Preparation and Characterization of Aqueous Polyurethane Dispersions Containing Ionic Centers

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ABSTRACT: Aqueous polyurethane dispersions were prepared from toluene di-isocyanate, polytetramethylene glycol, and 1,4-butanediol, with different weight percent of dimethylol propionic acid (DMPA) as anionic center. IR Spectroscopy was used to follow the polymerization reaction as well as the polymer characterization. The effect of DMPA content on the state of dispersion, particle size distribution, mechanical, and thermal properties of the emulsion-cast films were studied. Average particle size of the prepared emulsion polyurethanes decreased with increasing DMPA content. Tensile strength and hardness increase and elongation at break and contact angle decrease by increasing the ionic content. Glass transition temperature (T_g) shifted toward higher temperature and thermal stability decreased by increasing the DMPA content. The increased T_g and tensile properties are interpreted in terms of the increased hard segments and coulombic forces between ionic centers. The decreased contact angle is ascribed to the increase in the hydrophilicity of the polyurethanes because of the incorporation of more hydrophilic moiety in polymer backbone. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3931–3937, 2007

Key words: dispersions; polyurethanes; ionomers; TGA; thermal properties

INTRODUCTION

Aqueous polyurethane dispersions have been gaining importance in a wide-rang of application to reduce solvent emissions into the atmosphere.[1] Their excellent properties such as good chemical and abrasion resistance, high flexibility at low temperature, excellent adhesion to many polymers, and glass surfaces and film-forming ability at ambient temperature make them suitable for myriad of application.[2,3]

These types of polyurethanes can be classified into ionic and nonionic types. Nonionic types contain hydrophilic soft segment pendant group such as polyethylene oxide,[4] whereas the ionic types contain anionic or cationic centers in the polymer chains. These centers could be pendant acid or tertiary nitrogen groups, which are neutralized to form salts.[5] These groups are building up in the chain structure during the polymer formation.

Several processes have been developed for the synthesis of polyurethane dispersions.[6–9] All of these processes are common in the first step, in which a medium molecular weight prepolymer is formed by the reaction of suitable polyols with a molar excess of di-isocyanates. In this reaction mixture, an internal emulsifier is added to allow the dispersion of the polymer in water; this emulsifier is usually a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a nonionic group (polyethylene oxide).The internal emulsifier becomes part of the main chain of the polymer. The critical step in which the various synthetic pathways differ is the dispersion of the prepolymer in water and the molecular weight build up. The most important processes are the acetone process, the prepolymer mixing process, the melt dispersion process, and the ketimine process.[10] In the melt dispersion process, the hydrophilically modified chain extended prepolymer is directly mixed with water.

It is now generally accepted that the properties of PU ionomers are primarily due to the phase behavior of soft and hard segments as well as their ionic character. Since ions which are introduced into either hard or soft segments, impart many properties to the polyurethane matrix, attention being drawn to these polyurethane ionomers.[11–13] The existence of the hard segment domains also gives PU ionomers an excellent mechanical strength. The dispersion of polymers in water and properties of cast films are affected by type and content of ionic centers and polyols as soft segment.[14,15]

In this article we describe the preparations of ionic type waterborne polyurethane from polytetramethylene glycol (PTMG), dimethylol propionic acid

