SYNTHESIS and CHARACTERIZATION of NOVEL WATERBORNE POLYURETHANE DISPERSIONS

by

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Aileme...

SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF NOVEL WATERBORNE POLYURETHANES

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MATERIALS SCIENCE AND ENGINEERING, MASTER OF SCIENCE THESIS, 2014

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Keywords: waterborne polyurethanes, acetone process, halloysites, synthesis of polyurethanes, polyurethane elastomers

ABSTRACT

Novel aqueous dispersions of polyurethanes with sodium 2-[(2-aminoethyl)amino]ethanesulphonate as the ionic monomer have been successfully synthesized by acetone method. The effects of ionic content, hard segment content, type of polyol and degree of chain extension on the properties of polyurethane dispersions and their films have been systematically investigated. Furthermore, polyurethane/Halloysite nanocomposites have been prepared and the effects of key reaction parameters such as method of the incorporation of Halloysites into polyurethanes, Halloysite content and ionic content of the polyurethane on the final film properties have been studied. Polyurethane dispersion samples were characterized by particle size analyzer, whereas elastomeric films of synthesized polyurethanes were characterized using differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscopy, transmission electron microscopy and universal tensile testing machine in order to establish structure-property relationships in these novel polyurethane dispersions, their films and nanocomposites that are reported in the scientific literature for the first time.

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ÖZET

Özgün su bazlı poliüretan dispersiyonları iyonik monomer olarak 2-[(2-aminoethyl)amino]ethanesulphonate ve aseton metodu kullanılarak sentezlenmiştir. İyonik grup içeriği, sert segment içeriği, kullanılan polyol tipi ve zincir uzatma yüzdesinin sentezlenen poliüretan dispersiyonlarının ve bu dispersiyonlardan elde edilen filmlerin özellikleri üzerindeki etkileri sistematik olarak incelenmiştir. Buna ek olarak Poliüretan/Halloysite nanokompozitleri hazırlanmış ve Poliüretan/Halloysite karıştırma metodu, Halloysite miktarı ve poliüretanın iyonik grup yüzdesinin nanokompozit filmler üzerindeki etkileri araştırılmıştır. Poliüretan dispersiyonlarının partikül boyutu Dinamik Işık Saçılımı(DLS)tekniği ile belirlenmiştir. Elastomerik poliüretan filmlerinin termal ve mekanik özellikleri Diferansiyel Taramalı Kalorimetri (DSC), Dinamik Mekanik Analiz (DMA) ve Evrensel Test (UTM) cihazları ile ölçülmüştür. Taramalı Elektron Mikroskobu (TEM) ve Geçirmeli Elektron Mikroskobu (SEM) ile Poliüretan/Halloysite nanokompozit dispersiyonları ve filmleri incelenmiştir. Bu çalışmada kullanılan iyonik grup ile sentezlenen özgün poliüretan dispersiyonlarının ve Poliüretan/Halloysite nanokompozit filmlerinin yapı-özellik ilişkileri incelenmiş ve bilimsel literatürde ilk defa olmak üzere rapor edilmiştir.

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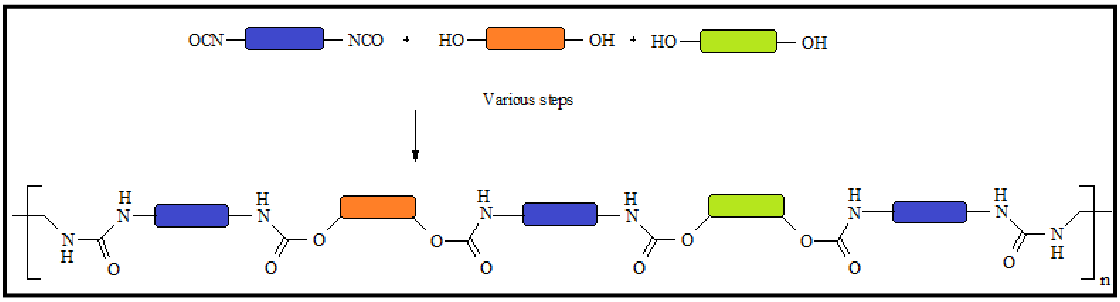
1. CHAPTER 1

1.1. Introduction

Polyurethanes are practically important class of polymers since 1970s. Polyurethanes in general are multi component systems. The chemical structure is formed from two segments: hard segments, which are formed from the reaction of di- or polyisocyanates with short diols or diamines, and soft segments, which are formed from oligomeric diols, so called polyols. General scheme for polyurethane synthesis is shown in Scheme 1. Other components used in polyurethane synthesis to help processing or to change the properties of the polymer are chain extenders, catalysts, blowing agents, emulsifiers, stabilizers, neutralizers and surfactants.



Scheme 1: Generalized scheme for polyurethane synthesis

The chemical composition of polyurethanes can vary widely depending on the specific polyol and di- or poly-isocyanate used in the synthesis. The many different chemical structures possible for polyurethane make it a versatile polymer which can be in the form of flexible or rigid foams, elastomers, thermoplastic sand fibers.

One of the properties that make the polyurethanes unique and versatile is the hydrogen bonding between the polymer chains. Hydrogen bonding between adjacent polymer chains forms a virtual crosslinking causing significant improvement in the physical/mechanical properties of the polymer.

The increasing need to reduce the volatile organic compounds (VOC) and hazardous air pollutants (HAP) are becoming more and more important nowadays. The legislative restrictions regarding the use of VOC and HAP made people to come up with the materials that do not contain hazardous solvents without compromising their properties. Waterborne polyurethanes are a subclass of polyurethanes, which have the most crucial advantage differentiating from solvent-based polyurethanes with their low or no volatile organic component (VOC) emission. They are both non-toxic and non-flammable. Another advantage of water-borne polyurethanes over the solvent-based ones is their high molecular weights at low viscosities as well as their good applicability. Although their preparation is more challenging because of the working in the aqueous solution, various synthetic methods are available overcoming these difficulties.

In this study, waterborne polyurethane dispersions were synthesized based on an anionic internal emulsifying agent sodium 2-[(2-aminoethyl) amino]ethanesulphonate(AEAS), as a co-monomer. Although AEAS based PUDs have been reported in the patent literature, structure-property relationships in such polyurethanes have not been systematically studied and reported in the scientific literature.[1-3]Therefore, the effects of key reaction parameters such as ionic content, type of soft segment, hard segment content and degree of chain extension on the properties of corresponding polyurethane films were investigated. In addition, novel waterborne polyurethane/Halloysite dispersions were prepared by the in-situ incorporation of Halloysites and characterization of corresponding polyurethane/Halloysite nanocomposite films was reported.

In CHAPTER 2, all experimental procedures carried out in this thesis were reported. In CHAPTER 3, Section 3.1.1.1, investigation of the effect of ionic content in the polyurethane structure has been discussed. Stable dispersions of polyurethanes with AEAS were successfully synthesized with controlled particle size and distribution. In Section 3.1.1.2, the effects of hard segment content on the final dispersion and film properties was discussed. The mean particle size of PUDs increased with increasing hard segment content because of increasing chain rigidity. On the other hand, as expected, with increasing hard segment content, tensile properties of films improved systematically. In Section 3.1.1.3, polyol type, corresponding to the soft segment structure in the polyurethane was varied and depending on the rigidity and hydrophilicity of the polyol, particle size was affected. Stable dispersions with four different types of polyols were successfully synthesized. Highest tensile strength at break and modulus values were achieved for polyurethanes when poly(tetramethylene oxide) and polycaprolactone were used as soft segment polyols. In Section 3.1.1.4, the degree of chain extension during the polyurethane synthesis was investigated and 50% and 60% chain extended polyurethane dispersions were found to yield unstable dispersions. The reason for obtaining unstable dispersions was uncontrolled reactions of remaining unreacted NCO groups in the prepolymer with water resulting in urea groups. Unexpected urea groups form bigger particles which are not included in polyurethane latex particles resulted in bimodal particle size distributions. Although chain extension ratio determines the molecular weight of the polyurethane; with 50% chain extension the tensile strength of the PU film was higher than 70% chain extension primarily because of the formation of extra urea groups upon reaction with water, resulting in increased hard segment content as well as tensile strength.

In Section 3.1.2.1, the incorporation of Halloysite Nanotubes (HNTs) PUDs in order to improve mechanical properties was reported and discussed. For the incorporation of HNTs, two different methods, post-blending and in-situ incorporation were used and the latter was found to be more successful. Differences between particle size distributions of blank PU and PU-HNT nanocomposite clearly evidenced that HNTs were successfully incorporated. With 1% HNT incorporation into PUDs in-situ, more than 50% tensile strength increase was achieved as discussed in Section 3.1.2.2 in detail. With 5% HNT incorporation the stability of PUDs was disturbed resulting in unstable dispersions as reported in Section 3.1.2.3. In conclusion, in this study the effect of key structural parameters such as ionic content, degree of chain extension, hard segment content and polyol structure on the properties of novel polyurethane dispersions and their films were systematically investigated and optimized for the first time in the scientific literature. And in-situ incorporation of HNTs into PU dispersions resulted in one-component, stable polymer-nanoparticle aqueous dispersions with dramatic increase in tensile and thermo-mechanical properties of their corresponding films compared to PU analogues without HNTs.

1.2. Waterborne Polyurethanes

Waterborne polyurethanes are fully reacted polyurethane chains dispersed in water in the form of latex particles. Waterborne polyurethane (PUD) materials form the basis for a environmentally-friendly chemistry of polyurethanes which have vast application areas for industry and high technology including artificial heart ventricles, automobile coatings, wall paints, imitation wood and wood coatings, mattresses and all other foam filled household. Compared to their solvent counterpart, waterborne polyurethane dispersions can offer the following advantages: viscosity and flow properties independent of molecular weight, the absence of external emulsifiers, flexibility, good behavior at low temperature and high strength, nontoxic, nonflammable, environmental safety, good adhesion and rheology characteristics that allows them to be use in wide application fields.

There are different methods to synthesize waterborne polyurethanes.

1) Prepolymer mixing process

2) Acetone process

3) Melt dispersion process

4) Self-dispersing of solids process

5) Ketamine process

6) Ketazine process

1.3. Cationic Polyurethanes

Cationic aqueous PUs (CAPU) is one of the types of waterborne polyurethanes, in which a cationic group is incorporated into the polymer backbone to render chains water dispersible. They are extensively used in the applications of adhesives, membranes, man-made leathers and coagulants. The physical properties of CAPU depend on both hard and soft segments as well as chain extender and dispersing center. The soft segment gives the film fine elasticity, flexibility and weatherability while hard segment provides the properties of tensile strength and hardness. [4]

N-methyl diethanolamine (N-MDEA), a short chain extending diol with a quaternizable tertiary amine, is one of the most common monomers to synthesize CAPUs. For example, Tsai et al. synthesized N-MDEA based CAPU dispersions containing polycaprolactone-polyethylene glycolpolycaprolactone (PCL-PEG-PCL) triblockcopolydiol in order to investigate the effects of different chain lengths for CAPUs. They studied how the PEG to PCL ratio affects the water vapor permeability (WVP). As the PEG content increased the particle size of PUD dispersion decreased, but the WVP of cast films from CAPU dispersions increased. N-MDEA was quaternized with glycolic acid in this study. [4]

In another example, Frisch et al. synthesized cationic PU dispersions using N-methyl diethanolamine (N-MDEA), bis (2-hydroxyethyl) benzylamine and bis (2-hydroxypropyl) aniline as the cationic dispersing center in order to discuss the effects of the soft segment on CAPU. It has been shown that the mechanical property of PU film was affected by Mn of PTMG also the tensile strength of PU containing N-MDEA is excellent, and the strength of PU film decreases with increasing Mn of PTMG. [5]

1.4. Anionic polyurethanes

Aqueous dispersions of polyurethanes are also commonly prepared from anionic PUs. For the preparation of anionic PUs, dimethylol-propionic acid (DMPA) is used in the prepolymer synthesis step, which is easily neutralized with a tertiary amine compound such as triethylamine to form a salt. Delpech et al. have synthesized anionic polyurethanes both in acetone and in water using isophorone diisocyanate (IPDI), ethylene glycol (EG), poly(propylene glycol) (PPG)as polyol and ethylene diamine (EDA) as chain extender. DMPA was used as the ionic monomer and the neutralizing agent was TEA. Prepolymer formation step is followed by the chain extension and then the polymer has been separated into two parts and reaction is carried on. The polyurethanes have been tested for their adhesion to the wood. Delpech et al. found out that as the soft segment chain length gets shorter the adhesive property of the polyurethane increases.[6] In another study, polycarbonate diol as polyol segment has been used by Cakic group in cationic PUDs. [7] The aim of the study is to investigate the effects of the Polycaprolactone diols to the soft segment structure in the cationic PUD, in which DMPA was the ionic monomer that was neutralized with TEA. It has been observed that the phase separation of hard and soft segments in poly (ester-urethane) is more pronounced than of poly (ether-urethane). As the phase separation degree increased glass transition temperature decreased proportionally.

1.5. Synthesis Methods of Polyurethane Dispersions

1.5.1. Prepolymer Process

Polyurethane synthesis methods with less or no solvent usage are gaining attention. Prepolymer method for the synthesis of waterborne PUDs is one of the promising methods for lessened amounts of solvent usage compared to solvent-borne synthesis. In this process prepolymer with terminal isocyanate groups are prepared and then ionic groups are introduced into the backbone. The reaction mixture is not very viscous for the stirring purposes at this point. However, viscosity can be reduced with addition of solvent. Water is introduced to the system and prepolymer is dispersed in water. At that point high shear rates are not necessary. Chain extension is done in the aqueous system but there is a risk of reacting hydrophilic prepolymer with water. So generally the chain extension is done quickly with a diamine. The polymer synthesis takes place in aqueous two-phase environment with the help of emulsifiers if necessary.

Prepolymer method is very simple to carry out but it has been constrained to specific NCO prepolymers. Nonionic dispersions are also possible to synthesize by this method. Lee et al. had synthesized waterborne polyurethane using polyethylene adipate glycol (PEA), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) and dimethylol-propionic acid (DMPA) using a prepolymer mixing process. The DMPA amounts are kept constant and by changing [NCO]/[OH] ratios and different molecular weight prepolymer are obtained. They observed that particle size decreases and emulsion viscosity increases with increasing Mp(molecular weight of the prepolymer) [8] At the constant polyurethane amount, the emulsion viscosity increases because of smaller particles’ hydrodynamic volume.

Nanda et al. showed that in order to have stable PU dispersions at least 4% DMPA content is necessary when prepolymer mixing method is used. However as discussed in the next section, when acetone process is used, the only necessary amount is 2% in this study. The reason for this difference could be because either the activity of the carboxylate groups on the surface of PU particles is lowered or the stability decreases for the prepolymer with low molecular weights. [9]

1.5.2. Acetone Process

The most remarkable property of polyurethanes is their ability to make stable dispersions with water under certain conditions is applied. Polyurethanes dispersions are basically binary colloidal systems, which is a discontinuous polyurethane phase and continuous water phase.[10]The acetone process allows the synthesis of aqueous polyurethanes with zero-VOC content. In this process, high molecular weight ionic polyurethane chains are formed by prepolymer synthesis, dissolution in acetone and chain extension in acetone. Then the ionic polyurethane/acetone solution is transferred into water under high shear, which results in the formation of latex particles. Finally, acetone is carefully removed from the system by vacuum distillation, resulting in stable, VOC-free PU dispersions. In addition to acetone, polar solvents such as tetrahydrofuran or methyl ethyl ketone can also be used. After the prepolymer formation, dissolving in acetone reduces the viscosity. At this point the system is an organic one-phase solution. Upon the chain extension, the molecular weight increases as well as the viscosity. Water dispersion step follows chain extension and final product is an aqueous dispersion. The conversion from an organic solution to an aqueous dispersion is a very interesting process. Details of this conversion are explained below.

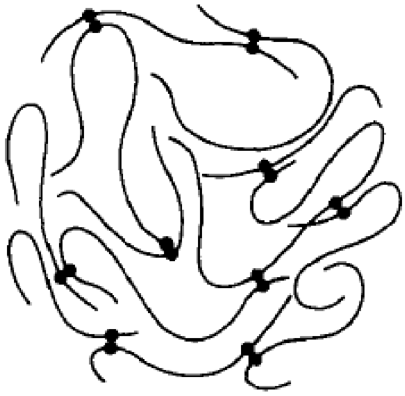


Figure 1: Polyurethane ionomer in organic solution, black dots shows the ionic centers[10]

Molecular weight increases as the ionic centers inside of a latex-like particle gets together. When water added drop wise to this mixture very interesting steps of polymer dissociation starts. With the first few milliliters of water it reduces the rearrangement of the ionic centers.

Figure 2: Water molecules which represented as “v” surrounded the ionic centers[10]

Water addition is continued and the viscosity increases even though the polymer concentration in total decreases. As the water amount increases in total this brings the decrease in the acetone concentration. Decrease in acetone concentration results in the reduction of the solvation heat of the hydrophobic segments of the polymer.

Hydrophobic segments are aligned in between each other and this alignment results in viscosity increase.

Figure 3: The hydrophobic chains are aligned in between[10]

Dispersion has been started with this step. As the water amount is increased the mixture becomes turbid. This shows that the dispersed phase is started to form.

Figure 4: Second step of the dispersion, turbid mixture occurs[10]

As the water amount increase the acetone concentration drops. With increase of water amount the turbidity increases and then viscosity drops. The clusters of polyurethane chains are rearranged and form into microspheres. These microspheres contain acetone inside of it while the outer environment is the continuous water phase.

Figure 5: Microspheres are formed at the end of water dispersion[10]

After the dispersion is obtained, the acetone must be removed. Microspheres will shrink following the removal of acetone and viscosity will decrease. These microspheres are also called latex particles.

