional groups formed in crosslinked polymers can be monitored using FTIR measurements. However, the FTIR technique is challenging to use since the expected new bands are masked by strong absorptions in the IR spectra of the reacting materials. For example, CX-100 and the WPUD exhibit a broad band in the carbonyl region which prevents the observation of significant spectral variation after the reaction [64]. The FTIR spectra of CX-100 containing film (CWPUD) is remarkably similar to that of neat WPUD film, the shift of the peak at 1723 cm−1 to 1726 cm−1 and its increase can be attributed to the curing reaction between the aziridine and the carboxyl group (Figure 4.2) [65].

Polyisocyanates are extremely reactive substances that can quickly react with WPUDs at room temperature or slightly higher to form a crosslinked structure. If the polyurethane structure contains OH, NH_2, COOH functional groups, isocyanates can react with one or more of these groups, resulting in urethane, urea, and amide groups, respectively (Figure 3.8). Water and isocyanate react to form unstable carbamic acid, which quickly decomposes to CO_2 and amine. Then, It will also quickly react with the other isocyanate functionality to produce urea links [66]. Figure 3.9 depicts the urea link formed during crosslinking when water is present. Bayhydur 3100 is a polyether modified hydrophilic aliphatic polyisocyanate crosslinker based on hexamethylene diisocyanate (Figure 3.7).

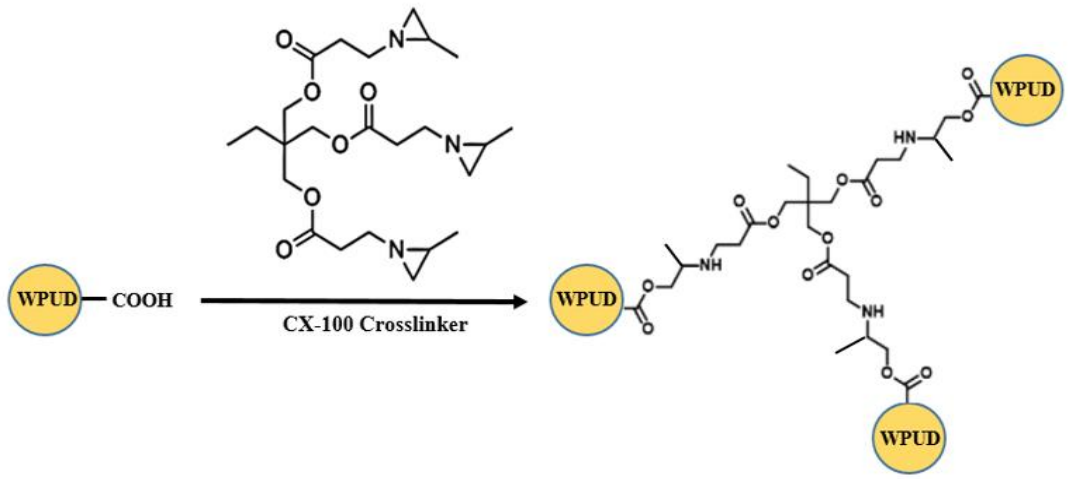


Figure 3.6 : Crosslinking reaction mechanism of WPUD with polyfunctional aziridine.

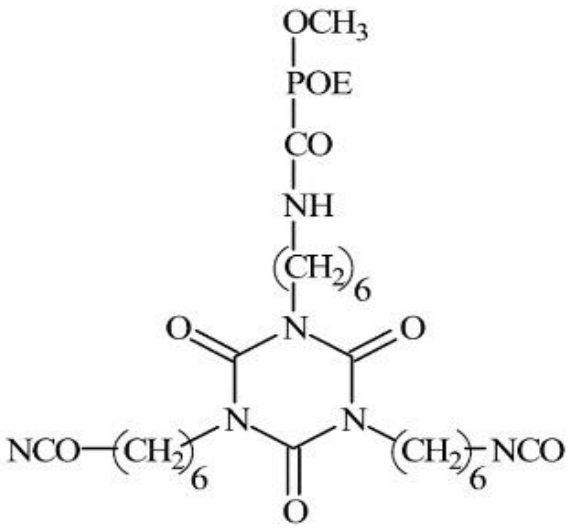


Figure 3.7 : Structure of Bayhydur 3100 [58].

FTIR spectra were used to examine the reactions of Bayhydur 3100 and WPUD. The absence of characteristic free NCO peaks in the FTIR spectra of neat WPUD between 2200 cm^{-1}- 2270 cm^{-1} suggested that the NCO group of the isocyanate reacted with the OH group of the polyol [67, 68]. The peak at 1,686 cm^{-1} can assigned to C=O stretching of urea (which can be produced by the side reaction between NCO and water) or to the C=O stretching modes of isocyanurate groups in Bayhydur 3100. The peaks at 765 cm^{-1} and 1465 cm^{-1} are associated with C-N skeletal stretching and CH_2 bending deformation vibrations, respectively [69- 71]. The FTIR spectra of neat WPUD and BWPUD (containing 5% Bayhydur 3100) films were compared based on the peaks at 1686 cm^{-1}, 1465 -1463 cm^{-1}, and 765 cm^{-1}, it was seen that the peaks in

BWPUD became stronger than neat WPUD. According to the FTIR result, it was deduced that isocyanate, which has a very similar structure to Bayhydur 3100 or Bayhydur 3100, may have been used for the pre-crosslinking of the neat WPUD.

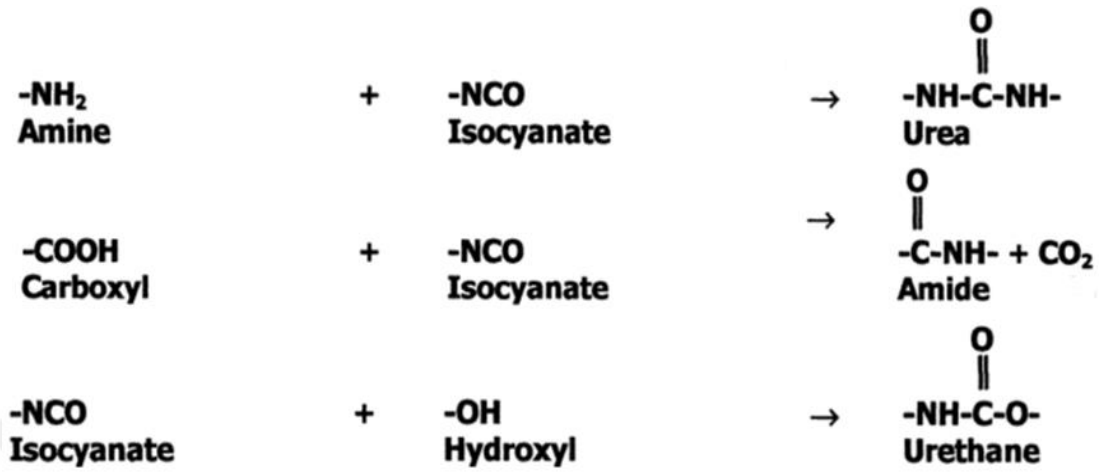


Figure 3.8 : Isocyanate reactions with functional groups of WPUDs [69].

For post-crosslinking of Neat WPUD, 5% wt of Bayhydur 3100 was added to the dispersion. The addition of Bayhydur 3100 increased the NCO/OH ratio of the WPUD. It is assumed that when the NCO/OH ratio increases, more urethane, and urea will be formed in the WPUD system, increasing the crosslinking density and hydrogen bond interactions [68, 69, 72].

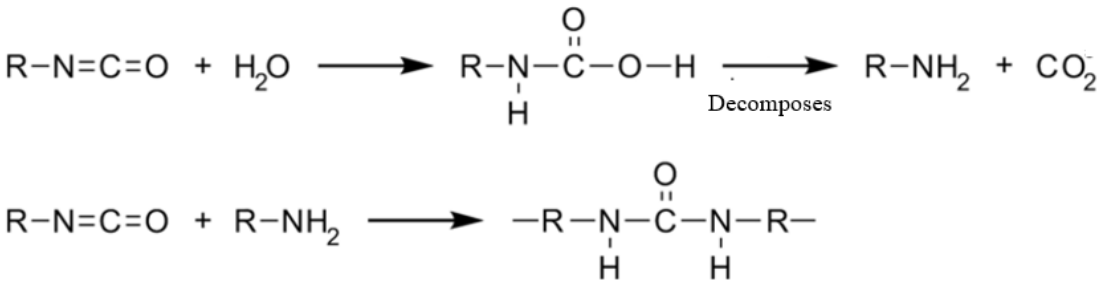


Figure 3.9 : Isocyanate reaction with water [66].

3.5 Characterization

FTIR-ATR

FT-IR spectra were measured using Bruker Alpha FTIR spectrophotometer (ATR sampling accessory), directly from the sample.

Scanning Electron Microscope (SEM)

Morphology of products was examined by scanning electron microscope, ESEM XL30 ESEM-FEG Philips, and the samples for the SEM measurement are prepared by platinum coating (Figure 3.10).

Figure 3.10 :ESEM XL30 ESEM-FEG Scanning Electron Microscope.

Scanning Electron Microscope Energy Dispersive X-Ray Analysis (SEM-EDAX)

Semi-quantitative element analysis was carried out with FEI-Philips XL30 Environmental Scanning Electron Microscope with Field Emission Gun that equipped with EDAX-Energy Dispersive X-ray Analysis Unit.

X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of samples were obtained with Rigaku D/Max-Ultima+/PC XRD instrument (Figure 3.11). Cu K α radiation with a wavelength of λ=0.15406 nm was applied in the range of 2θ=3° to 2θ=60° with a step width of 0.02 and a dwell time of 0.6 s.

Figure 3.11 : Rigaku D/Max-Ultima+/PC XRD.

Differential scanning calorimetry (DSC)

The DSC thermograms of the samples were measured with the EXSTAR DSC-7020 instrument (Figure 3.12). All samples about 5 mg were placed in an alumina ceramic crucible and heated under nitrogen atmosphere from 20 °C to 300 °C with a heating rate of 10 °C min^{-1}.

Figure 3.12 : EXSTAR DSC-7020 instrument.

Hardness

The hardness of the polyurethane films was determined according to the ASTM D2240 standard with the calibrated Shore D durometer. The Shore D hardness scale is 0 to 100; the higher the Shore D hardness value, the harder the material. The average of three experimental tests was used to determine Shore D hardness.

Optical Microscopy

Dried films appearance and transparency were examined by surface analysis of the material using nosepiece type microscope Nikon LV150NL equipped with objective CFI L Plan EPI 2.5x at magnification 25x. There was no extra sample preparation required before the measurement. Nikon LV150NL microscope is shown in Figure 3.13.

Figure 3.13 : Nikon LV150NL nosepiece type microscope.

Swelling measurements

For swelling study on films in water, the films were immersed in distilled water for 144 hours at room temperature. After the residual water was wiped from the sample surfaces with filter paper, the weight of swollen films was measured immediately. The water swelling of the samples was calculated by measuring its mass increase as a function of time, by the following equation:

$$\text{Swelling (\%)} = \frac{w\text{-}w_0}{w_0} \times 100 \qquad (3.1)$$

As seen in equation 3.1 the w_0 is the weight of the dried film prior to immersion in distilled water and w is the weight of the film after swelling over a certain period.

4. RESULTS AND DISCUSSION

4.1 FTIR Analysis

Fourier Transform Infrared Spectroscopy was used to characterize functional groups, and investigate the chemical structure of silicas, crosslinkers, and prepared films. The FTIR spectrum of HDI based polyether modified aliphatic polyisocyanate crosslinker Bayhydur 3100 is shown in Figure 4.1.

