Synthesis, Characterization and Properties of Waterborne Polyurethanes Based on Two Different Ionic Centers

Hengameh Honarkar, Mohammad Barmar*, and Mehdi Barikani

Polyurethane and Advanced Polymers Department, Faculty of Science, Iran Polymer and Petrochemical Institute, Tehran 14977 13115, Iran

Abstract: Two different series of waterborne polyurethanes based on anionic centers: dimethylol propionic acid (DMPA) and *N,N*-bis(2-hydroxy ethyl)-2-aminoethane sulfonic acid sodium salt (BES sodium salt) were prepared from hydrogenated MDI (H$_{12}$MDI), poly(εcaprolactone), and 1,4-butanediol (BDO). The BES-based dispersions showed a smaller average particle size, and higher viscosity in comparison to the DMPA-based series. Furthermore, the tensile strength, thermal stability, and modulus of the polyurethane films for the BES ionic center were higher than the DMPA-based films. These were due to the higher activity and more powerful degree of dissociation and electrostatic interaction of -SO$_3^-$Na$^+$ groups in comparison to the quaternary ammonium carboxylate groups of the neutralized DMPA.

Keywords: Waterborne polyurethane, Ionic center, Thermal stability, Tensile strength, Particle size

Introduction

In chemical industries, environmental aspects are the main driving force for the interest of research, development, production, and application.

Waterborne polyurethane dispersions, as a special class of colloidal dispersions, are important in many industrial applications, such as coatings, adhesives, ink binders, glass fibers, paper sizing, synthetic leathers, biomaterials, membranes, films for packaging and water proof textiles [1-3].

These environment-friendly polymers are non-toxic, non-flammable and they do not pollute the air or produce wastewaters. As only water evaporates during the process, these systems are not harmful to the environment. Besides ecosystem management, high flexibility, low temperature property, high tensile strength, excellent adhesion, improved rheological properties, good chemical, and abrasion resistance are specific properties of waterborne polyurethanes. As a result of the absence of dispersants in the formation of aqueous polyurethanes and their ionomeric character, they show excellent film forming properties [4,5].

In general, polyurethanes are hydrophobic in nature and insoluble in water, therefore, to disperse them in water, they must be modified by, for example, incorporating ionic groups and/or non-ionic hydrophilic segments into the polymer structure [6-8]. Thus, the waterborne polyurethanes (WPUs) can be prepared from PU ionomers or hydrophilic polyurethanes.

Aqueous polyurethane dispersions are classified into two types: ionic and non-ionic. The ionic types contain anionic, cationic, and zwitterion centers in the polymer chains. These centers can be pendant acid or tertiary nitrogen groups, which are neutralized or quaternized to form salts [9]. The non-ionic types contain hydrophilic soft segment pendant groups, such as polyethylene oxide [10]. These groups are incorporated in the polymer backbone during the polymer synthesis.

The hydrophilicity of ionic groups enables the polyurethane to disperse in the water without using any external emulsifier. Several processes have been used for the synthesis of polyurethane dispersion, such as the acetone process, the prepolymer mixing method, the melt dispersion, and the ketimine-ketazine process [11-15].

In polyurethane dispersion the particle size is roughly in the range of 20-200 nm. These particles have a high surface energy and this is a driving force for the preparation of the film after evaporation of water. In practical purposes, polyurethane dispersions are often stored for six months or more before use. The shelf life of these colloidal systems is influenced by their particle size distribution. Due to the type of ionic groups, a minimum ionic content is necessary for the preparation of a stable polyurethane ionomer [16].

The interaction between ions with opposite charges (ion and counter ion) is important to obtain a stable dispersion. The ionic content, the degree of neutralization, the type of ionic component, the counter ion used, the molecular weight for the soft segment, and the amount of cosolvent significantly affect the particle size of the waterborne polyurethane dispersions.

Chinwanitcharoen *et al.* investigated the effect of acetone on the particle size [17]. The mechanisms of polyurethane dispersions and the effect of the neutralizing base were also studied [18].

Jhon *et al.* followed the effect of chain extension on the properties of waterborne dispersions of polyurethanes [19].

This paper describes the synthesis of two series of anionic waterborne polyurethanes from two ionic centers with carboxylic acid (dimethylol propionic acid, DMPA) and sulfonic (*N,N*-bis(2-hydroxy ethyl)-2-aminoethane sulfonic acid sodium salt (BES sodium salt) pendant groups, poly(ε-

*Corresponding author: M.Barmar@ippi.ac.ir

caprolactone, PCL), hydrogenated MDI (H$_{12}$MDI) and 1,4-butanediol (BDO). The influence of the ionic centers on the mechanical properties, thermal stability, glass transition temperature (T_g), modulus, particle size distribution and viscosity of the synthesized emulsions was investigated.

It is important to point out that the BES sodium salt ionic center has not been studied in any system yet and no comparison between the two anionic centers has been made. Furthermore, the properties that impart to the waterborne polyurethane systems have not been investigated before. A detailed view of the individual reactions will be presented in the next sections.

