



Preparation and properties of waterborne polyurethane/epoxy resin composite coating from anionic terpene-based polyol dispersion



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ABSTRACT

An anionic polyol (T-PABA) dispersion was prepared by modifying terpene-based epoxy resin with para-aminobenzoic acid. Then T-PABA dispersion was crosslinked with a hexamethylene diisocyanate (HDI) tripolymer to prepare waterborne polyurethane/epoxy resin composite coating. The rheological properties and particle size distribution of the composite system were characterized by rotary rheometer and laser particle size analyzer. The crosslinked composite product has good thermal resistant properties, with glass-transition temperatures (T_g) about 40% and 50% weight loss temperatures (T_d) in the range of 400–420. The smooth and transparent film obtained from the composite product has good flexibility, adhesion, impact strength, antifouling and blocking resistance properties. The impact strength, pencil hardness, water-resistant and thermal-resistant properties of the composite products increased with the molar ratio of isocyanate group to active hydrogen of T-PABA.

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1. Introduction

Conventional solvent-based polyurethanes, with their excellent outdoor durability, outstanding chemical resistance and very good mechanical properties, are successfully used in various applications, such as original equipment manufacturer (OEM) coats, automotive repair coatings, industrial paints, furniture lacquers, plastic coatings and adhesives [1,2]. Recently, controlling the emission of volatile organic compounds (VOCs) is becoming the important driving force for resin developments. The substitution of solvent-based coatings with water-dispersed coatings is a major approach to reduce VOC emission. Two-component waterborne polyurethanes (2K-WPUs) coatings which integrate the environment-friendly property of water-dispersed coatings with the high performance of two-component polyurethanes, are gaining extensive research attention [3–6]. 2K-WPUs comprise a polyisocyanate component and a waterborne polyol component which results in various performances of the 2K-WPUs due to the various structures of the polyols. The most commonly used waterborne polyol is polyacrylate polyol which has been applied widely in the field of coatings and adhesive

[7–9]. However, the polyacrylate polymer has some shortcomings such as bad temperature adapt property and organic solvent resistibility. Polyurethane polyol is another promising hydroxyl group component for 2K-WPUs with its high comprehensive properties, while the use-cost of polyurethane polyol is quite expensive [10,11].

Most of these polyol components for 2K-WPUs originate from the unrenewable fossil resource. With the fossil resource being exhausted, the utilization of biomass resource for preparing polymer materials has been paid more attention to by many scholars all over the world [12,13]. Terpene-based epoxy resin (TME), an alicyclic epoxy resin with endocyclic structure, was synthesized from the raw material turpentine [14,15]. Recent investigations showed that it could also serve as precursors for the synthesis of TME-based polyols which could be crosslinked with polyisocyanate to prepare polyurethane/epoxy resin composite polymers [16]. In this article, an anionic polyol (T-PABA) dispersion was synthesized by reacting TME with para-aminobenzoic acid (PABA). Then a new two-component waterborne polyurethane–epoxy resin composite coating was prepared by crosslinking T-PABA dispersion with polyisocyanate. The purpose of this study was in order to obtain a wonderful composite polymer product from the bioresource turpentine, which could combine the rigidity and heat resistance of the epoxy resin (TME), the flexibility and tenacity of the polyurethane and the environmental friendliness and safety of the waterborne systems together.

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Table 1
Physicochemical parameters of T-PABA and T-PABA dispersion

T-PABA (solid resin)	
Appearance	Yellow transparent solid
Hydroxyl value (mg g ⁻¹)	168.9
Amine value (mg g ⁻¹)	125.9
Active hydrogen content (mmol g ⁻¹)	5.254
T-PABA dispersion	
Appearance	Yellow transparent liquid
Solid content (%)	30
Viscosity (mPa s, 25 °C)	400
Average particle size (nm)	40
Stability	No delaminating after 6 months

2. Materials and methods

2.1. Materials

The base material was the terpene-maleic ester-type epoxy resin (TME) with epoxy value of 0.34–0.38 mol 100 g⁻¹, which was synthesized from turpentine [14]. Para-aminobenzoic acid (PABA), technical grade, was purchased from Changzhou Sunlight Pharmacy Industry Co., Ltd., China. N,N-dimethyl ethanolamine and 2-butanone, chemically pure, were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. The hydrophilically modified hexamethylene diisocyanate (HDI) tripolymer (Fig. 1) with isocyanate (NCO) group content of 14 wt% and solid content of 85 wt%, technical grade, was supplied by Shanghai Sisheng Polymer Materials Co., Ltd., China.