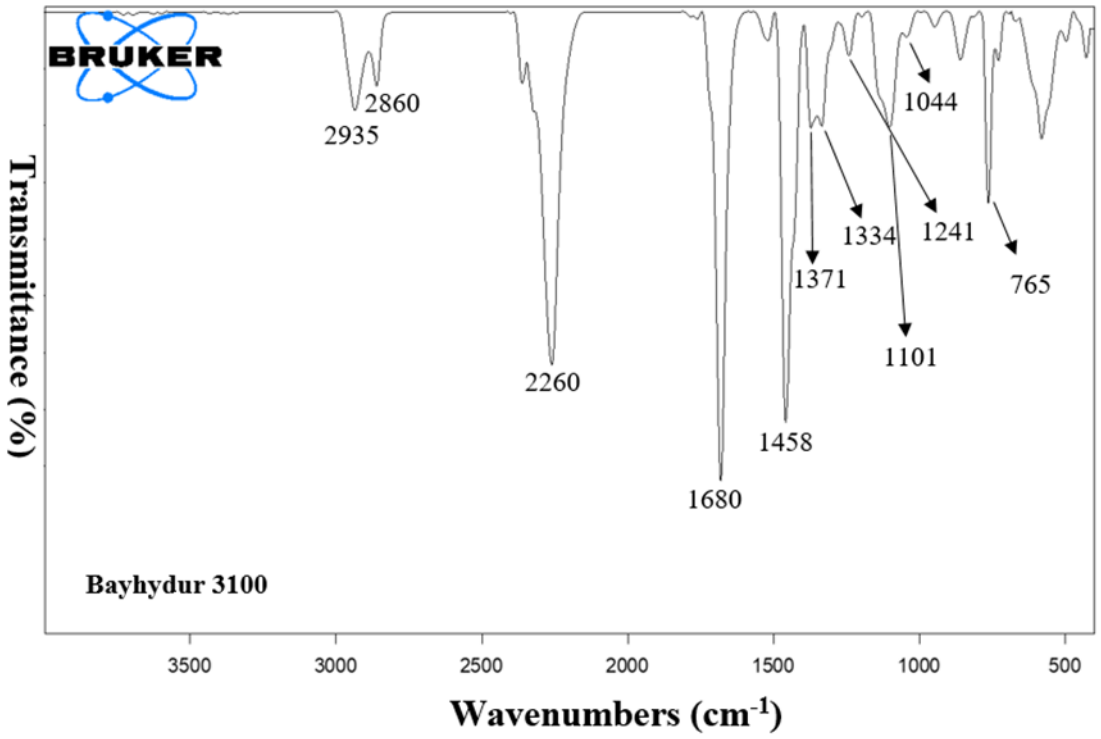


Figure 4.1 : FTIR spectrum of HDI based polyisocyanate crosslinker.

The peaks at 2935 cm^{-1} and 2860 cm^{-1} correspond to asymmetric and symmetric stretching vibration of the CH_2 group, respectively [70, 73]. The strong peak at 2260 cm^{-1} is referred to as N=C=O stretching vibration [74, 75]. The strong peak at 1680 cm^{-1} was attributed to the H-bonded C=O stretching modes in isocyanurates, while the peak at 1458 cm^{-1} presumably results from the C=N stretching [76]. The peak at 1241 cm^{-1} was assigned to stretching vibrations of (O=) C–O–C. The bonds at 1371 cm^{-1},

765 cm^{-1}, and 1334 cm^{-1} were referred to as asymmetric stretching of δ–C (CH_3), C-N skeletal stretching, NCO in phase/CH_2 vibrations, respectively. Lastly, the peak at 1101 cm^{-1} attributed to asymmetric stretching of C-O-C, and the peak at 1044 cm^{-1} attributed to the C-C skeletal vibrations [74, 71].

The FTIR spectrum of polyfunctional aziridine crosslinker CX-100 is shown in Figure 4.2. The CX-100 spectrum displays a strong peak at 1734 cm^{-1} attributed to carbonyl absorption (C=O) [77, 78], as well as peaks ranging from 1395 cm^{-1} to 1014 cm^{-1} related to aziridine ring stretching vibrations [79]. Furthermore, the peaks between 3045 cm^{-1} and 2839 cm^{-1} were assigned to C-H, CH_2 bonds in the structure [65, 79, 80].

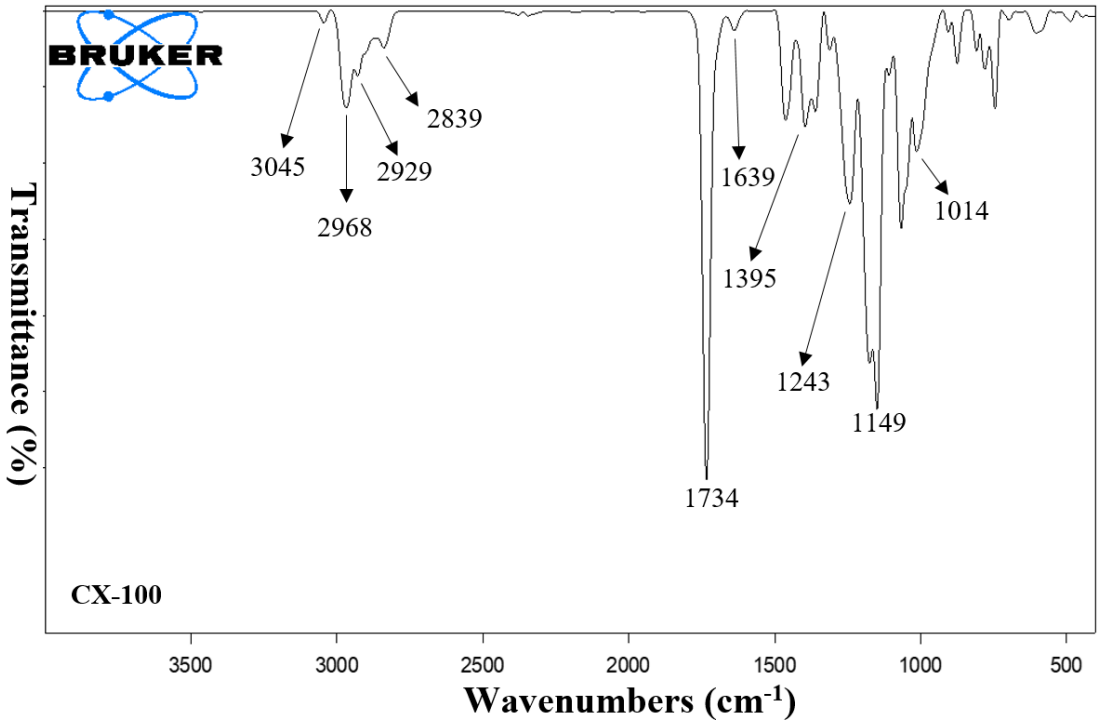


Figure 4.2 : The FTIR spectrum of polyfunctional aziridine crosslinker.

The FTIR spectra of both nanosilica are shown separately in Figure 4.3. In Figure 4.3 the characteristic peaks of Si-O-Si bonds for DDS treated fumed silica (Aerosil R 972) were observed at 456 cm^{-1}, 807 cm^{-1}, and 1065 cm^{-1}. The peak at 456 cm^{-1} is attributed to O–Si–O deformation bonds, at 807 cm−1 and 1065 cm−1 correspond to the symmetric and asymmetric stretching of Si-O-Si bonds, respectively [60]. In Figure 4.3 the characteristic peaks for surface treated silica dispersion in water were observed at 465 cm^{-1}, 1117 cm^{-1}, 1638 cm^{-1}, 2849 cm^{-1}, 2981 cm^{-1}, and 3355 cm^{-1}. The broad band near 3355 cm^{-1} was assigned for the stretching vibration of OH groups

(Si-OH). The peaks at 2981 cm^{-1} (Si-CH_3 asymmetric stretching) and 2849 cm^{-1} (Si-CH_3 symmetric stretching) can be related to alkyl groups of the organosilane modifier on the surface of the nanosilicas. The peak at 1638 cm^{-1} corresponds to O–H bending vibration of adsorbed molecular water, at 465 cm^{-1} and 1117 cm^{-1}attributed to a bending and asymmetric stretching vibrations of Si-O-Si bonds, respectively [81, 82].

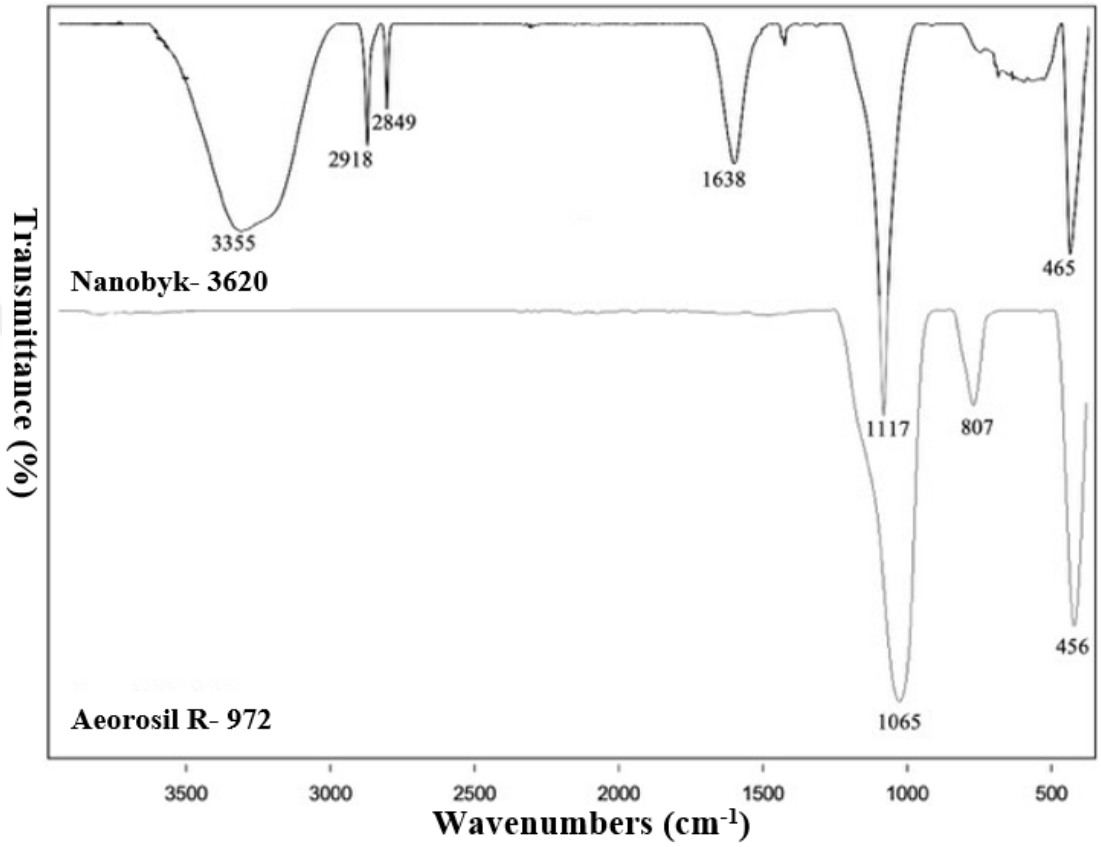


Figure 4.3 : The FTIR spectra of fumed silica and aqueous silica dispersion.

The FTIR spectrum of WPUD, BWPUD, and CWPUD films is shown in Figure 4.4. The absorption peak at 3307 cm^{-1} refers to urethane N-H stretching with the corresponding deformation vibration peak appearing at 1530 cm^{-1}, and the peak at 1723 cm^{-1} belongs to the stretching mode of C=O groups in urethane [83]. There is no peak at 2270 cm^{-1} indicating that the isocyanate group (- NCO) had fully reacted with the OH group of polyether polyol [84]. The peaks at 2938 cm^{-1}, 2854 cm^{-1}, and 2795 cm^{-1} are associated with C–H stretching vibration in CH_3 and CH_2 [85]. The peak at 1686 cm^{-1} was attributed to C=O stretching vibration [68]. The C-O-C stretching absorption peak corresponds to the ether oxygen of the polyether soft segment at 1103 cm^{-1} [86]. The strong peak at 1240 cm^{-1} belongs to the C–O and C–N stretching vibration [87].