Experimental

Materials

Poly(ε-caprolactone, Capa 225, PCL) with a molecular weight of 2000 g/mol from Solvay Chemical Company (UK), H$_{12}$MDI (mixture of isomers, 90 %), dimethylol propionic acid (DMPA) and *N,N*-bis(2-hydroxyethyl)-2-amino ethane sulfonic acid sodium salt (BES sodium salt) from Sigma Aldrich also, 1,4-butanediol (BDO) and triethylamine, TEA, from Merck were used in this project. PCL and 1,4 BDO were dried and degassed at 60 ^{o}C overnight under a static vacuum, separately, before use. *N*-methyl-2-pyrrolidone (NMP) (Merck) and dimethyl sulfoxide (DMSO) (Merck) were used as solvents after distillation.

Dibutyltin dilaurate (DBTDL) was used as a catalyst without further purification. TEA was dried over molecular sieves (4 Å) and diisocyanate was used as a received. Furthermore, DMPA and BES were dried overnight in a vacuum oven at 80 ^{o}C, separately.

Characterization

Particle size and distribution were measured by dynamic light scattering (Sema Tech, SEM-633, He-Ne laser, France) at room temperature. The samples were homogenized after dilution in deionized water to 0.5 %. The test was followed by the pinhole being set at 100 μm, at an angle of 90 ^{o} and for experiment duration of 120 s and refractive index of 1.33.

Solution viscosity was measured at 25 ^{o}C using a Brookfield viscometer (DV-II + Pro, UL Adapter spindle).

Infrared spectra were recorded on a FT-IR (Equinox 55-Bruker, equipped with HATR accessories and ZnSe crystal. The samples were scanned over the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} at room temperature.

The thermal behavior of the synthesized polyurethanes was analyzed by differential scanning calorimetry (Mettler Toledo, DSC1, Swiss) at a heating rate of 10 ^{o}C/min under nitrogen atmosphere from -100 ^{o}C until 150 ^{o}C.

The thermal stability of the samples was studied by using a thermogravimetric analyzer (Mettler Toledo, TGA/DSC1, Swiss) at a heating rate 10 ^{o}C/min in a nitrogen atmosphere from room temperature to 600 ^{o}C. The sample weight was 14 mg in all cases.

Dynamic mechanical thermal analysis (DMTA) was carried out with a Triton (Tritec 2000 DMA, UK) instrument at the deformation mode of tensile, a frequency of 1 HZ and a heating rate of 5 ^{o}C/min from -100 ^{o}C to 100 ^{o}C.

The tensile properties of the emulsion cast films were measured at room temperature by using a Santam Universal Testing Machine (STM-20), according to the ASTM D 638 type V at a crosshead speed of 10 mm/min. In these tests an average of at least five measurements was taken and the 200 N load cell was used.

Preparation of Polymer

A 250 m*l* round-bottom, four-necked flask including a mechanical stirrer with condenser connector, thermometer, nitrogen inlet, and pipette outlet was used as a reactor. The reaction was carried out in a constant temperature oil bath. At first, the dried PCL was loaded into the dried flask. While stirring, the system was heated up to 90 ^{o}C. Then, the isocyanate (H$_{12}$MDI) and two droplets of DBTDL were added slightly with a dropper funnel. In this mixture, a stoichiometric excess of diisocyanate was used. Therefore, a NCO-terminated prepolymer was obtained, after continuing the reaction for 4 h at 90 ^{o}C.

The value changes in the isocyanate (NCO) content during the reaction was determined with the standard dibutylamine back titration method (ASTM D 2572) [20]. The reactor was cooled to 65 ^{o}C, after reaching the theoretical NCO value. Then the solution of DMPA in NMP was poured into the reactor and the stirring was continued for 30 min. Next, butanediol was added at this temperature and the reaction was carried on for a further 30 min.

The termination point of the reaction was detected by the complete disappearance of the NCO peak (2270 cm^{-1}) by following the reaction and monitoring of the peaks in the FT-IR spectrum. TEA, as neutralizer, was poured into the reactor followed by the reactor being cooled to 45 ^{o}C. In all steps of the reaction, the stirring rate was 250 rpm. It is worth mentioning that for synthesis of the prepolymers based on the sulfonic ionic center (BES), BES was dissolved in DMSO (minimum amount) and added to the reactor, and no neutralization was conducted.
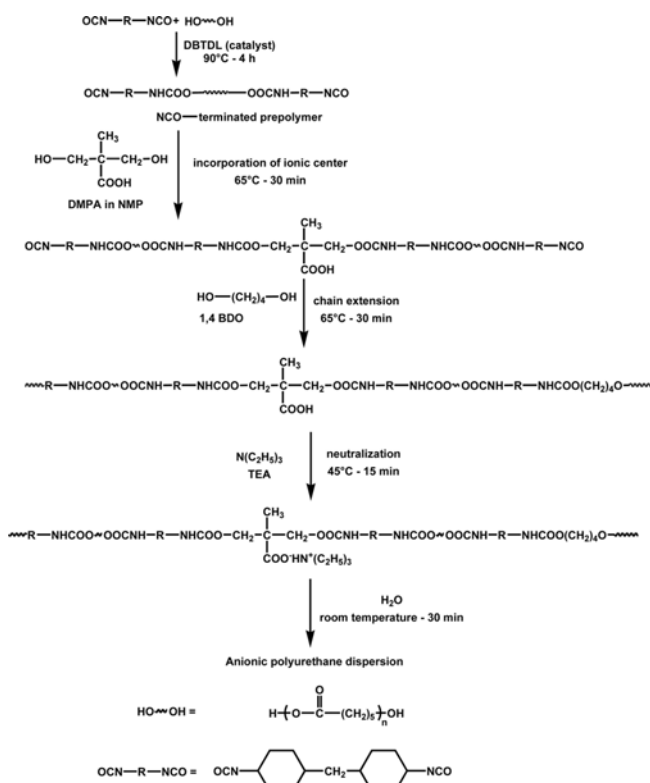
Dispersion

The deionized and double distilled water was slowly added drop wise after neutralization with TEA (15 min for the waterborne polyurethane based on DMPA). This was done at a rate of 750 rpm over 30 min.

