



# Synthesis of aqueous and hydroxy-terminated polyurethanes: Impacts of formulation parameters by orthogonal matrix design



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## ABSTRACT

Aqueous and hydroxy-terminated polyurethanes (AHPUs) were synthesized using poly(caprolactone) glycol, isophorone diisocyanate, dimethylolpropionic acid (DMPA) as main raw materials, trimethylolpropane (TMP) as crosslinking agent, ethylenediamine (EDA) as chain extender, and tris(hydroxymethyl) aminomethane as chain terminator. The optimum synthesis condition of AHPUs was elected by  $L_{16}(4^5)$  orthogonal experiments with the content of DMPA (A) and TMP (B), molar ratio of isocyanate to hydroxyl in the prepolymerization step (C) and the molar ratio of amino groups in EDA to residual isocyanate groups of prepolymerization (D) as factors and the transmittance, relative viscosity and particle size of dispersions as evaluation index, and the tack-free drying time, gloss, hardness, adhesion and water resistance of coatings were discussed, too. The results demonstrate that the synthetic AHPUs have good physical properties, such as relative viscosity, transmittance and particle size, what's more, the two-component films have good air-drying ability, gloss, hardness, adhesion and water resistance when synthesis parameters are  $A = 7.0 \text{ wt\%}$ ,  $B = 5.0 \text{ wt\%}$ ,  $C = 1.6$  and  $D = 0.2$ .

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## 1. Introduction

Aqueous polyurethane dispersions represent a versatile class of materials having a wide range of applications [1]. Due to rigorous limitations of chemical pollutants emission, a recent renaissance has occurred on water-based polyurethanes, which markedly lessen the environmental contamination coming from their solvent-based counterparts by greatly reducing the content of volatile organic compounds (VOCs). The water-based polyurethanes are expected to show superior performance compared to conventional solventborne systems [2]. Aqueous polyurethanes have earned more attention due to their exceptional properties such as in gloss, transparency, non-flammability, adhesion with most substrates, resistance to solvents and chemicals, and weather stability [3–5].

It is well known that aqueous resin dispersion is a binary colloidal system and there are some flaws such as long drying time, shrinkage and crackle to be resolved, which mainly result from large latent vaporization heat of water and the dominance of physical interaction in film formation process due to

low degree of crosslinking and few reactive functional groups. A proposed solution is increasing the functionality of the resin to improve its degree of crosslinking for self-crosslinking or two-component systems [6–13]. So the key is to find a polyfunctional substance used as a blocking reagent to achieve these ideas. Herein, tris(hydroxymethyl) aminomethane (THAM), a relatively inexpensive substance, was used as a polyhydroxyl introducing reagent and its structure has been shown in Fig. 1. Due to higher reactivity of amino groups than hydroxyl groups, amino groups will participate in the reaction with isocyanate groups, whilst hydroxyl groups will be retained.

As the experimental design involves multiple formulation parameters, orthogonal design method was particularly chosen to find out the optimum solution of the target product [14].

## 2. Experimental

### 2.1. Materials

Poly(caprolactone) glycol (PCL-210N) ( $M_n = 1000 \text{ g/mol}$ ) was purchased from Daicel Corporation (Osaka, Japan). PCL-210N was dried at  $120^\circ\text{C}$  for 2 h under vacuum to remove moisture before use. Isophorone diisocyanate (IPDI) and trimethylolpropane (TMP) were kindly provided by Chongqing Sanxia Paints Co.,

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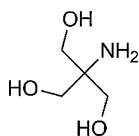


Fig. 1. The structure of tris(hydroxymethyl) aminomethane.

Ltd. (Chongqing, China). Dimethylolpropionic acid (DMPA) was purchased from Canto Chemical (Shanghai) Co., Ltd. (Shanghai, China). DMPA and TMP were dried at 100 °C for 5 h under vacuum before use. Tris(hydroxymethyl) aminomethane (THAM) was purchased from Guangdong Guanghua Chemical Factory Co., Ltd. (Shantou, China). Ethylenediamine (EDA) was purchased from Chengdu Kelong Chemical Reagent Company (Chengdu, China). Dibutyltin dilaurate (DBTDL) was purchased from Elementis Specialties, Inc. (Shanghai, China). Triethylamine (TEA) and acetone were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. (Chongqing, China). TEA was dried over 3 Å molecular sieves for 7 days prior to use. Acetone was redistilled after being mixed with anhydrous calcium sulfate overnight, and then dried over 3 Å molecular sieves prior to use. Bayhydur XP 2655 was purchased from Bayer MaterialScience, which was hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate having 20.7–21.7 wt% isocyanate groups and was used as curing agent for waterborne two-component polyurethane coating systems. All the materials mentioned above were used as received without further purification unless otherwise specified.

