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Preparation and properties of castor oil/pentaerythritol triacrylate-based UV curable waterborne polyurethane acrylate

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ABSTRACT

Castor oil (CO)/pentaerythritol triacrylate (PETA)-based UV curable waterborne polyurethane acrylate (UV-WPUA) was prepared by using isophorone diisocyanate (IPDI), poly(caprolactone diol) (PCL) and dimethylolbutyric acid (DMBA) as the main materials. A series of emulsions and films with different content of CO were obtained. The infrared spectra, together with the nuclear magnetic resonance spectroscopy, demonstrated the presence of CO and PETA in the UV-WPUA chains. The surface roughness of the curing film was measured by atomic force microscope. In addition, the effects of CO content on particle size, thermal properties, glass transition temperature and tensile performance of the emulsions and films were investigated. With the content of CO increasing from 1.72 to 8.58 wt%, the particle size of the UV-WPUA emulsion increased and the particle size distribution gradually widened. The appearance of the emulsions transformed from blue transparent into opaque and the stability decreased gradually. Water resistance, glass transition temperature for soft segment and thermal performance of the films were improved. The tensile strength of the films firstly increased and then decreased.

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1. Introduction

As the concept of environmental protection is becoming more and more popular, waterborne polyurethane (WPU) material with environmental protection has been paid more and more attention in recent years [1–3]. However, compared with aliphatic polyurethane and epoxy resin, application of pure aliphatic WPU is limited due to its poor mechanical properties, lower water resistance and lower hardness [3,4]. In order to improve the performance of WPU emulsion and film, organic fluorine [5], modified epoxy resin [6] and natural products [7] and other methods such as nanotubes were used to modify the performances.

UV curable coatings can be curable in a short period of time under UV irradiation and endow the coatings with more excellent performances. What's more, UV curable technology is noted for 5E, which stands for Efficiency, Enabling, Economical, Energy saving and Environmental friendly [8–10]. In view of these advantages, UV curing technology has been widely used in construction, sporting goods, electronic communications, packaging materials and other fields [11–13]. However, the conventional UV curable coatings have volatile solvent and are not zero-VOC emission. Therefore,

in order to overcome the disadvantages mentioned above, UV curable waterborne coating generates. UV-curable waterborne polyurethane, which has the advantages of both UV technology and waterborne coatings, has attracted much attention in recent years [14–16].

Pentaerythritol triacrylate (PETA), containing multiple acrylates and with good film-forming performance, was utilized as one of the most promising materials in UV-curing coating field [17]. In Hwang's study [18], WPU dispersions were synthesized using different end-capping groups such as 2-hydroxyethylmethacrylate, 2-hydroxyethylacrylate and PETA. The result showed that the pendulum hardness, curing rate and conversion of dispersion capped with PETA (with tri-acrylate functionality) were significantly higher than those of the other dispersions with mono-methacrylate or mono-acrylate functionality. However, single UV curable process was vulnerable to being influenced by oxygen inhibition and the bottom of the coating was cured more slowly and not completely, therefore, its practical application was restricted [19]. Castor oil (CO) is a kind of natural vegetable oil and can be used as cross-linking monomer with hydroxyl, whose average functionality is 2.7. And it can be cured in the presence of oxygen and drier to form a more compact network structure by partially replacing polyester diol or polyether glycol as soft segment [20]. Furthermore, its long nonpolar fatty acid chain endows the films with excellent hydrophobicity, toughness and cold resistance and causes

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widespread concerns in the polyurethane fields [20,21]. In Luo's study [22], a series of WPU were synthesized using polytetramethylene ether glycol, toluene diisocyanate, and epoxidized castor oil (ECO) as main materials. They found that increasing amount of ECO resulted in an improvement of the anti-water, thermal and mechanical properties of WPU films. However, literatures about introducing both CO and PETA into WPU molecules have rarely been reported so far.

In our previous studies, UV-curable polyurethane acrylate emulsion was obtained by using IPDI, DMBA and PETA as main materials. The effect of R (the molar ratio between $-NCO$ and $-OH$) value on the properties of the emulsions and the films was discussed. In this paper, the main objective was to improve comprehensive properties of the UV-curable polyurethane acrylate based on our previous studies. In view of this, both CO and PETA were introduced into waterborne polyurethane molecules and finally the castor oil/pentaerythritol triacrylate-based UV curing waterborne polyurethane acrylate (UV-WPUA) was prepared. The structure was characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR). The performances of both emulsions and coatings such as particle size, water resistance, thermal property, glass transition temperature and mechanical performance were investigated. Furthermore, the curing mechanism was postulated.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, AR), Poly (caprolactone glycol) (PCL, AR) and 2,2-dimethylol butanoic acid (DMBA, AR) were purchased from Taisen Chemical. Dibutyltindilaurate (DBTDL, AR) as catalyst, triethylamine (TEA, AR) and acetone were obtained from Tianjin Chem. Agent Inc. (China). Pentaerythritol triacrylate (PETA, AR) was purchased from Guangzhou Deco Composite Technology Co. Ltd. (China). Hydroquinone monomethyl ether (MEHQ, CR) was from Guoyao Chemical groups (China). Photoinitiator (Chemcure-73W, CR) was provided by Guangzhou Hengqiao Commerce Co. Ltd. (China). Castor oil (CO, CR) was purchased from Shandong Laiyang Fine Chemical Co. Ltd (China). Composite cobalt drier was supplied by Nanjing Anjing Drier Co. Ltd; PCL1000 and DMBA were dried overnight at 80 °C under vacuum in order to remove the moisture before use. Acetone was dehydrated by immersion in 4 Å molecular sieves for one week. All other materials were directly used without further purification.

