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Synthesis and Characterization of Anionic Polyurethane Dispersants for Waterborne Paints

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ABSTRACT

Anionic polyurethane dispersants (APUDs) were used as dispersing agents in formulation of waterborne paints. The APUDs were synthesized by three steps. In the first step, macromonomer diisocyanate having carboxylic acid was prepared by isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) in the presence of acetone as solvent and dibutyltin dilaurate (DBTDL) as catalyst. Then, carboxylic polyurethane was prepared by reaction macromonomer diisocyanate having carboxylic acid groups with alcohols. In this work, alcohols were 1,4-butanediol and 1,6-hexanediol as difunctional alcohols, trimethylol propane as trifunctional alcohol and pentaerythritol as tetrafunctional alcohol. The final step involved neutralization and dispersion in water, where acidic polyurethane was neutralized by the addition of triethylamine (TEA). The polymers have been characterized with ^{1}H-NMR and FT-IR. The dispersion of APUDs depends on their molecular weights and chemical structures. Dispersion of titanium dioxide in typical waterborne acrylic resin has been investigated. Prog. Color Colorants Coat. 7(2014), 147-154. © Institute for Color Science and Technology.

1. Introduction

The process of dispersing particles in liquid or polymeric matrix has attracted a wide range of interests both in theoretical studies and practical applications [1-3]. Steady and stable dispersion was formed via a dispersant that was usually added in liquid phase or polymeric matrix for improving properties. Dispersing agents provide electrostatic charges on the particles or steric hindrance to produce a barrier for preventing coagulation [4].

In recent years, new dispersing agents were designed and synthesized based on polymer structure with active groups to attach the surface of particles [5]. Because of interaction between surface of the particles for dispersing, it can be concluded that the ability of polymers is strongly affected by their chemical structure. Thus, the existence of functional groups and the hydrophobicity of polymers cause their dispersing ability [6, 7]. An advantage of polymers as dispersing agents refers to the ability to provide a high density of charges and an efficient steric hindrance. Molecular weight and

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*Corresponding author: fnajafi@icrc.ac.ir its dispersity is another factor which affects the ability of polymeric dispersant [8].

On the other hand, waterborne dispersion technology was developed in the last decade because of its environmental advantages such as elimination of organic solvents, monomers and odor. The polymeric dispersant used in the waterborne paint should be compatible with this system and needed to design the suitable molecular structure.

Polyurethane dispersions (PUDs) are one of the most important industrial waterborne polymers. PUDs have the ability to change the structure of the polymeric chain to achieve polymeric dispersant for using in waterborne systems. So, depending on the charge of the functional group in PUDs, these dispersants can be classified into ionic (anionic or cationic) and nonionic (with hydrophilic part) [9, 10]. The functional group in the polymeric dispersant must be able to absorb the mineral particles [11-13]. The most important functional groups which can be used in polymeric chain of the dispersant are: phosphoric, sulphonic, and carboxylic acid groups and their salts, ammonium, quaternary ammonium groups, amine, etc [14-17].

Polyurethane dispersant is produced by different methods and processes and it is similar to the preparation of PUDs [18-21]. Polyurethane dispersant is synthesized by a pre-polymer process which involves the preparation of a low molecular weight isocyanate terminated ionomer, dispersing the ionomer in water followed by chain extension [22]. The pre-polymer is prepared from ionic monomer, diol and excess diisocyanate. Then the chain of isocyanate terminated pre-polymer extended with a diamine or low molecular weight diol and finally neutralized by tertiary amine.

Water soluble dispersants are recommended for using in waterborne paint and coating formulations where they will provide a wide range of performances and formulation benefits and highly compatible with these systems.

In this research, linear, branch and hyperbranch anionic polyurethane dispersants (APUDs) were synthesized by difunctional alcohol (BDO and HDO), trifunctional alcohol (TMP) and tetrafunctional alcohol (pentaerythritol). Dispersion of titanium dioxide was investigated by APUDs in typical waterborne acrylic resin.

2. Experimental and instruments

Isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), dibutyltin dilaurate (DBTDL), 1,4-butanediol (BDO), 1,6-hexanediol (HDO), trimethylol propane (TMP), pentaerythritol, acetone, triethylamine (TEA) were supplied from Merck. Acrylic resin NA-58 and TiO_2 were provided from Simab resin Co. and Chemira (Iran). Acrylic resin NA-58 was a very soft nonionic self-crosslinking acrylic emulsion. Table 1 shows typical properties of the acrylic resin NA-58.

