

Synthesis and properties of aqueous polyurethane dispersions: Influence of molecular weight of polyethylene glycol

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Abstract—Aqueous polyurethane dispersions (PUDs) have recently emerged as important alternatives to their solvent-based counterparts for various applications due to increasing health and environmental awareness. A series of aqueous polyurethane dispersions containing carboxylate anion as hydrophilic pendant groups were synthesized through step growth polymerization reaction using hexamethylene diisocyanate (HDI), 1,4-butanediol (1,4-BDO), dimethylol propionic acid (DMPA) and polyethylene glycol (PEG) of different molecular weight. Effect of PEG molecular weight was investigated on molecular structure, contact angle measurement, and physical and adhesive properties of PU emulsions. Fourier transform infrared spectroscopy (FT-IR) was used to check the completion of polymerization reaction. Contact angle measurement indicated that the hydrophilicity of polymer increases by increasing molecular weight of PEG with a corresponding decrease in contact angle. Results of T-peel test showed a decrease in peel strength by increasing molecular weight of PEG. Moreover, solid contents%, drying time and storage stability suggested fast drying properties and greater stability of aqueous PU dispersions.

Key words: Polyurethane, FT-IR, Adhesive Properties, Hydrophilicity, T-peel Test

INTRODUCTION

Aqueous polyurethane dispersions (APU) represent a versatile class of materials having a wide range of applications [1]. Polyurethane elastomers (PUEs) are possibly the most versatile class of polymers as they can be molded, injected, extruded, recycled [2] and easily modified by varying the diisocyanate structure [3] and chain extender (CE) length using α , ω -alkane diols [4,5]. Synthesis, characterization of UV-curable and waterborne polyurethane dispersions [6,7], effect of blocked polyisocyanate based PU composites [8] and PU/natural rubber blends [9,10] have been studied comprehensively.

Due to high demand because of chemical pollution, a recent renaissance has occurred on water-based polyurethanes that expressively lessen the environmental contamination coming from their solvent-based counterparts. These water-based polyurethanes are expected to display superior performance relative to that of conventional solvent borne systems [11]. Aqueous polyurethanes have earned more importance due to their exceptional properties such as glossiness, transparency, quick drying time, flexibility and temperature impact resistance, abrasion resistance, non-flammability, and adhesion with most substrates. In addition, APUs are also resistant towards solvents and chemicals, offering good weather stability [12, 13]. Aqueous polyurethane dispersion is a binary colloidal system having dispersed in water polyurethane particles. Generally, PU is water incompatible because of the presence of hydrophobic isocyanates which are not dispersible in water but also react with water. Hydrophilic modification of poly (diisocyanates) has been used to

facilitate water dispersibility by incorporation of hydrophilic groups, distributed along the chain of polyurethane prepolymer. Water-based polyurethane (WBPU) coatings are developed by incorporating ionic groups into PU backbone [14,15]. Depending on these ionic groups, PU dispersions can be classified into cationic, anionic and nonionic types. Nonionic types contain hydrophilic soft segment pendant groups such as polyethylene oxide. Dispersions containing N-methyl diethanol amine and poly(tetramethylene adipate diol) are cationic dispersions whereas poly(tetramethylene glycol) (PTMG), poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG) and dimethylolpropanoic acid (DMPA) are categorized as anionic dispersions. The ionomers are neutralized to form salt. These groups are built in the chain structure during the polymer preparation [16,17].

PU dispersions can be achieved in a variety of ways. A choice must be made on which process to select and which type of chemistry to use in order to run the polyurethane into a water-based coating. Most important processes used to prepare WBPU are acetone process, prepolymer mixing process, the melt dispersion process and the ketamine process [18]. However, these methods have common characteristics that are the preparation of NCO-terminated PU prepolymer of their respective molecular weights. Molecular weight is controlled by mole ratio of NCO/OH and chain extender, so synthesis processes mostly vary in chain extension step that is generally performed using diamines ($-NH_2$) and diols ($-OH$) [14]. The preparation of PUDs by the prepolymer mixing process has received much attention in the literature. PU-prepolymer is synthesized by reacting macrodiol and diisocyanate, followed by the introduction of hydrophilic groups such as dimethylolpropanoic acid which acts as an internal emulsifier and becomes the part of main chain of polymer. Then the chain extension step is carried out by adding the diamine or diol to the aqueous dispersion. PU disper-

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sions are generally made with aliphatic diisocyanates, because of their lower reactivity with water than aromatic ones [15,19].