For the waterborne polyurethane based on BES, after the chain extension step, water was added in the same condition. Furthermore, incorporation of the ionic center and chain extension were carried out within a period of 15 min for

Table 1. Feed compositions of waterborne PUs with various ionic centers

Sample	Capa(225) (g)	H$_{12}$MDI (g)	DMPA (g)	1,4 BDO (g)	BES (g)	TEA (g)
1 D	20	7.99	2.68	-	-	2.02
2 D	20	7.99	2.01	0.45	-	1.52
3 D	20	7.99	1.34	0.9	-	1.01
4 D	20	7.99	0.67	1.35	-	0.5
1 B	20	7.99	-	-	4.7	-
2 B	20	7.99	-	0.45	3.53	-
3 B	20	7.99	-	0.9	2.35	-
4 B	20	7.99	-	1.35	1.18	-

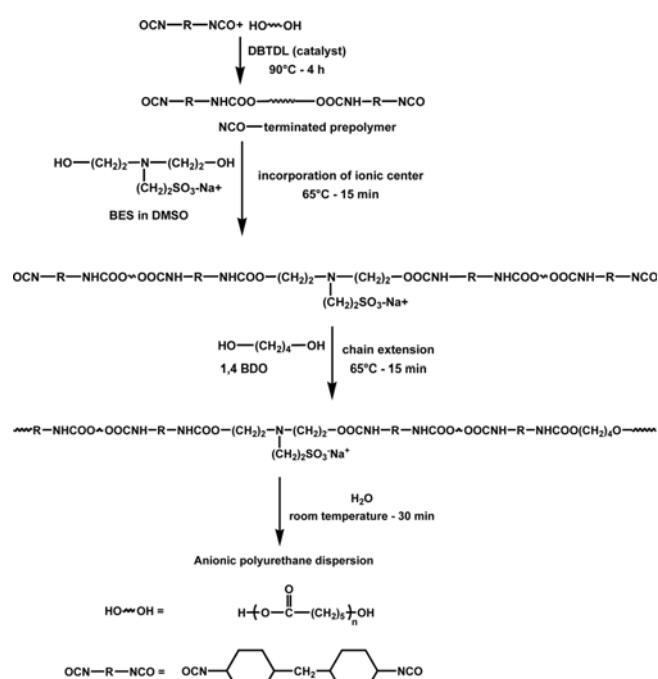**Scheme 1.** Synthesis of PU dispersion based on DMPA.

Scheme 2. Synthesis of PU dispersion based on BES.

each step.

In this way, the waterborne polyurethanes with 30 % solid content were obtained. The rate of water addition is of crucial importance for obtaining a stable dispersion. Water should be added with a dropping funnel or a dosing pump at a constant flow rate.

After adding a small amount of water, the associates, which were formed between chains, were dissolved by hydratization of the ionic group. Since the ionic groups are located on the droplet's surface, the turbidity and increment of viscosity are observed, which confirms a water-in-polymer emulsion formation.

In the free volume between the droplets, the apolar segments are compacted and the mobility of segments is prevented and, therefore, a white highly viscous paste is formed. At this time, phase inversion occurs and the aqueous dispersion is obtained and a sharp decrease in viscosity is observed. Therefore, the hydrophilic groups are submerged in the continuous aqueous media. The samples were prepared using different percentages of the ionic centers and 1,4 BDO. The compositions and their amounts (in weight) are shown in Table 1.

The reaction scheme for the prepolymer synthesis and processes of dispersion and chain extension based on DMPA and BES have been shown in Schemes 1 and 2, respectively.

Preparation of Films

The films were prepared by casting the aqueous dispersions onto a Teflon plate at room temperature, followed by drying for 3 days. Afterwards, the mold was put in an oven at 100 °C: 18 h and 8 h for the DMPA and the BES-based

samples, respectively. After demolding, the films were stored in a desiccator at room temperature for further analysis.

Results and Discussion

IR Spectroscopy

The IR spectra of waterborne polyurethane based on 100 % DMPA (1D) and 100 % BES (1B) are shown in Figure 1. The characteristic absorption peaks are: 2926 (1B), 2937 (1D) cm^{-1} and 2857 (1B), 2856 (1D) cm^{-1}, which are due to alkane -CH asymmetric and symmetric stretching vibration of CH$_2$ groups, respectively.

Absorptions at 1530 (1B) and 1527 (1D) cm^{-1} are due to the CHN vibration of associated secondary urethane groups (-NH bending), 1455 (1B) and 1456 (1D) cm^{-1} due to CH$_2$ bending, 1357 (1B) and 1393 (1D) cm^{-1} due to C-N stretching. 1311 (1B) and 1305 (1D) cm^{-1} are attributed to CH$_2$ wagging.

The C-O-C stretching absorption band corresponds to the ether oxygen of the soft segment at 1159 (1B), 1149 (1D) and 1228 (1B), 1232 (1D) cm^{-1}. This also provides strong evidence for the formation of PU.