Figure 6: Latex particles of polyurethane has been formed[10]

The size of these latex particles is determined mainly by the ionic content of the polymer. It varies between 20 nm to 500 nm. With the change in particle size the physical appearance of the dispersion changes from a clear dispersion with blue tint to opaque milky dispersion.

Nanda et al. have worked on identifying the effects of the acetone process in polyurethanes based on poly (hexyleneadipate-isophthalate) polyester diol and isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) and1,4-butane diol (BD).[9]In PU dispersion the particle size is very critical. It can be controlled to some extent by changing emulsification conditions like speed of mixing and temperature but mainly the ionic group’s concentration is effective. To observe the effects of the ionic group they varied DMPA content from 2 to 7 wt%. As DMPA percent increases the particle size decreases. They have shown that for DMPA concentration higher than 5%, no additional particle size lowering occurs. The increase in viscosity with the concentration of the polymer is higher in acetone process compare to prepolymer mixing process. [9]

1.5.3. Melt Dispersion Process

The synthesis route for PUDs by melt dispersion process is the following: First NCO prepolymer is prepared in melt, from a polyester or polyether diol, diisocyanate with a glycol containing a tertiary amino group. Secondly this prepolymer reacts with urea to get biuret groups and afterwards alkylating agent is introduced into the system so that bis-biuret ionomer is formed. This structure has hydrophilic groups enabling the formation of a homogeneous phase when methylolated with formaldehyde. Finally, water is introduced to form a stable dispersion. In this dispersion if the pH is decreased polycondensation of polymer starts. Polycondensation process will result in high molecular weight polyurethane. [10]

1.5.4. Self Dispersing of Solids Process

The self-dispersing of solids process uses the idea of dispersing oligomers with high ionic group content. If the melt of polyurethane ionomers’ molecular weight is between 3000 and 10000 and the system is cooled, quasi-dissolving process takes place in water and dispersion is formed. Decreasing the temperature means the cooling of free NCO groups which in turn leads to quasi-dissolving process. After that the product can be obtained as 100% solid. [10]

1.5.5. Ketimine Process

The reactivity of chain extending amines with NCO prepolymers is very high in the presence of water. Ketones, however, are able to slow down this reaction by reacting reversibly with amines. Acetone is highly effective reducing the reaction rate of amines with NCO prepolymers. In order to reduce the solvent amount, the acetone is introduced just enough to mask an amine and form bis-ketimine or mono-ketimine.

Ketimines can be mixed with NCO prepolymers without any further reaction. Water added to this system and a stable dispersion occurs. The ketimine hydrolyzes to an amine enabling the chain extension of polymer chains. Acetone process with less solvent is possible with ketimine process. [10]

1.5.6. Ketazine Process

Similar to ketimine process, ketazine process also works by the logic of masking the NCO prepolymer. Masking agent is changed from ketimine to ketazine or aldazine or hydrazone. Prepolymer is reacted with ketazine before introduced in water. This results in a slower hydrolysis of ketazines. Hydrolysis is slower when compared to that of ketimines.

Slower hydrolysis is advantageous since it allows aromatic NCO groups to be introduced into the system. This is not possible with other methods because aromatic groups could not be dissolved or melted. Another advantage of ketazine method is the stabilizing effect of the carbazide groups that makes the resultant products resistant to UV light and oxidation.

1.6. Applications of Polyurethane Dispersions

Polyurethanes, in general, present good adhesive properties due to their elastomer properties, enhanced by the soft segments of the polyol, and by the polar character of the urethane groups. The applications of polyurethane adhesives include substrates such as glass, wood, leather, plastics, rubber, metals, concrete and ceramic. Polyurethane aqueous dispersions are becoming an increasingly important class of materials in the surface coatings industry. Their application includes areas such as construction, automotive, packing, transportation, electronics, textiles, tape, paper and footwear.[11]Polyurethane coatings are useful in the industry of marine coatings.[12]

Tsai et al. applied the CAPUs with various polyester diols onto the nylon fabric and examined their water vapor permeability. The different polyester diols durability is given as: PEG-PU > PTMG-PU > PPG-PU > PCL-PU. After application and washing the fabric, all samples have 80% washing durability. [4]

Liminana et al. have investigated the effect of the hard to soft segment ratio to the adhesive properties of PUD. Prepolymer mixing process is used. 1, 4-butanediol polyadipate (Mw = 2500), m-TMXDI, tetramethylxylylene diisocyanate, Diethyleneglycol, DMPA, TEA and monohydrated hydrazine are used to synthesize the PU. Diisocyanate/diol (NCO/OH) ratio is varied from 1.4 to 2.0. The mean particle size and prepolymer viscosity increases as the NCO/OH molar ratio decreases. On the other hand, as the NCO/OH ratio gets smaller, molecular weight of the PU decreases and crystallinity of the polyurethane increases.[13]

The demand for the durable press cotton fabrics which are easy to maintain, wrinkle resistant and comfortable has been increased in textile industry. Pigment printing is one of the easiest methods to print the fabrics. More than 80% of the printed fabrics based on this method.[14] This method uses kerosene as the thickening agent in the emulsion and as in the drying and curing process it gets evaporated. During the evaporation the oven must be ventilated continuously otherwise volatile hydrocarbon volume will increase and it will possibly cause explosions. Based on these safety issues and other economical reasons the use of kerosene is decreased. Other synthetic thickening agents have formaldehyde emissions.[14] The cut-and-dried chemicals in order to prevent or lessen the wrinkles is N-methylol reagents and polyfunctional carboxylic acids.[15] The problem with N-methylol reagents is that these agents leave free formaldehyde on the fabric so the usage of such chemicals carries risk of health problems. Polyfunctional carboxylic acids possess good qualities apart from being expensive. Since waterborne polyurethanes release only water vapor during the curing process it is applicable for printing purposes.

Li et al. have reported the synthesis of waterborne polyurethanes using polyether diol (PETO) (molecular weight 2000), isophorone diisocyanate (IPDI), modified dimethyloldihydroxyethyleneurea (SDP), maleic anhydride (MAA), citric acid (CA) and trimethoxysilylpropyldiethylenetriamine (SCA).[15] SDP serves as the finishing agent decreases the tear strength and tensile strength of the fabric. The fabric which waterborne polyurethane has applied shows the characteristic peaks of the FTIR spectra: –NCO (2264 cm^{-1}), NHC=O (3324.8 cm^{-1}), and C=O groups (1718.7 cm^{-1}) from urethane linkages.[15]It is a prospective material since it improves the wrinkle resistance without causing a decrease in the tensile and tear strength and having any yellowing effects. Due to the elastic behavior of the polymer, it forms films on the fibers of the fabric, which results in the wrinkle resistance and other properties. [15]

Another issue with the fabrics is pilling because it spoils the look of the fabric. Factors affecting the pilling tendency are the fiber characteristics, yarn construction, fabric construction, fabric finishing, humidity, rinse, and softener.[16] As Montazer et al. pointed out the increasing polyester content mixed with cotton increases the pilling and formaldehyde releasing resins decrease the pilling. Also silicone-based fabric softeners decrease the pilling however the adhesion of these softeners to the fabric is low since the particle size of the softener in the emulsion is crucial for binding to the fabric. As the particle size gets larger adhesion strength gets weaker. [16] Also fabrics treated with citric acid and untreated fabrics adsorb water droplets very quickly close to zero seconds. However fabrics with polyurethane resin have longer water droplet adsorption time. [16]

Fabrics that are pretreated with cationic aqueous polyurethane contain different amounts of quaternary hydrogen. Cationic aqueous polyurethane interacts with the carboxylic groups in the acrylic fabrics enabling the acid dyeing. Kantouch et al. have used polyethylene glycol, IPDI, DBTDL, methyl ethyl ketone, diethanolamine (DEA) to synthesize PU. It is shown that cationic PU treated fabrics have greater affinity to the dyes. Also printed fabrics show good fastness properties. The interaction between the cationic aqueous PU and the fabrics is happening through the quaternary nitrogen of the CAPU. The remaining nitrogens are also the favorable sites for the acid dyeing. The pick up of CAPU by the fabric is found to be increasing with increasing time. [17]

Pan et al. synthesized anionic PUD in order to use it for plush finishing. PUD was prepared from polypropyleneglycol, 4, 4-diphenylmethane diisocyanate, dimethylol propionic acid, TEA and butanediol. The glass transition temperature of the PUD is -46 °C and the onset temperature for thermal degradation of the PUD is 265 °C. PUD presents more advantages for plush coating compared to commercially used polyacrylate resin. [18]

1.6.1. Nanoparticle Incorporation into Polyurethane Dispersions

The idea of adding some external materials to a system to improve several properties has always been appealing to scientists. Various kinds of nano-sized materials are available for such purposes. The effect of the added nanoparticles can change with the shape, size, hydrophobicity, hydrophilicity, wettability and surface roughness of the nanoparticles. For instance tubular structures like carbon nanotubes and the spherical silica nanoparticles will result in interesting property improvements on the final nanocomposite product due to their aspect ratios.

Halloysites are aluminosilicate clay materials with tubular structure. External diameter of the halloysite tube is 50-80 nm and length is around 1000 nm.[19] Because of the tubular structure they are referred as halloysite nanotubes (HNT). HNTs are two-layered alumina silicate clay $Al_2Si_2O_5(OH)_4$.[19] The outer surface contains hydroxyl groups. The inner part of the tube makes HNTs as specific target carrying agents. The controlled release of different agents makes HNTs useful for many different applications such as anticorrosion, antimicrobial, flame retardancy and micro crack self-healing. As HNTs are obtained from soil, it is an environmentally-friendly, sustainable and inexpensive material. HNTs are advantageous compared to its close relative CNTs as the CNTs bear the problem of toxicity, dispersibility and cost.

Pan et al. synthesized waterborne PU/attapulgite (AT) nanocomposites using the method of direct emulsion blending. Attapulgite (AT) is a type of natural crystalloid hydrous magnesium–aluminum silicate mineral. During the synthesis of PUD, polytetramethylene glycol, 4,4-diphenylmethane diisocyanate, dimethylolbutanoic acid and triethylamine are used. SEM images show that AT has an irregular dispersion through the PUD network. Addition of AT increased the glass transition temperature. Tensile strength and elongation at break also increased. [20]

Zhao et al. used hydroxyapatite to make the nanocomposites with PUD. Hydroxyapatite particles were first reacted with IPDI and grafted. These are used as cross-linkers, then these grafted hydroxyapatite particles further polymerized and PUD/HA particles are obtained. These particles are dispersed in the polyurethane matrix less than 2% wt. Mechanical strength and elongation at break is highly improved. [21]

Yun et al. investigated the properties of waterborne polyurethane-urea/sodium alginate (SA) blends for coating purposes. Poly(tetramethylene oxide) glycol [PTMG, number-average molecular weight (Mn) = 2000], IPDI, methyl ethyl ketone(MEK), EDA, TEA and NMP are used. PUD and sodium alginate blends are prepared by solution blending. Resultant polymer film is applied to nylon fabric. As the SA content increases, the water vapor permeability increases significantly as well as the viscosity of the PUD/SA emulsion. [22]

Polyurethane/clay composites are investigated by Rahman et al. In order to prepare four different PUD/clay nanocomposites different countercations are used: TEA, lithium hydroxide, LiOH, copper hydroxide $Cu(OH)_2$ and a mixed countercation of TEA and $Cu(OH)_2$ (1:0,5). Water resistance, tensile strength and adhesive strength increased to an optimal value with the increasing clay content. The nature of countercation is highly effective on the properties of the resultant material. For monovalent countercation optimum clay amount is found to be 1.0; for divalent countercation 0.5 and for mixed countercation 1.0 wt%. [23]

1.6.2. Halloysite Nanoparticles and their Polymer Nanocomposites

Shchukin et al. have studied the loading-reloading ability of HNTs. In order to encapsulate the anti-corrosion agent of benzotriazole, first they have modified HNT surface with polyelectrolyte. The comparison of loading ability is made between modified HNTs, silica nanoparticles and polyelectrolyte capsules. Shchukin et al. reported an increase with all of the nanocontainers in aqueous solution at alkaline or acidic pH. Even though complete loading could not be achieved by this group; it was achieved to load up to 80% for HNT based nanocontainers. After 5 cycles of reloading, the efficiency decreases to 20%. For the controlled release applications, they have suggested to use one weak one strong polyelectrolyte to achieve better results. [24]

Abdullayev et al. have used HNTs as corrosion inhibitor carrier and compared the activity of three different agents and loaded HNTs with these agents. In order to entrap the anti-corrosion agents in HNTs, Abdullayev et al used saturated solutions of agents in acetone and mixed these solutions with dry HNT powder. Vacuum is applied to the beakers of HNT-acetone-agent solutions. Slight fizzing is observed which indicates that the air inside the HNT is removed while the agents are going inside HNTs. Vacuum is applied for 3 hours and then released. The process is applied 3 consecutive times to be able to increase the loading efficiency. After this stage HNTs are washed with water and dried. To incorporate the agent loaded HNTs to the self-healing coating, the processed HNTs are dispersed in water based acrylic paint. After the application of paint to the surface, a scratch is formed intentionally on the surface. Scratched coating is then dipped into 0,5 M NaCl solution and the copper level is monitored. They claim that the inhibitor loaded HNTs are significantly improved the corrosion resistance. The corrosion is retarded at the initial stage as the agents in HNTs were leaking due to the cracks in HNTs. [25]

Another application for HNTs is the drug delivery area. Schmitt et al. have tried to incorporate drug which is 5-aminosalycylic acid (5-ASA) into HNTs together with starch nanocomposites. Schmitt et al. also investigated the swelling properties and the degradability. Their degradability tests have resulted in 24% stabilized weight loss which is the level for starch plasticizers. It is claimed that the overall results prove that HNTs are a potential candidate for drug delivery applications. [26]

As various fillers are in use to increase the mechanical properties of polyurethane coatings, Li et al. investigated the effect of HNTs incorporated into 2-component polyurethane coatings. To incorporate the filler into HNTs they have silanized HNT surfaces using (3-aminopropyl)-triethoxysilane, APTES. An increase in pencil hardness from B level to 2H level is achieved with the addition of less than 10% of HNTs. Li et al. claim that due to the mechanical network formation dependent to HNTs' elongated tubular structure an increase in the pencil hardness is observed. [27]

Another mechanical improvement of polymer resin with the help of HNTs is stated by Du's group. They show that the increase in flexural modulus, flexural strength and impact strength as well as the improvements in thermal stability and flame retardancy can be improved by addition of HNTs. [28]

Du et al. have detailed their investigation about the flame retardancy of HNTs and used polypropylene (PP) nanocomposites. The nanocomposites are prepared by using two-screw extruder to make pellets and then injection molded. The claim about why HNTs are flame retardants is due to the fact that walls of HNTs are acting as a barrier to the mass and heat transport. It is claimed that HNTs are new and inexpensive thermal stabilizer and flame retardant. [29]

Another aspect of HNTs is using their hollow tubular structure intercalation and polymerization. Aniline is introduced to the system with HNTs and the presence of polyaniline on both internal and external walls have been observed. [30] This observation proves that HNTs can act as molecular wires. Aniline in vapor phase has been sorbed onto the outer surface of HNTs and oxidized more. [30]

Silanization of HNT surfaces is very popular concerning the pre-treatment of HNTs. One of the examples to silanization is the work that Liu group has made. The outer surface of HNTs is silanized using APTES solution. In this work HNTs are dispersed onto the reduced graphene oxide sheets via electrostatic self-assembly process. The positive surface of HNTs and the reduced surface of graphene oxide are assembled. This product is showed superior performance as an electrode material in super capacitors. [31]

In contrast to its close relative CNTs HNTs are biocompatible and at the same time extremely cheap compared the CNTs. As the supply of HNTs is thousands of tons CNT production is in the range of grams. [19]The controlled release properties of HNTs are studied by Lvov et al. Lvov et al. shown that there is an initial burst of agent in nearly 10 minutes. Than it is prolonged release lasts 8-10 hours. By changing the viscosity of the solvent changes the initial leak time and also the release time. As HNT is a biocompatible material it is promising for the biomedical and drug related applications however the carrier part aluminosilicate part should not dissolve. So Lvov et al. claim that the applications of HNT may be limited to dermal applications, dental uses or medical implants. [32]

A very important application area for most of the nanofillers is the crack prevention. During the film formation crack formation is very prominent issue for most of the polymers. Qiao et al. incorporated HNTs, CNTs, silica and Titania to compare the effects. Poly (acrylic acid) is used as dispersing agent. The authors have suggested using of HNT incorporated films as a potential scaffold for enzyme immobilization. To incorporate HNTs to the polymer matrix first they have mixed 15% wt HNT with water mixed and sonicated. As HNTs are forming sediments even after sonication Qiao et al. added poly (ethylene glycol) (PEG) as a stabilizer. The PEG/HNT ratio is 1/5. HNT dispersion and latex dispersion is mixed with a magnetic stirrer. Qiao et al. claim that the HNT content of 10 vol % has prevented the crack propagation. The critical cracking thickness has improved and brightness is increased. Isotropic dispersion of HNTs have been achieved.[33]

2. CHAPTER 2

2.1. Experimental

2.1.1. Materials

Polyol of diethyleneglycol/adipate diol (Mn=2000, Desmophen S-1011-55), polyol of ethylene glycol/adipic acid/butane diol (Mn=2000, Desmophen 1652), polyol of poly(propylene oxide) (Mn = 2000, Acclaim 2200), hexamethylene diisocyanate (HDI),isophorone diisocyanate (IPDI) were kindly supplied by Bayer MaterialScience. Polytetramethyleneoxide (Mn=2000 g/ mol, PTMO), ethylene diamine (EDA), acetone (99.5%),dry toluene and di-*n*-butylamine were purchased from Sigma-Aldrich. sodium 2-[(2-aminoethyl)amino]ethanesulphonate (Vestamin A95, AEAS) was kindly donated by Evonik Industries

2.1.2. Synthesis of Waterborne Polyurethane Dispersions

The waterborne polyurethane (PUD) dispersions were prepared using the acetone method. For this purpose, first the NCO-terminated polyurethane prepolymer was synthesized by charging a four-necked, 1-L glass round-bottomed-flask equipped with a heating mantle, stirrer, condenser and a thermocouple with polyol and diisocyanate components and allowing the mixture to polymerize at 80-85°C until theoretical NCO content was reached. The NCO content of the reaction mixture was determined by the standard di-butyl amine back titration method (ASTM D2572-97). Upon reaching the theoretical NCO value, the reaction mixture was allowed to cool to 48 °C while dissolving in acetone to obtain a solution with 35-40 wt% solids content. Once the prepolymer completely dissolved in acetone, the chain extension step was carried out by adding EDA and AEAS mixture dropwise at 48°C. Then the prepared polyurethane polymer was dispersed in water by slowly adding distilled water into the flask while cooling the mixture to 40°C. Finally, acetone was removed from the reaction mixture by vacuum distillation and complete removal of acetone was ensured at 42°C, 50 mbar. If needed, solids content was adjusted to 40% and then the final product, waterborne polyurethane dispersion was collected by filtering through a 50 micron filtration media. Polyurethane films from each PUD that was synthesized were cast onto a glass substrate on a leveled surface and allowed to dry at room temperature for 12 h and then at 60°C for 24h.Films were removed from the glass substrate and conditioned at ambient temperature/humidity for 24 h prior to any characterization. Throughout this study the nomenclature of ND-1-XX is used in which “ND” stands for the initials, “1” stands for the notebook number and “XX” stands for the reaction number.