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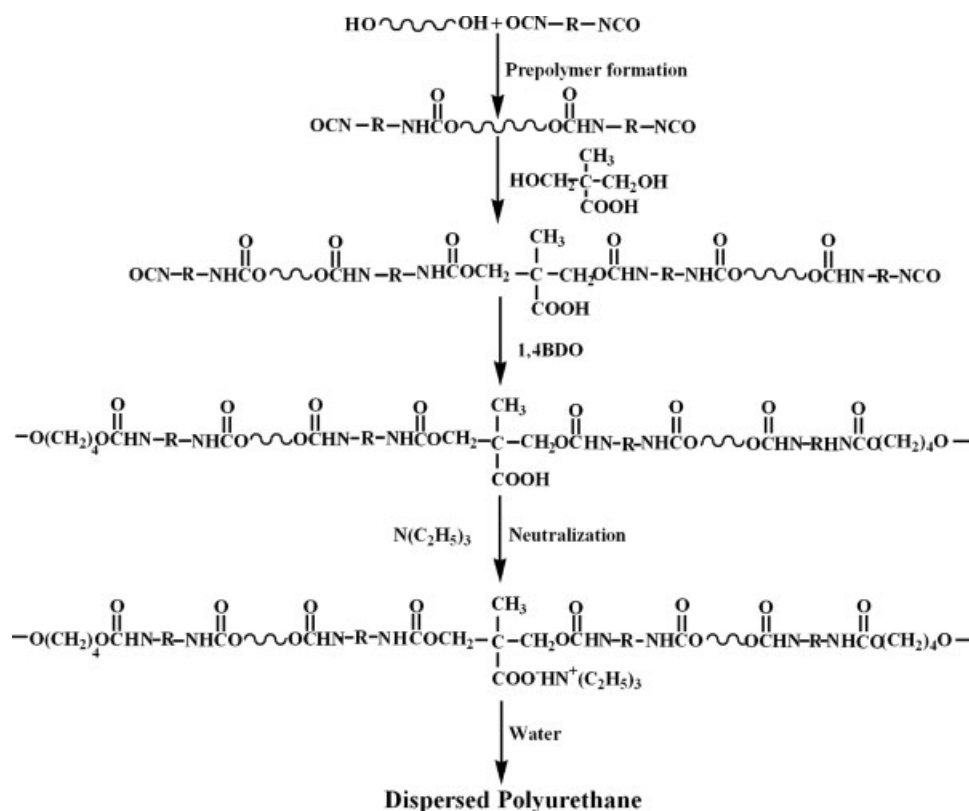
Scheme 1 Formation of PU dispersion with anionic center.

(DMPA), 1,4-butanediol (1,4-BD), and toluene di-isocyanate (TDI). The effect of ionic content and chain extension on the physical, mechanical, and thermal properties of emulsion-cast films, contact angle, glass transition temperature, and particle size were studied.

EXPERIMENTAL

Materials

PTMG ($M_n = 2000$) supplied by Arak Petrochemical (Iran) were dried and degassed at 80°C, and 1–2 mmHg for 5 h before use. 1,4-butanediol (1,4-BDO) (Merck, Germany) was dried and degassed for 2 h at 50°C and 1–2 mmHg. DMPA (Aldrich, UK) was dried at 100°C for 2 h in an oven. Dimethylformamide (DMF) (Merck, Germany), triethylamine (TEA)(Merck, Germany), were dried over molecular sieves (4 Å), and TDI (Merk, Germany) was used as received.

Preparation of polymer

A 250 mL round-bottom, four-necked flask equipped with a mechanical stirrer, thermometer, condenser, nitrogen inlet, and pipette outlet was used as reactor. Reaction was carried out in a constant temperature oil bath. PTMG was charged into dried flask. While stirring, the system was heated to 98°C, and then TDI was

added slightly with dropper funnel. The mixture was heated at 98°C for 2 h to obtain NCO terminated prepolymer. After that, solution of DMPA in DMF was added and stirred continuously for 1 h. Then the system was cooled to 60°C. Butanediol was added at this temperature and after 15 min the neutralizing solution TEA dissolved in DMF charged into the reactor. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in Scheme 1. The block ratio for this reaction was 1 : 3.05 : 2 for PTMG, di-isocyanate, and chain extenders, respectively, and chain extenders were DMPA and 1,4-BDO. Samples were prepared by changing the carboxylic group content via different percentage of DMPA in formulation. The ionic group plays a major role in making a stable dispersion in water. The composition of the prepared polyurethanes is given in Table I.