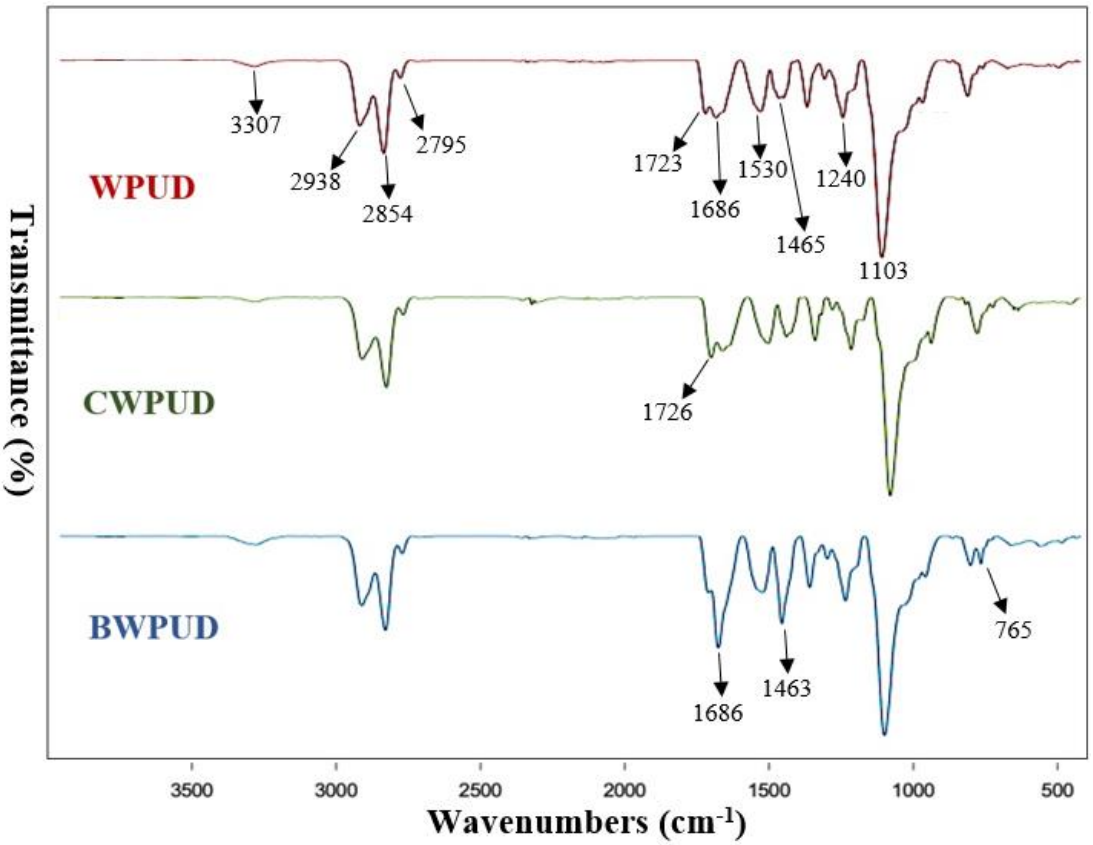


Figure 4.4 : FTIR spectra of WPUD, CWPUD and, BWPUD films.

Compared to the WPUD IR spectrum, IR spectrums of BWPUD (containing 5% HDI based polyisocyanate crosslinker Bayhydur 3100) and CWPUD (containing 2% polyfunctional aziridine crosslinker CX-100), it was observed in the BWPUD spectrum the peaks at 1686 cm^{-1} and 765 cm^{-1} were stronger, the peak at 1465 cm^{-1} cm shifted to 1463 cm^{-1} and was stronger, the peak at 1448 cm^{-1} disappeared. The impact of Bayhydur 3100 is confirmed by a stronger peak at 1686 cm^{-1}, 765 cm^{-1}, which can arise from C=O stretching vibration in the isocyanurate ring of Bayhydur 3100 or C=O stretching of ureas (which can be produced by the side reaction between NCO and water) and C-N skeletal stretching vibration in the isocyanurate ring, respectively [75]. Although the spectra of CWPUD is remarkably similar to that of WPUD, the shift of the peak at 1723 cm^{-1} to 1726 cm^{-1} and its increase can be attributed to the curing reaction between the aziridine and the carboxyl group [65].

The FT-IR spectra of films containing silica (Nanobyk- 3620 or Aerosil R-972) are similar to that of neat WPUD, as shown in Figure 4.5. This is because the characteristic absorption peak of Si-OH (960 -900 cm^{-1}) and Si-O-Si (1100-1000 cm^{-1} and 800-700 cm^{-1} for asymmetric and symmetrical stretching vibration) are overlapped with neat

WPUD. The peak at 475 cm^{-1} in both CNPU-3 and BNPU-3 spectra was attributed to the Si-O-Si bending vibration of aqueous silica dispersion [88].

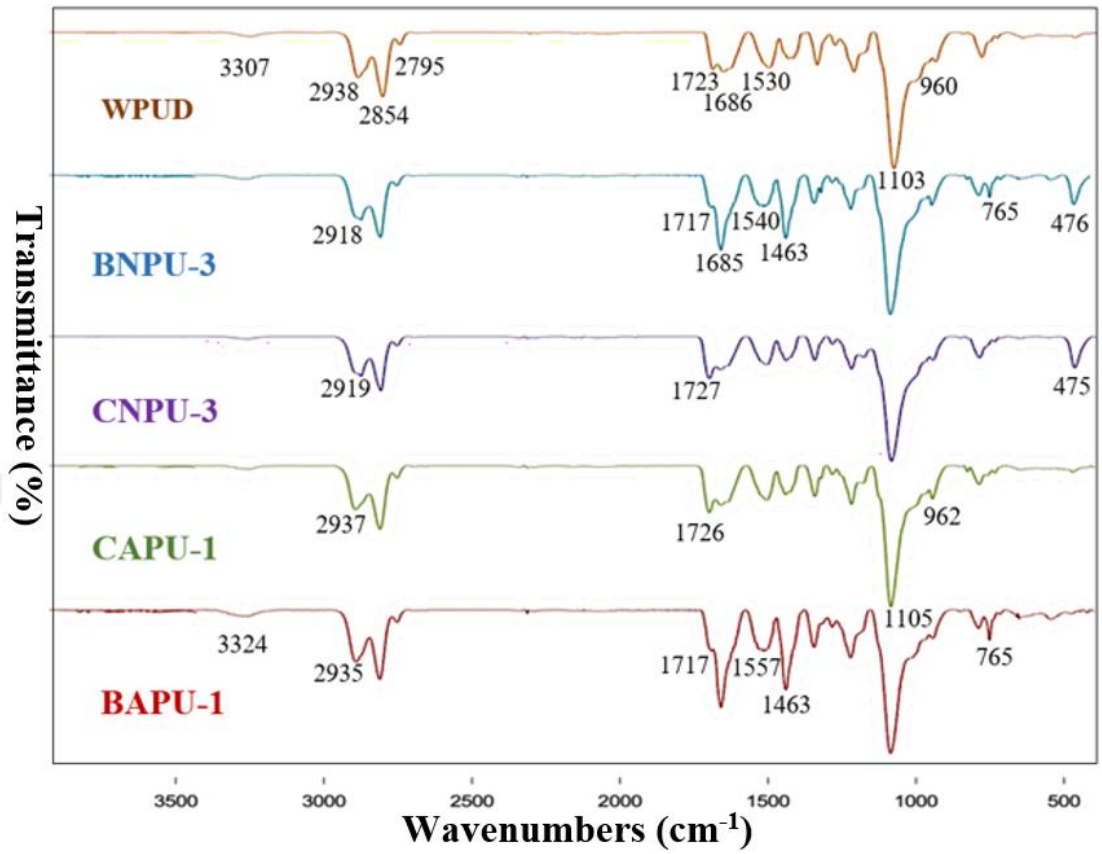


Figure 4.5 : FTIR spectra of WPUD, BNPU-3, CNPU-3,CAPU-1, and BAPU-1 films.

4.2 Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry (DSC) was used to investigate the thermal characteristics of prepared films. DSC thermograms, of the neat WPUD film and crosslinked films with Bayhydur 3100 or CX-100 were shown in Figure 4.6 and Figure 4.7, respectively. In Table 4.1, the results of the analysis from the various DSC thermograms were listed.

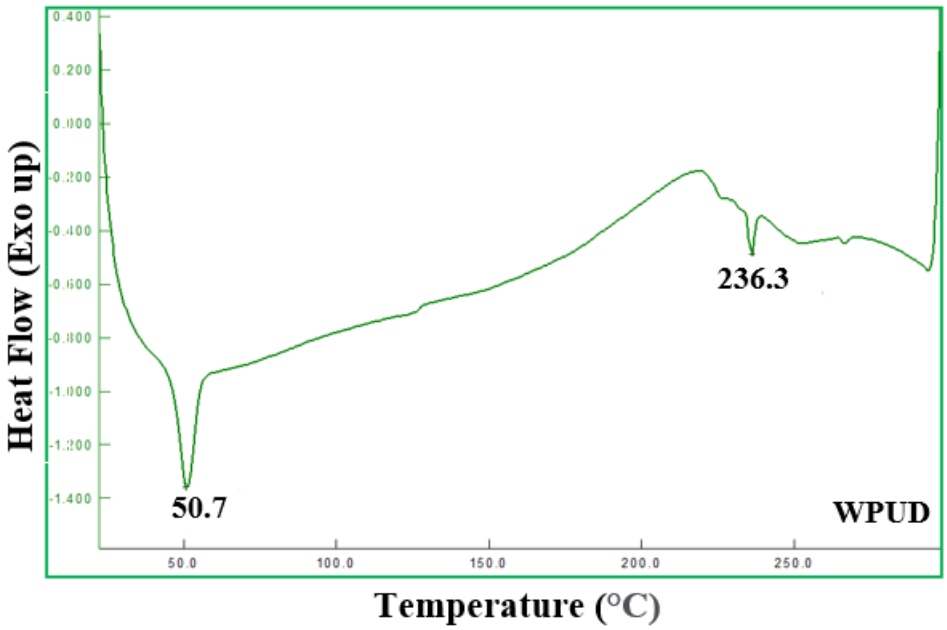


Figure 4.6 : DSC thermogram of WPUD film.

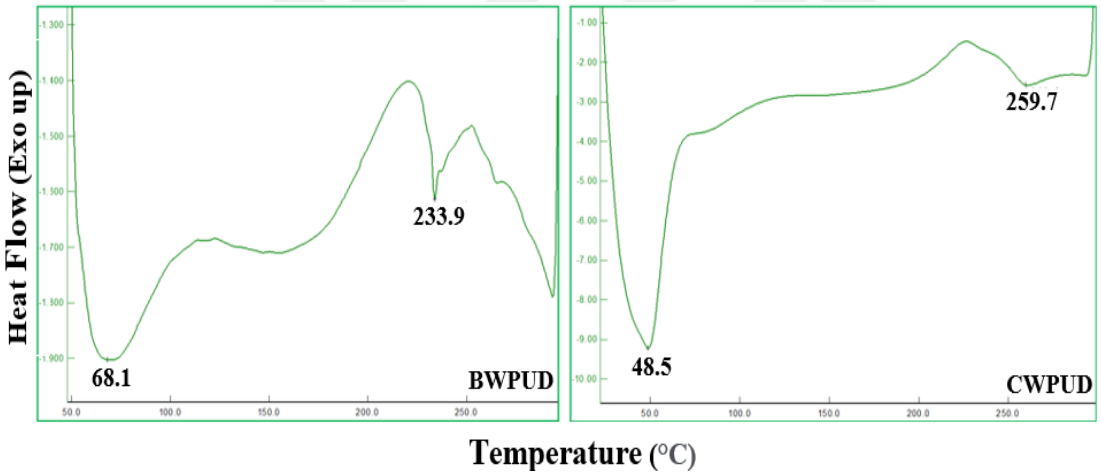


Figure 4.7 : DSC thermograms of BWPUD and CWPUD films.

As seen in Dsc thermograms, It was observed that WPUD, BWPUD, and CWPUD films display significant endothermic melting peaks (Tm_1) in the interval of 48.5 °C – 68.1 °C, corresponding to the crystalline melting temperature of the soft segments [89- 91]. In addition to this, WPUD, BWPUD, and CWPUD films showed an endothermic peak (T_d) at 236.3 °C, 233.9 °C, and 259.7 °C, respectively. This peak attributed to the beginning of polyurethane degradation [90, 92].