^{1}H-NMR 500 MHZ Bruker, FT-IR Nicolet 6700 and GPC 150C Waters were used for characterization of APUDs. Molecular weight was determined in accordance with ISO 13885-1. Thus, 0.01g of each APUDs was dissolved in THF then filtered and injected to GPC 150C Waters. The standards for calibration of GPC were polystyrene. For dispersing of TiO_2 by APUDs a mixer (IKA Co.) was used and the particle size was measured by Grindometer (Brave Co.) according to ASTM D1210 standard test method.

2.2. Methods

2.2.1. Synthesis of macromonomer diisicyanate having COOH group

The macromonomer diisocyanate having carboxylic acid group was synthesized by stirring of 4.44 g (0.02 mol) isophorone diisocyanate (IPDI) and 1.34 g (0.01 mol) dimethylol propionic acid (DMPA) in 15 g acetone as solvent and 0.03g of dibutyltin dilaurate (DBTDL) as catalyst in 55°C for 4h until a homogeneous mixture was obtained.

Table 1: Typical properties of acrylic resin NA-58.

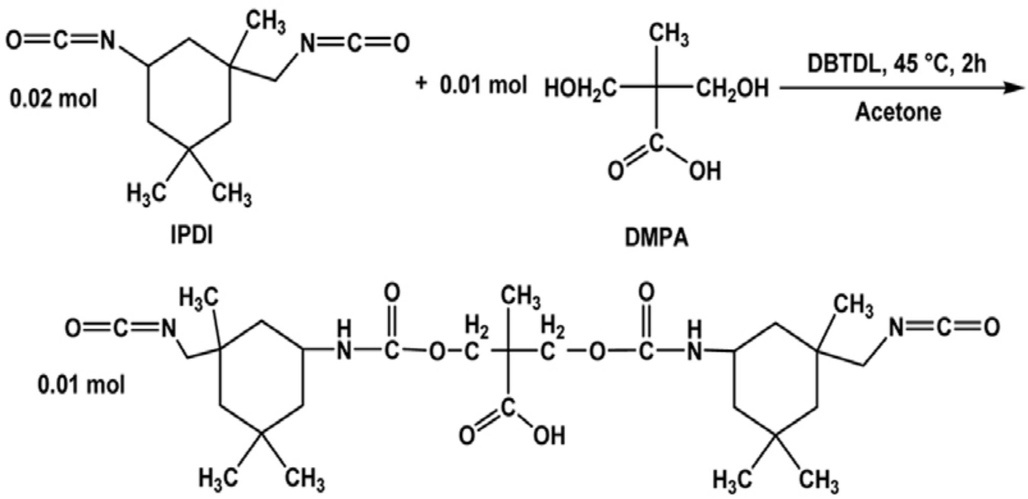
Solids (%)	45 ± 1
pH	2-3
T_g (ºC)	-14
Viscosity (as packed)*(cP)	Max.1000

Scheme 1 shows the synthesis of macromonomer diisocyanate having carboxylic acid group.

2.2.2. Synthesis of APUDs

APUDs were synthesized by the reaction of macromonomer diisocyanate having carboxylic acid group with several alcohols. Table 2 shows the amounts of raw materials for the synthesis of APUDs. Each alcohol was reacted with macromonomer diisocyanate in 15 g acetone as solvent and 2 drops of dibutyltin dilaurate (DBTDL) as catalyst in 55°C for 4 hours.

In the next step, acidic polyurethane was neutralized by the addition of 2 g triethylamine (TEA), then 15 g distillated water was slowly added to the neutralized acetone solution and in the final step, APUD solutions were heated to 70 °C for 1h until acetone was removed from APUDs.



Scheme 1: Synthesis of macromonomer diisocyanate having carboxylic acid group.