2.1.3. Preparation of Waterborne Polyurethane/Halloysite Nanocomposite Blends

In An aqueous HNT suspension and PUDs were physically blended with the aid of a mechanical stirrer and the HNT content varied between 0.25 to 5 wt%. HNT suspension was introduced into the PUD in a drop wise manner and mixed for 15 min at room temperature. Films of mixtures have been casted without further delay to obtain homogeneous films before the precipitation of HNTs.

2.1.4. Synthesis of Waterborne Polyurethane/Halloysite Nanocomposite Dispersions

Dispersions of PU/HNT nanocomposites were prepared using the procedure of PUD synthesis described in Section2.1.2; however, immediately after the chain extension and before the dispersion steps, pre-determined amount of HNT suspension was introduced into the reaction mixture by drop wise addition and then the dispersion step continued in the same manner.

2.2. Characterization

Particle size values and distribution of PUDs were measured by a particle size analyzer (ZetaSizer, Malvern Instruments). Approximately 0.1 mL of dispersion was diluted with deionized water to an appropriate concentration in the cell and measured at 25°C. Refractive index of polyurethane is 1.50 and for water index is 1.30.

Thermo-mechanical analyses of PU films were carried out using dynamic mechanical analyzer (DMA, Netzsch) with tensile mode at a heating rate of 3°C/min and a frequency of 1 Hz in a temperature range between -120 to 250°C. The sample size was10*6 mm with varying thicknesses.

Mechanical properties of PU films were tested on a universal testing machine Zwick Roell Z100 UTM, with a load cell of 200 N and a crosshead speed of 25 mm/min according to the testing method determined by ASTM D1708-10, standard test method for tensile properties of plastics by use of micro- tensile specimens. The initial grip separation was 22 mm and average of at least five replicates of each specimen was reported.

Films of PU/Halloysite nanocomposite dispersions were analyzed using a JEM-2010HT transmission electron microscope (TEM) operated at an accelerating voltage of 80 kV. Drops of pre-diluted aqueous dispersion of PU/HNTs (0.05%, w/w) were deposited on electron microscope grids and allowed to dry in a vacuum chamber.

Field-emission Scanning Electron Microscopy (FE-SEM) (SUPRA 35VP, LEO, Germany) was utilized to analyze the PU/Halloysite nanocomposite films' cross-sections after tensile tests. Samples were previously coated with gold.

Differential scanning calorimetry was performed using a DSC 204 Phoenix Differential Scanning Calorimetry (Netzsch, Germany) instrument. Samples were first heated up to 150 °C at 10 °C/min and cooled down to -120 °C with 40°C/min rate before scanning to erase thermal history of PUD films and then heated to 150 °C at 10 °C/min.

3. CHAPTER 3

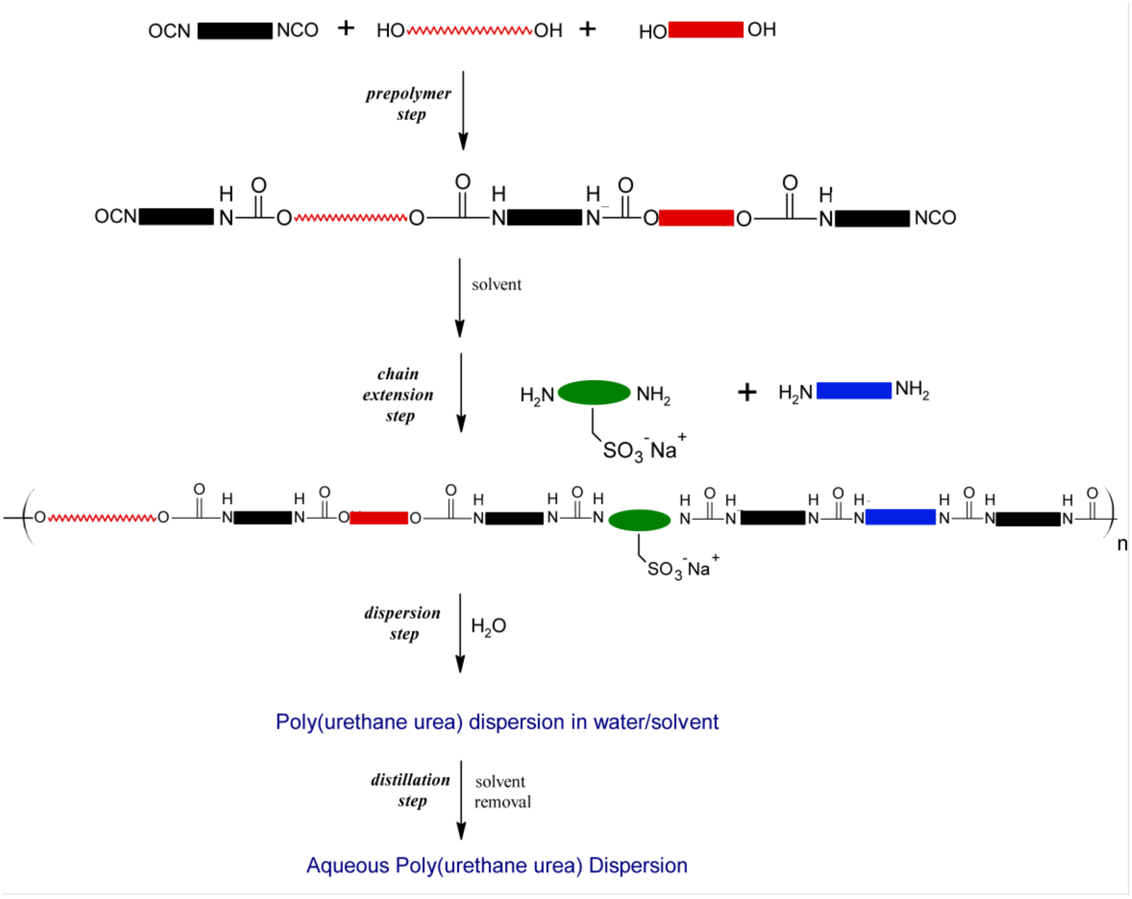
3.1. Results and Discussion

3.1.1. Synthesis and Characterization of Waterborne Polyurethane Dispersions

In this study PUDs were synthesized using the “acetone process” that was explained in CHAPTER 1, Section 1.5.2 in detail. As shown in Scheme 2, the synthesis method comprised of prepolymer synthesis, chain extension, and dispersion and acetone distillation steps. While AEAS Figure7 was used as an ionic co-monomer and incorporated into the polyurethane chain in the chain extension step, it was critical to optimize key reaction parameters in each step to obtain stable aqueous PU dispersions with high molecular weight polymer chains resulting in thermoplastic elastomeric films. In the prepolymer synthesis step, reaction temperature between polyols and diisocyanate was kept at 80 – 85 °C in order to maintain the reaction without any side reactions or vaporization of reactants. It was critical to determine the NCO content of the reaction mixture during the prepolymer reaction using the back titration method (ASTM D2572-97) at any time and an experimental NCO content equal to or slightly smaller (<15%) than the theoretical NCO content showed the completion of the prepolymer synthesis.

Upon the completion of the prepolymer synthesis, the NCO-terminated prepolymer was dissolved in acetone in order to carry out the chain extension and dispersion steps. For this purpose, a prepolymer concentration of 35-40 wt% in acetone was found to be optimum to carry out these two processes without any viscosity increase or solubility issues. It is also important to note that acetone was a key solvent for the synthesis of these PUDs. While acetone was capable of dissolving the polyurethane prepolymer and the chain extended, fully reacted polyurethane, its miscibility with water enabled us to obtain waterborne PU dispersions and its low boiling point (than water) enabled us to easily and completely remove from the final mixture to obtain a solvent-free product.

In addition to key reaction parameters such as temperature and concentration that were optimized in each step in order to obtain stable PU dispersions as discussed above, there are key structural parameters that have a pronounced effect on the final properties of PUDs and their PU films. Our study focused on the investigation of the effect of key structural parameters such as the ionic content, hard segment content, degree of chain extension and the type of soft segment on the final properties of PU dispersions containing AEAS as the ionic emulsifying agent and thermoplastic elastomer PU films from them.



Scheme 2: Synthesis scheme for waterborne polyurethanes by acetone method

3.1.1.1. The Effect of Ionic Content

As discussed in the “Introduction” section in detail, aqueous PU dispersions are obtained by carefully constructing ionic polyurethane chains that are hydrophilic enough to emulsify them, yet, once dried, their corresponding films or coatings are hydrophobic and water resistant for a various applications. For this purpose, it was critical to control the particle size and distribution of PU dispersions as a function of the content of ionic groups in the polyurethane backbone. During the synthesis of PU dispersions, particle size can also be affected by some of the emulsification conditions such as mixing rate and temperature during emulsification. But the concentration of ionic content has the highest impact on particle size. In our studies, AEAS was used as the source of the ionic groups during the synthesis of PUDs, which possesses two amino-and a sodium sulfonate ionic group per molecule as shown in Figure7.

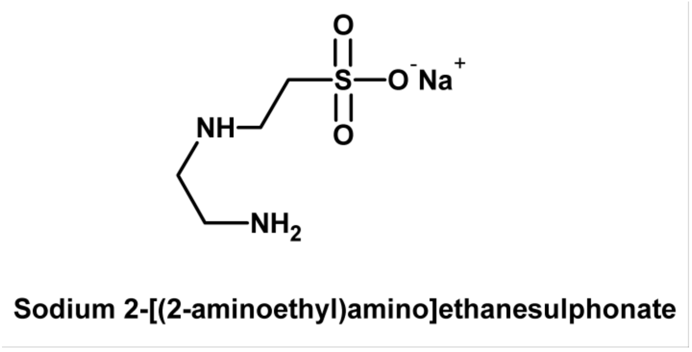


Figure7: Chemical structure of ionic group sodium 2-[(2-aminoethyl)amino]ethanesulphonate (AEAS)

As discussed in CHAPTER 1in detail, DMPA, possessing two hydroxyl and a carboxylic acid group is the most commonly used monomer in PUD synthesis that can form a carboxylate group upon neutralization with triethylamine. Although it is not as common, sulphonated polyurethane ionomers have also been reported. Interestingly, sodium salt of both sulphonate group and carboxylate group have been incorporated into same PU compositions and it has been found out that sulphonate groups tend to lead to the formation of smaller latexes as explained by Mequanint et al.[24]The ionic co-monomer, AEAS, used in our study, is an alternative source of sulphonate sodium salt that can be incorporated into polyurethanes and thus it was critical to optimize the content of sulphonate groups in the total polyurethane polymer for optimum particle size and distribution.

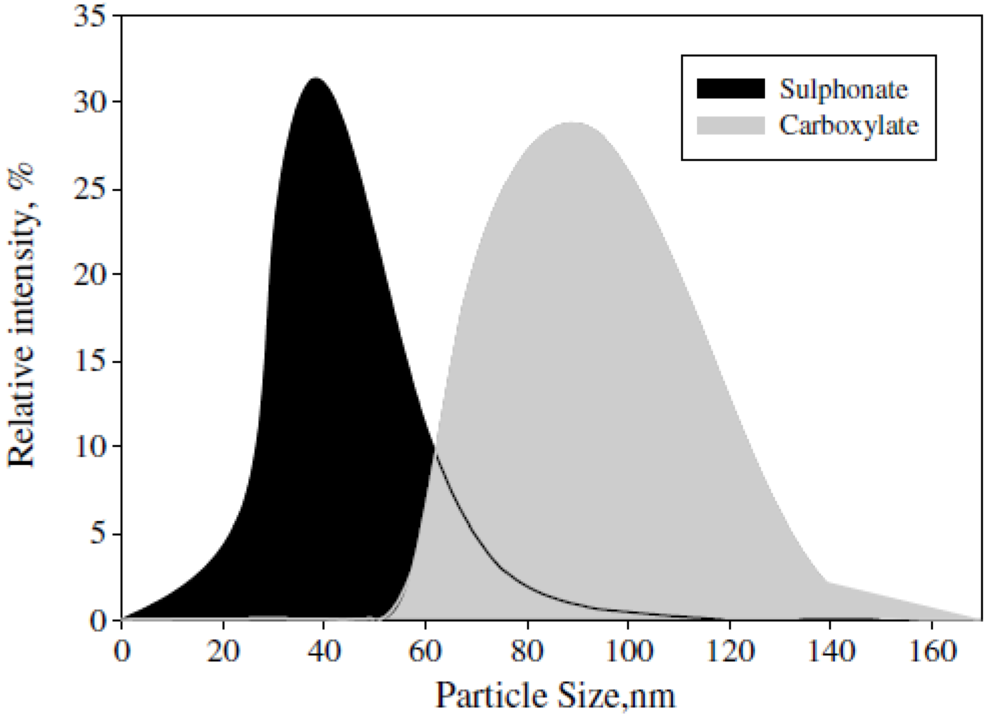


Figure 8: The effect of two different ionic structures on particle size distribution of polyurethane dispersions shown by Mequanint et al.

Polyurethanes that were synthesized for this purpose composed of a prepolymer prepared by reaction a polyester polyol of diethylene glycol/adipate diol (DEG/ AD) (2000 g/mole) and IPDI, which was then chain extended with EDA and AEAS. The effect of ionic content (SO_3 wt% in total polymer) on the final particle size of PUDs was investigated by varying the ionic content value between 1.05 and 1.10 wt%. Meanwhile other critical parameters were kept constant, such as hard segment content was17% and chain extension was 85%.

Table 1: Properties of PUDs synthesized with different SO_3 ionic contents

Effect of Ionic Content			
Sample #	**ND-1-24**	**ND-1-32**	**ND-1-36**
Ionic Content, %	1.05	1.07	1.10
Hard Segment, % wt	20	20	20
Chain Extension, %	85	85	85
Tensile Strength at Break, MPa	1.38 (±0.2)	1.34 (±0.1)	0.83 (±0.2)
Percent Elongation, %	2030 (±33)	2020 (±118)	1680 (±78)
Youngs Modulus, MPa	1.025 (±0.03)	1.47 (±0.2)	1.17 (±0.2)
Particle Size, nm	955	67	56
NCO/OH ratio	1.86	1.85	1.85
Polyol: Diethylene glycol / adipate diol; Isocyanate: IPDI			

As summarized in Table 1, the mean particle size value of PUDs systematically decreased with increasing ionic content as expected. In PU dispersions, particle size is critical depending on the application as well. For instance relatively large particles are preferred in many surface coatings to facilitate rapid drying. However smaller latex particles are crucial when deep penetration of the dispersion into the substrate is essential. Therefore, it is always critical to control the particle size PU dispersions. Figure 9shows the particle size distributions of polyurethane dispersions synthesized in our studies. As the ionic group concentration increases the particle size is expected to decrease as observed. This decrease has been observed. The stabilizing mechanism of ionic groups is effective in this change. Ionic type PU dispersions are stabilized by the electrical double layers which diffuse throughout the dispersion. These layers increase with increasing ionic concentration. Another important parameter is the hydrophilicity, which may arise from other components of the polymer chain, such as a non-ionic hydrophilic polymer, and affect the particle size.