Table 4.1 : DSC data of neat WPUD, crosslinked WPUDs, and WPUD/silica nanocomposites.

Sample	Tm_1 (°C)	Tm_2 (°C)	T_d (°C)
WPUD	50.7	-	236.3
BWPUD	52.1	-	233.9
CWPUD	48.5	-	259.7
BAPU-7	49.7	-	258.2
BNPU-3	-	120.1	249.5
BNPU-4	50.9	123.5	-
BNPU-7	-	123.4	245.7
CNPU-7	45.7	119.5	-

In general, the initial degradation of polyurethanes is associated with the degradation of the urethane/urea bonds, whereas the following degradation is associated with the decomposition of ether or ester bonds in the structure of the soft segment (due to polyol), utilized in the production of polyurethanes [93, 94].

The DSC thermograms of WPUD/silica composite films containing Nanobyk- 3620 and Aerosil R972 at different %wt can be seen in Figure 4.8 and Figure 4.9. Unlike the films without silica, a new endothermic peak (Tm_2) was detected in these DSC thermograms of BNPU-3, BNPU- 4, BNPU-7, and CNPU-7 between 119.5 °C and 123.5 °C. Also, soft segment melting peak (Tm_1) was not observed in BNPU-3 and BNPU-7 films. This data about Tm_1 indicates that any strong interfacial interaction between the amorphous nanosilica particles and the soft segments in the polymer chains may prevent crystallization of the soft segments. At BNPU-3, and BNPU-7 films, the nanosilicas were possibly well dispersed in the WPU matrix compared to other silica containing films, and the resulting larger interfaces strongly prevented the soft segments from crystallizing in the WPUD/silica composites [95, 96].

The endothermic peak (Tm_2) observed between 119.5 °C – 123.5 °C can be associated with the physical crosslinking disruption of highly organized (or crystalline) hard segments in polyurethane/silica composites [97, 98]. Hassanajili et al. proposed that in the situation of WPUD/silica composites, endothermic peaks could be linked to a strong interfacial interaction between silica and polyurethane molecules [99, 100]. As shown in Table 4.1, the polyurethane degradation temperature (Td) increased with crosslinking and silica addition (except for BWPUD, which decreased slightly). According to these results, it was observed that crosslinkers and nanosilicas increased the thermal stability of the films.

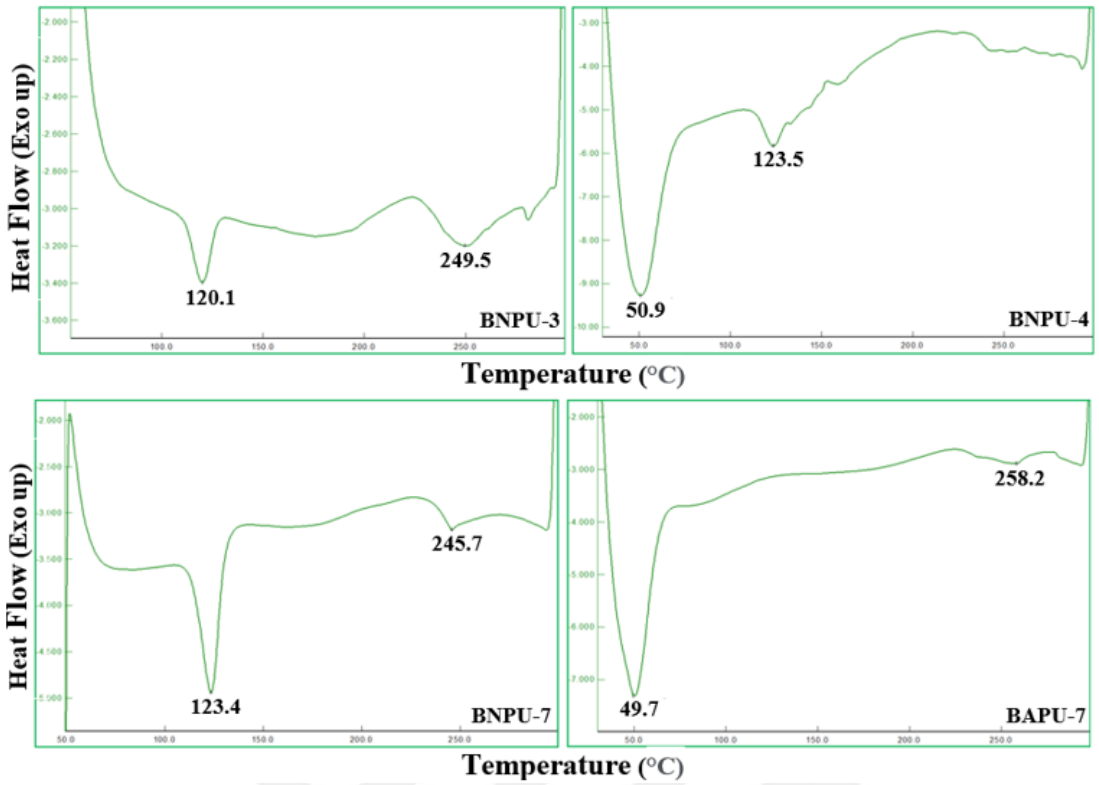


Figure 4.8 : DSC thermograms of BNPU-3, BNPU-4, BNPU-7 and BAPU-7 nanocomposites.

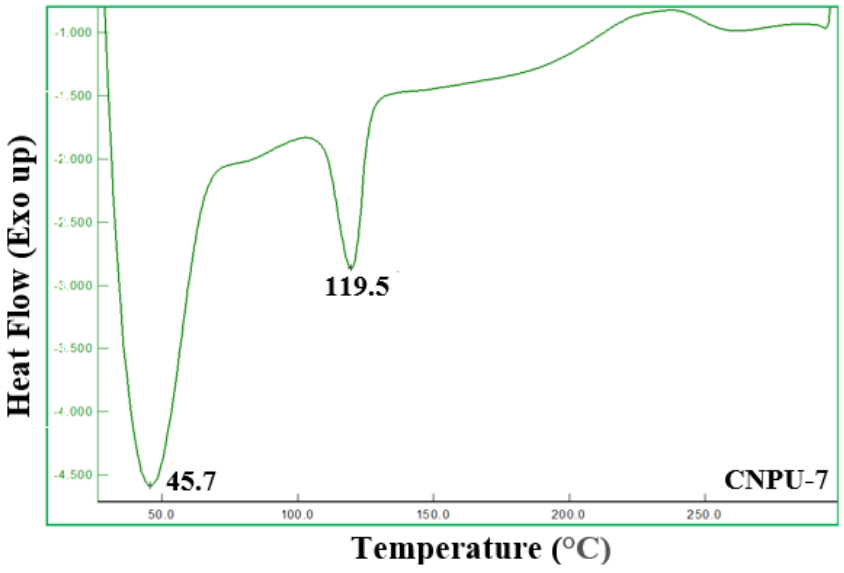


Figure 4.9 : DSC thermogram of CNPU-7 nanocomposite.

4.3 X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) measurement was used to investigate the crystallinity of films as well as to examine the effect of crosslinkers and nanosilicas on crystallinity.

Figure 4.10 depicts the XRD curves of neat WPUD, BWPUD (5% wt Bayhydur 3100 content), and CWPUD (2% wt CX-100 content) films. The neat WPUD display diffraction peaks at 19.1°, 19.9°, 21.2°, and 23.2°, implying the presence of crystalline structure in the WPUD [91, 101, 102]. Furthermore, similar 2θ degrees of diffraction peaks to neat WPUD film were detected in the BWPUD and CWPUD film's XRD curves. While these peaks were detected in BWPUD at 19.1°, 19.9°, and 23.3°, the peaks were observed in CWPUD at 19.1°, 19.9°, 21.2°, 22.8°, and 23.2°. However, as compared to neat WPUD, the intensity of the diffraction peaks increases slightly in BWPUD, while it decreases dramatically in CWPUD.

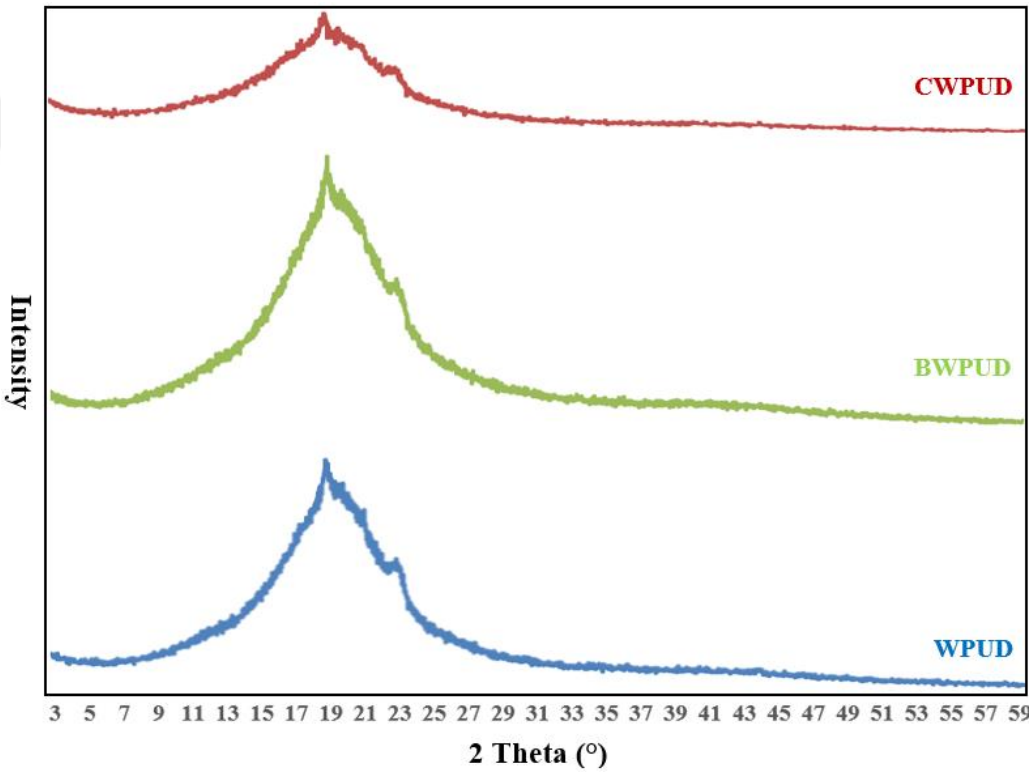


Figure 4.10 : X-ray diffractograms of WPUD, BWPUD, and CWPUD films.

As shown in Table 4.2 the intensity order of the diffraction peaks 19.1° and 19.9° is BWPUD > WPUD > CWPUD, meaning that crystallinity decreased with the addition of CX-100 (polyfunctional aziridine) and increased with the addition of Bayhydur 3100 (HDI based polyisocyanate). The decrease in crystallinity of CWPUD may be due to COOH groups in WPUD reacting with aziridine to create a three-dimensional network structure, thereby decreasing the flexibility of soft segments and inhibiting their entire backbone mobility, as well as hindering soft segment crystallization in PU [29, 103]. The increased crystallinity of BWPUD compared to WPUD may be

attributed to the fact that the NCO/OH ratio increased with the addition of Bayhydur 3100 (HDI based polyisocyanate), resulting in more urethane/urea crosslinking in the structure, making it more rigid and crystalline [104, 105].

Table 4.2 : XRD data of neat WPUD, and crosslinked WPUDs.

	2 Theta degree (2θ°)				
Sample	19.1	19.8-19.9	21.2	22.8	23.2-23.3
	Intensity				
WPUD	2165	1943	1698	-	1242
BWPUD	2546	2195	-	-	1379
CWPUD	1127	979	840	639	614

Figure 4.11 depicts the XRD curves of samples containing CX-100 - nanosilica (Aeorosil R 972 and Nanobyk- 3620). The diffraction peaks of CAPU-1 (0.1% wt Aerosil R 972), CNPU-3 (5% wt BYK 3620), and CNPU-7 (25% wt Nanobyk- 3620) nanocomposites between 19.1° and 26.5° 2θ degrees, and the intensities of these peaks are shown in Table 4.3.

Table 4.3 : XRD data of polyaziridine crosslinked WPUD/silica nanocomposites.