It is important to mention that the asymmetric and symmetric stretching vibration of -SO$_3^-$Na$^+$, at 1175-1195 cm^{-1} and 1050-1065 cm^{-1}, respectively, and the asymmetric and symmetric stretching vibration of -COO$^-$ at 1550-1610 cm^{-1} and 1335-1420 cm^{-1}, respectively, are covered by the above absorption peaks [21].

The FTIR spectra showed the characteristic bands of urethane NH groups at 3361 and 3360 cm^{-1} (N-H stretching) for 1B and 1D, respectively. Furthermore, 1727 (1B) and
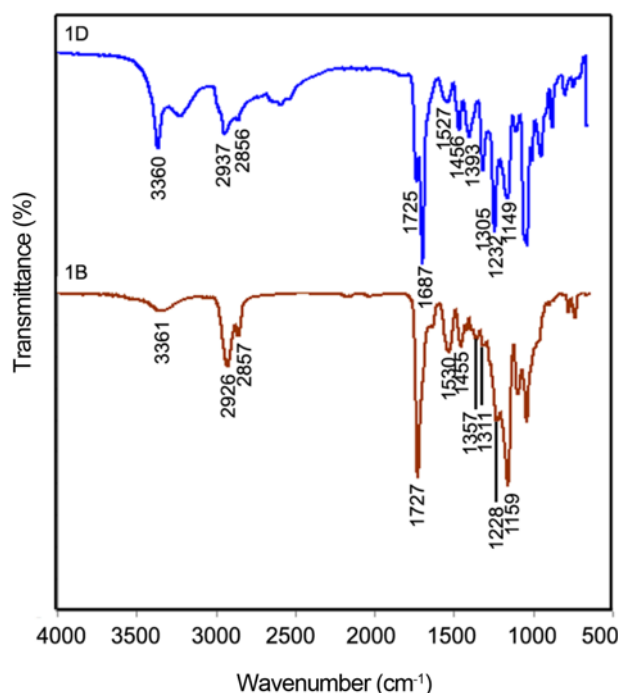
Figure 1. IR spectra of 1D: 100 % DMPA and 1B: 100 % BES.

Table 2. The characteristic peaks in the synthesized polyurethanes based on BES and DMPA

Groups/bands	Wavenumber (cm^{-1})	
	BES	DMPA
N-H stretching	3361	3360
CH stretching	2926 (asym.)	2937 (asym.)
CH stretching	2857 (sym.)	2856 (sym.)
C=O stretching	1727	1725, 1687
N-H bending	1530	1527
CH$_2$ bending	1455	1456
C-N stretching	1357	1393
CH$_2$ wagging	1311	1305
C-O-C stretching	1228,1159	1232,1149

1725 (1D) cm^{-1} are due to carbonyl (C=O) stretching of urethane and ester groups. The sharp band at 1727 cm^{-1} in the spectrum of the 1B sample becomes evident, which suggests that stronger H-bonded carbonyl groups are formed for the samples from the BES ionomer. Consequently, an increased intermolecular interaction of the hard segments with the soft segments occurs. Furthermore, the peak of the urethane group in 1B is broader than of 1D.

The characteristic peak in 1687 cm^{-1} in the spectrum of 100 % DMPA sample corresponds to the carbonyl group of DMPA. It is observed that this peak is much sharper than 1725 cm^{-1}.

In these spectra, the isocyanate group absorption peak (-NCO, 2270 cm^{-1}) disappeared, indicating the end group of -NCO of the synthetic prepolymers has reacted completely with the chain extender. The characteristic peaks observed for different groups are summarized in Table 2.

Effect of the DMPA and the BES Contents on Particle Size and Viscosity

The effect of the DMPA and the BES contents on viscosity of the PU dispersions and the particle size distributions are shown in Figures 2 and 3, respectively.

It seems that by increasing the DMPA and the BES contents the particle size decreases: from 213 to 28 nm for the DMPA-based and from 168 to 8.3 nm for the BES-based samples. In other words, the particle size decreases with the increasing of ionic centers. Each particle in the dispersion is absorbed by a thin layer of water due to the presence of hydrophilic -COO$^-$HN$^+$(C$_2$H$_5$)$_3$ and -SO$_3^-$Na$^+$ groups on the surface of the particles in the DMPA and the BES-based samples, respectively. In the water-based polyurethane dispersion it is generally seen that the greater the hydrophilicity, the smaller the particle size [22]. It is reasonably assumed that the anionic centers are naturally hydrophilic and significantly located on the surfaces of PU particles in continuous aqueous phase.

The number of particles increases with decreasing the
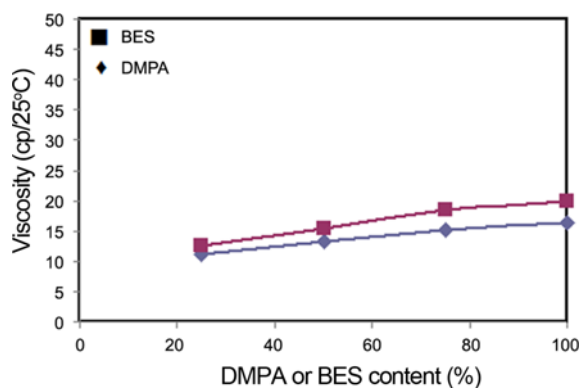
Figure 2. The effect of the DMPA and the BES contents on the viscosity.

particle size [23]. The decrease of the particle size with increasing the ionic center content is due to the stabilizing mechanism of the ionomer dispersion. The coulombic repulsion between the colloidal particles occurs and can impart stability. The counter ions in the dispersion medium increase the electrical double layers that surround the colloidal particles [24].