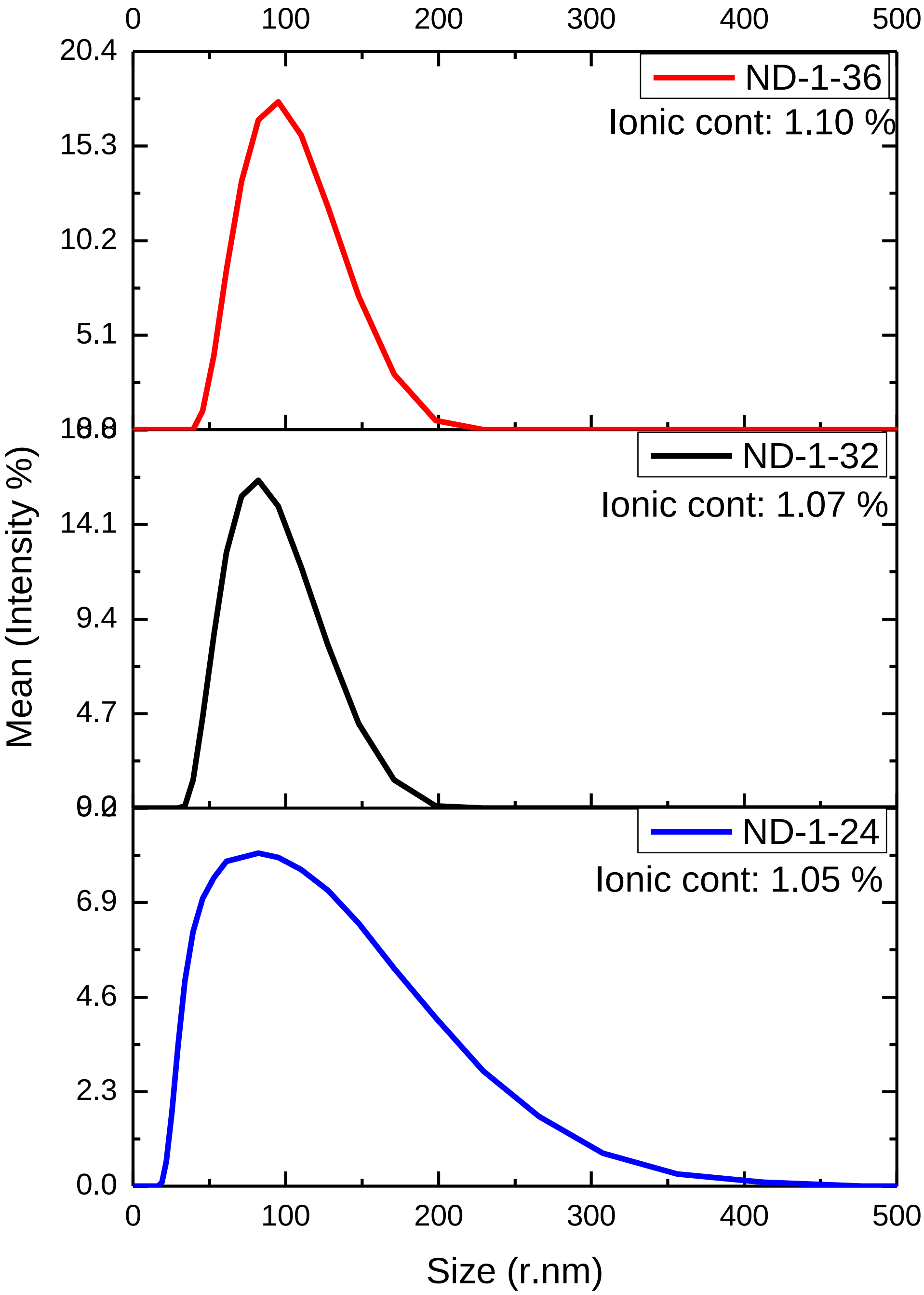


Figure 9: Particle size distributions of PUDs with different ionic content values

The mechanical properties of PU films prepared from dispersions synthesized in this series showed poor, non-elastomeric properties as shown in Figure 10. The main reason for both low tensile strength at break values such as1.34 - 0.83 MPa and non-elastomeric behavior was presumed to be the asymmetric nature of the diisocyanate, IPDI, used in these syntheses, which inhibits the formation of well-defined hard segment domains that are responsible for high modulus and good recovery in PU films .As a result of asymmetric nature of IPDI, a hard segment content of 17% was found to be very low for this series of PUDs. In order to improve the mechanical properties HS value could have been increased. On poly(ester- urethane) elastomers it has been known that low levels of hard segment content leads to either; mixed segment systems since microphase separation is mostly depends on hard segment-soft segment incompatibility or microphase separated structures which contain hard segments which are dispersed in soft segments. Low mechanical properties, low modulus values are due to the little interaction between hard segments which lie in the soft segments.[29] The reason why the IPDI containing polyurethanes did not give proper tensile strength values is explained by the relationship of hard and soft segments and polyurethane morphology. Upon the increase in hard segment, wt% the morphology of the backbone changes from interconnecting to isolated hard domains. Three dimensional hydrogen bonds between hard segments give strong hard domain cohesion. Hydrogen bonds play a direct role in the mechanical properties. [34]

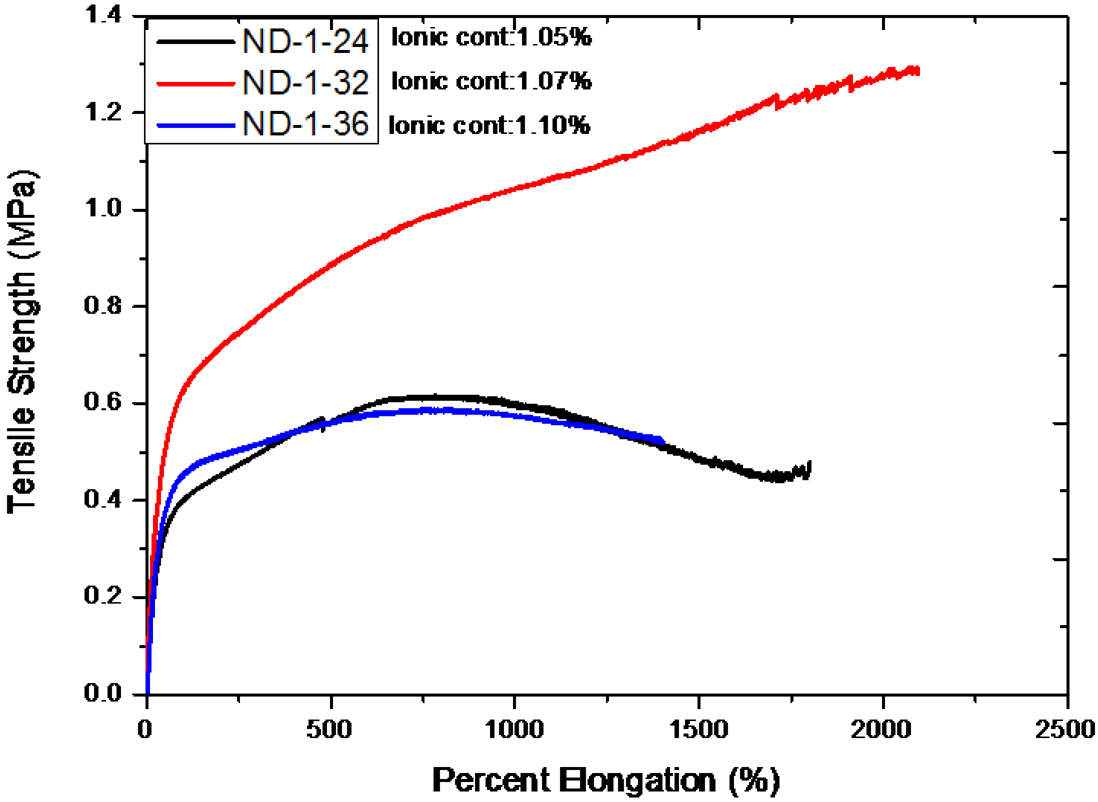


Figure 10: Mechanical characterization of PUDs with different ionic content values

Another reason for such poor mechanical behavior was presumed to be the poor incorporation of isocyanate to the PU backbone. IPDI has been used as isocyanate in this series and it bears two different NCO groups with different reactivity values. As the type, position and structure of isocyanate group affect the reactivity with nucleophile affecting the overall physical properties. Primary and secondary NCO groups of IPDI have different reactivities due to their stereo electronic configurations are different. Thus the reactivity difference of two isocyanates in IPDI could have limited the molecular weight increase of these polymers. In order to address these issues, in the forthcoming studies in this thesis, the type of diisocyanate was changed from IPDI to HDI, which is a symmetrical molecule and both isocyanates have almost equal reactivity.

3.1.1.2. The Effect of Hard Segment Content

In order to investigate the effect of hard segment content on the final PUDs and film properties, a prepolymer synthesized from the reaction of polyol of adipic acid/butane diol/ethylene glycol (200 g/mole) with HDI was chain extended with EDA and AEAS synthesize PUDs at a fixed ionic group concentration, 1.20wt %, and chain extension, kept at 70 %. The hard segment content in PUs is determined by calculating the weight fraction of the mass of diisocyanate and chain extenders in the whole polymer and reported as wt% in total polymer. In this study, for the given composition above, hard segment values were varied from 16 to 17, 18 and 20 wt %.

Table 2: Properties of PUDs and their films different hard segment ratios

Effect of Hard Segment				
Sample #	**ND-1-52**	**ND-1-58**	**ND-1-54**	**ND-1-56**
Hard Segment, % wt	16	17	18	20
Chain Extension, %	70	70	70	70
Ionic Content, %	1.20	1.20	1.20	1.20
Tensile Strength at Break, MPa	18.2 (±0.7)	22 (±1.0)	27.3 (±0.8)	35.3 (±0.3)
Percent Elongation, %	1900 (±29)	1610 (±9)	1470 (±39)	1200 (±35)
Youngs Modulus, MPa	1.8 (±0.1)	3.4 (±0.1)	3.6 (±0.1)	6.2 (±0.9)
Particle Size, nm	70	87	72	152
NCO/OH ratio	1.84	1.98	2.13	2.43
Polyol: Adipic acid/ Butane diol/ Ethylene glycol; Isocyanate: HDI				

Main difference of this series is the isocyanate group has been chosen as HDI instead of IPDI. Because of issues arose with IPDI as discussed in the previous section, HDI molecule with two isocyanate groups with almost equal reactivities was chosen from now on.

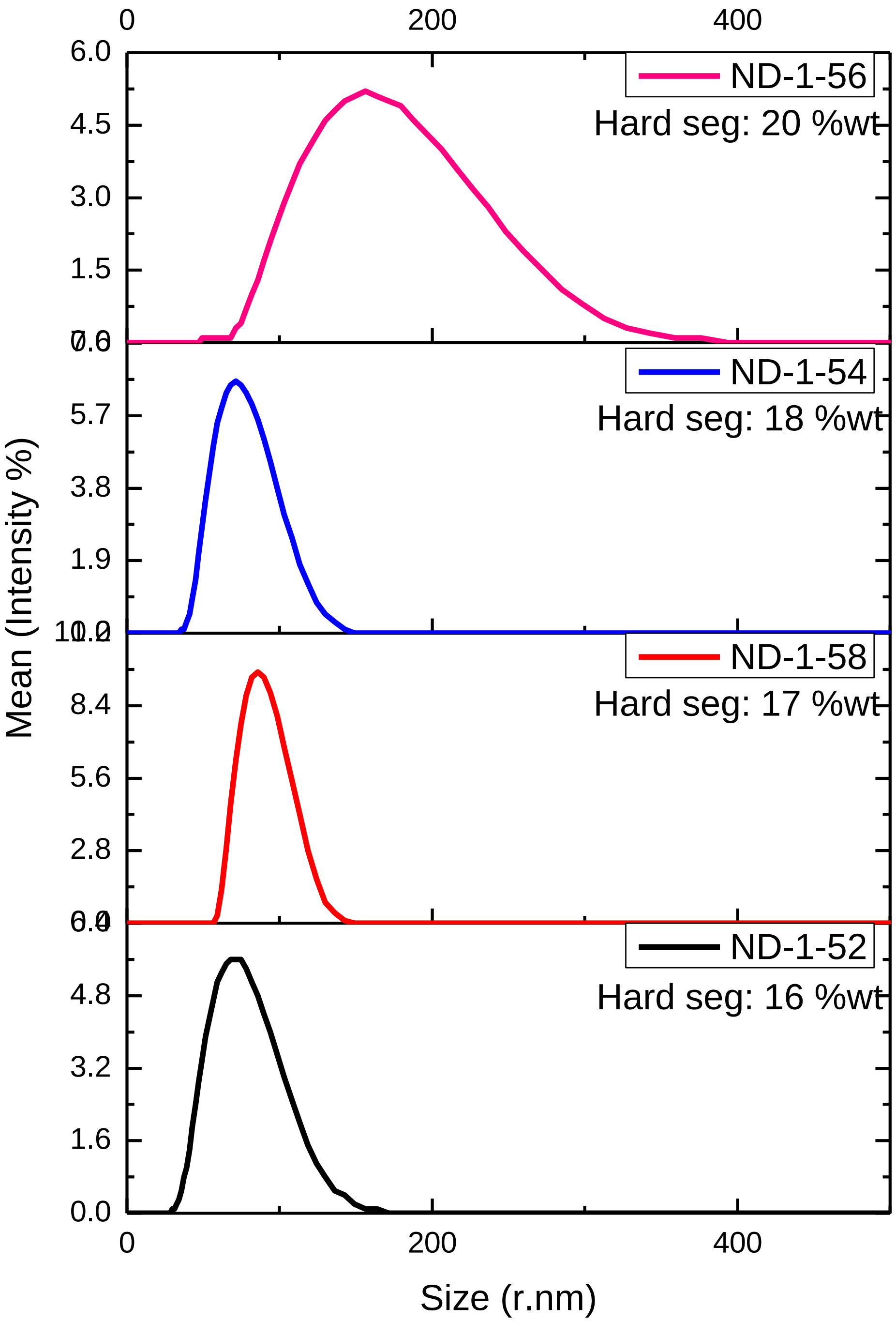


Figure 11: Particle size distributions of PUDs with different hard segment values

As shown in Figure 11 the mean particle size of PUDs increased as a function of hard segment content. Considering the fact that the chains' rigidity is expected to increase as the hard segment content increases, and the ionic parts on the polymer backbone are located on the surfaces of PU latex particles, it is expected to become harder for more rigid polymer chains to rearrange ionic centers and form a sphere. With increasing rigidity it is then expected to be less possible to form regular latex particles with the proper hydrophobic-hydrophilic arrangement of chains. This situation was presumed to cause larger particle sizes during the phase inversion part as the hard segment content increased.

Broadest particle size distribution was observed for the PUD which contains 20 wt% hard segments. One of the main reasons for this broad distribution is 20 wt% hard segment in polymer backbone corresponds to the most rigid chain in the series as explained above. As the chain rigidity increases the ability to fold inside and form latex decreases resulting in a broad particle size distribution.

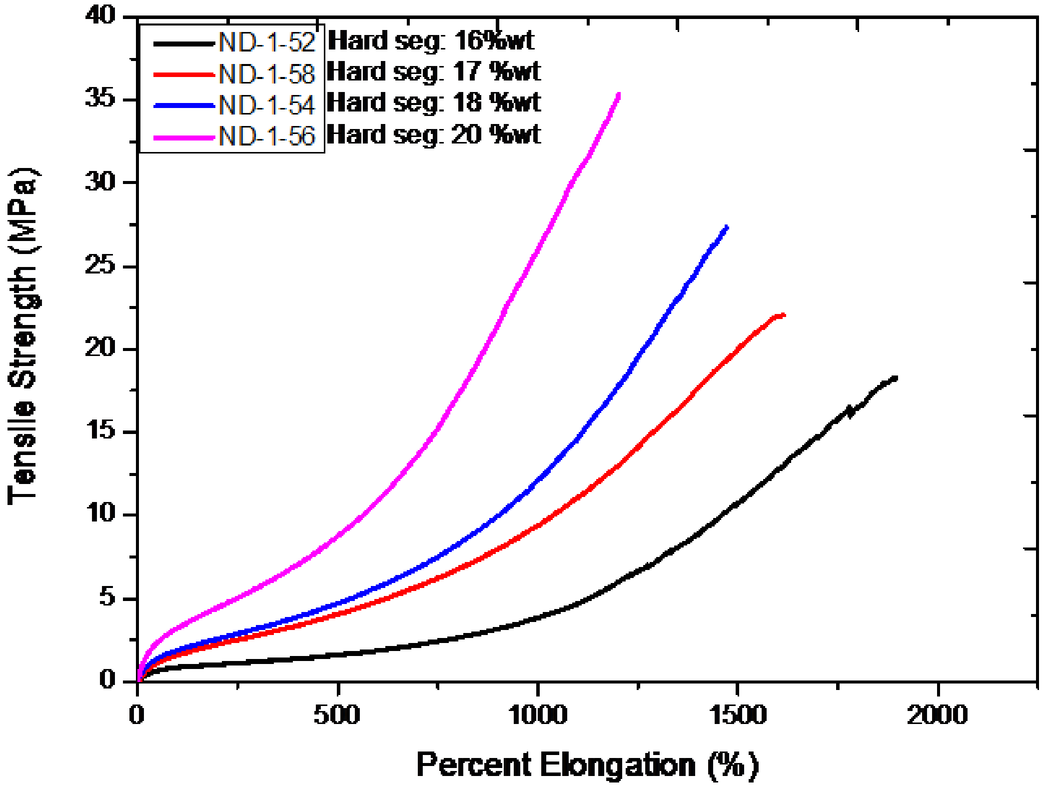


Figure 12: Mechanical characterization of PUDs with different hard segment ratios

Mechanical properties of thin films cast from each PUD are shown in Figure 12. All films showed an elastomeric behavior, which is typical for high molecular weight thermoplastic polyurethanes. As hard segment content increased the tensile strength at break value also increased systematically. Young’s modulus values also followed the same trend as summarized in Table 2. Elasticity, in other words the percent elongation of films exhibits a reverse relationship with increasing hard segment. The reason for this behavior is as the amount of hard segments groups in the PU backbone increases chains become more rigid because the number of urethane bonds and their hydrogen bonding interactions increase. So the decrease in the content of soft segment chains will decrease the elasticity since the amorphously dispersed soft chains from polyols are the main reason for elastic behavior.