	2 Theta degree (2θ°)					
Sample	19.1	19.7-19.9	20-21.5	22.8	23-24	25-26.5
	Intensity					
CAPU-1	1237	1069	993	-	691	372
CNPU-3	1982	1840	1710	-	1203	-
CNPU-7	-	1768	2403	-	1247	793

XRD diffraction peaks of CAPU-1 and neat WPUD were examined, it was found that the peak intensities of CAPU-1 were weaker than WPUD, and a new peak appeared at 26.5°. When the intensities of XRD diffraction peaks of CNPU-3 and CNPU -7 nanocomposites were examined, it was determined that the peak intensities of CNPU-3 were weaker than WPUD except for 21.4° and, the peak intensities of CNPU-7 were higher than WPUD except for 19.8° also new peak appeared at 25°.

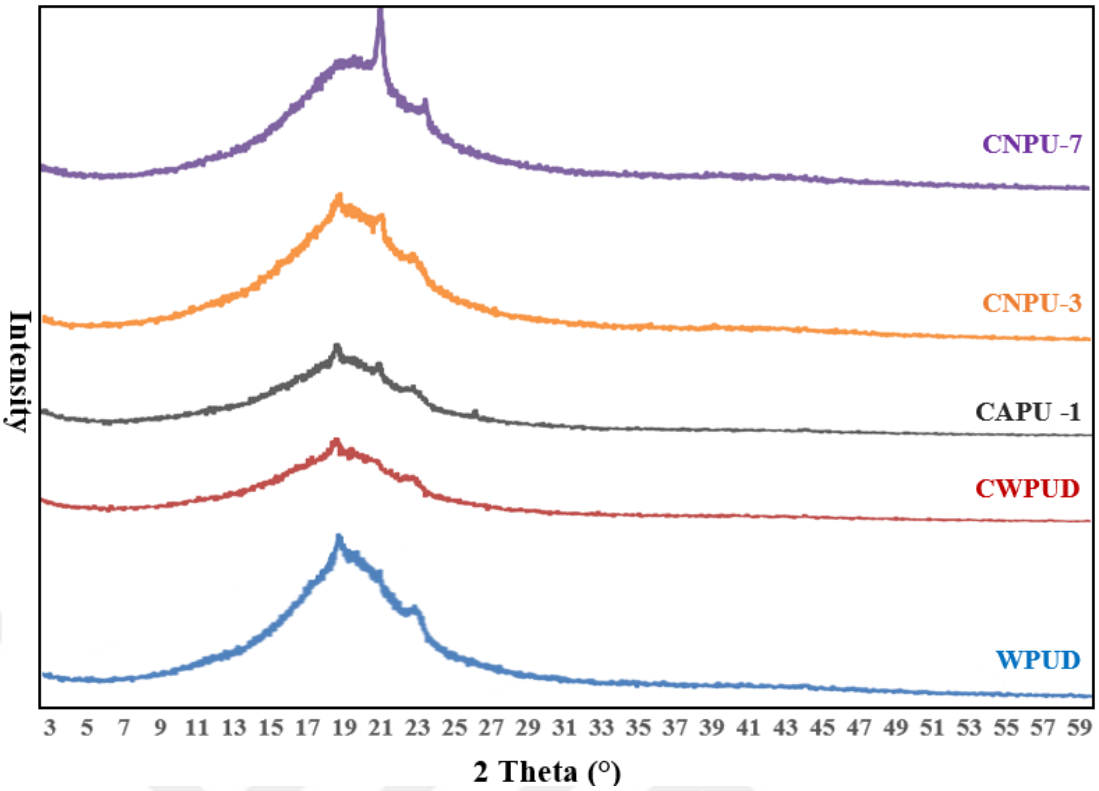


Figure 4.11 : X-ray diffractograms of WPUD, CWPUD, CAPU-1, CNPU-3, and CNPU-7 films.

Compared to neat WPUD, the diffraction peak intensities at 2θ 19.1° and 19.7° - 19.9° for samples containing CX-100 and nanosilica are in the order WPUD > CNPU-7 > CNPU-3 > CAPU. This indicates that the addition of nanosilica decreased the WPUD's crystallization capability. This result can be attributed to an increase in phase separation with the addition of nanosilica particles or the creation of new bonds with the addition of SiO_2 particles since these bonds restrict the mobility of the chains in the structure and prohibit the formation of new crystalline particles [28, 106].

Figure 4.12 depicts the XRD curves of polyisocyanate crosslinked WPUD/silica (Aerosil R972) films. The diffraction peaks of BAPU-1 (0.1% wt Aerosil R 972), BAPU-4 (0.5% wt Aerosil R 972), BAPU-7 (2% wt Aerosil R 972), and BAPU-8 (3% wt Aerosil R 972) films, and the intensities of these peaks are shown in Table 4.4.

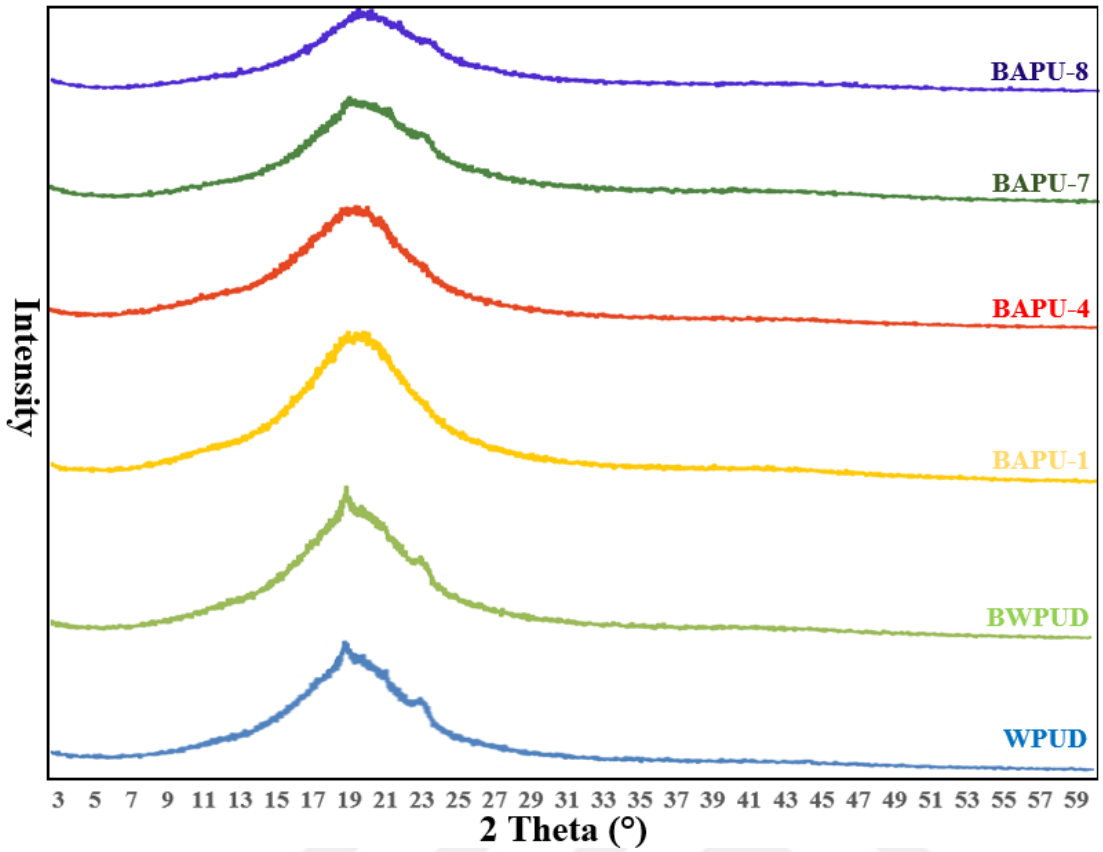


Figure 4.12 : X-ray diffractograms of WPUD, BWPUD, BAPU-1, BAPU-4, BAPU-7, and BAPU-7 films.

As seen in Figure 4.12, it was observed that the diffraction peaks became weaker and broader as the amount of Aerosil R 972 increased. This proved that the crystallinity of the films decreased with the addition of Aerosil R 972. This result can be attributed to the creation of new bonds with the addition of SiO_2 particles since these bonds restrict the mobility of the chains in the structure and prohibit the formation of new crystalline particles [28, 106, 107].

Table 4.4 : XRD data of polyisocyanate crosslinked WPUD/silica nanocomposites.

Sample	2 Theta degree (2θ°)					
	12°-15°	19°-19.5°	19.6°-19.9°	20°-22°	23°-24°	26.3°
	Intensity					
BAPU-1	-	-	2518	2520	-	-
BAPU-4	-	-	2068	1749	1050	-
BAPU-7	-	1775	1710	1583	1225	-
BAPU-8	-	-	1401	1245	964	-
BNPU-3	-	-	2567	2260	1387	-
BNPU-4	806	-	2144	2312	123	-
BNPU-7	472	1676	-	2348	1248	706

Figure 4.13 depicts the XRD curves of polyisocyanate crosslinked WPUD/silica (Nanobyk- 3620) films. The diffraction peaks of BNPU-3 (5% wt Nanobyk- 3620), BNPU-4 (10% wt Nanobyk- 3620), and BNPU-7 (25% wt Nanobyk- 3620), and the intensities of these peaks are shown in Table 4.4.

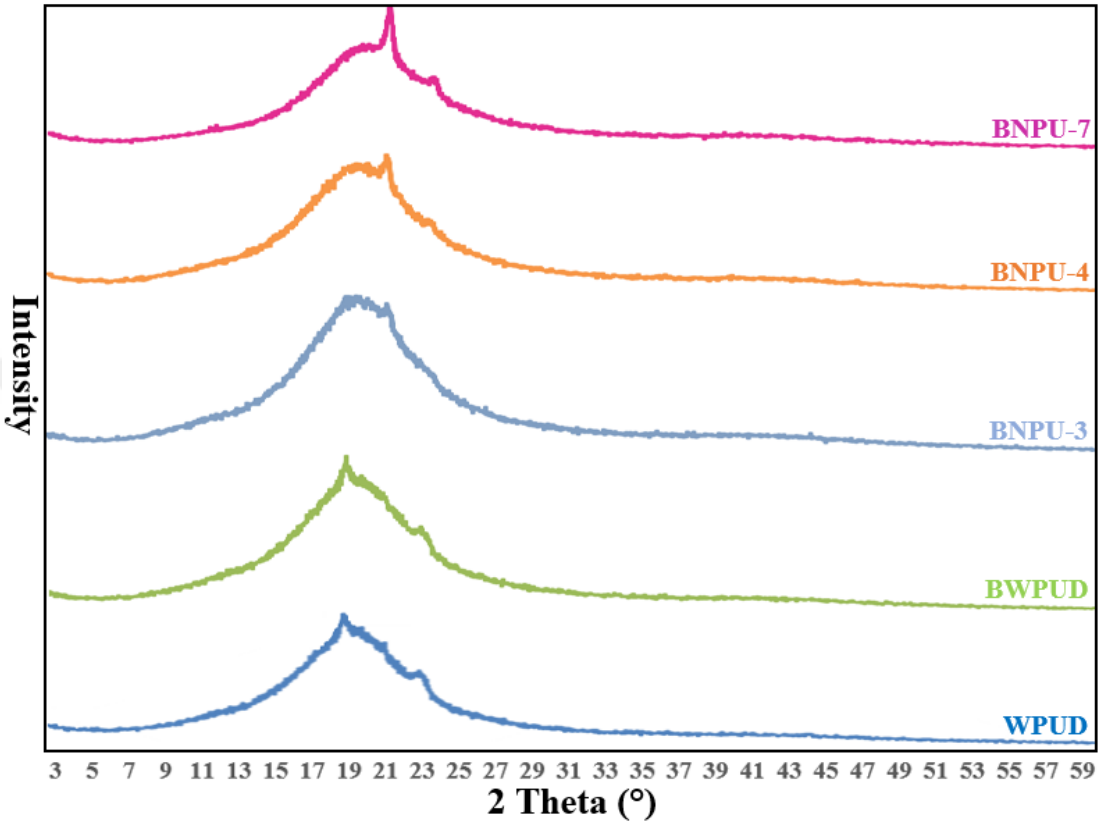


Figure 4.13 : X-ray diffractograms of WPUD, BWPUD, BNPU-3, BNPU-4, and BNPU-7 films.