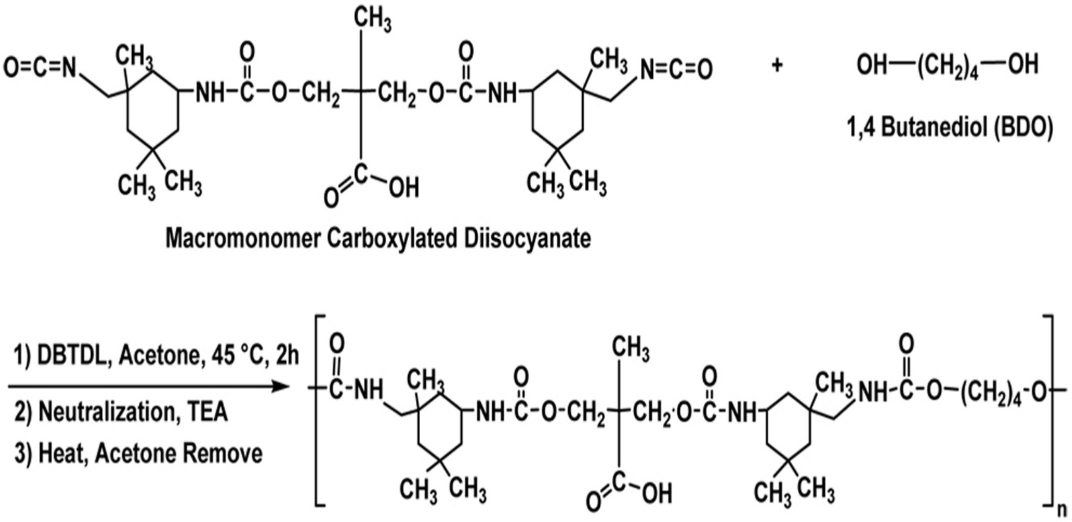
Table 2: The amounts of raw materials for the synthesis of APUDs.

Anionic polyurethane dispersants	IPDI	DMPA	BDO	HDO	TMP	Pentaerythritol
APUD1	0.02 mol (4.44 g)	0.01 mol (1.34 g)	0.01 mol (0.9 g)			
APUD2	0.02 mol (4.44 g)	0.01 mol (1.34 g)		0.01 mol (1.18g)		
APUD3	0.02 mol (4.44 g)	0.01 mol (1.34 g)			0.0066 mol (0.89 g)	
APUD4	0.02 mol (4.44 g)	0.01 mol (1.34 g)				0.005 mol (0.68 g)

Scheme 2 shows the synthesis of APUDs with 1,4 butanediol.

3. Results and discussion

Figure 1 shows the ^{1}H-NMR spectrum of the anionic polyurethane dispersant (APUD1) in $CDCl_3$. In the FT-IR spectrum of the APUD1 (Figure 2), stretching bonds of isocyanate groups (2265 cm^{-1}) were disappeared, and carbonyl groups of urethane bands were appeared in 1694 cm^{-1}.



Scheme 2: Synthesis of anionic polyurethane dispersant (APUD1).

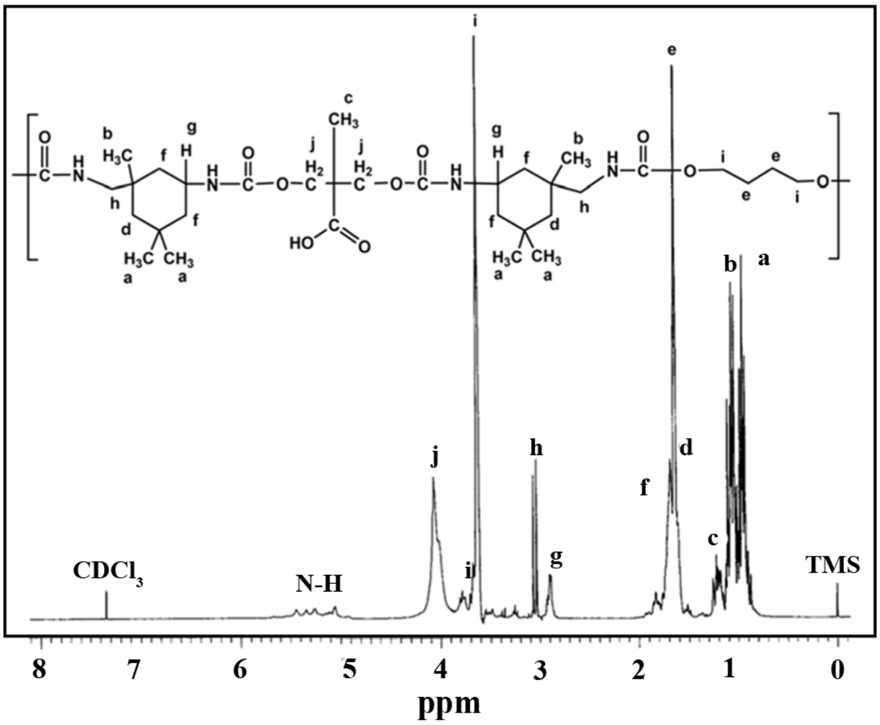


Figure 1: ^{1}H-NMR spectrum of anionic polyurethane dispersant (APUD1).

Molecular weight and acid value of APUDs are presented in Table 3.