3.1.1.3. The Effect of Polyol Type

It is well-known that the chemical structure and length of the soft segment in PUs are critical factors in determining the final polymer properties by affecting the micro-phase morphology that is composed of hard and soft segment phases. For example, in order to investigate the effect of soft segment length, Hartmann et al showed that while keeping the hard segment length constant, increasing the molar mass of soft segment will increase the tendency for the hard segment domains to be isolated in the soft segment matrix.[35]

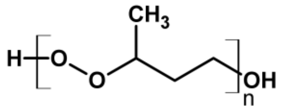
The chemical structure of the soft segment is also expected to play a critical role on the properties of PUs. Yilgor et al has investigated the effect of molecular weight of the soft segment in thermoplastic polyurethanes using polytetramethyleneoxide (PTMO) as polyol and molecular weights of about 1000, 2000, 2900 and 3500 g/mol has been used. p-Phenylenediisocyanate (*p*PDI)was used as the diisocyanate and 1,4 butanediol was the chain extender. As the molecular weight of PTMO increased the micro phase separation also increased. The soft segment which is composed of PTMO had melted before the ambient temperature, which means there is no contribution from soft segment to tensile strength or stiffness. As the length of soft segment increased the incompability between the hard segment and soft segment also increased. Following the increased incompability between hard and soft segments, micro phase separation consequently increased. [29]

In this study the effect of the soft segment structure (while keeping the soft segment length constant) on the final properties of polyurethane dispersions and their films was investigated by synthesizing a series of polyurethanes. As shown in Figure 13, four different types of polyols, a polyol of ethylene glycol/adipic acid/butane diol, a polyol of diethylene glycol/adipate diol, poly (tetra methylene oxide) and poly (propylene oxide) that constituted the soft segment of polyurethanes. The molecular weight of polyols, thus the length of soft segment in the PU chain, was kept equal (2000 daltons). . In addition, other parameters such as chain extension (70%), hard segment content (17 wt %) and ionic content (1.20 wt %) were kept constant during the synthesis of PUDs as summarized in Table 3Therefore, it was ensured that the hard segment and soft segment lengths of all polyurethanes were statistically equal to each other and only the effect different soft segment structures on the properties of PUDs and their films was investigated.

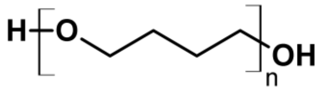
Table 3: Properties of PU dispersions and their films with different polyol types incorporated to the soft segment

Effect of Polyol Type				
Sample #	**ND-1-64**	**ND-1-72**	**ND-1-86**	**ND-1-88**
Polyol Type	Diethylene glycol/Adipate diol	Ethylene glycol/Adipic acid/Butane diol	Poly(tetra methylene oxide)	Poly(propylene oxide)
Hard Segment, % wt	17	17	17	17
Chain Extension, %	70	70	70	70
Ionic Content, %	1.20	1.20	1.20	1.20
Tensile Strength at Break, MPa	22.6 (±0.4)	12.8(±2.1)	26.9(±1.6)	5.51 (±0.1)
Percent Elongation, %	1580 (±17)	1660 (±104)	730 (±14)	2070(±26)
Youngs Modulus, MPa	2.7 (±0.1)	2.2(±0.4)	6.4 (±0.2)	2.5 (±0.2)
Particle Size, nm	99	157	154	144
NCO/OH ratio	1.98	1.91	1.88	1.88
Isocyanate: HDI				

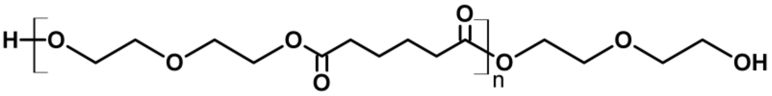
It should be noted that all synthesized polyurethanes formed stable dispersions. Mean particle sizes varied between 99 to 157 nm. The main component which is effective on the particle size of PU latexes is the ionic group content of that specific PU, and the ionic content the same for all PUs in order to observe the effects of only different soft segment structures. It is clear that the mean particle size value and distributions reveal stable dispersion for each type of polyol. The variation of the particle size properties could be due to the fact that the chemical structures of soft segments are different from each other by means of rigidity and more importantly hydrophilicity/hydrophobicity. It was already discussed that chain flexibility affects the particle size distribution as also reported by Mequanint et al. that more flexible chains are easier to deform, so the flexibility of soft segment is also effective on the particle size of latexes[24]. In our studies, relative hydrophilicity of each polyol was assumed to play a role in final particle size distributions. When the chemical structure of each soft segment is investigated in Figure 13 the polyol of diethylene glycol/adipic acid reaction is expected to give the most hydrophilic structure, which in fact yielded a product with the lowest mean particle size values as well as the hard segment content.



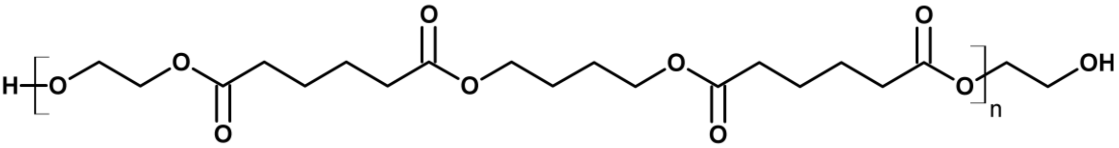
Poly(propylene oxide)



Poly(tetramethyleneoxide) (PTMO)



Polyol of (Diethyleneglycol/ Adipic acid) (DEG-AA)



Polyol of (Ethylene glycol/Adipic acid/Butane diol) (EG-AA-BD)

Figure 13: Chemical structure of different polyols used in synthesis

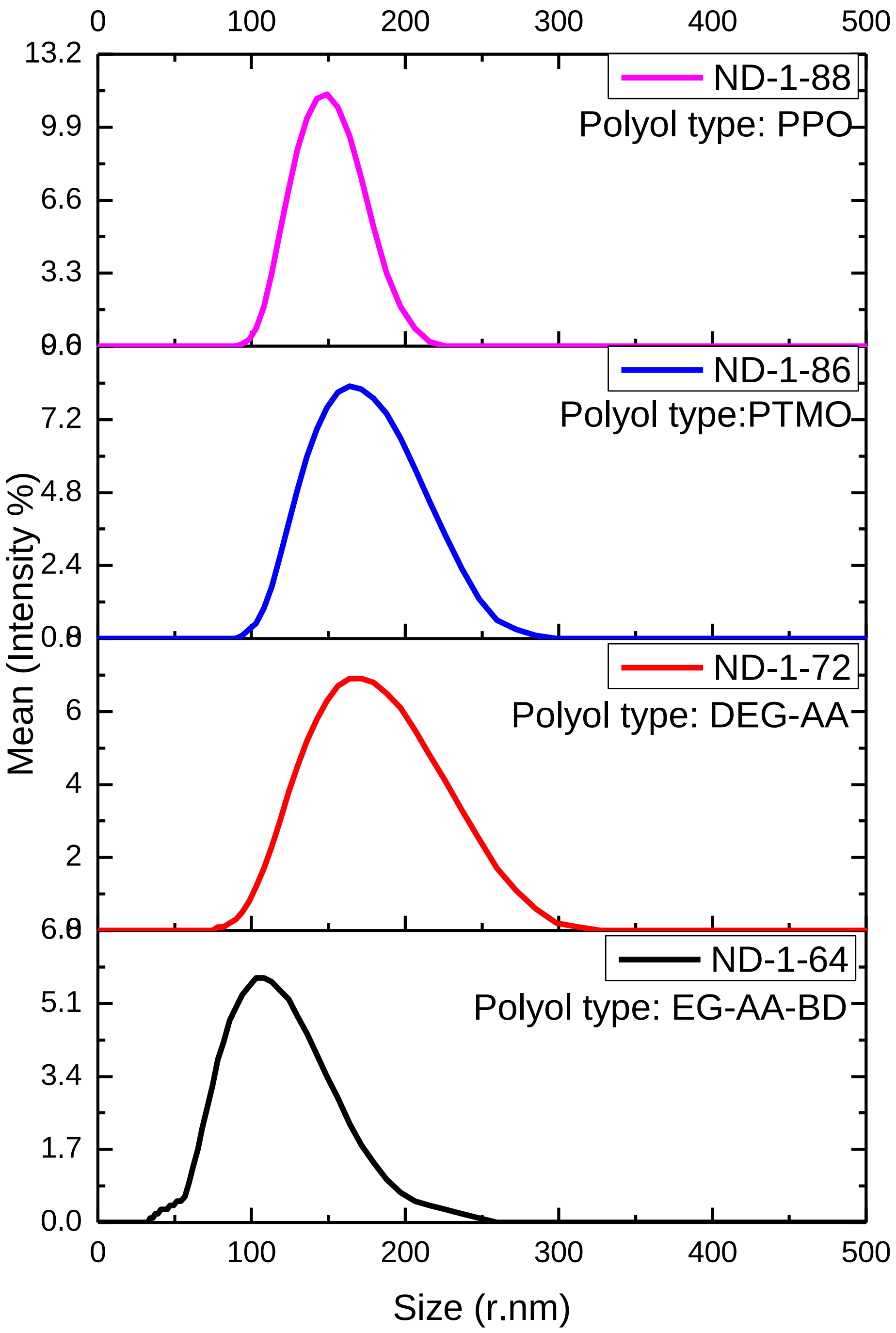


Figure 14: Particle size distributions of PUDs with different soft segments

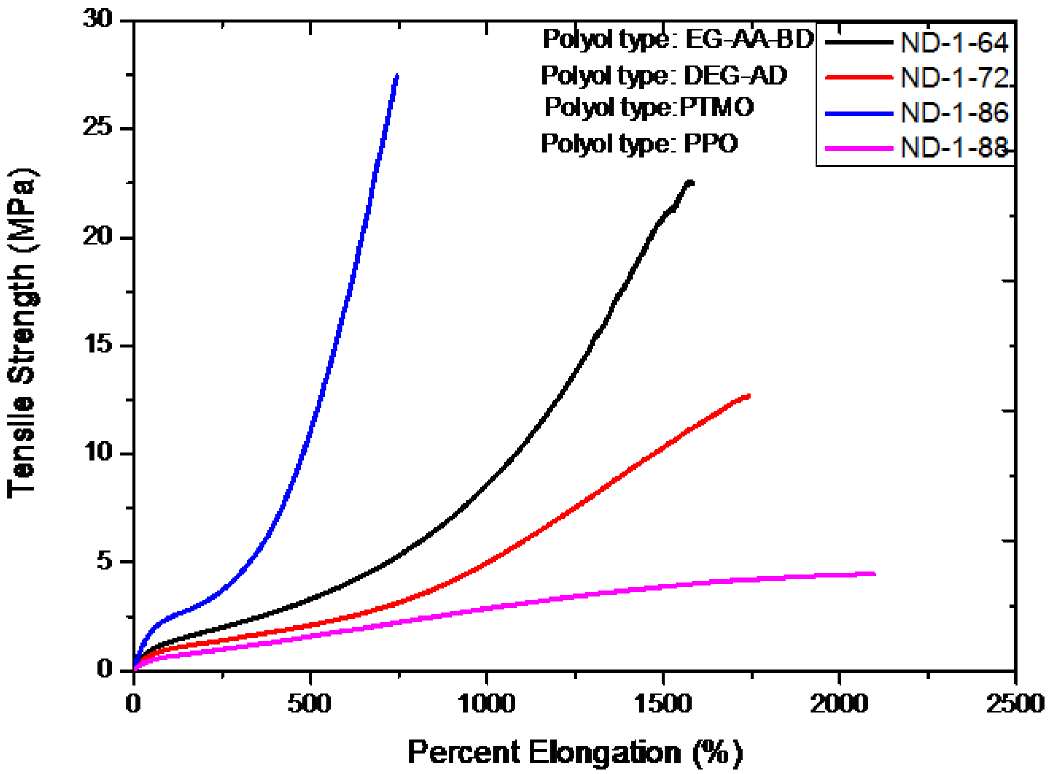


Figure 15: Mechanical characterization of PUDs with different soft segment structures

Phase-separation in polyurethanes is a well-known phenomenon and by Cooper unique properties of polyurethanes have been associated with this behavior. Thermodynamic and kinetic forces as well as the solubility parameters of hard and soft segments are effective on phase separation.[36]By using different polyols as starting materials that constitute soft segments, the solubility parameters also change and as a result micro-phase morphology of each polyurethane structure changes, which is reflected on the mechanical properties of corresponding films. The polyurethane sample with PTMO as the soft segment is expected to result in higher ratio of phase-separated morphological structure compared to polyester polyols of ethylene glycol/adipic acid/butane diol (EG/AA/BD), polyol of diethylene glycol/adipate diol (DEG/AA). In fact, ester carbonyls in these polyester polyols are expected to participate in hydrogen bonding interaction with the hard segments, resulting in phase mixing. This situation leads to lower tensile strength values in polyurethanes containing polyester-based soft segments, ND-1-64 and ND-1-72. As expected, polyurethanes films with PPO-based soft segment gave the lowest tensile strength values, due to the fact that PPO chains are the most flexible structures among all PTMO based polyurethane films exhibit exceptionally high tensile strength at break values, with a different stress-strain behavior compared to the rest, which is primarily due to the fact that PTMO segments in PU chains show strain-induced crystallization effect after ~400% elongation during the test. This phenomenon, which renders PTMO-based PUs very unique, has been previously reported in the literature in detail.

3.1.1.4. The Effect of the Degree of Chain Extension

During the synthesis of PUDs by acetone process, the isocyanate-terminated prepolymer is dissolved and chain extended in acetone. During the chain extending step, the concentration of isocyanate end-groups is precisely determined by the back titration method (ASTM D2572-97) and then these end-groups are chain extended with a diamine. However, typical diamine structures including EDA have limited solubilities in acetone. In addition, AEAS monomer, both the chain extender and ionic source used in our studies is only available in 50% aqueous solution form. For the chain extension reaction to take place, the aqueous chain extenders are slowly added into the PU/prepolymer solution. It is also well-known that although they are more reactive towards hydroxyl or amino-groups, isocyanates react with water as well. In addition, since the degree of chain extension primarily determines molecular weight of final polymers, at high degrees of chain extensions (typically >85%) issues with poor solubility of very high molecular weight polyurethanes in acetone may arise as well. Therefore, in an acetone process, minor reactions of isocyanate end-groups and poor solubility of high molecular weight polymers in acetone need to be taken into account and an optimum degree of chain extension with diamino-compounds need to be determined for every polyurethane composition. In order to study the effect of the degree of chain extension on the properties of PUDs and their films and to establish a relationship between the two, adipic acid/butane diol/ethylene glycol based polyol (2000 g/mole) and HDI were used as the prepolymer’s constituents, which was then chain extended with EDA and AEAS to form the ionic polyurethane. The ionic content was set to 1.20 wt %, and the hard segment content of each sample varied slightly since the amount of chain extenders varied depending on the degree of chain extension. The degree of chain extension varied from 50 to 70 wt % as summarized in Table 4.

Table 4: Table of PUD properties with different chain extension ratios

Effect of Degree of Chain Extension				
Sample #	**ND-1-60**	**ND-1-62**	**ND-1-58**	**ND-1-64**
Chain Extension, %	50	60	70	70
Hard Segment, % wt	17	17	17	17
Ionic Content, %	1.20	1.20	1.20	1.20
Tensile Strength at Break, MPa	27.5 (±3.4)	19.7 (±0.1)	22 (±1.0)	22.6 (±0.4)
Percent Elongation, %	1140 (±36)	1205 (±27)	1610 (±9)	1580 (±17)
Youngs Modulus, MPa	4.9 (±0.2)	3.7 (±0.1)	3.4 (±0.1)	2.7 (±0.1)
Particle Size, nm	503.6	101.4	86.7	98.9
NCO/OH ratio	2.13	1.98	1.98	1.98
Polyol: Adipic acid/ Butane diol/ Ethylene glycol; Isocyanate: HDI				

The degree of chain extension directly determines the molecular weight and content of urea bonds, which are formed by isocyanate and amine reactions. Alternative to chain extension with short diols, which give urethane bonds, urea groups increase hydrogen bonding interactions between hard segments.[37]

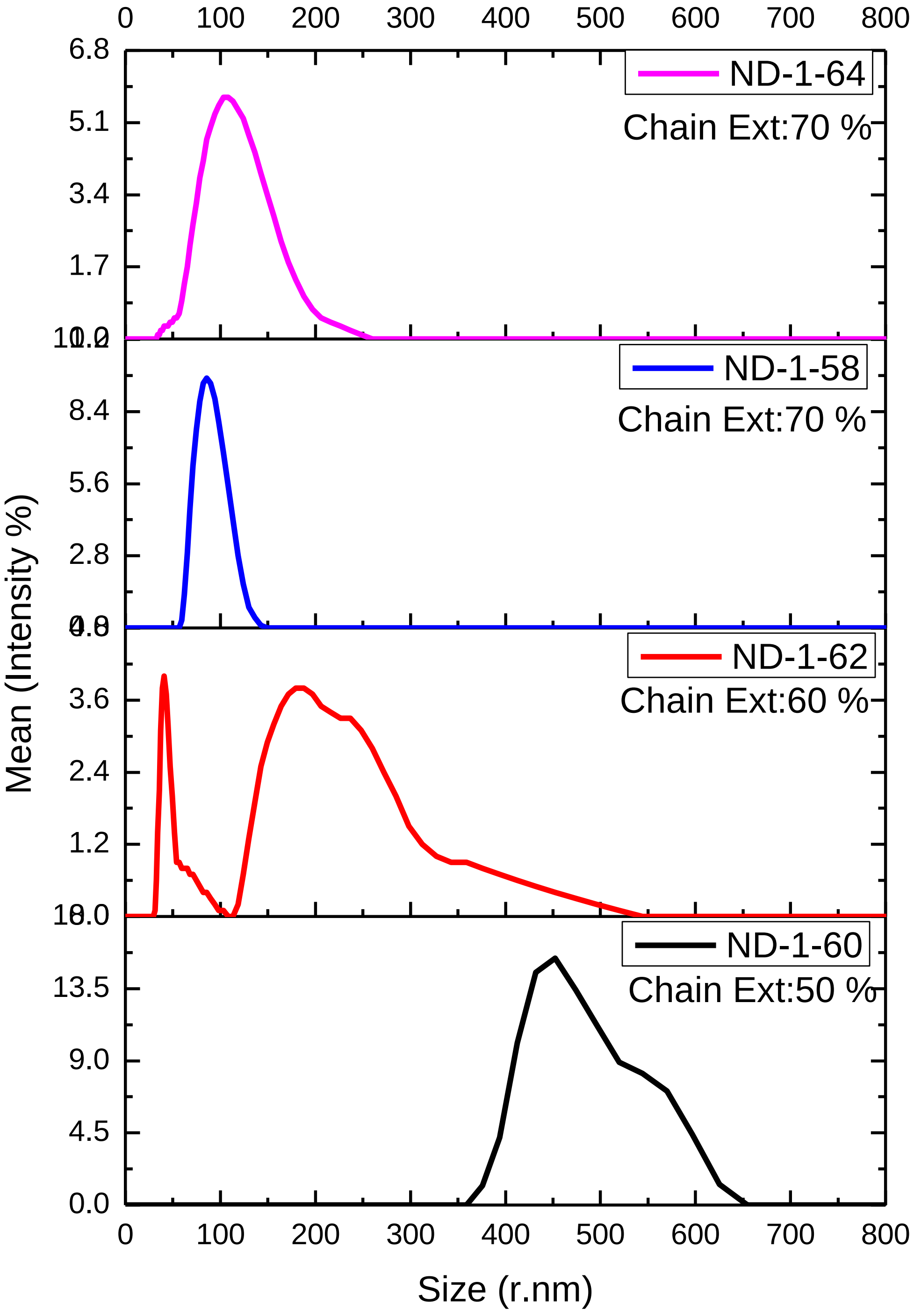


Figure 16: Particle size distributions of PUDs with different chain extension ratios

In our syntheses, PUDs samples, namely “ND-1-64” and “ND-1-58” (both having 70% chain extension) have very narrow particle size distributions with acceptable mean particle sizes close to each other. However, PUD samples with 50% and 60% chain extensions showed multi-model particle size distributions are bimodal and contain particles larger than acceptable value for stable dispersions. In fact, when shelf-life stabilities of these samples were compared, ND-1-60 with 50% chain extension immediately precipitated within days, ND-1-62 with 60% chain extension slightly precipitated within weeks and ND-1-64 and ND-1-72 samples with 70% chain extension were stable. The main reason for multi-modal particle size distributions at low chain extension degrees was due to increased amount of unreacted isocyanate end-groups, which are more likely to react with excess water in the reaction mixture and uncontrollably form urea particles, which do not readily disperse in water and are observed on the larger end of particle size distributions. This study was therefore very essential to determine the optimum degree of chain extension when AEAS was used as both the chain extender and ionic source. Similar when the 70% chain extended reaction was repeated.