The viscosity of the polyurethane dispersion increases when the average particle size decreases because, with decreasing particle size, there is an increase in the number of particles, effective surface, and subsequently surface interaction.

The particle size of BES samples is smaller than that of DMPAs and consequently, they are more viscous than DMPA samples. This is due to more activity and hydrophilicity of the $-SO_3^-Na^+$ group. Furthermore, emulsions from DMPA and BES were stable for 5 and more than 8 months, respectively.

DSC Analysis

The thermal properties of the synthesized waterborne polyurethane films were studied by differential scanning calorimetry (DSC), with the following thermal cycles: heating from -100 $^{\circ}$C to 150 $^{\circ}$C, quenching at -100 $^{\circ}$C, and reheating from -100 $^{\circ}$C to 150 $^{\circ}$C at a heating rate of 10 $^{\circ}$C/min under a nitrogen atmosphere. The variations of glass transition temperature (T_g) of the soft segment of synthesized polyurethanes are shown in Table 3. As can be seen, T_g of the soft segment (-61 $^{\circ}$C) is increased with increasing the ionic center. The DSC curves of the synthesized samples are shown in Figure 4.

The results showed that the effect of DMPA and BES on T_g was almost similar and T_g of the soft segment increased in both cases.

Thermogravimetric Analysis (TGA)

Figure 5 depicts the thermal stability of the samples as a function of the ionic center. The initial decomposition temperature ($T_{d, onset}$), temperature of half decomposition ($T_{d, 1/2}$), and temperature of the maximum decomposition ($T_{d, max}$) for

Table 3. Thermal analysis by DSC

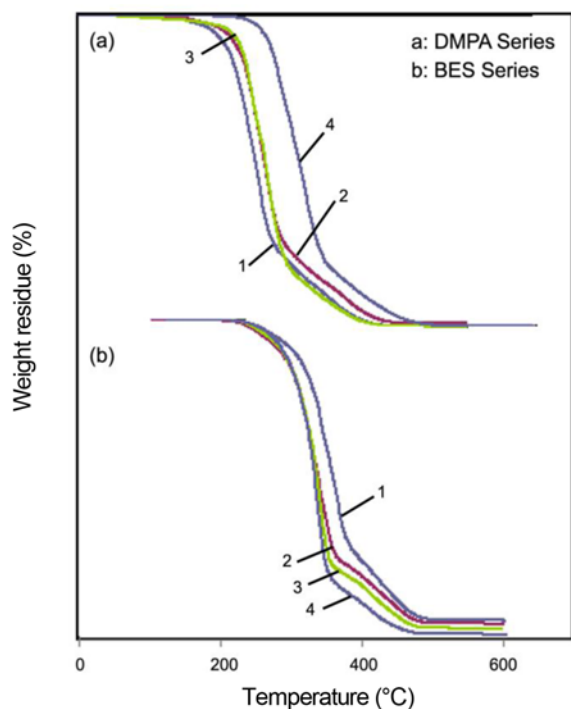| Sample	Percentage of ionic center	T_g based on DMPA ($^{\circ}$C)	T_g based on BES ($^{\circ}$C)
1	100	-49.59	-49.96
2	75	-51.89	-50.83
3	50	-52.82	-53.56
4	25	-52.15	-54.54
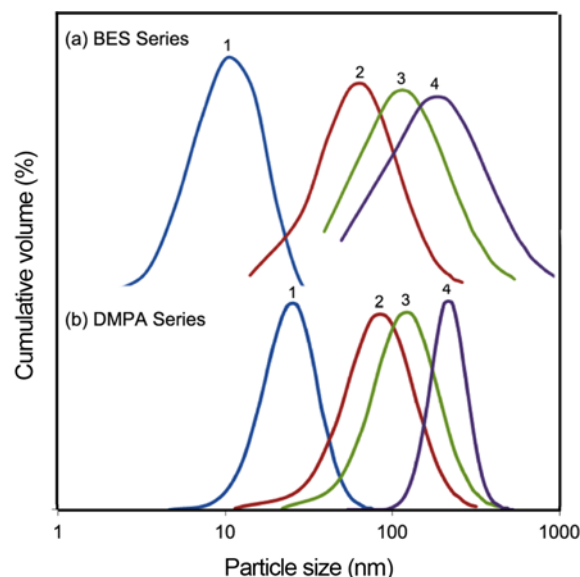
Figure 3. The particle size distribution for the emulsions based on (a) BES Series: 1 (100 % BES), 2 (75 % BES), 3 (50 % BES), 4 (25 % BES), and (b) DMPA Series: 1 (100 % DMPA), 2 (75 % DMPA), 3 (50 % DMPA), 4 (25 % DMPA).
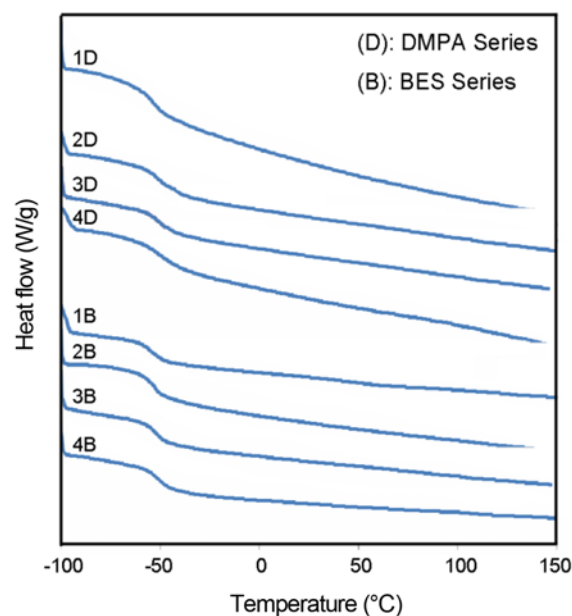
Figure 4. The DSC curves for synthesized samples based on BES and DMPA.