Reducing the particle size of TiO_2 in water base paints is an important factor in dispersion process. Also reduced particle size is an effectiveness parameter for selecting dispersant. Increasing the rate of dispersion leads to decreasing the cost.

The APUDs were formulated in water base acrylic resin according to Table 4. The dipersing of TiO_2 particles were considered in water base acrylic resin (NA 58) in 35 minute.

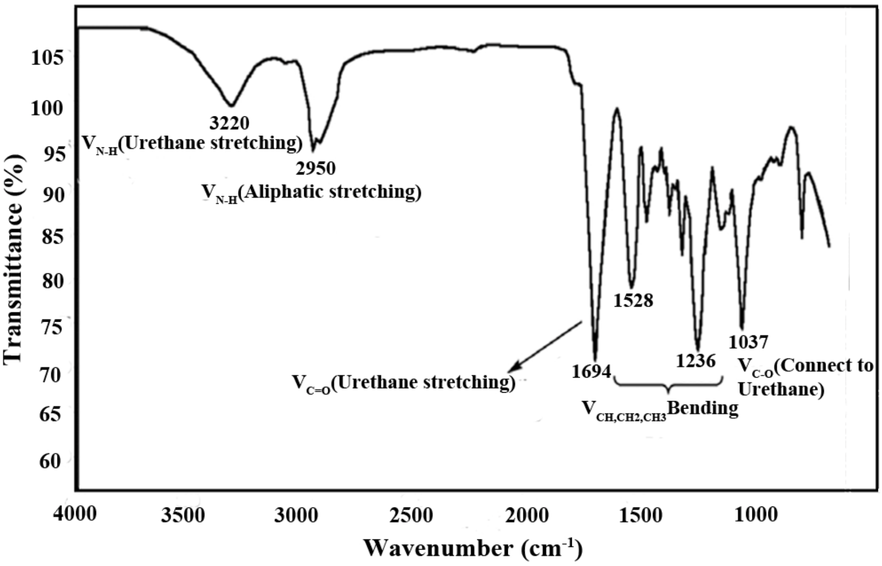


Figure 2: FT-IR spectrum of anionic polyurethane dispersant (APUD1).

Table 3: Properties of anionic polyurethane dispersants.

Anionic polyurethane dispersants	Chemical structure of copolymer	Mw	Acid value (mg KOH/g)
APUD1	Linear	6680	83
APUD2	Linear	6960	81
APUD3	Branch	13340	84
APUD4	Hyperbranch	19380	87

Table 4. Typical formulation of water base acrylic coating.

Ingredients	Weight (%)
Water base acrylic resin NA58-Simab resin	60
TiO_2 (Chemira)	30
Anionic polyurethane dispersants (APUD1)	0.5
Water	9.5

At first, the maximum particle size in each formulation was 100 micron. The results show that the rate of decreasing TiO_2 particle sizes by APUD3 in acrylic resin (NA 58) is higher than other dispersants. Figure 5 shows the decrease of TiO_2 particle size in water base acrylic resin (NA58). Maximum rate of dispersion was obtained when the surface of particles and the chains of the resin were bonded to each other [23-25]. The dispersion of APUSs is mainly through the electric stabilization.

The APUD1 and APUD2 are linear copolymers but APUD3 and APUD4 are branch copolymers; linear polymeric polyurethane dispersants have been synthesized by difunctional alcohols (1,4 butanediol and 1,6 hexandiol) but branch polymeric polyurethane dispersants have been synthesized by trifunctional (trimethylol propane) and tetrafunctional (pentaerythritol) alcohols.

Hydrophobic back bone of APUDs lengthens on the inorganic filler and pigments in the waterborne paints and the repulsion of anionic centers of carboxylic groups in APUDs prevents inorganic particles from sedimentation in water base paints.

Hydrocarbon segments of APUDs that have been formed by di-, tri- and tetra- alcohols are hydrophobic segments and TiO_2 particles were wetted by these hydrophobic segments. Therefore, wetting and dispersion of APUDs with long hydrophobic segments is better. Hydrophobicity of APUD2 is higher than APUD1 because of using 1,6 hexandiol in the synthesis of APUD2 which is more hydrophobic than 1,4 butanediol. Therefore, dispersion and stability of inorganic particles by APUD2 was better than APUD1 (Figure 3).