Polyurethanes are segmented polymers consisting of alternating soft and hard segments that constitute a unique micro phase separated. PU ionomers contain ionic groups which are introduced either into hard or soft segments yielding prescribed properties. The dispersion of polymer in water and properties of cast films are affected by types and contents of ionic centers and macrodiols as soft segments. Moreover, reaction conditions like temperature of reaction, stirring speed, the rate of addition of ingredients and sequence of addition had a significant effect on the properties of aqueous dispersion [20]. This article describes the preparations of ionic type water-based PU dispersions containing different molecular weight of polyethylene glycol (PEG), dimethylol propionic acid (DMPA), 1,4-butanediol (1,4-BDO) and, hexamethylene diisocyanate (HDI). The prepared WBPU dispersions were characterized by Fourier transform infrared spectroscopy (FT-IR). The influence of macrodiols molecular weight on mechanical strength, surface wettability and physical assets of dispersions were examined by T-peel test and contact angle measurement.

EXPERIMENTAL

1. Materials

Polyethylene glycol (PEG) with various molecular weights ($M_n = 200, 400, 600, 800, 1,000$ and $1,500$) was procured from India and dried and degassed at 80°C and at some optimum pressure (1-2 mmHg) for 3 h before use. 1,4-Butanediol (1,4-BDO) (Merck) was dried and degassed at 50°C and 1-2 mmHg for 2 h. Dimethylol propionic acid (DMPA) (Aldrich) was dried at 100°C for 2 h in an oven. Methyl ethyl ketone (MEK) (Merck) was dried using anhydrous CaSO_4 and triethylamine (TEA) (Merck) was dried over molecular sieves. Dibutyltin dilaurate (DBTDL) (95%, Aldrich), N,N -Dimethylformamide (DMF) (99% Aldrich) and hexamethylene diisocyanate (HDI) (99% Aldrich) were used as received.

2. Preparation of Water-based Polyurethane Dispersions

Water-based polyurethane dispersions were synthesized by conventional prepolymer process. WBPU dispersions were synthesized without any emulsifier. Mole ratio was kept constant throughout the synthesis, but polyethylene glycol (PEG) with different molecular weight was used. Typical procedure for synthesis was as follows: Following prepolymer mixing process PU-prepolymer was synthesized in a round-bottom glass reactor equipped with a mechanical stirrer, a thermometer, a reflux condenser, a temperature controller and a nitrogen inlet. Reaction was carried out in a nitrogen atmosphere. First, 0.25 moles of PEG was charged into reactor with constant stirring at 80°C for 15 minutes. After that, 0.5 moles of DMPA was charged into the reactor and the mixture was heated at 80°C for 30 minutes. Then under vigorous stirring 1 mole of HDI was added dropwise. Meanwhile 1-2 drops of dibutyltin dilaurate (DBTDL) was added as catalyst with the help of a micro syringe. Reaction proceeded for 2 h at $70\text{--}80^\circ\text{C}$ to obtain hydrophilic NCO-terminated PU prepolymer. After obtaining NCO-terminated PU prepolymer, neutralization was performed. TEA (0.5 moles) was used as neutralizing agent to react with carboxylic groups present in DMPA molecules in polymer chain. Small amount of methyl ethyl ketone (MEK) (about 5 ml) was used to reduce the viscosity of prepoly-

