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Synthesis and Characterization of Anionic Polyester-Polyurethane Dispersion as Environmentally-Friendly Water Based Resins

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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 (green chemistry). Anionic polyester-polyurethane dispersions 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 percent of acetone as solvent and dibutyldtin dilaurate (DBTDL) as catalyst. Then, carboxylic polyurethane was prepared by reaction macromonomer diisocyanate having carboxylic acid with linear aliphatic polyester (Mw=2000), trifunctional polyester (Mw=2800) and butanediol (BDO) as chain extender. The next step involved neutralization and dispersion in water, where acidic polyurethane was neutralized by the addition of triethylamine (TEA). Factors influencing the synthesis of polyurethane dispersion mainly involve reaction temperature, reaction time, the concentration of catalyst, DMPA content and BDO content, were studied. The polymers have been characterized with DSC and FTIR.

Key words: Anionic polyester-polyurethane dispersions, green chemistry

INTRODUCTION

The evaporation of volatile organic compounds (VOCs) during the formulations of coatings, ink, and paints cause a wide variety of air quality problems. Consequently, governmental organizations such as the Environmental Protection Agency (EPA) in the United States and Local Air Quality Regulators have stepped up their efforts to limit the amounts of VOCs released to the atmosphere. These regulations and consumer demands are forcing industries to develop environmentally friendly products that will minimize adverse consequences to the environment (Tirpak *et al*, 1986; Seneker *et al*, 1992; Kim *et al*, 1994).

Amongst several options to develop new technology, water is the best choice to use as a medium in formulating coatings systems. To reduce or eliminate organic solvents from the formulations, solvents should be partially or completely replaced with environmental benign solvents (e.g., water), in the coating formulations to achieve little or no VOC content (Dieterich *et al*, 1970; Eisenberg 1970; Visser *et al*, 1991; Kim *et al*, 1991; Kim *et al* , 1996; Coutinho *et al*, 1996; Chen *et al*, 1997; Jhon *et al*, 2001; Narayan *et al*, 2006).

Due to the strong demands for low-pollution chemical industry, a recent renaissance has occurred in the area of aqueous polyurethanes, which has the potential to significantly reduce current environmental pollution from industries that are accustomed to using organic solvents that are costly and harmful to the environment. In the past 60 years, a number of studies aimed at improving the production technology and quality of waterborne polyurethanes have been reported in journal publications and patents.

For example, the work of Dieterich and his colleagues in Bayer AG is noteworthy because it pioneered the field and inspired much of the work in this area (Dieterich *et al,* 1970; Dieterich, 1981)

Today, waterborne polyurethanes have begun to penetrate new application areas previously reserved almost exclusively for their solvent borne analogs, especially as coatings for various fibers, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes, and textile dyes.

Modern polyurethane dispersion technology allows the preparation of the high-molecular-weight polymer dispersions which can produce surface coatings exhibiting many of the characteristic advantages of polyurethanes (e.g., good abrasion resistance and hardness) (Szycher's handbook of polyurethanes 1987).

As conventional polyurethane is insoluble in aqueous media, for making it dispersible in water, ionic and/or nonionic hydrophilic segments should be incorporated in its backbone structure. Important

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class of waterborne PUDs is ionic type among which anionic type is dominant where PU ionomers possess pendant acid groups (anionomer) incorporated into their backbone.
(Frisch *et al*,1987;Oertel , 1985;David *et al*, 1969 ;Lee *et al*,1992)

MATERIAL AND METHODS

Materials

Linear aliphatic polyester (Mw=2000), trifunctional polyester (Mw=2800) as polyol and 1,4-butane diol (BDO) as chain extender and dimethylol propionic acid (DMPA) that was dried at 40°C under vacuum, overnight. Isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) as catalyst and triethylamine (TEA) purchased from Merck Company (Germany).

Procedure

General procedure for synthesis of anionic polyester-polyurethane dispersion: In this process, a mixture of 4.44 g isophorone diisocyanate (IPDI), and 1.34 g dimethylol propionic acid (DMPA) in percent of 15 g acetone as solvent and 2 drops of dibutyldtin dilaurate (DBTDL) as catalyst, were stirred under reflux conditions, (T=45°C, 2h) and stirring was continued until a homogeneous mixture was obtained. In the next step 14 g linear aliphatic polyester (Mw=2000) was added and stirred for 30 min, then 0.27g butanediol (BDO) as chain extender was added and stirring was continued for 1 h in 45°C.

In the next step, acidic polyurethane was neutralized by the addition of 2g triethylamine (TEA) for 30 min and formation of the dispersion was accomplished by slowly adding 15g water to the neutralized acetone solution of the polyurethane polymers at 80 °C over 30 min.

RESULTS AND DISCUSSION

Anionic polyester-polyurethane dispersions were synthesized by three-step. In the first step, macromonomer diisocyanate having carboxylic acid was prepared by isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) in percent of acetone as solvent and dibutyldtin dilaurate (DBTDL) as catalyst. Then, carboxylic polyurethane was prepared by reaction macromonomer diisocyanate having carboxylic acid with linear aliphatic polyester (Mw=2000) or trifunctional polyester (Mw=2800) and butanediol (BDO) as chain extender. The next step involved neutralization and dispersion in water where acidic polyurethane was neutralized by the addition of triethylamine (TEA). Figure 1 shows the synthesis of polyurethane dispersion based on linear aliphatic polyester. Factors influencing the synthesis of polyurethane dispersion were studied that mainly involve reaction temperature, reaction time, the concentration of catalyst, DMPA content and BDO content,.