TABLE I
Feed Compositions (g) of Dispersion Polyurethanes with Variable DMPA Content

Sample	PTMG	TDI	DMPA	1,4-BDO	TEA
SD1	29.56	8.84	4.46 (100)[a]	0 (0)	3.36
SD2	29.56	8.84	3.35 (75)	0.75 (25)	2.52
SD3	29.56	8.84	2.23 (50)	1.50 (50)	1.68
SD4	29.56	8.84	1.11 (25)	2.25 (75)	0.84

[a] Values within parentheses are percentages.

Dispersion

Aqueous dispersion of PU was obtained by adding deionized water (30°C) to the polymer mixture (60°C). The temperature of the mixture is gradually decreased by the addition of deionized water. The rate of water addition is very important and is a critical parameter to obtain stable dispersion. It should be added with a dropping funnel at a constant flow rate. The phase inversion was happened and the dispersion was obtained. The emulsion was stable over 5 months at room temperature.

Preparation of films

Films were prepared by casting the aqueous dispersion onto a Teflon plate at room temperature, followed by drying at 40°C (1 day), at 60°C (1 day), at 70°C (1 day), and at 85°C (1 day). This trend of drying is just for slow drying. It is also possible to evaporate the solvent at a fixed temperature either room or elevated temperature. After demolding, the films were stored in a desiccator at room temperature for further studies.

Measurements

The IR spectra of the PU polymer films were obtained with an EQUINOX55 Fourier transform infrared spectrometer from Bruker by H.ATR accessories equipped with ZnSe crystal. It is possible to use polymer film as a strip with ATR (Attenuated Total Reflectance) technique without further preparation.

Particle size was measured by laser light scattering (SemaTech, SEM-633, He–Ne laser) at room temperature. The samples were first diluted by deionized water to 0.5%, and the dispersions were homogenized. The particle size measured in this study was an average particle size.

Contact angle was measured at room temperature with water as a liquid by Gl0 (KRUSS) instrument through sessile drop method.

The thermal degradation behavior of the PU films was recorded with a thermogravimetric analyzer (Perkin–Elmer pyris 1) at a heating rate of 10°C/min under nitrogen atmosphere from room temperature to 700°C. The sample weight was 7–9 mg in all cases. During the heating cycle, the weight loss and the temperature difference were recorded as a function of temperature.

Tensile properties of the emulsion cast films were measured according to ASTM412, using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least five measurements was taken and a 1-kN load cell was used. The dimension of the specimens was $70 \times 5 \times 3 \text{mm}^3$.

Dynamic mechanical tests were performed with a PL-DMTA instrument (Polymer Laboratory) from -100 to $100°C$ at the frequency of 1 Hz with a sample size of $1 \times 3 \text{ cm}^2$.

RESULTS AND DISCUSSION

Preparation of aqueous polyurethane dispersion with different weight percent of DMPA was achieved. The polyurethane was prepared by the reaction of stoechiometric amount of polyol/diisocyanate/chain extender according to synthetic route as depicted in Scheme 1. DMPA, a carboxylic acid containing diol,[16] can be used to form water-dispersible urethane prepolymer without any significant reaction between the carboxylic and isocyanate group because the hydroxyl groups are much more reactive than the carboxylic in reaction with aliphatic isocyanate component.

IR spectroscopy

IR spectroscopy of the cast film is shown in Figure 1. This analysis was used to check the completion of the polymerization reaction, verifying the disappearance of the v NCO at 2265 cm^{-1} and the appearance of the v N—H at 3000–3400 cm^{-1}. Presence and disappearance of the expected peaks imply that the reaction is completed and the predesigned polyurethane is formed. IR spectra also contained all the information relating to the primarily structure of the final polymer.

An absorption band is observed for the N—H stretching at 3291 cm^{-1}, aliphatic C—H stretching at 2795–2938 cm^{-1}, carbonyl (C=O) stretching at 1726 cm^{-1}, N—H bending vibration at 1532 cm^{-1} and C—O—C stretching at 1000–1150 cm^{-1}.These vibrations are strong evidences for the formation of PU.