4.4 Scanning Electron Microscope (SEM) Analysis

SEM was used to investigate the morphology of the neat WPUD film as well as the impact of crosslinkers (polyisocyanate and polyaziridine) and nanosilicas (fumed silica and aqueous silica dispersion) on morphology. The cross-sectional SEM images of the neat WPUD, CWPUD (polyaziridine crosslinked), BWPUD (polyisocyanate crosslinked) films are shown in Figure 4.14. The surface of the Neat WPUD was examined, and a rough surface was observed, containing PU particles ranging in size from nano to micron, as well as phase separations. In recent years, there have been many studies in which WPU dispersions with a wide particle size distribution, which form a rough surface and provide a matte appearance and good tactile feeling (rubbery, silky, soft), have been synthesized [108, 109].

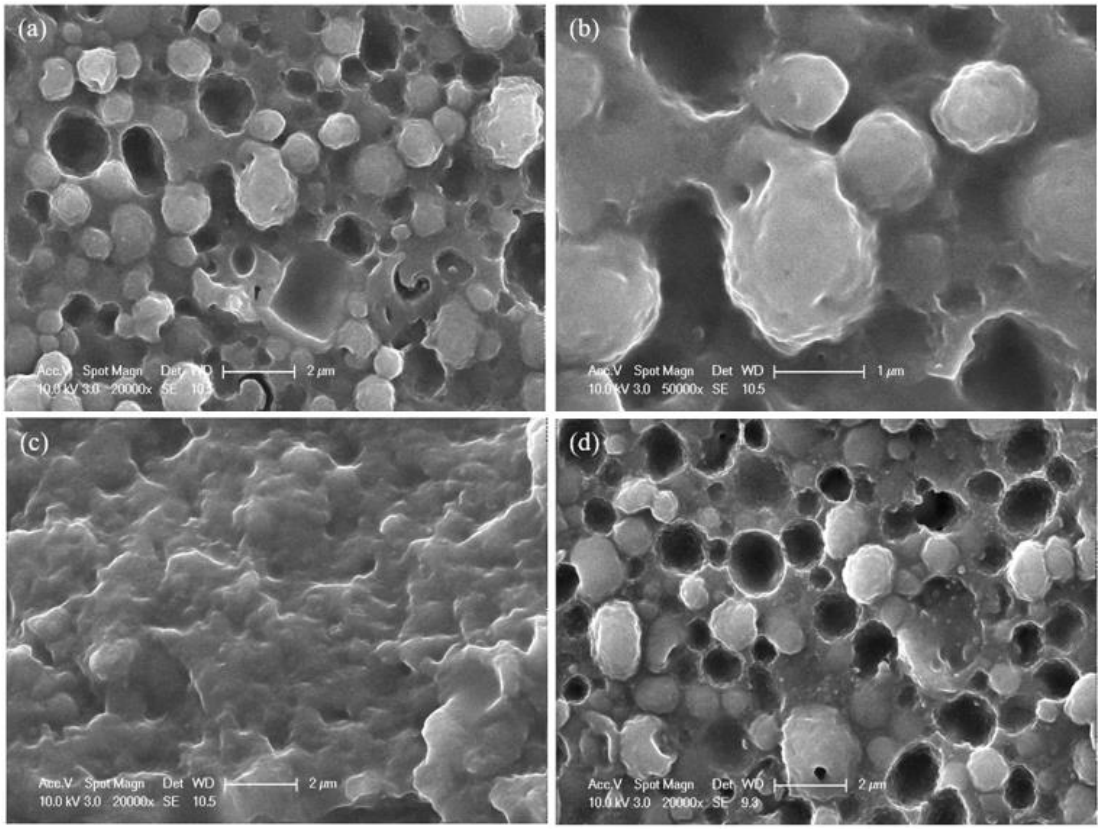


Figure 4.14 : Cross-sectional SEM images of (a) neat WPUD at 20 kx magnification, the scale bar 2 μm, (b) neat WPUD at 50 kx magnification, the scale bar 1 μm, (c) CWPUD at 20 kx magnification, the scale bar 2 μm, (d) BWPUD at 20 kx magnification, the scale bar 2 μm.

The fractured surface of the CWPUD film which contained 2 wt% polyaziridine was examined, it was observed that the phase separations decreased with the effect of crosslinking and the surface had a more uniform structure. On the other hand, the fractured surface of the BWPUD film containing 5 wt% polyisocyanate was examined, it was observed that the phase separations increased compared to neat WPUD.

Cross-sectional SEM images of BNPU-3 (5% silica- 5% polyisocyanate) , BNPU-7 (25% silica- 5% polyisocyanate), CNPU-3 (5% silica- 2% polyaziridine), and CNPU-7 (25% silica- 2% polyaziridine) films that containing varying amounts of Nanobyk-3620 (aqueous silica dispersion) are shown in Figure 4.15. The surface of the films containing Nanobyk- 3620 was examined. It was found that the surface became rougher compared to the BWPUD and CWPUD films, and the roughness increased as the silica ratio increased. Besides, no obvious silica agglomeration was observed, which indicates that the nanosilicas are uniformly dispersed in the WPU matrix.

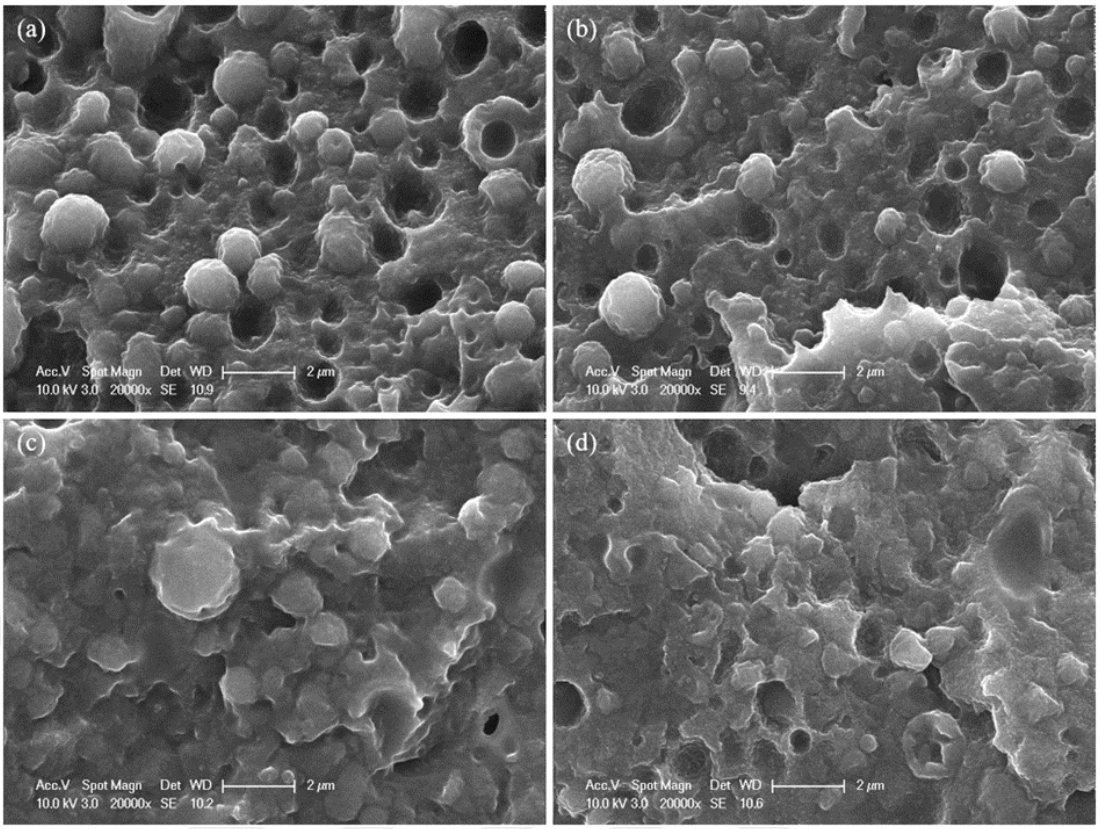


Figure 4.15 : Cross-sectional SEM images of (a) BNPU-3, (b) BNPU-7, (c) CNPU-3, (d) CNPU-7 films, at 20 kx magnification. The scale bars are 2 μm.

Figure 4.16 shows the cross-sectional SEM images of polyisocyanate crosslinked BAPU-1 (0.1% silica), BAPU-4 (0.5% silica), BAPU-7 (2% silica), and BAPU-8 (3% silica) films with various amounts of Aerosil R 972 (fumed silica). Similar to the films containing Nanobyk- 3620, it was observed that the films with the addition of Aerosil R972 formed a rougher surface compared to the BWPUD film, and the roughness increased as the amount of silica increased. However, unlike the films containing Nanobyk-3620, significant agglomerations were detected in the films containing Aerosil R 972 and it was observed that the agglomeration increased as the silica ratio increased. The high agglomeration potential of Aerosil R 972 caused difficulty to produce homogenous dispersion in WPU/nanosilica composite particularly filled with a high amount of nanosilica particles [110, 111].

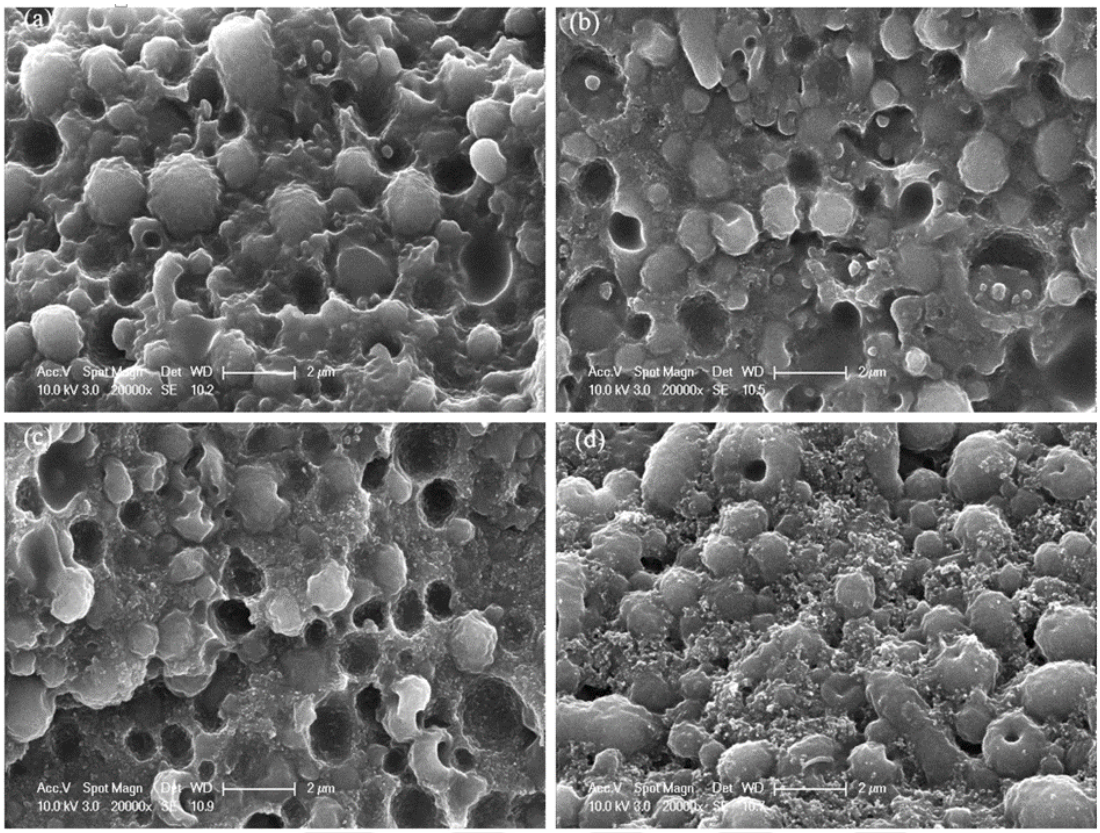


Figure 4.16 : Cross-sectional SEM images of (a) BAPU-1, (b) BAPU-4, (c) BAPU-7, (d) BAPU-8 films, at 20 kx magnification. The scale bars are 2 μm.