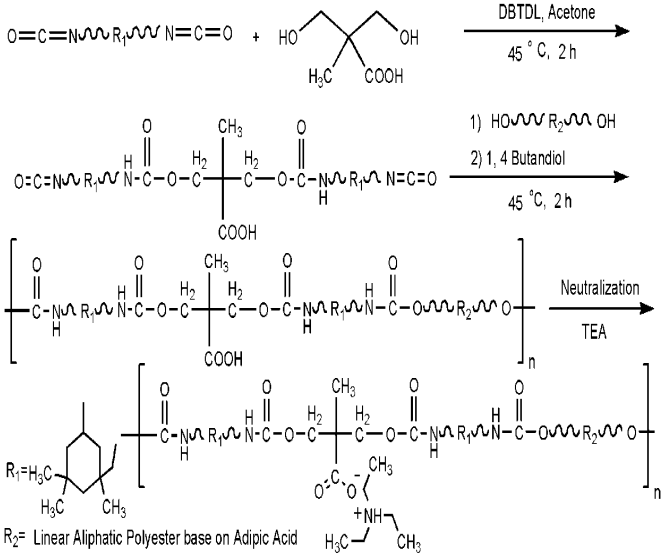

Fig. 1: Synthesis of polyurethane dispersion base on linear aliphatic polyester

In FT IR spectrum of anionic aliphatic polyester polyurethane dispersion (Figure 2), a broad absorption band of the N-H stretching was in 3336 cm-1. Aliphatic C-H stretching appeared in 2800-2990 cm^{-1}. Stretching absorption of carbonyl groups was seen in 1728 cm^{-1}. The stretching band of C-O appears in 1000-1150 cm^{-1}.

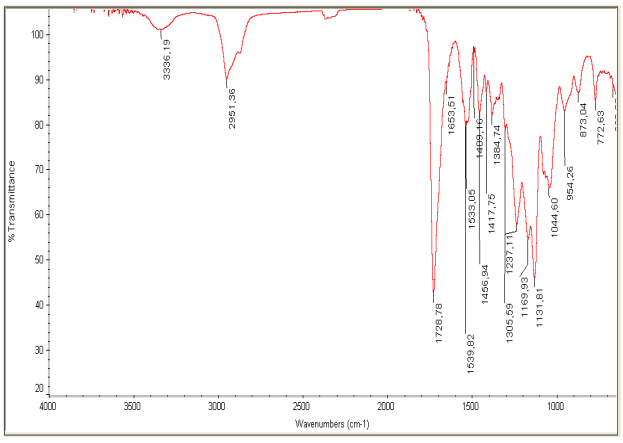

Fig. 2: FT-IR Spectrum of Anionic Aliphatic Polyester Polyurethane dispersion

Figure 3 and 4 show DSC of PUD based on difunctional polyester and trifunctional polyester,

respectively. As shown in figures 3 and 4 trifunctional polyester (Mw=2800) Tg is higher than Tg linear aliphatic polyester (Mw=2000) because trifunctional polyester has a higher molecular mass and it is nonlinear.

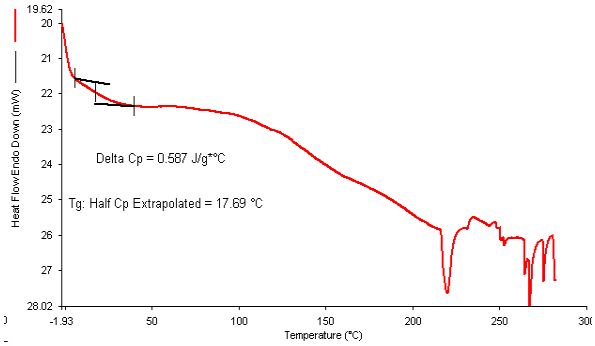

Figure 3: DSC of PUD base on liner aliphatic polyester Mw=2000

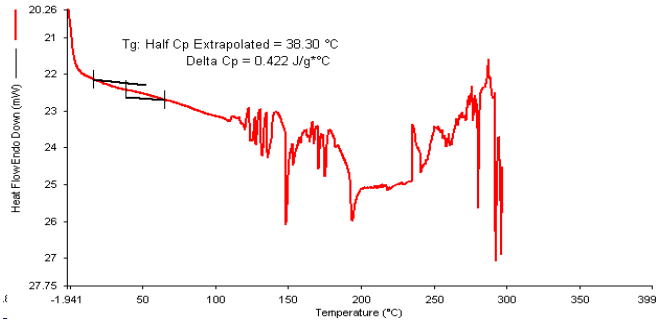

Figure 4: DSC of PUD base on trifunctional aliphatic polyester Mw=2800

CONCLUSION

Waterborne polyurethane has been developed in this study in order to reduce pollution due to organic solvent. This study describes the preparation of ionic type waterborne polyurethane with using internal emulsifier and synthesis method was acetone process. The results show that Tg of PUD with trifunctional polyester (Mw=2800) is higher than Tg of PUD with linear aliphatic polyester (Mw=2000) because PUD with trifunctional polyester has a higher molecular mass and it is nonlinear.

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