Figure 5. TGA thermograms of PU emulsion cast films; (a) DMPA series: 1 (100 % DMPA), 2 (75 % DMPA), 3 (50 % DMPA), 4 (25 % DMPA) and (b) BES series: 1 (100 % BES), 2 (75 % BES), 3 (50 % BES), 4 (25 % BES).

Table 4. Thermal degradation behavior of the PU films based on DMPA and BES

Samples	$T_{d, onset}$ (°C)	$T_{d, 1/2}$ (°C)	$T_{d, max}$ (°C)
1D (100 %)	210	312	597
2D (75 %)	215	314	599
3D (50 %)	220	315	599
4D (25 %)	250	320	599
1B (100 %)	260	363	603
2B (75 %)	240	338	601
3B (50 %)	234	337	599
4B (25 %)	220	334	598

different samples at a heating rate of 10 °C/min are shown in Table 4.

In this table the initial decomposition temperature ($T_{d, onset}$) is the temperature at which the loss of weight during heating is just measurable. The temperature of half decomposition ($T_{d, 1/2}$) is the temperature at which the loss of weight reaches 50% and ($T_{d, max}$) denotes the maximum decomposition and means the temperature at which the loss of weight reaches its final value. This is seen by increasing the percentage of BES, as a result of which the thermal stability of cast films is increased, however, in the samples based on DMPA, with

increasing the content of DMPA, thermal stability decreases and degradation occurs in lower temperatures.

There are two stages in the thermal degradation of aqueous polyurethanes: the first stage is caused by the degradation of hard segments and the second stage is due to soft segment degradation. In the above both series, the degradation of the synthesized samples occurs in two steps.

The early stage degradation in the hard segment urethane groups first undergoes depolymerization and results in the formation individual monomers, which then further react to produce carbon dioxide. Three mechanisms of decomposition of urethane bonds have been proposed by Petrovic *et al.* [25]: dissociation to isocyanate and alcohol, formation of a primary amine and olefin, and formation of secondary amine and carbon dioxide.

In the DMPA-based samples, the decreasing of the thermal stability is due to the increase of COOH groups in a polymer backbone as a result of more DMPA. It is possible to associate with the presence of tertiary carbon atoms connected with the carbonyl group. It is accepted that the tertiary carbon is more easily attacked by organic radicals to form new active species [26,27].

In the BES-based samples, there is stronger electrostatic interaction between sodium sulfonate groups and hence, thermal stability is higher.

DMTA Studies

The dynamic mechanical properties (storage modulus and tanδ) of the emulsion cast films based on BES and DMPA are shown in Figures 6 and 7, respectively.

It can be seen that the glass transition temperature (T_g) of PU (tanδ) moves toward higher temperatures as DMPA and BES values are increased. Furthermore, storage modulus increases with increasing DMPA and BES quantities. However, these incremental increases are more significant for the BES-based than the DMPA-based samples due to higher intermolecular interaction.
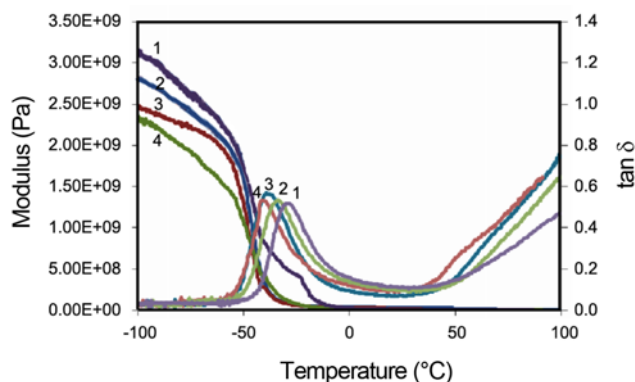
Figure 6. Storage modulus and tan δ of the samples based on BES as a function of temperature: 1 (100 % BES), 2 (75 % BES), 3 (50 % BES), 4 (25 % BES).
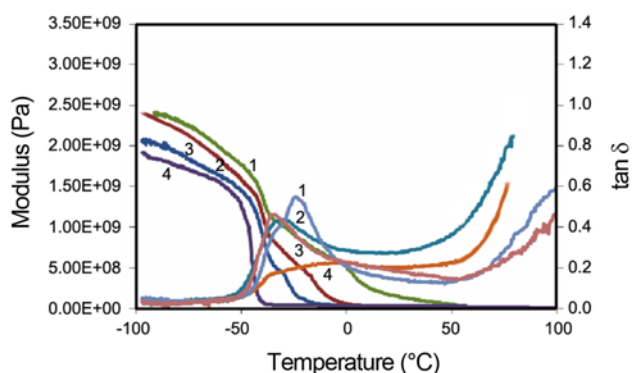
Figure 7. Storage modulus and tan δ of the samples based on DMPA as a function of temperature: 1 (100 % DMPA), 2 (75 % DMPA), 3 (50 % DMPA), 4 (25 % DMPA).