## 2.2. Synthesis of AHPUs

### 2.2.1. Prepolymer synthesis

Aqueous and hydroxy-terminated polyurethane were prepared via the acetone process [15]. A 500 mL three-necked round bottom flask equipped with a mechanical stirrer, thermometer, and condenser was charged with a calculated amount of DMPA and PCL-210N. The polymerization temperature was maintained using a thermostatic heating mantle. When heated up to 75 °C, the reactor was stirred until a homogenized mixture was obtained.

IPDI and DBTDL (0.03 wt% based on the total solid) which were dissolved in acetone (12 wt% based on the total solid) in advance were added drop wise within 20 min followed by heating up to 80 °C under reflux conditions. The isocyanate content of the prepolymers was determined by acetone–dibutylamine titration method upon obtaining the theoretical value, which aimed to monitor the progress of the reaction [16].

TMP was added to participate in the cross-linking reaction after dissolved in acetone (24 wt% based on the total solid). As soon as the theoretical endpoint of this reaction was reached, which was monitored by titrating the content of isocyanate group, the mixture was cooled down to 40 °C and acetone was added for adjusting the prepolymer viscosity.

TEA was diluted using acetone and then added to neutralize all the carboxylic acid groups for 30 min followed by cooling down to ambient temperature.

After that chains extended by the addition of solution of EDA in acetone, and allowed to react for 1 h to form isocyanate-terminated polyurethanes. During this time, THAM was dissolved in deionized water and stood in the refrigerator.

### 2.2.2. Dispersion and chain termination

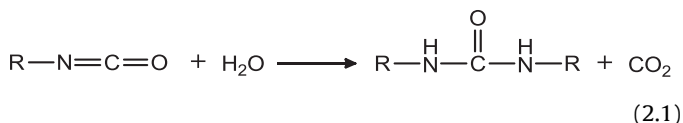
Aqueous dispersion of polyurethane was accomplished by adding the neutralized prepolymer to aqueous solution of THAM in 30 min with vigorous stirring. Additionally, the stirring was continued for 1 h. After that aqueous dispersion was filtered with rapid qualitative filter paper and then acetone was removed at 35 °C on a

rotary evaporator. The resultant aqueous polyurethane dispersion had the solid content of about 40% by weight.

The reaction scheme for the preparation of polyurethane prepolymer and the processes of dispersion and chain termination are shown in Fig. 2.

## 2.3. Application of films

Generally, to obtain the good performance of films, the moles of isocyanate groups should be equal to the moles of hydroxyl groups. However, because of the following side reaction (shown in Eq. (2.1)), an excess of isocyanate group with respect to the hydroxyl was needed.



Bayhydur XP 2655, a commercially available product, was used as curing agent for waterborne two-component polyurethane systems. The homemade AHPUs and Bayhydur XP 2655 were thoroughly mixed with the moles ratio of isocyanate group to hydroxyl being 1.5:1, just before the application of their films onto the substrates. The films were allowed to cure at ambient conditions (25 °C and relative humidity of approximately 45%) for at least 168 h before tests for mechanical and chemical properties were carried out.

## 2.4. Characterizations

### 2.4.1. Properties of dispersion

Transmittance of AHPUs dispersions following quadruple dilution with deionized water was tested by T60 UV–Vis spectrophotometer at 480 nm with deionized water as the reference sample. The relative viscosity of dispersions was measured using an Ubbelohde viscometer with 4 mL measuring bulb and 0.57 mm capillary in diameter (from Taizhou Glass Instrument Factory, Taizhou, China). After three repeated measurements, the average was taken to calculate the relative viscosity. In addition, particle size of AHPUs dispersions was performed using zetasizer nano ZS90 (from Malvern Instruments Ltd., Worcestershire, UK). The gel permeation chromatography (GPC) of six representative samples was measured by Shimadzu Prominence GPC. The experiments were performed on two Shodex GPC KF-806L columns (8.0 mm × 300 mm) using tetrahydrofuran as eluent with a flow rate of 1.0 mL/min at 40 °C. Polystyrene standards were used for the calibration.

### 2.4.2. Properties of coatings

All tests for tack-free drying time were carried out as described in ASTM D1640-03. And gloss tests were executed by WGG-60 portable specular gloss meter (from Toongfuh Guangahou Co., Ltd., Guangzhou, China). Three different points of each sample were tested and the average was taken as result.

According to ASTM D3363-05, film hardness was determined by pencil test including gouge hardness and scratch hardness. Analogously, film adhesion was detected by cross-cut tape test with tinfoil as the substrate subject to ASTM D3359-09.

Importantly, characterization for water resistance was carried out by measuring the water absorption of films. The films applied on microscope slide were weighed  $W_0$  firstly before being immersed in deionized water at ambient temperature for 12 h, then taken out to wipe surface water immediately with filter paper and weighed  $W_1$ . Water absorption was calculated as shown in Eq. (2.2).

$$\text{Water absorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2.2)$$

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