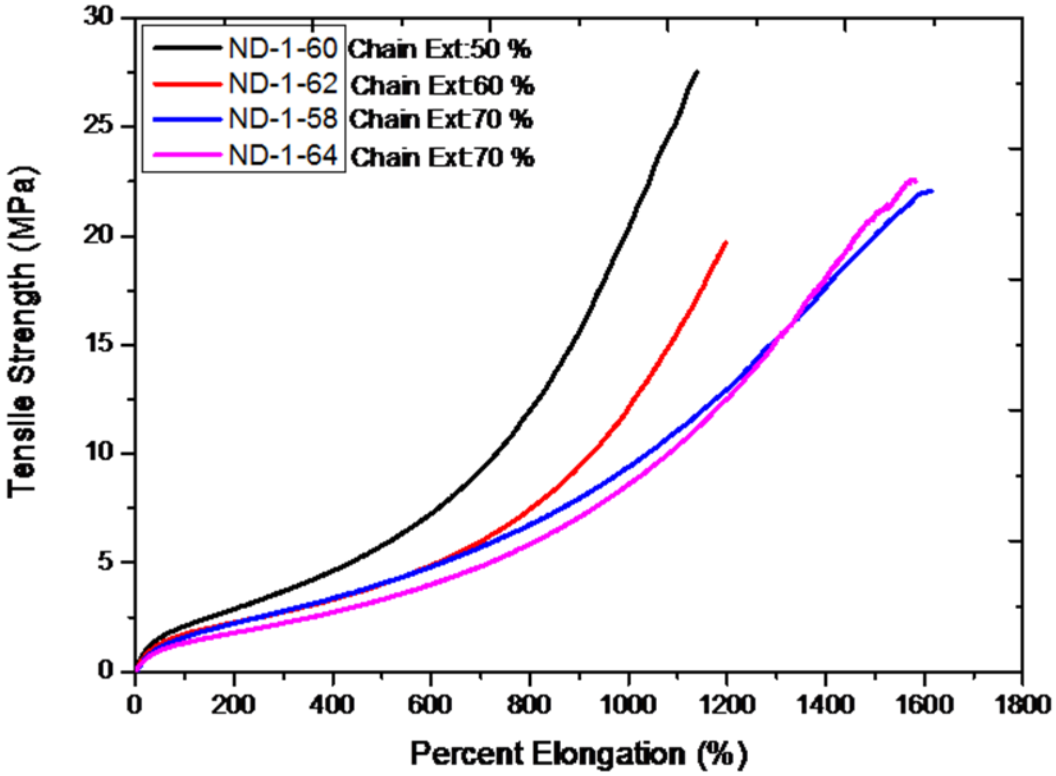


Figure 17: Mechanical characterization of PUDs with different chain extension ratios

3.1.2. Synthesis and Characterization of Waterborne Polyurethane/Halloysite Nanocomposite Dispersions and their Films

In addition to syntheses and characterization efforts on the investigation of key structural parameters for new PU dispersions reported in this thesis, novel PU/Halloysite dispersions and their nanocomposite films were also prepared and characterized. For this purpose, Halloysite nanoparticles (HNT) were incorporated into PU dispersion either during the synthesis (in-situ)or by directly blending into a previously synthesized PUD that had exactly the same structural parameters and composition with the in-situ added PUD. These two incorporation methods were compared by testing the final casted thin PU/HNT nanocomposite films for mechanical and thermal properties.

HNTs are a type of naturally abundant clay materials with crystalline structures. Depending on variety of crystallization conditions and geological occurrence, HNTs are found in nature as in tubular, spheroidal and plate-like shaped particles. Typically, the inner diameter, outer diameter and length of HNTs are 1–30 nm, 30–50 nm and 100–2000 nm, respectively.[28]

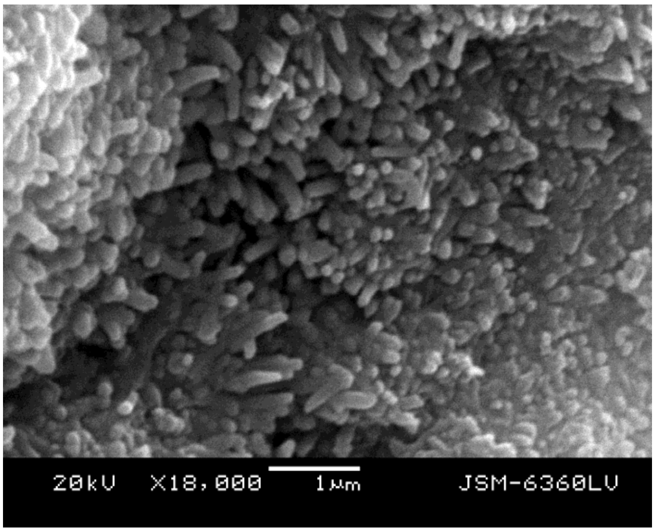


Figure 18: SEM image of Halloysite nanotubes in cluster: SEM image of Halloysite nanotubes in clusters[29]

As shown in Figure 18 HNTs are found in nature in clusters and therefore, HNTs that were used in this study were supplied in a pre-suspended form in an aqueous solution by Eczacibasi ESAN Figure 19 shows the TEM images of HNT particles that were deposited on a TEM grid and dried. The inner hollow part of nanotubes is especially interesting to observe under TEM.

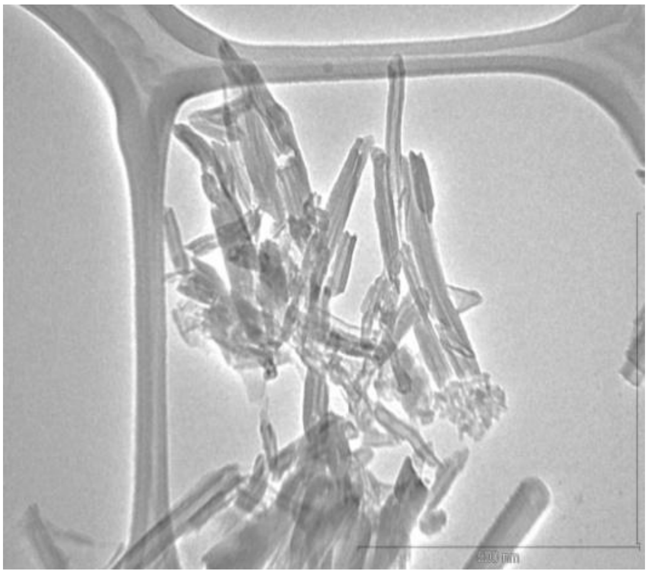


Figure 19: TEM image of pure HNTs dried on carbon coated Lacey formvar film supported in 300 mesh copper TEM grids.

Two different methods of incorporation of HNTs into the PU matrix, effect of HNT content and effect of ionic content of PUD on the final film properties were then investigated in this part of the study.

3.1.2.1. The Effect of Nanoparticle Content using Blending Method

In this series HNTs were blended into a pre-synthesized PUD under mechanical agitation with contents ranging from 0.25 to 5 wt% and then corresponding nanocomposite films were cast and characterized. HNTs were supplied in the form of 10 wt% suspension.

Table 5: Effect of different HNT contents blended into PUDs

Effect of Nanoparticle Content using Blending Method						
Sample #	**ND-1-68**	**ND-1-70-A**	**ND-1-70-B**	**ND-1-70-C**	**ND-1-70-D**	**ND-1-70-E**
Nanofiller Content,%	Blank	0.25	0.5	1	3	5
Hard Segment, % wt	20	20	20	20	20	20
Chain Extension, %	70	70	70	70	70	70
Ionic Content, %	1.20	1.20	1.20	1.20	1.20	1.20
Tensile Strength at Break, MPa	20.4 (±0.9)	14.0 (±0.3)	6.9 (±3.46)	14.2 (±1.2)	6.2(±1.4)	10.7(±3.7)
Percent Elongation, %	1190 (±58)	1530 (±10)	1600 (±290)	1550 (±45)	1630 (±57)	1555 (±4)
Youngs Modulus, MPa	3.3 (±0.3)	2.3 (±0.1)	2.2 (±0.5)	2.6 (±0.5)	2.5(±0.5)	2.5(±0.7)
Particle Size, nm	98	101	104	98	105	107
NCO/OH ratio	1.98	1.98	1.98	1.98	1.98	1.98
Polyol: Adipic acid/ Butane diol/ Ethylene glycol; Isocyanate: HDI						

Particle size distributions of these PU/HNT dispersions are shown inFigure 20. Noimportant shift from the main peak of blank PU is observed in all of size distribution graphs. The mean particle size of blank PUD is at 98 nm while 5 wt % HNT containing PUD gives a mean particle size of 107 nm. However, there is a clear broadening of the particle size distribution with a shoulder appearing on the higher particle size end. Due to this behavior, it was concluded that there was no encapsulation of HNTs into latex PU particles. In fact, this conclusion was supported by the fact that HNTs in these samples phase separated and precipitated at the bottm of containers by forming aggregates within one day.

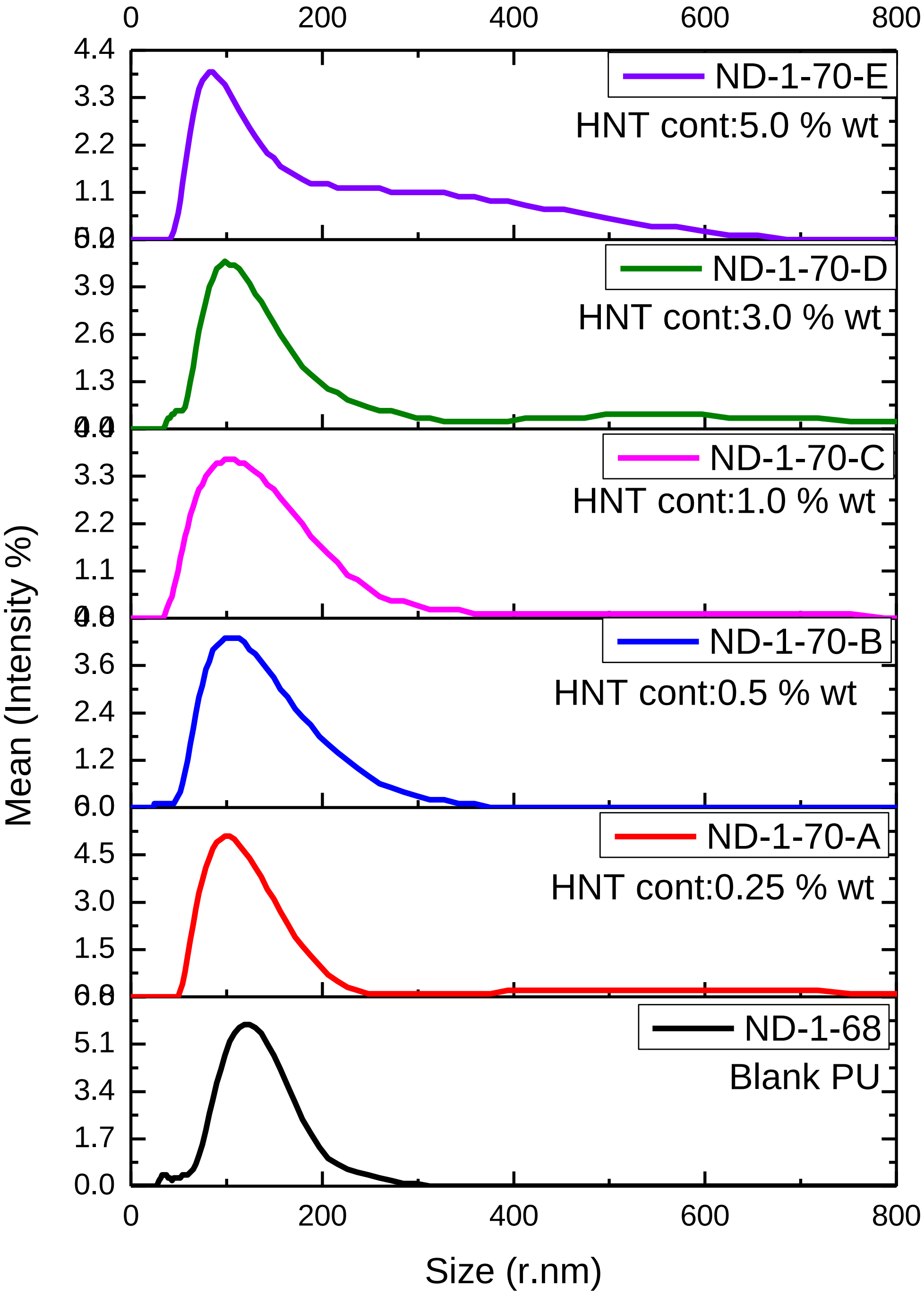


Figure 20: Particle size distributions of PUDs with different nanoparticle concentrations

Mechanical behavior these PU/HNT nanocomposite films are shown inFigure 21 and average values are given inTable 5.

Upon the addition of HNTs into previously synthesized blank PU, a decrease in the tensile strengthand a slight increase in elongation at break values were observed gradually as a function of the HNT content. Interestingly, following the increase of HNT content in the PU film from 0.25 to 0.5 wt%, tensile strenght sharply dropped from 14.0 to 6.9 MPa. This gradual decrease was observed up in all samples to a 5 wt % HNT addition.

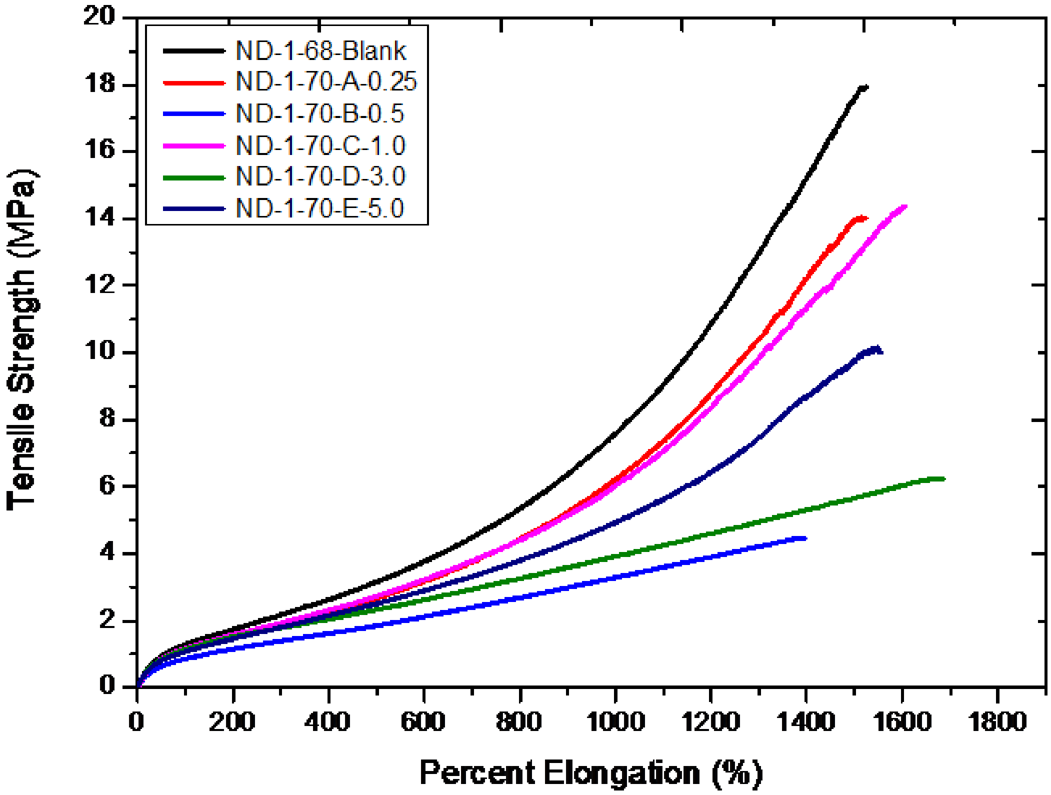


Figure 21: Mechanical characterization of PUDs with different nanoparticle concentrations

The reason for such a significant decrease in the tensile strength values upon the incorporation of HNTs into the polyurethane matrix was presumed to be due to poor dispersion of externally added HNTs that could have formed clusters in the PU matrix during the film formation due to lack of any interactions between polymer chains or latex polymer particles and HNT nanoparticles. It is already known that the uniform distribution of nanoparticles in such polymer nanocomposites is important because the matrix will distribute the force to the fillers and the nanofillers carry most of the applied load.