Table 5. T_g values based on DMTA analysis

Sample	Percentage of ionic center	T_g based on DMPA (°C)	T_g based on BES (°C)
1	100	-24.4	-27.37
2	75	-30.4	-32.73
3	50	-32.6	-35.8
4	25	-39.8	-38.9

DMPA and BES contribute to the hard segment domains of the PU films. The hard segments improve the mechanical property, such as storage modulus. Therefore, E' increases with increasing DMPA and BES.

An increase in T_g of the soft segment indicates the presence of the hard segments dispersion in the amorphous soft segment microdomains. The chain mobility of the soft segments is hindered by the confined hard segments and this causes the T_g value of the soft microdomain to increase. The variations of T_g for the samples based on DMPA and BES are shown in Table 5.

Mechanical Properties

The mechanical properties of PUs with respect to DMPA and BES values are shown in Table 6. Figure 8 shows stress-strain curves of the emulsion cast films based on BES and DMPA. It can be seen that as DMPA and BES contents increased, the tensile strength of the PU films significantly increased. The increases in the tensile strength with the DMPA and the BES contents are mainly due to the increased hydrogen bonding forces between the ionic centers and urethane linkages, and also coulombic forces between the ionic centers [4,28]. As a result of the presence of $SO_3^- Na^+$ groups in BES, which belongs to the salt of a strong acid and a strong base, the electrostatic interaction of BES is stronger than that of DMPA. Therefore, the tensile strength is higher than the DMPA-based samples.

Table 6. Mechanical properties of waterborne PU films based on DMPA and BES

Samples	Modulus (MPa)	Tensile strength (MPa)	Elongation-at-break (%)
1D (100 %)	15.4±0.79	17.93±0.03	1236±57.33
2D (75 %)	13.33±0.57	8.43±0.19	1136±31.21
3D (50 %)	8.47±0.37	5.06±0.26	508±14.5
4D (25 %)	3.33±0.15	2.25±0.05	168±8.02
1B (100 %)	22.83±0.06	19.85±1.35	313±9.53
2B (75 %)	17.13±0.32	13.77±0.37	330±10.4
3B (50 %)	11.67±0.25	12.85±0.83	400±15.1
4B (25 %)	5.8±0.91	7.81±0.065	596±18.5
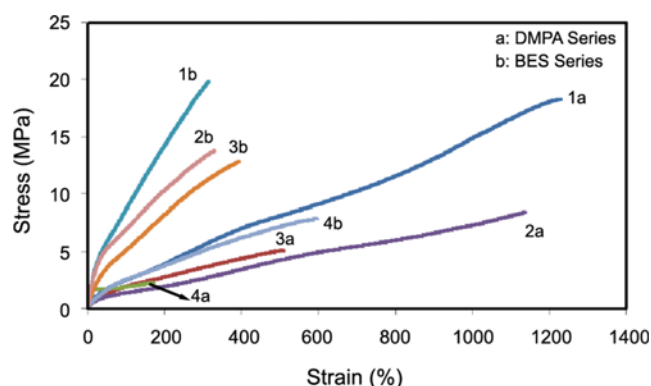
Figure 8. Stress-strain curves of the emulsion cast films based on DMPA and BES; 1a (100 % DMPA), 2a (75 % DMPA), 3a (50 % DMPA), 4a (25 % DMPA) and 1b (100 % BES), 2b (75 % BES), 3b (50 % BES), 4b (25 % BES).

Jang *et al.* [29] showed that the molecular weight of water-based polyurethane dispersion decreased with increasing DMPA content. Therefore, if there is no significant difference in reactivity between polyol and DMPA, the prepolymer chain would be shortened as the DMPA content increased at a constant NCO/OH. The hard segment increased as the DMPA content increased because DMPA molecules formed hard segments in the polyurethane main chain. With increasing the DMPA content, the soft segment portion decreased and a homogeneous network of the hard segments was formed. DMPA provides a more polar character to the hard segments and the increase of the tensile strength with the DMPA content is directly due to the increased number of urethane linkages and interchain interaction of the PU ionomers via coulombic forces [30]. On the other hand, in the DMPA-based samples, toughness increases with increasing the DMPA content, indicating the ductile nature of the resulting materials. Heterogeneity leads to points in the structure, resulting in a relatively low elongation-at-break. Toughness is the resistance of a material to fracture when stressed. In general, brittle materials have low toughness, while ductile

materials are very tough. The much higher percentage of elongation-at-break results from the homogeneous network structure [31]. So, BES-based samples formed a heterogeneous network with low elongation-at-break and DMPA-based samples organized a homogeneous network with high elongation-at-break.

Conclusion

Aqueous polyurethane dispersions were synthesized by the prepolymer mixing process from H_{12}MDI, PCL, 1,4 BDO, DMPA and BES with different amounts of anionic centers.