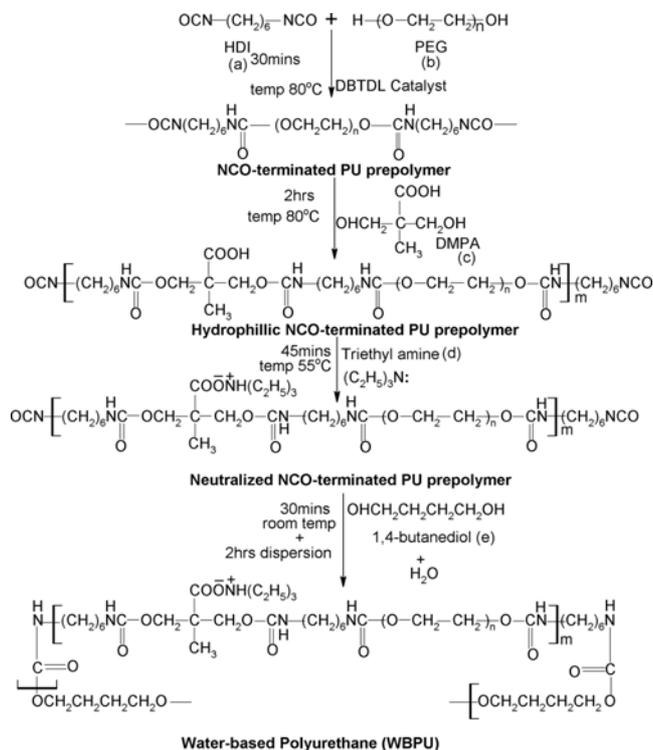


Fig. 1. Synthesis of water-based Polyurethane (WBPU) based on (a) HDI, (b) PEG, (c) DMPA, (d) TEA and (e) BDO.

mer. Neutralization was performed for 45 minutes at 55°C in the presence of nitrogen atmosphere. Afterwards, the neutralized water dispersible PU prepolymer was extended with 0.25 moles of 1,4-butanediol (BDO). The BDO, a chain extender, was added to react with remaining isocyanate groups of PU prepolymer. Chain extension was performed for next 30 minutes. After that, a calculated amount of distilled water was added dropwise with dropping funnel and stirring rate was increased. Dispersion formation proceeded for next 2 hours at room temperature. A stable dispersion with 33% solid content was obtained.

The reaction scheme for the PU prepolymer preparation and the processes of dispersion and chain extension are shown in Fig. 1. A series of samples were prepared by varying molecular weights of polyethylene glycol (PEG) with constant ionic content and chain extender.

3. Measurements

3-1. Fourier Transforms Infrared (FT-IR) Spectroscopy

Fourier transform infrared spectroscopy experiments were conducted on a Thermo Scientific FT-IR spectrometer equipped with ATR accessories and ZnSe crystal over the range $4,000\text{--}400\text{ cm}^{-1}$ at room temperature.

3-2. Contact Angle Measurement

To confirm the surface structure of the dry films cast from the emulsions, surface tension was determined by contact angle measurement. WBPU samples were applied on glass slides and were completely dried at room temperature for contact angle measurement using sessile drop method at constant room temperature.

3-3. Peel Strength (T-peel Test)

Peel strength of prepared polyurethane dispersions was measured by relevant standard D1876-95. Test specimens were condi-

tioned for seven days at relative humidity of 50% at 23 °C. An autographic recording of load versus head movement or load versus distance peeled was obtained.

3-4. Physical Properties

Different physical characteristics of synthesized water-based polyurethane dispersions such as solid contents %, tack free dryness and storage stability of dispersions were measured according to standard procedures. Drying time of WBPU samples was determined according to the relevant polish standard ASTM D1640-95.

RESULTS AND DISCUSSION

Aqueous PU dispersion was prepared via different molecular weight of polyethylene glycol (PEG), i.e., PEG 200, PEG 400, PEG 600, PEG 800, PEG 1000 and PEG 1500, keeping all other components constant. All of the PEGs were used separately to prepare different samples of water-based polyurethane. The PU was prepared by reaction of stoichiometric amount of PEG/HDI/1,4-BDO/DMPA with

ratios of 0.5 : 2 : 0.5 : 1 according to synthetic route as depicted in Fig. 1. Stable dispersions with 33% solid contents were made and all the tests were performed at these solid contents.