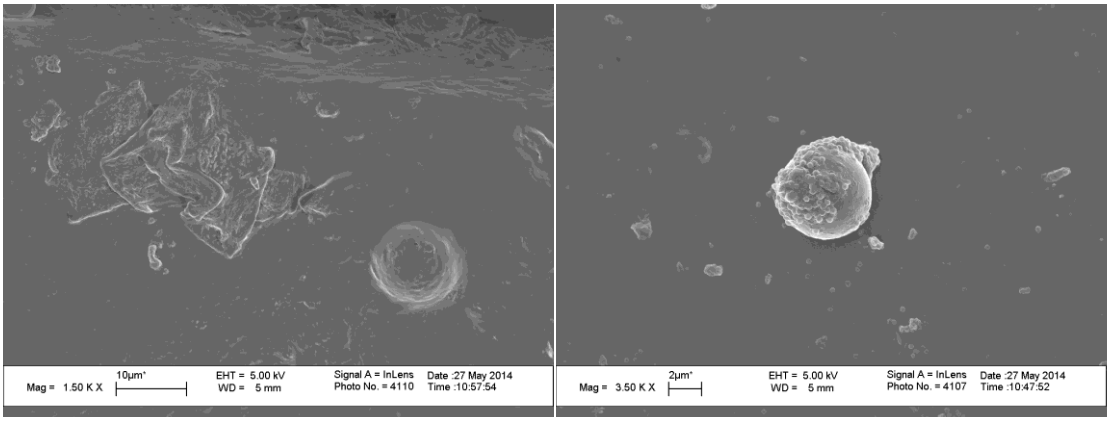


Figure 22: SEM images of (a) pure polyurethane film, (b) polyurethane with 1 wt % HNT added by direct blending method.

SEM image of blank PU film’s cross-section obtained after the mechanical testing exhibits the structure shown in Figure 22a,-b shows the cross-section of PU film with 1 wt % HNT added by direct blending method. A clear presence or good dispersion of HNTs in the PU-HNT nanocomposite film was not observed and the nod-shaped particle that was observed as a micron-sized defect introduced by HNT agglomerates could have been the main reason for significant reduction of tensile strength values. As stated earlier, in order to observe an enhancement in the properties of nanocomposites dispersion of nanoparticles has to be homogeneous all over the polymer matrix. There are several factors which affect the dispersion quality, intrinsically matrix-filler compatibility and surface energy of the particles as well as the extrinsic parameters like mixing method and conditions.[38] In this part of the study, the blending method was not found to effectively improve any properties of PU films.

3.1.2.2. Effect of the Method of HNT Incorporation

Alternative to the blending method discussed in the previous section, HNTs were introduced into PUDs during the synthesis, specifically by adding the calculated amount of HNT suspension dropwise into the reaction mixture immediately after the chain extension, before the dispersion step. For this purpose, a PUD sample containing 1 wt%

HNT (with respect to total PU solid content) was prepared (ND-1-76)and compared to sample containing no HNTs (ND-1-68) and the sample containing 1 wt% HNT prepared by blending (ND-1-70-C). It is important to note that during the synthesis of ND-1-76, the chemical composition and all other parameters were exactly same as ND-1-68.After the slow addition of HNTs into the reaction mixture, dispersion and acetone removal steps steps were carried out in the same manner to obtain the final polyurethane dispersion and thin films of each sample were cast immediately.

Table 6: Effect of different methods of HNT incorporation on the properties of PUDs and their films

Effect of HNT Incorporation			
Sample #	**ND-1-68**	**ND-1-70-C**	**ND-1-76**
Incorporation Method	Blank	Blending	In-situ Addition
Nanofiller Content,%	0	1	1
Hard Segment, % wt	20	20	20
Chain Extension, %	70	70	70
Ionic Content, %	1.20	1.20	1.20
Tensile Strength at Break, MPa	20.4 (±0.9)	14.2 (±1.2)	31.6 (±0.7)
Percent Elongation, %	1190 (±58.3)	1550 (±45)	1350 (±39)
Youngs Modulus, MPa	3.3 (±0.3)	2.6 (±0.5)	3.68 (±0.9)
Particle Size, nm	98	98	432
NCO/OH ratio	1.98	1.98	1.98
Polyol: Adipic acid/ Butane diol/ Ethylene glycol; Isocyanate: HDI			

The particle size comparison of this set of samples is given in Figure 23and a clear increase in the mean particle size and particle size distribution for the in-situ HNT incorporated sample (ND-1-76) was observed. This increase in particle size of PU latex particles clearly indicate that HNT nanoparticles were encapsulated in the latex polymer particles, which resulted in increased particle size and distribution.

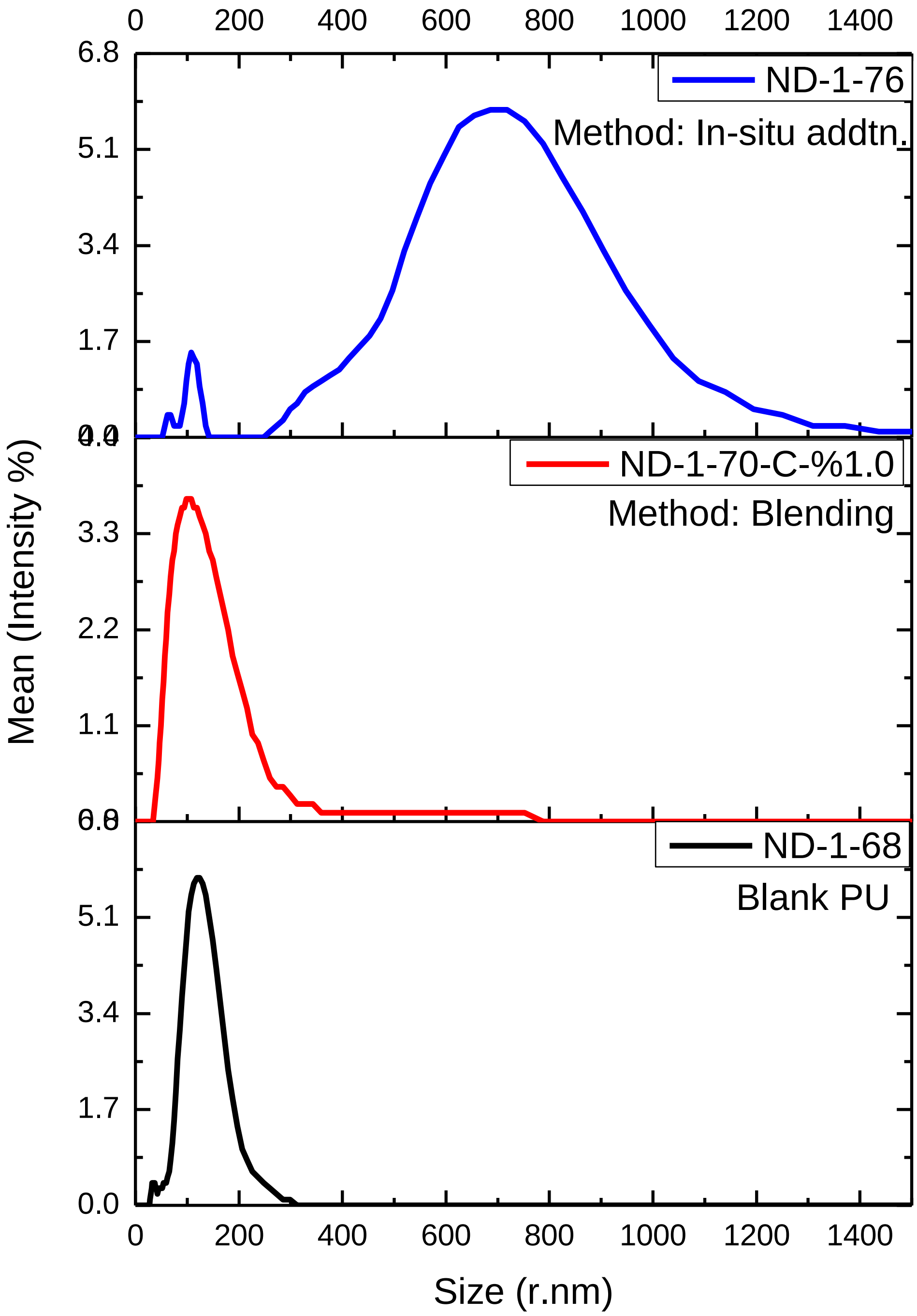


Figure 23: Particle size distributions of PU/HNT dispersions prepared by different methods

When, the effect of the two incorporation methods, direct blending and in-situ incorporation, on the mechanical and thermo-mechanical properties of final PU/HNT filmswere compared,while the blank PU filmhad20.4 MPa of tensile strength at break and this value decreased to 14.2 MPa for the PU film that containing 1 wt% HNTs incorporated by blending,the PU film containing 1 wt% HNTs incorporated in-situ had a tensile strength of 31.6 MPa at break(Figure 24andTable 6). Such a dramatic increase in the tensile strength corresponds to more than 50% improvement in the tensile strength with 1 wt% HNT incorporation. These results indicate that HNTs werefinely dispersed throughtout the polymer matrix. SEM images of the films' cross-sections also evidence a good dispersion of HNTs in the PU polyurethane matrix as shown in Figure 24

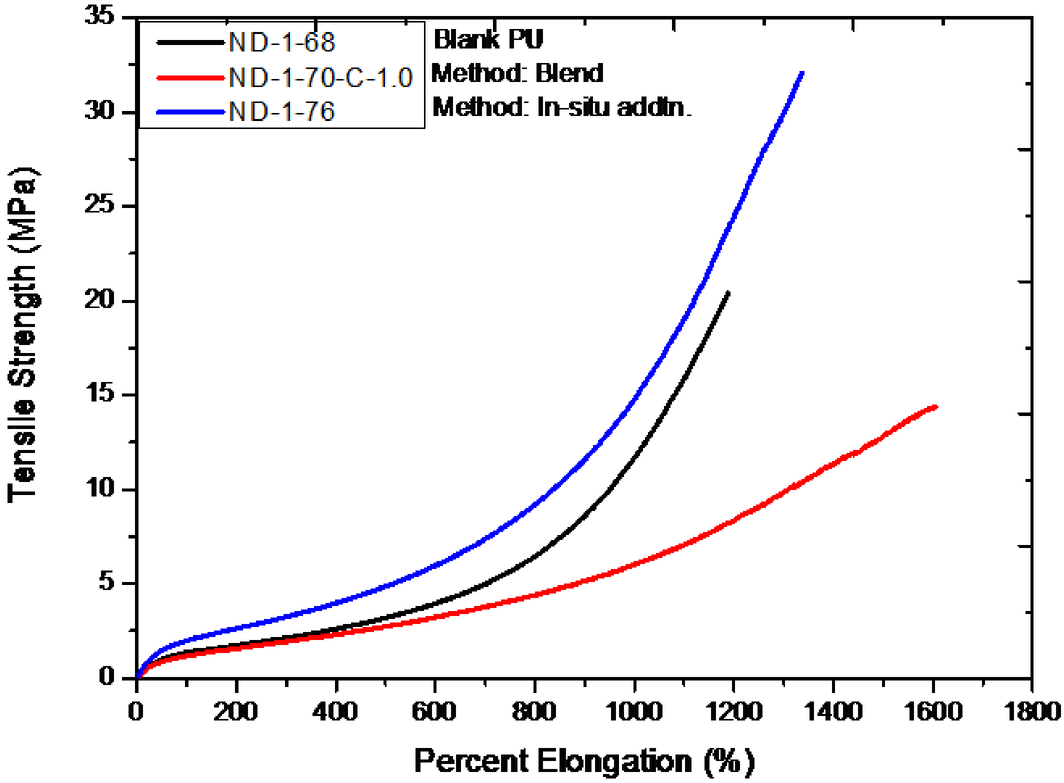


Figure 24: Mechanical behavior of PU-HNT nanocomposite films

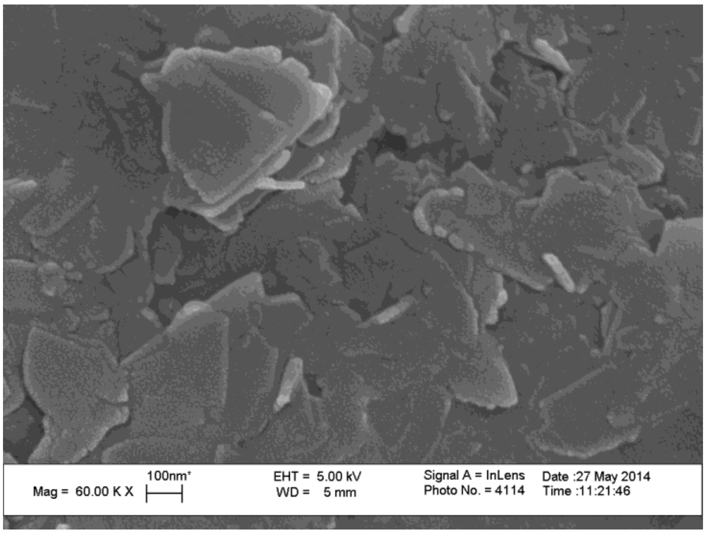


Figure 25: TEM image of PU-“ND-1-76”dispersion dried on carbon coated Lacey formvar film supported in 300 mesh copper TEM grids

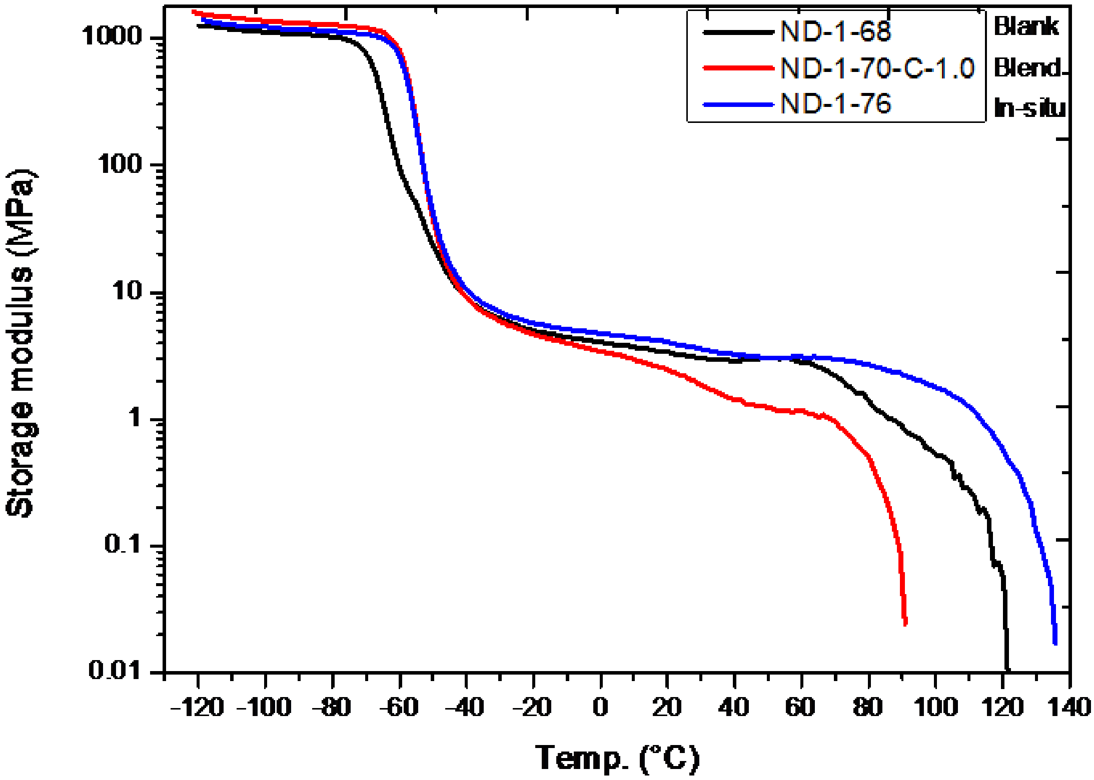


Figure 26: Dynamic mechanical analysis of PU films with different methods of HNT incorporation