4.5 Energy Dispersive X-Ray (EDX) Analysis

The EDX spectra of the neat WPUD and crosslinked WPUD/silica films are shown in Figures 4.17 and 4.18. All of the expected atoms C, N, and O were found in the instance of neat WPUD. Moreover, the characteristic Si atom also exists in the nanosilica added WPUDs, along with C, N, and O. The EDX data of neat WPUD and WPUD /silica films are shown in Table 4.5.

Table 4.5 : The EDX data of the cross-sections of neat WPUD & WPUD/silica films.

Sample	C		O		N		Si	
	At%	Wt%	At%	Wt%	At%	Wt%	At%	Wt%
WPUD	78.65	73.95	16.92	21.15	4.43	4.89	-	-
BAPU-1	77.63	72.12	18.22	22.55	3.38	3.66	0.77	1.66
BAPU-7	70.94	63.41	19.99	23.8	5.9	6.15	3.17	6.63
BNPU-4	75.11	68.57	20.33	24.72	2.84	3.02	1.73	3.69
BNPU-7	69.59	61.63	22.02	25.98	4.79	4.94	3.6	7.45
CNPU-3	76.45	69.94	17.99	31.92	3.51	3.74	2.05	4.39
CNPU-7	66.33	58.68	26.92	31.73	4.21	4.35	2.53	5.24

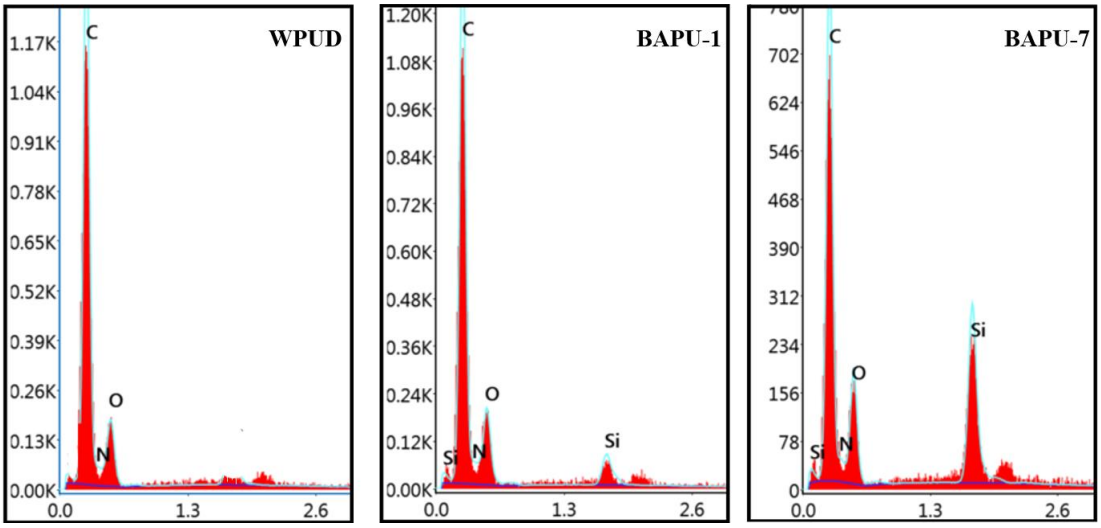


Figure 4.17 : EDX spectrum of neat WPUD, BAPU-1, and BAPU-7 films.

The EDX spectra of BAPU-1 and BAPU-7 which contain 0.1% and 2% fumed silica (Aerosil R 972) by weight, respectively, were examined and it was observed that the intensity of the Si peak increased as the amount of fumed silica increased.

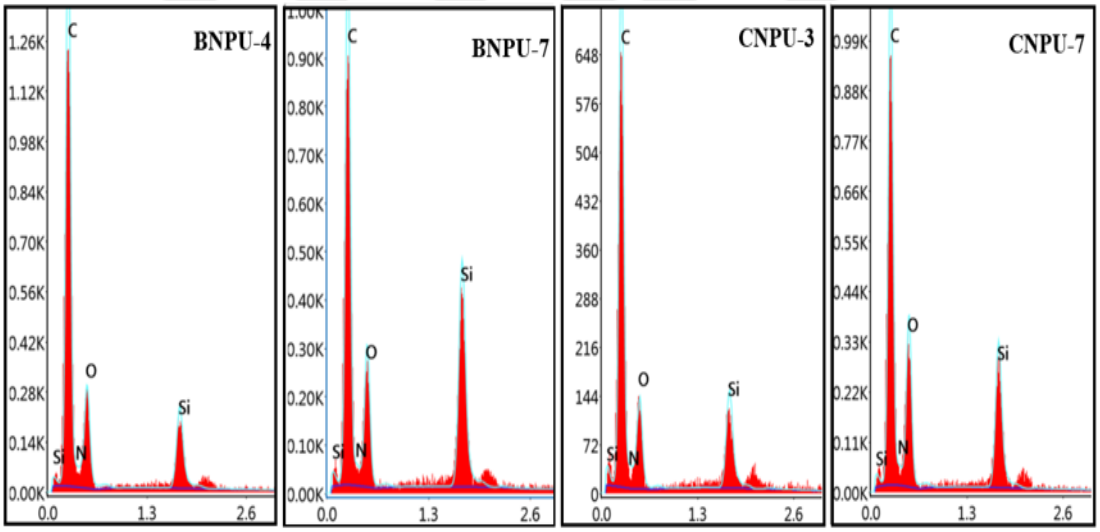


Figure 4.18 : EDX spectrum of BNPU-4, BNPU-7, CNPU-3, and CNPU-7 films.

BNPU-4, BNPU-7, CNPU-3, and CNPU-7 samples contain 10%, 25%, 5%, and 25% by weight aqueous silica dispersion (Nanobyk- 3620), respectively. The EDX spectra of these films were examined, it was determined that the intensity of the Si peak increased as the amount of Nanobyk- 3620 increased.

4.6 Swelling of the Films in Water

Water sensitivity and resistance of PU films are key priorities in most coating or adhesive applications. PU film-water interactions may produce some unwanted effects, such as plasticization, degradation of mechanical properties, microcrack, and deterioration of the matrix/filler interfaces [112]. Many variables affect the swellability of PU films, such as the hydrophilicity of the polymer chains, crosslink density, polyol type, NCO/OH ratio, chain extender type, inorganic fillers in the structure [113, 114]. Figure 4.19 shows the degree of water swelling versus time of neat WPUD, polyisocyanate crosslinked BWPUD and polyaziridine crosslinked CWPUD films.

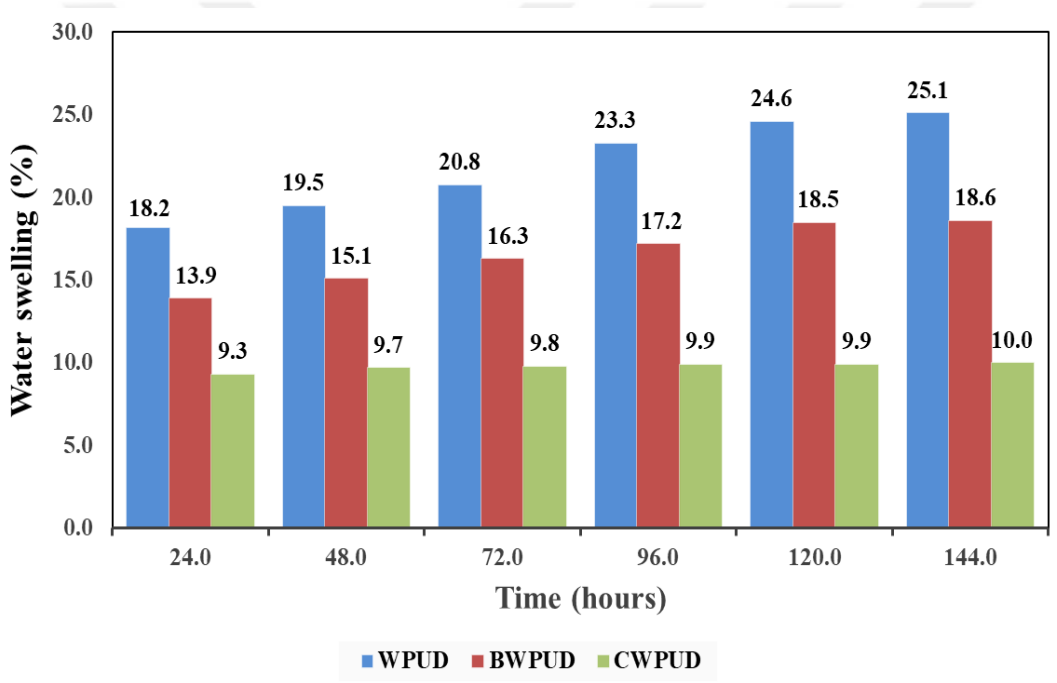


Figure 4.19 : Water swelling of neat WPUD and crosslinked WPUD films.

As shown in Figure 4.19, the swelling of the films increases with time, and after a while, the swelling decreases and remains stable, also water absorption of the films dramatically decreases with the addition of crosslinkers. The water swelling degrees of the neat WPUD film, BWPUD film, and CWPUD film were determined to be 25.1 %, 18.6 %, and 10%, respectively, after 144 hours. Generally, the water resistance reduced with raising the –COOH content because hydrogen bonding was easier to form between water molecules and –COOH groups in the hydrophilic microdomains. For this reason, lowering the amount of –COOH groups might enhance water resistance.

The decrease in swelling degree in CWPUD and BWPUD films may be due to the formation of cross-linking reaction between aziridine or isocyanates and –COOH groups [68, 115, 116]. Additionally, the crosslinked networks structure increases the interaction force between molecules and creates the molecular chains to become more compacted. As a result, water cannot readily enter the interior of the film; however, when cracks formed, solvents may be absorbed into the interior parts and easily access the hydrophilic segments [117]. Figures 4.20 and 4.21 show photos of the films after 144 hours of swelling in water.

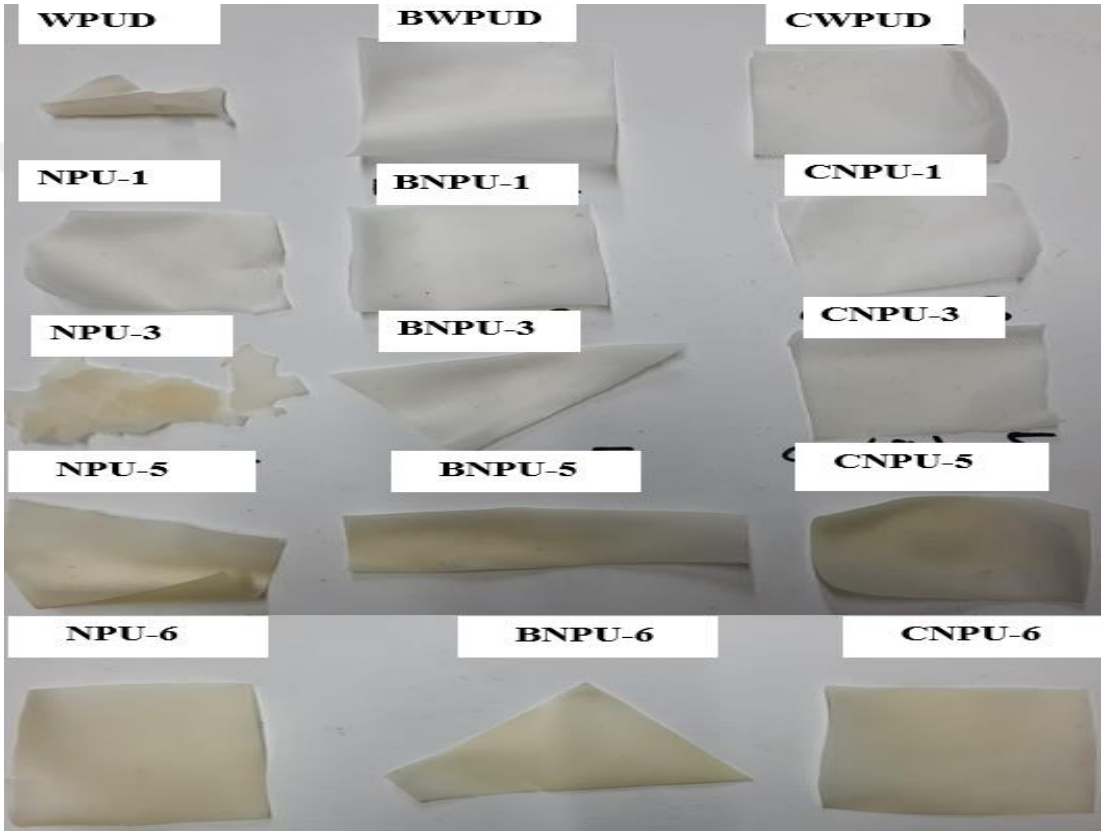


Figure 4.20 : The photos of neat WPUD crosslinked WPUDs and WPUD/ silica (aqueous silica dispersion) films after swelling in water.