The N—H group in polyurethane could form hard–hard segment H-bonding with the carbonyl oxygen and hard–soft H-bonding with the ether oxygen. The stronger hard–hard segment H-bonding acts as physical crosslinks leading to a difficult segmental motion of the polymer chain, which results in a more significant phase separation between the hard and soft segments. The phase separation improves mechanical properties of polyurethanes but reduces their flexibility and solubility.[17]

Effect of ionic content

Particle size

The effect of DMPA content on the particle size of the PU dispersions is shown in Figure 2. For these samples, the NCO/OH ratio (1.05) was kept constant in formulation and only the weight percent of DMPA was changed (Table I). The block ratio was
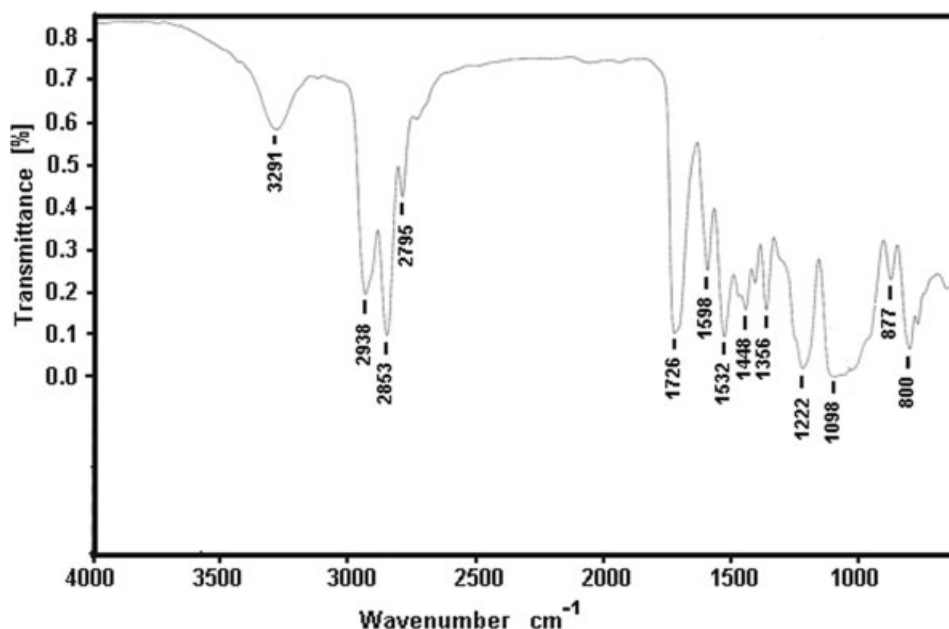
Figure 1 IR spectrum of polyurethane ionomer.

1 : 3.05 : 2 for PTMG, di-isocyanate, and chain extender, respectively.

The particle size decreases markedly from 453 to 94 nm with the increasing the DMPA content from 2.6 to 11.3 wt %, and then decreases slowly or remains constant. This may be due to introducing ionic content in polyurethane backbone, which affects the polymer solubility in aqueous media. By increasing the DMPA content and stoechiometric amount of TEA [N (C$_2$H$_5$)$_3$], the number of —COO$^-$HN$^+$(C$_2$H$_5$)$_3$ ionic groups in PU dispersion increases. Each particle in the dispersion is surrounded by a thin layer of water because of the presence of hydrophilic-COO$^-$HN$^+$(C$_2$H$_5$)$_3$ groups on the surface of the particle. By decreasing the size of the polymer dispersion particles, the relative size of the water layer to total particle size is increased. With decrease of the particle size, there is also an increase in the number of particles.[18–20]