2.2. Preparation of UV-WPUA

The mixtures of PCL and IPDI were added into a three-necked flask equipped with mechanical stirrer, reflux condenser and nitrogen. Hydrophilic chain extender DMBA dissolved in acetone was added in the presence of DBTDL as a catalyst. The reaction temperature was kept at 70–80 °C for 1.5 h. Subsequently, a certain amount of CO was added into the reaction system. After 1 h reaction, PETA with 0.7 wt% of MEHQ was added to cap the polyurethane and addition of MEHQ was to protect the double bonds of PETA and CO from radical polymerization at this stage. Followed by reaction for 2 h, the reactants were cooled to about 40 °C and then the carboxylic group in the side chain was neutralized by TEA (the molar ratio between TEA and DMBA was about 1.1), which lasted for 30 min. Finally the polymer was emulsified with suitable deionized water under high speed shearing. Then UV-WPUA dispersion was obtained after removal of the acetone by rotary vacuum evaporation. The solid content and pH of obtained emulsions were 30% and 7.8–8.2, respectively. The synthetic route of UV-WPUA was shown

in Fig. 1. A series of emulsions with different compositions were obtained by varying the content of CO following the same procedure and the detailed experimental compositions were illustrated in Table 1. For comparison, pure UV-WPUA0 was prepared according to the same procedure as above-mentioned, except that no CO was added.

2.3. Preparation of UV-WPUA films

UV-WPUA films were formed by casting the formulated dispersions with suitable photoinitiator 73-W (based on 1% of the amount of emulsion) and composite cobalt drier based on the amount of resins onto a polytetrafluoroethylene plate at room temperature for two days and followed by radiation under medium pressure mercury lamp for 40 s. The UV irradiation conditions were as follows [23]: the main wavelength was 365 nm, the UV light intensity at the sample was 50 mW cm⁻² and the irradiation distance was 8–10 cm. After demolding, the films were kept into a desiccator to avoid moisture. The thickness of the obtained film was about 0.5–0.6 mm. In order to form a uniform solution between the photoinitiator and UV-WPUA, about 1 mL of acetone should be added into the system and stirring was necessary.

2.4. Characterization and performance test

To evaluate the stability of emulsions, all the emulsions were placed at room temperature for six months and were centrifuged by L3660D low-speed centrifuge (made in Shanghai, China) at a speed of 3000 rpm min⁻¹ for 5 min to observe whether the precipitation was formed.

The Fourier transform infrared spectroscopy (FT-IR) of CO, UV-WPUA0 and UV-WPUA3 were recorded on a VERTEX 80 FT-IR spectrometer (BRUKER, Germany) scanning from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹ using ATR method.

¹H NMR and ¹³C NMR were conducted by ADVANCE III 400 MHz NMR spectrometer (made in Germany, BRUKER company). CO, PETA, NCO-terminated UV-WPUA3 prepolymer and UV-WPUA3 were dissolved in CDCl₃ before tests.

The average particle size and the particle size distribution of the UV-WPUA dispersions were analyzed by zetasizer nano ZS dynamic light scattering (Malvern Instruments Ltd., UK). Before tests, the dispersions were diluted (500×) with distilled water and dispersed by a sonicator.

The bibulous rate (*Q*) of the UV-WPUA films was determined as follows: UV-WPUA films were cut into small squares (2 cm × 2 cm) and weighed and immersed in water for 24 h at room temperature. Then the samples were removed from the water and *Q* was calculated by the equation: $Q = (m_2 - m_1) / m_1 \times 100\%$, where *m*₁ and *m*₂ are the weight of the initial and the films immersed in water, respectively. Contact angles were measured by the sessile drop method at 25 °C, using a JJC-I contact angle goniometer (Changchun Optical Instrument Company, China).

A TGA Q500 thermogravimeter (TA, America) was used to measure the weight loss of the UV-WPUA films with different CO content under an N₂ atmosphere. The sample was heated from 25 to 600 °C at a heating rate of 10 °C min⁻¹. Generally, 5–10 mg samples were used for the thermogravimetric analysis.

The DSC test was carried out by DSC-Q2000 (TA, America) and the temperature was heated from 25 to 150 °C at the heating rate of 10 °C min⁻¹. The dosage of sample was about 10 ± 0.2 mg.

The tensile strength and elongation at break of the films were measured on a multifunctional electronic TS 2000-S strength tester (Scientific and Technological Limited Company of High Iron in Taiwan), and the results reported were the mean values of three replicates.

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