1. FT-IR Spectroscopy

The prepared ionic WPU dispersions were characterized by using FT-IR spectroscopy. Fig. 2 shows representative FT-IR spectra of WBPU1, WBPU2, WBPU3, WBPU4, WBPU5 and WBPU6. The intriguing aspect of this analysis is the insight into the reaction mechanism obtained from the profiles. IR studies have been carried out by focusing principal regions -CH stretching ($2,700\text{--}2,950\text{ cm}^{-1}$), C=O stretching ($1,620\text{--}1,740\text{ cm}^{-1}$), -NH stretching ($3,300\text{ cm}^{-1}$) and C-O-C stretching ($1,050\text{--}1,150\text{ cm}^{-1}$). In the prepared WBPU, there was no signal at $2,270\text{ cm}^{-1}$ (-NCO stretching) and $3,590\text{ cm}^{-1}$ (O-H stretching), indicating that the synthesis of ionic water-based PU had been completed. The absorption bands of N-H stretching vibrations were observed at 3319.40 cm^{-1} .

NH deformation bands were observed in the range of $1,500\text{--}1,600\text{ cm}^{-1}$. The sharp peaks ranging from $1,690\text{--}1,700\text{ cm}^{-1}$ indicate C=O stretching vibrations of urethane/allophanate, which are functional groups used to anchor PEG moieties to HDI, imparting water dispersibility. Aliphatic C-H stretching mode of $2,880\text{--}2,929\text{ cm}^{-1}$ and carboxylic stretching absorption band at $3,735\text{--}3,770\text{ cm}^{-1}$ were observed. Moreover, IR spectra showed the characteristics C-O-C stretching bands of soft segment at $1,045\text{ cm}^{-1}$, $1,099\text{ cm}^{-1}$, $1,097\text{ cm}^{-1}$, $1,095\text{ cm}^{-1}$ and $1,103\text{ cm}^{-1}$. These vibrations are strong evidence for the formation of PU. Otts and Urban [21] suggested that when the NCO/OH ratio decreases, the carbonyl urethane group -C=O peak shifts to the left. According to these the NH peak in WBPU1, WBPU2, WBPU3, WBPU4, WBPU5 and WBPU6 samples remains almost constant (at about $3,320\text{ cm}^{-1}$). Therefore, it can be concluded that the molecular weight of polyethylene glycol does not have any considerable effect on hydrogen bonding of water-based polyurethane. Presence of expected peaks implies that the reaction was completed and the predesigned PU was formed. IR spectra also contain all the related information of the primarily structure of the final polymer.

2. Effect of Molecular Weight of PEG on Contact Angle Measurement

WBPU surface hydrophilicity, as characterized by static water contact angle, is reported in Fig. 3. Water absorption was measured to determine the polymer bulk hydrophilicity as this was expected to have a substantial impact on hydrolytic degradation. As can be seen, there is a remarkable difference in contact angle between different molecular weights of PEG, where it decreased from 83 for