It is known that aqueous polyurethane dispersions are two-phase systems, in which water is the continuous phase. The dispersed phase is a solid polymer, although the obtained aqueous polyurethane dispersions are seemed to be clear solutions. The particle size of the polymer ionomer dispersions depends on a variety of parameters, which the most important one is the number of ionic group in the polymers.[21] It is well known that the particle size has a direct effect on the polyurethane dispersion stability thus the larger average particle size (>1000 nm) is generally unstable with respect to sedimentation.[22] It is reasonably presumed that the anionic centers are hydrophilic in nature and predominantly located on the surfaces of PU particles in aqueous media. However, with the decrease in ionic center, deformation of hydrophobic–hydrophilic spherical structure in water is less possible and these lead to a larger particle size at the stage of emulsification (Table II).
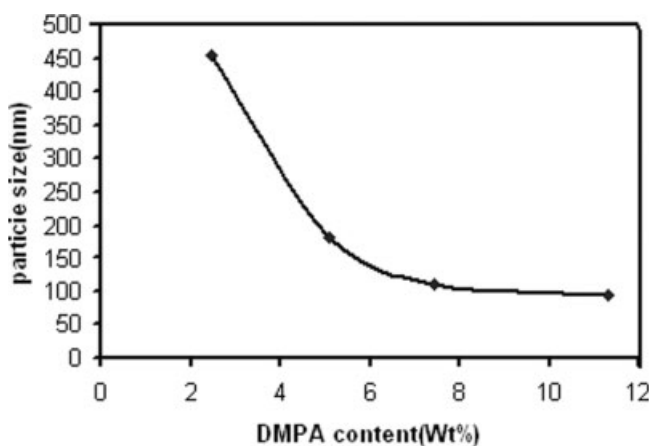

Figure 2 Particle size of PU ionomers versus DMPA content.

TABLE II
The Variation of Particle Size and Contact Angle with Different Weight Percent of DMPA in Polyurethane Dispersion

Sample	DMPA (wt %)	Contact angle (degree)	Particle size (nm)
SD1	11.3	74.8	94
SD2	7.4	86.0	110
SD3	5.09	90.7	182
SD4	2.6	–	453
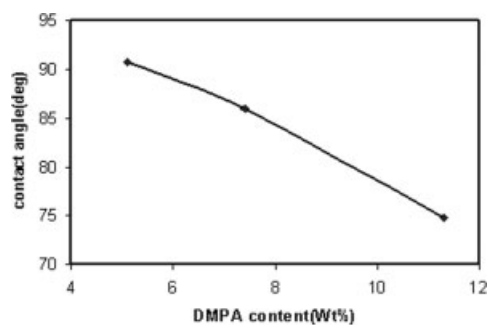
Figure 3 Contact angle of PU ionomers versus DMPA content.

Figure 4 Tensile properties of emulsion cast films with various DMPA content.

Contact angle

Hydrophilicity of the samples with different weight percentage of DMPA were evaluated by measuring the contact angle formed between water drops and the surface of the samples using contact angle measuring system G 10 (KRUSS). For this purpose, the drops of water were placed on three different areas of the surface using a micro syringe. Results presented as the mean value of three measurements on different parts of the film are shown in Figure 3.

As it can be seen, there is a remarkable difference in contact angle between different weight percentage of DMPA, where it reduces from 90.7 with 50% DMPA to 74.8 with 100% DMPA. This means that hydrophilicity increases with increasing of DMPA content. The carboxylic ion of DMPA in the polymer is a hydrophilic group and serves as an internal emulsifier for polyurethane dispersions. The contact angle was not measured for SD4 sample because of the due to lack of possibility for a good film formation (Table II).

Mechanical properties

The mechanical properties of PUs with respect to DMPA content are presented in Table III. It can be seen that tensile strength, load at yield, yield stress and hardness are increased with increasing DMPA content. SD1 (100% DMPA) showed the largest tensile strength among the others. This may be due to the pendant carboxylic group contents for the same NCO/OH ratio and a higher hydrogen bonding density. The elongation at break is also decreased with

increasing DMPA content. The stress–strain curve of the samples are shown in Figure 4.