The effects of the DMPA and the BES contents on the particle size, viscosity, mechanical, and thermal properties were investigated. The results showed that the average particle size of the prepared polyurethane emulsions decreased with increasing the ionic center of DMPA and BES and viscosity increased with decreasing the particle size. Thermal stability, modulus and tensile strength also increased with increasing the ionic center. Moreover, glass transition temperature (T_g) increased with increasing the amount of ionic centers. In all tests, BES showed better performance and improvement in properties since the $So_3^-Na^+$ group in BES was more active than the COOH in DMPA. This is because BES is the salt of a strong acid and a strong base and is freely dissociated in water. The nature of free dissociation and strong electrostatic interaction of sodium sulfonate groups of BES would strongly impact on the properties of the final waterborne polyurethane emulsions and films.

References

1. Y. H. Guo, J. J. Guo, S. C. Li, X. Li, G. S. Wang, and Z. Huang, *Colloid Surf. A-Physicochem. Eng. Asp.*, **427**, 53 (2013).
2. C. Fang, X. Zhou, Q. Yu, S. Liu, and D. Guo, *Prog. Org. Coat.*, **77**, 61 (2014).
3. E. H. Kim, W. R. Lee, S. W. Myoung, J. P. Kim, Y. G. Jung, Y. S. Nam, W. S. Kyoung, and H. Cho, *Prog. Org. Coat.*, **67**, 102 (2010).
4. D. Dieterich, *Prog. Org. Coat.*, **9**, 281 (1981).
5. C. Hepburn, "Polyurethane Elastomers", Chap. 10, pp.268-278, Applied Science, England, 1982,
6. Z. Ge and Y. Luo, *Prog. Org. Coat.*, **76**, 1522 (2013).
7. V. Garcia- Pacios, J. A. Jofre-Reche, V. Costa, M. Colera, and J. M. Martin-Martinez, *Prog. Org. Coat.*, **76**, 1484 (2013).
8. H. Chen, D. Chen, Q. Fan, and X. Yu, *J. Appl. Polym. Sci.*, **76**, 2049 (2000).
9. Y. S. Kwak, S. W. Park, Y. H. Lee, and H. D. Kim, *J. Appl. Polym. Sci.*, **89**, 123 (2003).
10. S. M. Seyed Mohaghegh, M. Barikani, and A. A. Entezami, *Iran. Polym. J.*, **14**, 163 (2005).
11. C. Y. Li, W. Y. Chiu, and T. M. Don, *J. Polym. Sci. Pol. Chem.*, **43**, 4870 (2005).
12. R. Arnoldus in "Waterborne Coating, Surface Coating" (A. D. Wilson, J. W. Nicholson, and H. J. Prosser Eds.), Vol. 3, Chap. 5, pp.186-188, Elsevier Applied Science, London, 1990.
13. A. K. Nanda, D. A. Wicks, S. A. Madbouly, and J. U. Otaigbe, *J. Appl. Polym. Sci.*, **98**, 2514 (2005).
14. A. K. Nanda and D. A. Wicks, *Polymer*, **47**, 1805 (2006).
15. A. Barni and M. Levi, *J. Appl. Polym. Sci.*, **88**, 716 (2003).
16. C. Chinwanitcharoen, S. Kanoh, T. Yamada, K. Tada, S. Hayashi, and S. Sugano, *Macromol. Symp.*, **216**, 229 (2004).
17. C. Chinwanitcharoen, S. Kanoh, T. Yamada, S. Hayashi, and S. Sugano, *J. Appl. Polym. Sci.*, **91**, 3455 (2004).
18. K. Mequanint and R. D. Sanderson, *Macromol. Symp.*, **178**, 117 (2002).
19. Y. K. Jhon, I. W. Cheong, and J. H. Kim, *Colloid Surf. A-Physicochem. Eng. Asp.,* **179**, 71 (2001).
20. ASTM D2572-97, "Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers", 2010.
21. G. Socrates, "Infrared and Raman Characteristic Group Frequencies", 3rd ed., Chap.16, pp.220-221, Wiley, London, 2004.
22. J. W. Rosthauser and K. Nachtkamp in "Advances in Urethane Science and Technology" (K. C. Frisch and D. Klempner Eds.), Vol. 10, pp.128-131, Technomic, Lancaster, 1987.
23. K. Mequanint and R. Sanderson, *Polymer*, **44**, 2631(2003).
24. D. H. Napper, "Polymeric Stabilization of Colloidal Dispersions", Chap.1, pp.8-9, Academic Press, London, 1983.
25. Z. S. Petrovic, L. Yang, A. Zlatanic, W. Zhang, and I. Javni, *J. Appl. Polym. Sci.*, **105**, 2717 (2007).
26. M. G. Lu, J. Y. Lee, M. J. Shim, and S. W. Kim, *J. Appl. Polym. Sci.*, **85**, 2552 (2002).
27. N. Grassie and G. Scott, "Polymer Degradation and Stabilisation", Chap. 2, pp.39-41, Cambridge University, London, 1985.
28. C. K. Kim and B. K. Kim, *J. Appl. Polym. Sci.*, **43**, 2295 (1991).
29. J. Y. Jang, Y. K. Jhon, I. W. Cheong, and J. H. Kim, *Colloid Surf. A-Physicochem. Eng. Asp.*, **196**, 135 (2002).
30. H. Koch, G. Mennicken, F. Muller, H. Toepsch, H. Traubel, and W. Wieczorrek in "Polyurethane Handbook" (G. Oertel Ed.), Chap. 10, pp.538-539, Hanser, New York, 1985.
31. Y. Lu and R. C. Larock, *Prog. Org. Coat.*, **69**, 31 (2010).