Table 4.6 shows the water swelling degrees of films containing different amounts of silica (Nanobyk-3620 or Aerosil R 972) and different crosslinker (Bayhydur 3100 or CX-100). As shown in Table 4.6, the swelling percentages of films containing both silica types decreased until the silica content reaches a particular level, and after this silica ratio, % swelling of films started to increase again. The lowest % swelling in the samples that contained Nanobyk- 3620 was determined to be 17.5% in the NPU-5 sample with 15% by weight of silica. The lowest % swelling in the samples with

Aerosil R 972 was determined to be 16.8 % in the APU-3 sample with 0.3% silica by weight.

Table 4.6 : Swelling degree (%) of the films.

Sample	wt% silica	% Swell	Sample	% Swell	Sample	% Swell
WPUD	-	25.1	BWPUD	18.6	CWPUD	10
NPU-1	1	23.2	BNPU-1	16.3	CNPU-1	8.7
NPU-3	5	21.5	BNPU-3	14.5	CNPU-3	6.4
NPU-5	15	17.5	BNPU-5	12.3	CNPU-5	4.7
NPU-6	20	18.2	BNPU-6	12.4	CNPU-6	4.8
APU-1	0.1	20.3	BAPU-1	15.8	CAPU-1	7.8
APU-3	0.3	16.8	BAPU-3	12.2	CAPU-3	4.2
APU-5	0.75	19.4	BAPU-5	12.5	CAPU-5	4.6
APU-6	1	22.7	BAPU-6	13.6	CAPU-6	5.2

In general, the % swelling of WPUD films in water reduces progressively as the amount of silica nanoparticles increases, this effect can be explained by the fact that silica can behave as crosslinking points in the WPUD matrix through interactions with polyurethane molecules [118, 119]. Whereas swelling increases when the amount of silica nanoparticles reaches a particular level. Because of the agglomeration of silica particles or phase separation between polyurethanes and silica nanoparticles, caused by high nanosilica content. As a result, more water migrates to the WPUD/nanosilica films [120, 121].

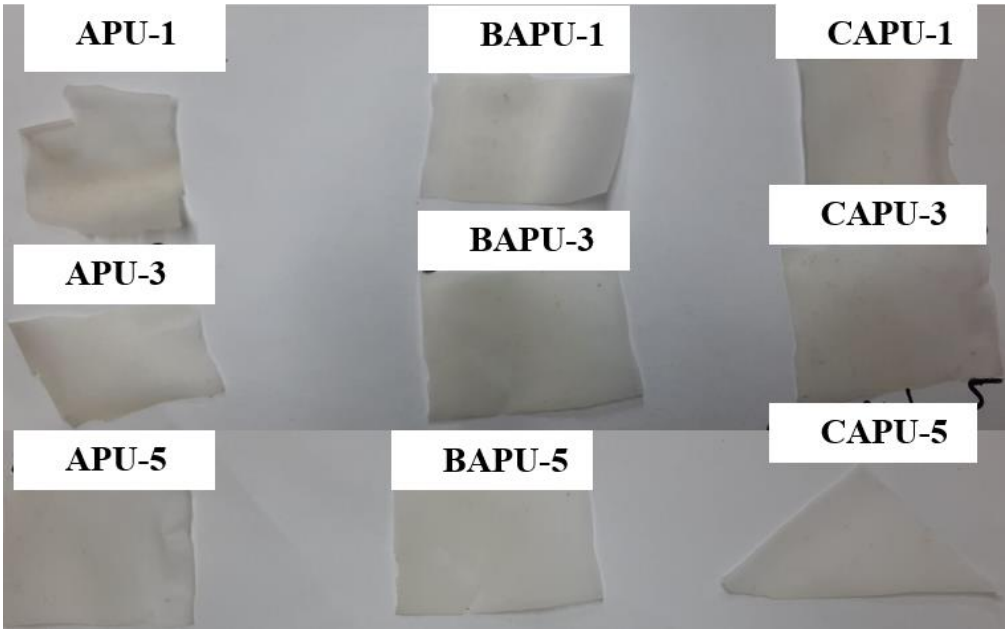


Figure 4.21 : The photos of WPUD/silica (fumed silica) films after swelling in water.

Table 4.6 also shows the degree of swelling in the water of crosslinked WPUD/silica films. The results were analyzed and crosslinked WPUD/silica films were determined to have lower swelling degrees. Also, it was determined that films containing polyaziridine (CX-100) had a lower swelling degree than films containing polyisocyanate (Bayhydur 3100). The lowest swelling degree was measured as 4.2% in the CAPU-3 film that contained 0.3 wt% Aerosil R 972 and 2 wt% CX-100. Based on these results, it can be concluded that the samples containing polyaziridine and silica had a higher crosslinking density and formed a more uniform and compatible film with silicas.

4.7 Transparency of the Films

Transparency is an essential feature of coating and adhesive materials since it indicates the capability of light transmission through a sample. On the other hand, the incorporation of silica particles commonly increases the nanocomposites opaqueness due to light scattering caused by silica particles [122, 123]. Figure 4.22 shows optical microscopy images of chosen samples containing various concentrations and types of the nanosilica.

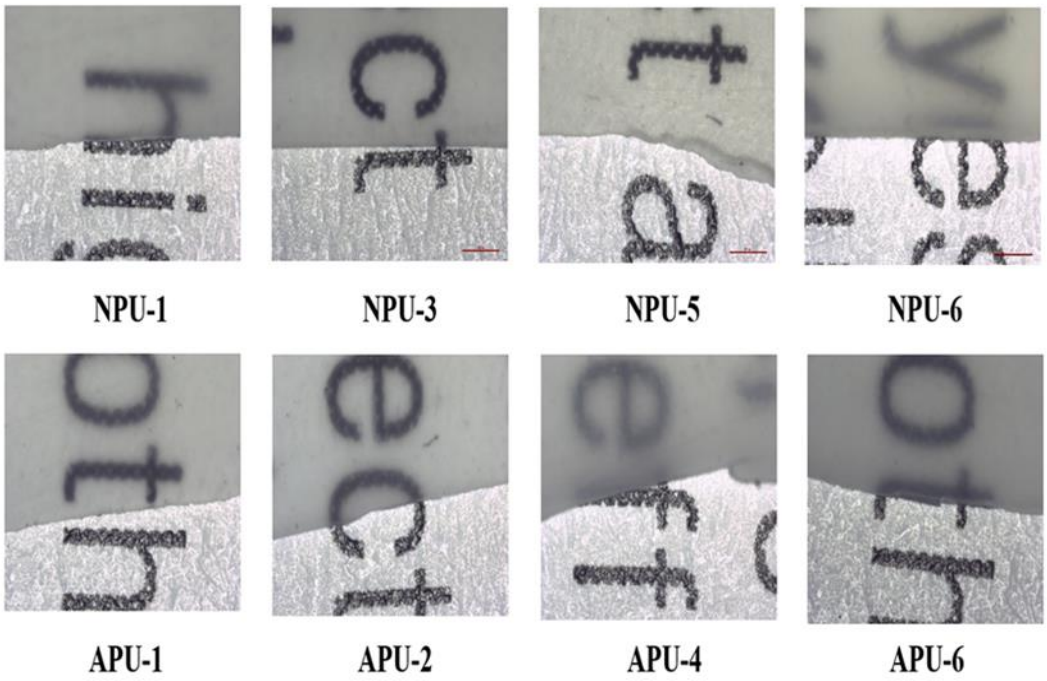


Figure 4.22 : Optical microscopy images of the WPUD/silica films at x25 magnification.

The transparency of the films was verified by measuring the films against the same background under the same conditions. The results of the transparency tests reveal that the transparency decreases with the increase of the amount of both types of nanosilica. In addition, samples containing Nanobyk- 3620, as the silica amount increased, the films became more opaque and yellower, as shown in the NPU-1 and NPU-6 samples containing 1 wt% and 20 wt% Nanobyk- 3620, respectively.

4.8 Hardness of the Films

As shown in Table 4.7, the Shore D hardness of the films increased with the addition of crosslinkers. It was determined that CX-100 increased Shore D hardness more than Bayhydur 3100. It was also determined that silica nanoparticlesNanobyk- 3620 and Aerosil R 972 increased the hardness of the films. These increases can be attributed to the formation of additional molecular networks as a result of the increase in crosslinking density with the addition of crosslinker [80, 124], as well as the reinforcing effect of nanosilicas with high surface hardness [49, 125]. However, for the films containing Nanobyk- 3620, the highest hardness was obtained in BNPU-4 film containing 10 wt% Nanobyk- 3620. A decrease in hardness was observed at BNPU-7 film that containing 25 wt% silica. This decrease in hardness can be attributed to the increase in agglomerates due to the increase in silica amount, and as a result, the increase in phase separations between silicas and WPU matrix [120].

Table 4.7 : Shore D hardness values of the neat WPUD crosslinked WPUDs and WPUD/silica nanocomposites.

Sample code	Shore D Hardness
WPUD	26
BWPUD	27
CWPUD	33
CAPU-1	34
BAPU-7	33
BNPU-3	36
BNPU-4	39
BNPU-7	27
CNPU-7	31

5. CONCLUSION

The aim of this study is to prepare various formulations using aliphatic polyether-based WPU dispersion, two different crosslinkers (polyaziridine and HDI-based polyisocyanate), and two different nanosilicas (fumed silica and aqueous silica dispersion), and then curing the prepared dispersions/nanocomposites to form films, and investigate the effect of nanosilicas and crosslinkers on prepared films with various characterization methods.

Chemical structures of crosslinkers and nanosilicas were analyzed by FTIR. Characteristic polyurethane peaks were detected in the WPUD film FTIR results. Successful crosslinking reactions were determined by the changes in the peaks. In addition, it was determined that nanosilica was also incorporated in the WPUD structure.

The DSC data revealed two distinct melting temperatures and thermal degradation temperatures. The variations in these temperatures were determined with the addition of crosslinker and silica. It was determined that the WPU dispersion could contain crystalline structures, and it was also observed that the thermal stability of the films increased with the addition of nanosilica. In XRD results, it was observed that films containing polyaziridine crosslinker and fumed silica had lower crystallinity than neat WPUD film and other films.

Morphological structures of the films were examined by SEM. When the fractured surface of the Neat WPUD film was examined, it was observed that the surface was a rough surface consisting of nano and micron-sized polyurethane particles, and phase separations were observed on the surface. It was also observed that the surface roughness increased with the addition of silica. The expected C, O, N atoms in the neat WPUD film were detected using EDX analysis. Additionally, Si atom was detected in the nanosilica-added films, and the peak intensity increased as the silica amount increased.

The degree of swelling of the films in water was measured. According to the swelling measurement results, it was found that crosslinking and the addition of a certain amount of nanosilica reduced the degree of swelling.

The transparency of the films was examined using an optical microscope, and it was shown that as the amount of nanosilica increased, the transparency of the films decreased.

As a result of the hardness measurements carried out with Shore D Durometer, it was observed that the hardness value increased with crosslinking, and the hardness increased with the addition of a certain amount of nanosilica, and then the hardness was decreased with the addition of excessive nanosilica.

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