TG studies

The TG and DTG curves of samples as a function of DMPA content are shown in Figures 5 and 6, respectively. The initial decomposition temperature, $T_{d,onset}$, the temperature of half decomposition, $T_{d,1/2}$, and the temperature of the maximum rate of decomposition, $T_{d,max}$, for different samples at heating rate of 10°C/min are also listed in Table IV.

The initial decomposition temperature corresponds to the intercept of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve.[23]

The TG curves show three discrete stages of degradation. These stages are clearly distinguished in DTG curve. It can be seen that by increasing the amount of DMPA in polyurethane structure, thermal stability of cast films decreases. The degradation temperature of PU films based on 100% DMPA is lower than PU films based on 75 and 50% DMPA. Although the detailed mechanism is not clear, it is
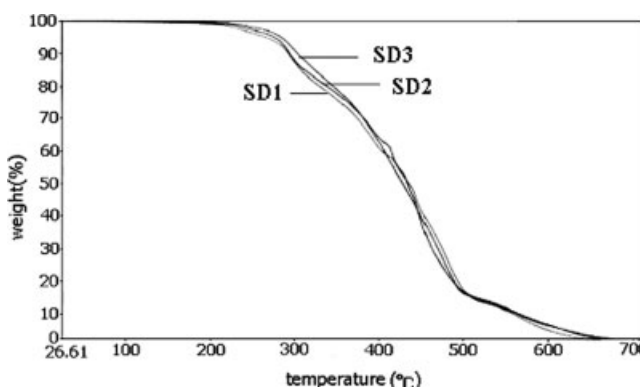
TABLE III
Mechanical Properties of Emulsion PU-Cast Films

Sample	Tensile strength (MPa)	Elongation at break (%)	Load at yield (N)	Yield stress (MPa)	Hardness (Shore A)	T_g (°C)
SD1	6.189	1266	2.60	0.838	71.5	−1.2
SD2	3.749	1284	2.12	0.584	64.2	−21.3
SD3	0.473	2032	1.49	0.499	63.6	−54.8

Figure 5 TG thermograms of emulsion cast films: SD3 (50% DMPA), SD2 (75% DMPA), SD1(100% DMPA).
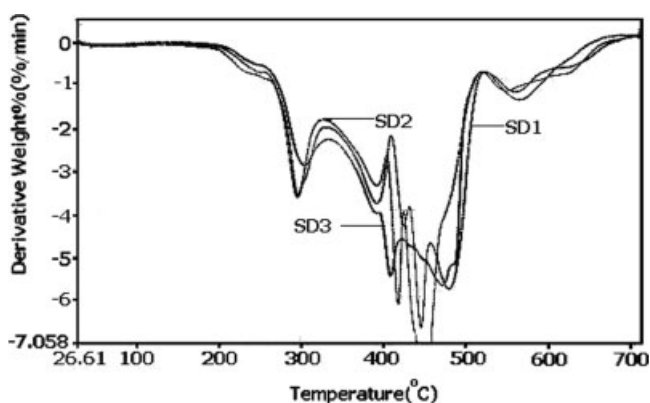
Figure 6 DTG thermograms of emulsion cast films: SD3 (50% DMPA), SD2 (75% DMPA), SD1(100% DMPA).

possible to associate it with the presence of tertiary carbon atom connected with carboxyl group. It is commonly accepted that the tertiary carbon is more easily attacked by organic radical to form new active species.[24] It is said that the early stage degradation occurred mainly in the hard segment where urethane groups first undergo depolymerization, resulting in individual monomers, which then they further react to produce carbon dioxide.[25] The subsequent stages of the degradation correspond to the soft segments, formed from polyol.[26] These results also verified that the thermal degradation or thermal stability was influenced by chain extender type. Comparing SD1 (0% 1,4-BDO) with SD3 (50% 1,4-BDO) showed the influence of chain extender type on thermal stability of polyurethanes.

TG studies of PU films showed that the degradation of PU films starts at 220°C and ended at 550°C. The degradation at 500°C corresponds to char forming of the films.