APUD3 and APUD4 were branch polyurethane dispersants. Hyrophobicity of APUD3 and APUD 4 was higher than APUD1 and 2 because of their branch structure and high molecular weight. Dispersion and stability of inorganic particles by APUD3 in preparation of waterborne paints was better than APUD4. APUD4 as dispersing agent was weak because of higher molecular weight and higher branch in comparison with APUD3 and hydrophobic segments of APUD4 can not be lengthened on inorganic fillers and pigments in the formulation of waterborne paints (Figure 3).

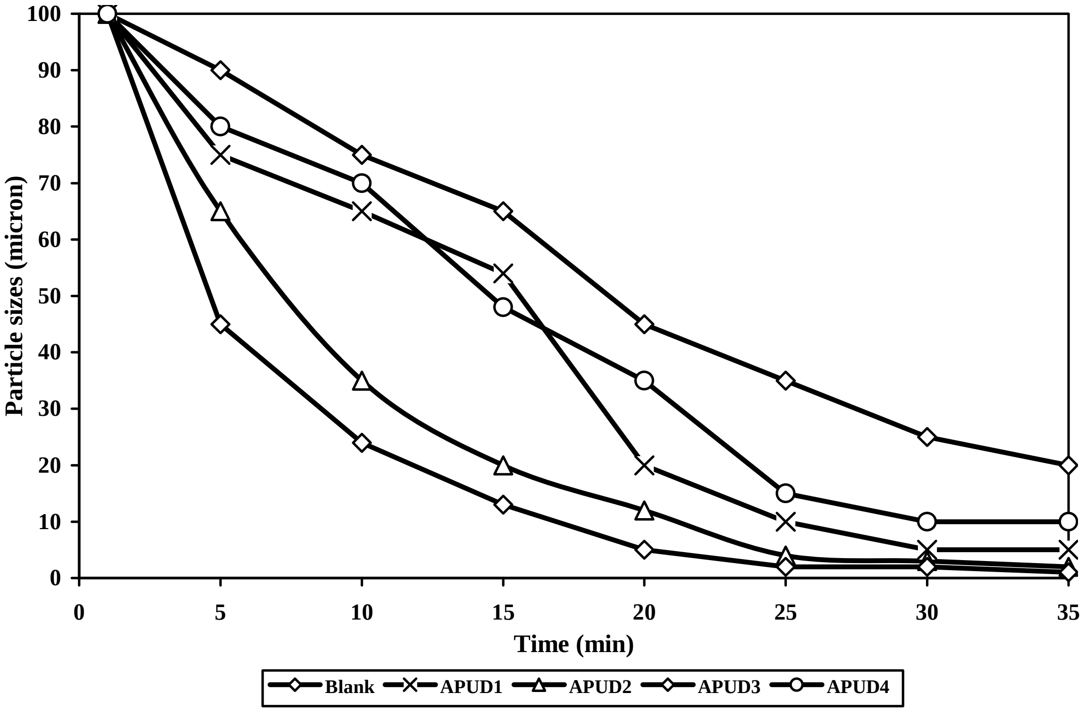


Figure 3: Decreasing particle sizes of TiO_2 in water base acrylic resin (NA58).

4. Conclusions

Anionic polyurethane dispersants (APUDs) were used as dispersing agents in formulation of waterborne paints. The APUDs were synthesized using isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) and alcohols with different functionality. The linear, branch and hyperbranch anionic polyurethane dispersants (APUDs) were synthesized by 1,4-butanediol and 1,6-hexanediol as difunctional alcohols, trimethylol propane as trifunctional alcohol and pentaerythritol as tetrafunctional alcohol.

The dispersion mechanism of synthesized APUSs is mainly the electric stabilization. Hydrophobic back bone of APUDs lengthens on inorganic fillers and pigments in the formulation of waterborne paints and the repulsion of anionic centers of carboxylic groups in APUDs prevents inorganic particles from sedimentation in water base paints. Dispersion of titanium dioxide was investigated by obtained APUDs in typical waterborne acrylic resin. The results show that decreasing the rate of TiO_2 particle sizes by APUD3 in water base acrylic resin is higher than other dispersants.

Hydrophobicity of APUD2 was more than APUD1. Therefore, dispersion and stability of inorganic particles in waterborne paints by APUD2 were better than APUD1. The hyrophobicity of APUD3 and APUD4 was more than APUD1 and 2 because of their branch structure and high molecular weight. Better results obtained using APUD3 as polymeric dispersant than APUD4. Because of its higher molecular weight and higher branch, APUD4 as dispersing agent was weak in comparison with APUD3. Hydrophobic segments in APUD4 can not be lengthened on inorganic fillers and pigments in the formulation of waterborne paints.

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