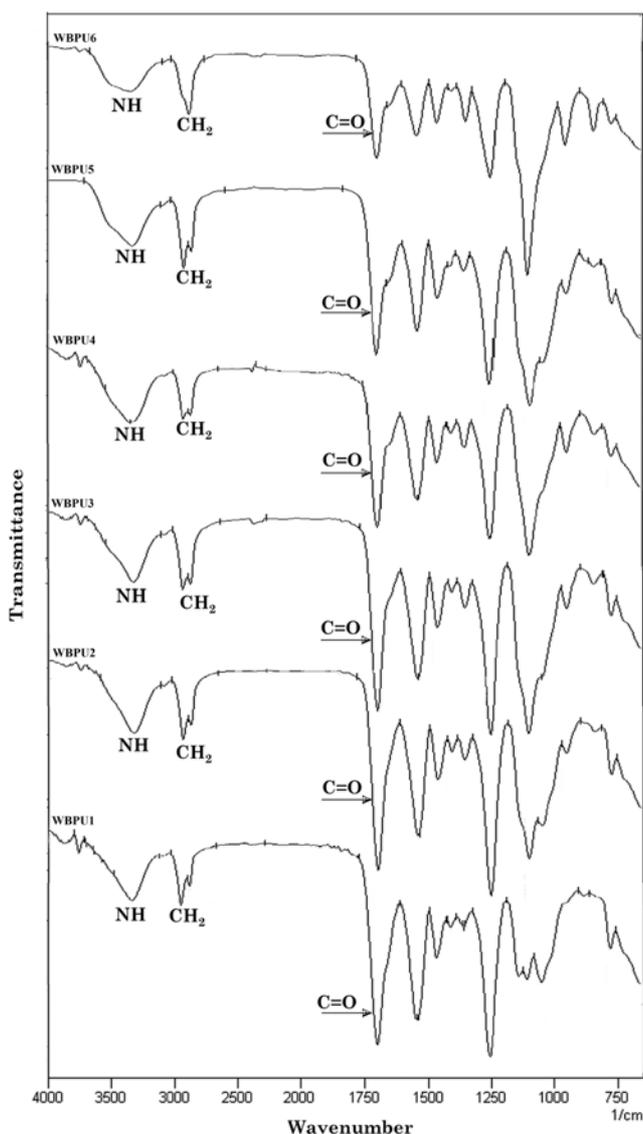


Fig. 2. FT-IR spectra of water-based polyurethane samples (WBPU1 to WBPU6).

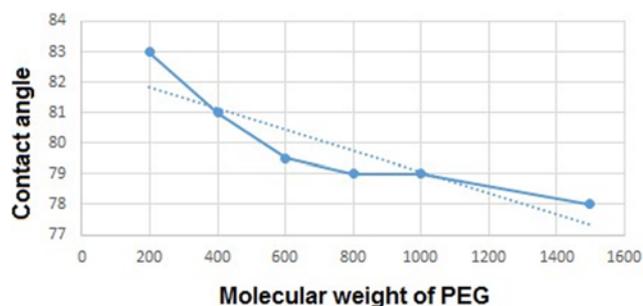


Fig. 3. Contact angle (θ) measurement of the prepared WBPU samples varying molecular weight of polyethylene glycol (PEG).

PEG 200 (WBPU1) to 78 for PEG 1500 (WBPU6). This means that hydrophilicity, chain flexibility, and phase separation increased with increasing molecular weight of PEG [22]. An increase in PEG content from 14% in WBPU1 to 30 wt% in WBPU6 decreased the contact angle from 83 to 78.

Gong et al. [23] suggested that amino groups improve hydrophilicity of polyurethane because of the presence of polar functional groups such as OH groups or NH₂ groups, resulting increases the hydrogen bonding interactions and, therefore, the contact angle decreases. This result can be ascribed to the higher amount of hydroxyl groups relative to the other compounds, which leads to an increase in hydrophilicity. We know that polyurethane dispersions are two phase systems, in which water is a continuous phase. The dispersed phase is a solid polymer, although the aqueous PU dispersions (APU) obtained are seemingly clean solutions. Smaller molecular weight of macrodiol causes lesser deformation of these two hydrophobic and hydrophilic centers and increase of particle size of dispersion leading to decrease in hydrophilicity of polymer and increase in contact angle value [20]. Polyurethane dispersions are ionomeric. It is reasonably presumed that the anionic centers are hydrophilic and predominantly located on the surfaces of PU particles in aqueous media. Larger number of these ionomers causes larger phase separation and lower contact angle. Chain flexibility also plays an important role in hydrophilicity of water-based polyurethane dispersion as chain rigidity does not allow these ionic groups to come near the particle surface, which in turn decreases hydrophilicity of dispersion.

3. Peel Strength

Basic structure-property relationships in PU indicate that the soft segments contribute to low-temperature properties, whereas the hard segments contribute to the modulus, strength and high-temperature properties. Peel strength was gradually decreased from 1.07 to 0.14 N/25 mm as molecular weight of PEG was increased. Presence of polar groups in polyurethane leads to improved wetting time, resulting in decrease in adhesion properties as shown in Table 1. Subaramani et al. [19] suggested that increase in hard segment content causes increase in tensile and adhesive properties of polyurethane. Moreover, peel strength is adversely moisture sensitive: the higher the moisture content, the lesser is the peel strength. By increasing the molecular weight, the soft segment content increased, resulting in decrease in adhesive/peel strength of polyurethane. Tensile strength, elongation at break and peel strength also depend upon many other factors such as DMPA content, hard segment content and ionic cross-linking