DMTA studies

Variations of tan δ and storage modulus with temperature for the emulsion PU cast films are shown in Figures 7 and 8, respectively. The glass transition temperature (T_g) of PU moves toward the higher temperatures as the DMPA concentration increases (Fig. 7). The tan δ peak located at about −54°C is shifted to about −1°C as the DMPA weight percent increases from 50 to 100%. The increase of T_g with DMPA concentration is mainly driven by the

TABLE IV
Thermal Degradation Behavior of the PU Films with Different DMPA Content

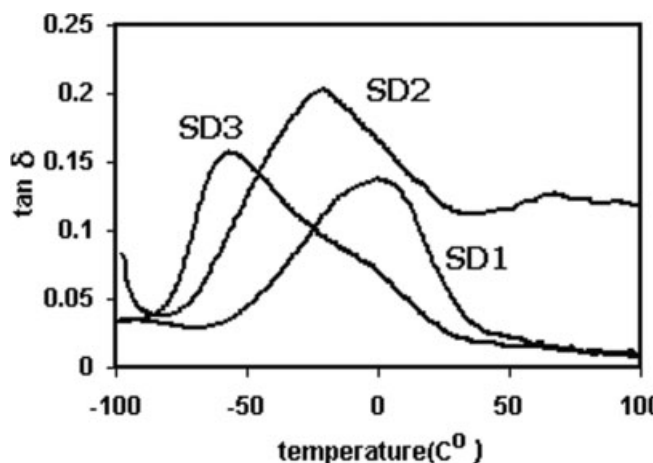| Sample	$T_{d,\mathrm{onset}}$ (°C)	$T_{d,1/2}$ (°C)	$T_{d,\mathrm{max}}$ (°C)
SD1	222.1	406.2	537
SD2	233.9	412.5	540
SD3	244.7	418.3	543

Figure 7 Variations of tan δ of emulsion cast films with different DMPA content.

increase of hard segment and coulombic forces between ionic centers. The value of storage modulus (E') is also presented in Figure 8. It is shown that stiffer polyurethanes are produced by higher percentage of DMPA as a chain extender.

CONCLUSIONS

Aqueous polyurethane dispersions were prepared from TDI, PTMG, 1,4-BDO, and different amounts of DMPA as ionic center. The effect of DMPA content on the state of dispersion, particle size, mechanical, and thermal properties are studied and considered. The average particle size of the prepared polyurethane emulsions decreases by increasing the DMPA content. Tensile strength and hardness increase and elongation at break and contact angle decrease with the increase of ionic content. Thermal property and thermal stability is also affected by the content of DMPA and thermal stability decreases with increasing
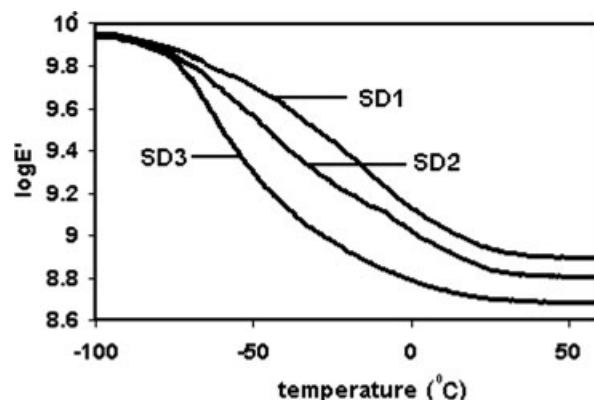

Figure 8 Variations of storage modulus (log E') of emulsion cast films with different DMPA content.

DMPA content. Glass transition temperature (T_g) shifts toward higher temperatures as the DMPA content is increased. The increase of T_g and tensile properties are interpreted in terms of increasing hard segments and coulombic forces between ionic centers. Also, the decreased contact angle is ascribed to the increase of the hydrophilicity of the polyurethanes.

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