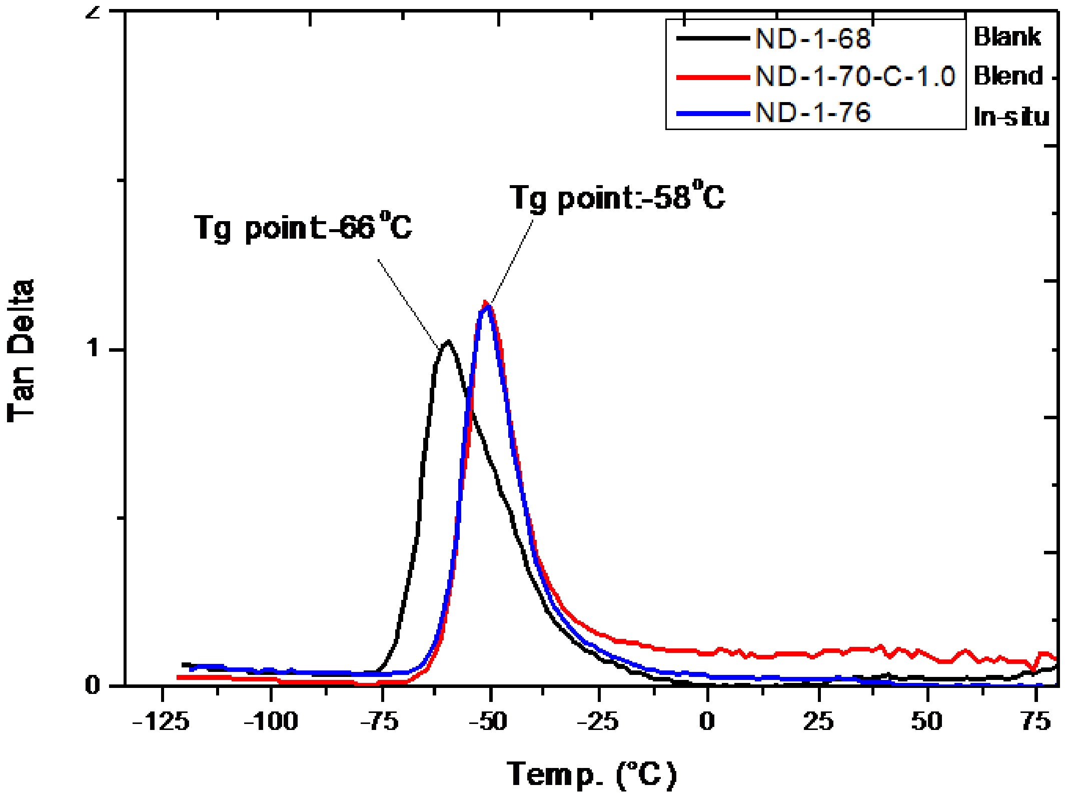


Figure 27: Dynamic mechanical analysis of PU films with different HNT incorporation methods applied, tan delta graph is shown

As shown in Figure 26interesting thermo-mechanical behaviors were observed for HNT containing PU films depending on the incorporation method. First of all, HNT incorporation into PUs by method, blending or in-situ, has resulted in a significant increase from -66 °C to -58 °C compared to the blank PU film as observed in tan delta plots in Figure 27. This increase suggests that independent from how they were incorporated; HNTs readily interacted with and restricted the mobility of soft segment chains of polyurethanes. On the other hand, there was a slight decrease and slight increase in the storage modulus of blended and in-situ incorporated samples, respectively, in the rubbery plateau region compared to the blank PU sample (Figure 26) In addition, the dissociation temperature, which is also associated as hard segment dissociation, of the PU film was significantly influenced by how HNTs were incorporated. While the blank PU film’s hard segment dissociation begun after 60 °C, the PU film with 1 wt% in-situ incorporated HNTs showed an extended rubbery plateau up to 80 °C. On the other hand, the thermo-mechanical behavior of the PU film with 1 wt% blended HNT in the rubbery plateau was negatively affected and a continuous dissociation behavior was observed after 0 °C.

The reason for poor distribution of HNTs in the polymer matrix prepared by the blending method could be explained by stronger filler-filler interaction than the filler-polymer interaction since the polymer was previously formed.[39] The in-situ incorporation method, however, resulted in dramatic improvement of tensile and thermo-mechanicalproperties of the PU film because HNT nanoparticles were assumed to readily interacted with polymerizing polymer chains since they were introduced during the chain extension step, this enabled them to interact and disperse better in the polymer matrix. According to the DMA results, the in-situ incorporation approach especially improved the interaction of HNTs with the hard segment, which resulted in the extended rubbery plateau, thus improved heat stability of the corresponding film. The in-situ incorporation process needs to be closely investigated in this study. First of all when HNTs were introduced into the reaction mixture immediately after the chain extension step, it was very likely that unreacted, residual isocyanate groups were still present. On the other hand, it is also well-known that HNT surface may possess residual hydroxyl groups. Thus, such dramatic improvement in tensile and thermo-mechanical properties of in-situ incorporated sample can be explained by the presumption that HNTs interact with the hard segments by covalent interactions as depicted in . Such interactions enable HNTs to be finely dispersed within the hard segment domains.

3.1.2.3. Effect of Ionic Content on HNT Incorporation

With the presumption that in-situ incorporation of HNTs resulted in their encapsulation into the latex polymer particles, the effect of ionic content, which is responsible for the stabilizing mechanism of these latex particles in water, on the ability to increase HNT content and achieve a stable PU/HNT dispersion was studied. Based on the encapsulation mechanism proposed, higher ionic content was presumed to stabilize higher HNT content in latex particles. For this purpose, the ionic SO_3content in the PU chain was increased from 1.20 wt% to 1.40 wt%. Then in addition to a new blank PU sample that contained 1.40 wt% SO_3, two PU/HNT dispersions with 1 wt% and 5 wt% HNTs were synthesized by their in-situ incorporation as summarized in Table 7

Table 7: Effect of different ionic content on the in-situ incorporated HNT containing PUDs and their films

Effect of Ionic Content on HNT Incorporation			
Sample #	**ND-1-82**	**ND-1-78**	**ND-1-80**
Incorporation Method	Blank	In-situ Addition	In-situ Addition
Nanofiller Content,%	0	1	5
Hard Segment, % wt	20	20	20
Chain Extension, %	70	70	70
Ionic Content, %	1.40	1.40	1.40
Tensile Strength at Break, MPa	14.4 (±1.2)	27.0 (±1.1)	12.0 (±1.6)
Percent Elongation, %	1890 (±90)	1470(±15)	1640 (±49)
Youngs Modulus, MPa	1.66 (±0.1)	3,54 (±0.1)	1.9 (±0.3)
Particle Size, nm	69	243	203
NCO/OH ratio	1.98	1.98	1.98
Polyol: Adipic acid/ Butane diol/ Ethylene glycol; Isocyanate: HDI			

As shown in Figure 28, the mean particle size of blank PUD was around 69nm while 1 wt % HNT added PUD showed a dramatic broadening and increase to 240 nm and 5 wt % HNT added PUDwas200 nm with more broadening. However, when the shelf-life stability of the two PU/HNT dispersions were evaluated, the 1 wt% HNT containing dispersion was stable, whereas the 5 wt% HNT containing dispersion showed signs of slow precipitation within a week.

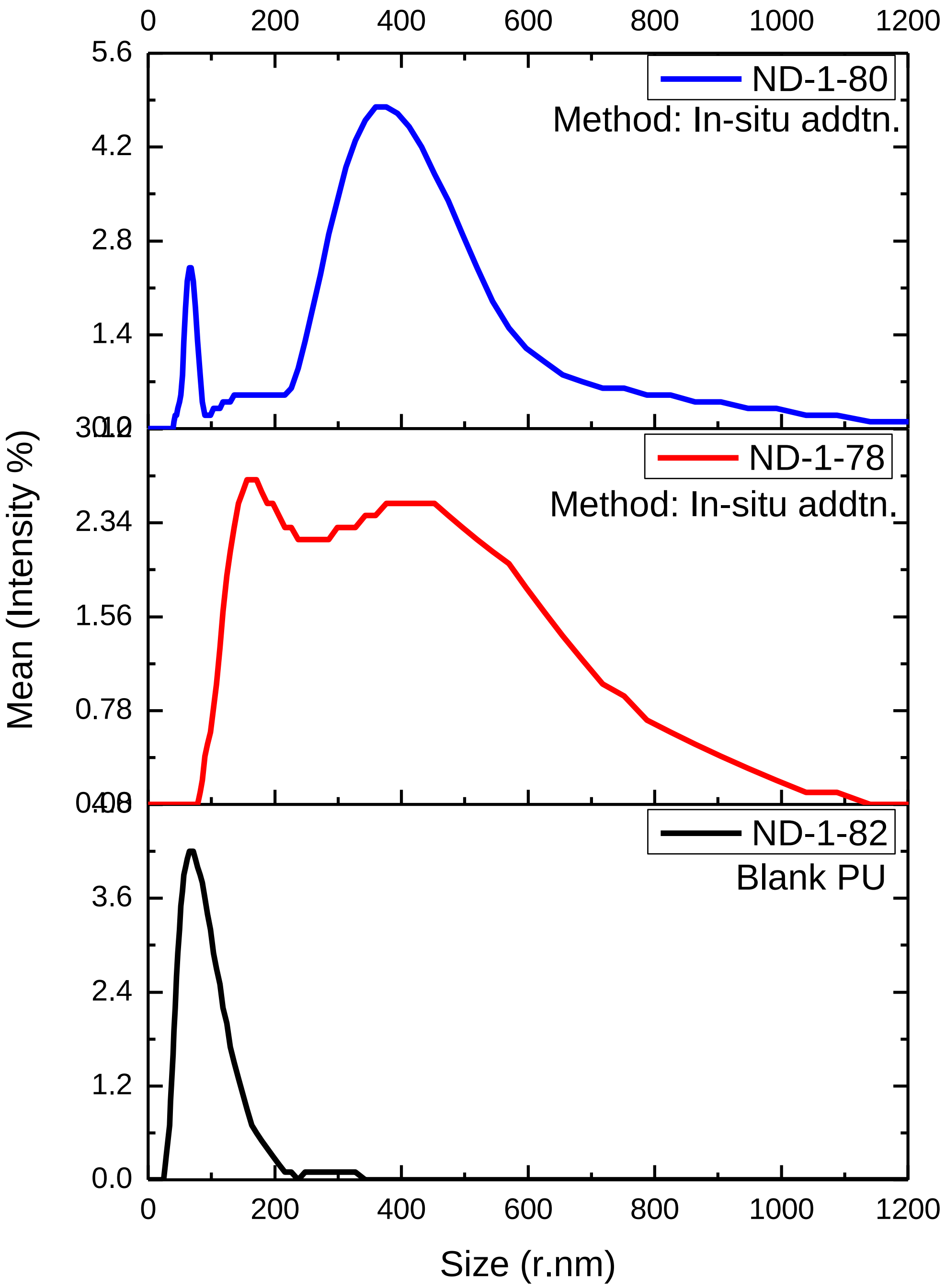


Figure 28: Particle size distributions of PU/HNT dispersions

When the stress-strain behavior of corresponding PU/HNT films were evaluated as shown in Figure 29, a dramatic increase in the tensile strength at break value of 1 wt% HNT containing PU films showed an almost 90% improvement and a 25% decrease in elongation compared to the blank PU film. However, 5 wt % HNT containing PU films exhibited a lower tensile strength than the blank PU film, which was presumably due to agglomeration of HNTs and formation of structural defects in the PU film. Such phenomenon, poor distribution of nanoparticles and formation of structural defects resulting in poorer physical properties of polymer nanocomposites is well established in the literature.[40]Fine dispersion of HNTs in the 1 wt% sample (ND-1-78) and agglomeration of HNTs in the 5 wt% sample (ND-1-80) were evidenced by preliminary TEM analyses as shown in Figure 30and Figure 31, respectively. In Figure 30 distribution of individual HNTs can be observed in the PU film. However, as seen in Figure 31the dispersion quality was very poor with 5 wt % addition of HNTs due to the presence of large HNT agglomerates in the PU film. As a result, these results suggest that although 1 wt% HNTs were successfully incorporated into PUDs and dispersed in the PU matrix, 5 wt% HNT content was too high to be properly incorporated into the PU matrix even if the ionic content was increased.

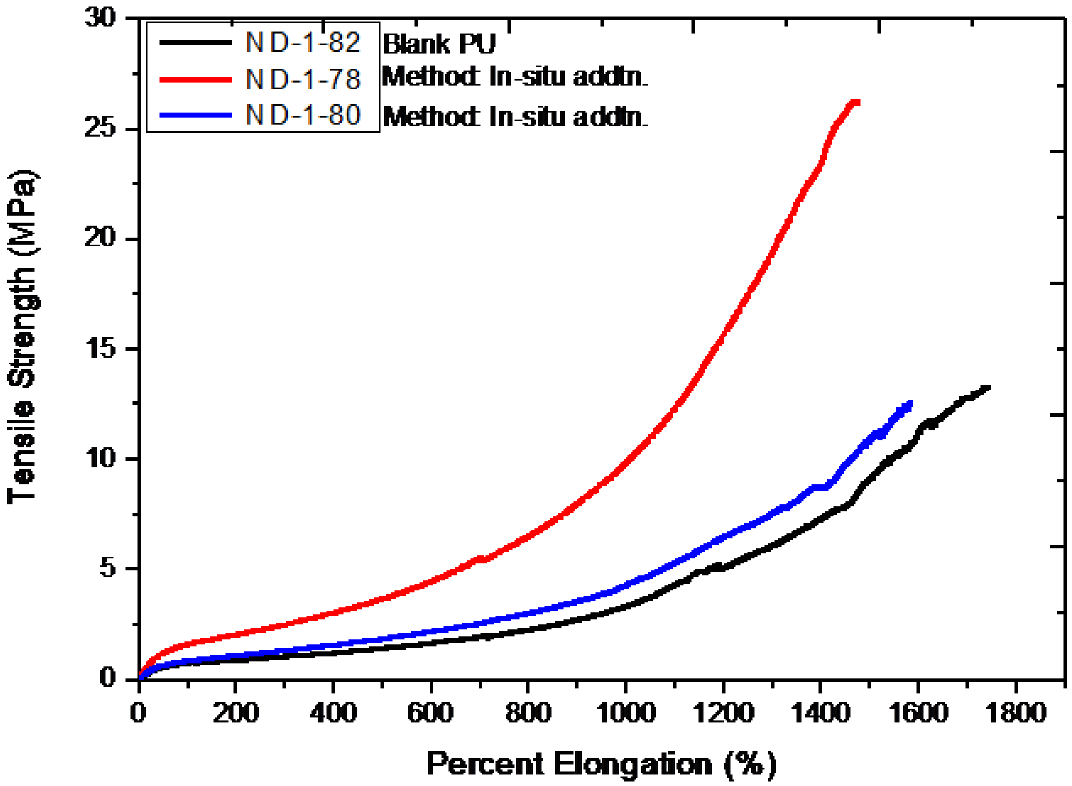


Figure 29: Mechanical behavior of PUD-HNT nanocomposite films with 1 wt% and 5 wt% HNT content

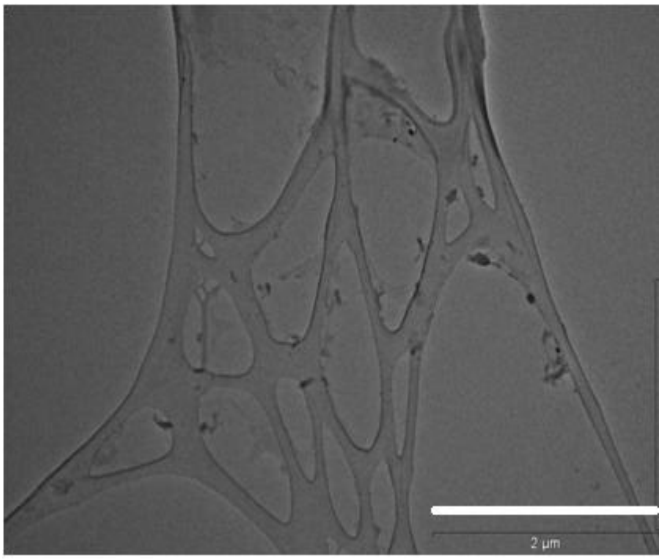


Figure 30: TEM image of PU-“ND-1-78” dispersion dried on carbon coated Lacey formvar film supported in 300 mesh copper TEM grids.

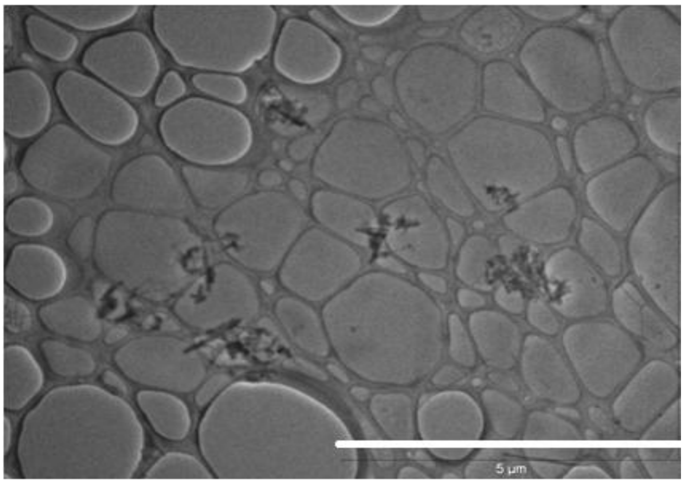


Figure 31: TEM image of PU-“ND-1-80” dispersion dried on carbon coated Lacey formvar film supported in 300 mesh copper TEM grids.

3.2. Conclusion

Novel aqueous dispersions of polyurethanes with sodium 2-[(2-aminoethyl)amino]ethanesulphonate as ionic group have been successfully synthesized by acetone method. Effect of different structural parameters such as the ionic content, degree of chain extension, hard segment content and, polyol type on the properties of aqueous dispersions and their corresponding films has been systematically investigated for the first time in the scientific literature. While it was demonstrated that the mean particle size and width of the particle size distribution decrease as a function of increasing ionic content, it was suggested that an optimum ionic content needs to be determined for each specific polyurethane structure. Similarly, an optimum degree of chain extension of 70% was determined that yielded both stable dispersions and gave elastomeric PU films with decent mechanical properties. Furthermore, it was demonstrated that by varying the hard segment content and/or the soft segment structure (type of polyol), stable polyurethane dispersions with tunable mechanical properties can be synthesized. Lastly, nanocomposites of polyurethanes containing Halloysite nanoparticles have been prepared. It was reported for the first time that HNT incorporation method plays a critical role on the final properties of PU/HNT dispersions and their corresponding films. In-situ incorporation of HNTs into PU dispersions resulted in stable dispersions with dramatic increase in tensile and thermo-mechanical properties of their corresponding films compared to PU analogues with exactly the same structure, without HNTs.

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