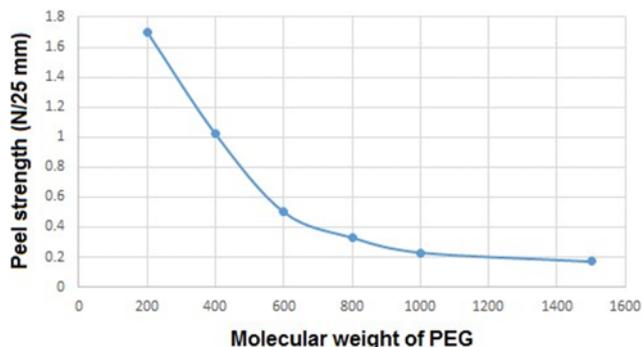


Fig. 4. Peel strength (N/25 mm) of the prepared WBPU samples varying molecular weight of polyethylene glycol (PEG).

which remained constant in the present research work [24]. The results of the peel strength (N/25 mm) of the prepared WBPU samples varying molecular weight of polyethylene glycol (PEG) are shown in Fig. 4.

4. Physical Properties

The solid content of the dispersions was adjusted to 33% and all measurements were based on 33% solids content. The carboxylic groups of DMPA were completely neutralized by TEA in all the experiments. Aqueous polyurethanes are mostly used in coatings. In WBPU physical properties are important parameters.

The storage stability of the anionic blocked isocyanate containing urethane pre-polymer dispersions was measured at room temperature (25 °C) for five months to check stability of dispersions, and the results are tabulated in Table 1. The storage stability, which is an important parameter, depends on many functions like pH, solid content, particle size and viscosity of the medium. Water-based polyurethane dispersions synthesized by using polyethylene glycols (PEG) of different molecular weights stored at room temperature were stable for more than four months. This is due to the low solids content of the dispersions. The dispersion containing higher molecular weight of macrodiol was more stable, whereas a little phase separation was observed in dispersion synthesized from PEG of Mn 200 (WBPU1) after four months. This was due to lower hydrophilicity of dispersion having lesser contents of soft segment, which is hydrophilic in nature. The hydrophilic character of polymer effectively maintains the properties of PU dispersions, i.e., the higher is the hydrophilic character, the smaller is the average particle size and larger is the number of particles, which in turn decreases the phase separation

Table 1. Sample code designation and different properties of water-based polyurethane dispersions

Sample code	Molecular weight of PEG ^b (\bar{M}_n)	Property			
		Peel strength (N/25 mm)	Drying time (minutes)	Stability (months)	Solid contents (%)
^a WBPU1	200	1.07	30	4	33
WBPU2	400	0.486	60	5	33
WBPU3	600	0.300	59	5	33
WBPU4	800	0.22	31	5	33
WBPU5	1000	0.19	30	5	33
WBPU6	1500	0.14	61	5	32

^aWater based polyurethane

^bPolyethylene glycol

and increases dispersion stability [20]. The results of storage stability of the dispersions showed that the stability of the dispersions increases by increasing molecular weight of PEG

Polyurethane chains are composed of flexible segments, derived from polyols, and rigid or hard segments formed by the urethane linkages. Drying time of polyurethane dispersions was calculated by standard method ASTM D1640-95. WBPU samples were dried at room temperature. If a thumb impression was formed on the film by applying some pressure, then it was not said to be dry until the thumb impression was not observed and tack-free film was formed. The results of drying time shown in Table 1 suggest that these dispersions have fast drying time. The drying time can be related to existence of C=O groups present in polyurethane. Therefore, in the presence of suitable driers the oxygen activation of methylene groups is further accelerated, which in results in faster drying time.

CONCLUSION

Novel water-based polyurethane dispersions were synthesized by using HDI, 1,4-BDO, DMPA and polyethylene glycols of different molecular weight: PEG 200, PEG 400, PEG 600, PEG 800, PEG 1000 and PEG 1500. The spectroscopic characterization of WBPU dispersions confirmed the structure. Effects of PEG on contact angle, mechanical and physical properties are studied and concluded. Contact angle measurement indicated that hydrophilicity of polymer increases by increasing molecular weight of PEG with a corresponding decrease in contact angle. This was because of presence of more ether residues in PEG of higher molecular weight. Peel strength of dispersions was decreased by increasing molecular weight of polyethylene glycol. Moreover, fast drying time, lower solid contents revealed good fastness properties of these dispersions.

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