2.2. Synthesis of T-PABA and T-PABA dispersion

A 500 ml four-necked flask equipped with stirrer, thermometer, condenser and heating mantle was charged with 30.6 g TME, 10.6 g PABA, and 16.5 g 2-butanone. After the PABA was all resolved in the 2-butanone under heating and stirred, the reaction was continued for 4 h at 80–90 °C. The 2-butanone was removed with vacuum distillation after reaction. The product (T-PABA) was neutralized with 4.8 g N,N-dimethyl ethanolamine, then dispersed with 96.0 g distilled water by churning at 500–1000 rpm, at 50–70 °C. A yellow transparent anionic dispersion (T-PABA dispersion) with solid content of 30% was obtained (Scheme 1). The physicochemical parameters of T-PABA and T-PABA dispersion were described in Table 1.

2.3. Preparation of the composite coating

A composite dispersion was prepared by mixing T-PABA dispersion with the hydrophilically modified HDI tripolymer at the molar ratio of active hydrogen to isocyanate group ranging from 0.8 to 1.4. The solid content of the blending was about 32% (by mass) as applied in this work. After mixed, the blending was cast on tinplates or glass slides to form 40 μm (±3 μm) thick dry films. The

crosslinked product of the composite dispersion was obtained by keeping the films in the room temperature for 24 h and then curing them in an oven at 70 °C for 6 h.

2.4. Measurements

Nicolet IS10 infrared spectrometric analyzer (Nicolet Instrument Co., U.S.A) was used to record the FT-IR spectra of polyol and composite product samples in the range of 400–4000 cm⁻¹.

¹³C NMR spectra were recorded on Bruker AV-300 NMR spectrometer at 300 MHz. Deuteroacetone was used as a solvent and tetramethylsilane (TMS) was served as internal standard.

Rheological properties of the T-PABA dispersion (30% solid content) and the composite dispersion (32% solid content) were performed with a Haake Mars-III rotational rheometer using coaxial cylinder technique.

Particle size analysis was carried out on a Nano-ZS ZEN3600 Zeta-sizer (Malvern Instrument Co., UK). The T-PABA dispersion and the composite dispersion were diluted with distilled water to 0.5% solid content.

The morphology of the composite product was characterized by atomic force microscope (AFM) performed on a SPM9600 AFM (Shimadzu, Japan). To prepare AFM sample, the composite sample was cast a film on silicon substrate.

Mechanical properties of the composite product were evaluated according to standard test methods (impact strength GB/T 1732-93 [17], adhesion GB/T 1720-89 [18], flexibility GB/T 1731-93 [19], pencil hardness GB/T 6739-96 [20]). Water resistance, antifouling and blocking resistance properties are measured according to standard test method GB/T 23999-2009 [21].

PerkinElmer Diamond differential scanning calorimeter (U.S.A) was used to record the differential scanning calorimetry (DSC) thermograms of the composite products at a heating rate of 20 °C min⁻¹ under a nitrogen gas flow of 20 ml min⁻¹.

NETZSCH STA 409 PC/PG thermogravimetric analyzer (Germany) was used to perform thermogravimetric analysis (TGA) of the composite products at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

3. Results and discussion

3.1. Characterization of T-PABA

The synthesis of T-PABA was carried out with the addition reaction between oxirane group and primary amine group (Scheme 1). The chemical structure of T-PABA was characterized with FT-IR (Fig. 2) and ¹³C NMR (Fig. 3) spectra. Compared with the spectra of TME, the significant enhancement of O–H stretching peak at 3480 cm⁻¹ and the disappearance of the absorption peak at 908 cm⁻¹ in the spectra of T-PABA denoted the occurrence of addition reaction of oxirane ring and amine group [22]. FT-IR spectra of T-PABA show significant absorption peaks at 3200–3700 cm⁻¹ (N–H and O–H stretching), 2400–2800 cm⁻¹ and 1680 cm⁻¹ (COOH stretching), 1605 and 1530 cm⁻¹ (benzene

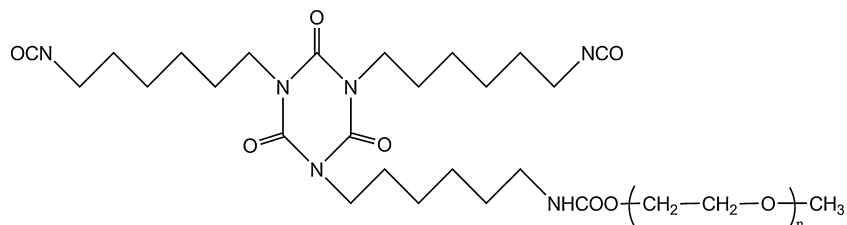


Fig. 1. Chemical structure of the hydrophilically modified HDI tripolymer.

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