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Synthesis of a novel UV crosslinking waterborne siloxane–polyurethane

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ABSTRACT

A novel UV crosslinking waterborne siloxane–polyurethane (UV-WPU) was synthesized using isophorone diisocyanate (IPDI), glycidyl azide polymer (GAP), polytetramethylene glycol (PTMG), dihydroxybutyl terminated polydimethylsiloxane (DHPDMS), dimethylol propionic acid (DMPA) as main materials. The structure of UV-WPU was verified using Fourier transform infrared spectroscopy (FTIR). Attenuated total reflectance (ATR) was used to study the UV crosslinking reaction kinetics of UV-WPU under UV irradiation. The properties of UV-WPU coatings by UV and thermal curing was comparatively analyzed by thermal gravimetric analysis (TGA), as well as gel fraction, water resistance and water contact measurements. The gel fraction and TGA analyses also confirmed the formation of crosslinking structure in the UV-WPU structure after UV curing process. UV-WPU cured by UV showed good thermal stability, surface properties and water resistance.

1. Introduction

Waterborne polyurethane (WPU) has some advantages such as non-toxic, no pollution to the environment, safe use compared with solvent based polyurethane [1]. WPU has been successfully used leather processing, coating and adhesive of textile, automobile, wood, building materials, paper, and become the main direction of the waterborne materials [2–4]. However, WPU shows some disadvantages such as poor water resistance, mechanical properties and surface performance because of its molecular structure containing a hydrophilic segment, which greatly limits its use in anti-corrosion, waterproof, anti oxidation and other fields. In order to improve the water resistance and surface hydrophobicity of waterborne polyurethane films, WPU is often modified by using polysiloxane. There are many papers about the preparation and properties of siloxane-modified waterborne polyurethane [5–10]. However, the siloxane-modified waterborne polyurethane showed poor mechanical properties because of the polysiloxane's bad mechanical properties. WPUs modified by the UV crosslinking method have been most extensively studied in recent years because of their versatility, environmental friendliness and excellent mechanical performance [11–14]. There are also some investigations on UV crosslinking waterborne siloxane–polyurethane [15–18]. Most UV crosslinking waterborne polyurethanes were prepared by using acrylates. However, these UV crosslinking waterborne polyurethanes based on acrylate have such major limitations as oxygen inhibition, unpleasant odor and toxicity originated from small molecule photoinitiators [3,19,20].

Azide group is well-known to easily photolyze upon UV irradiation to generate a highly reactive intermediate, nitrene, which can react with neighboring organic matter to form a covalent bond through C–H insertion or abstraction and/or C=C addition reaction [21]. Azides are effectively used as good UV crosslinking agents for polymer materials [22–24]. In these publications, it was found that the azide UV-photolysis process can be conducted at ambient temperature and even with higher reaction rate. It is a good UV crosslinking method using materials containing azide as UV crosslinking agents. Additionally, this method needs not any photoinitiators. Therefore, the incorporation of azide group into waterborne polyurethane is a potentially effective UV crosslinking technology that can overcome the above shortcomings of the UV acrylate-WPU.

In this work, a novel UV crosslinking waterborne siloxane–polyurethane was synthesized by using glycidyl azide polymer (GAP) as the crosslinking agent. The structure of the novel waterborne siloxane–polyurethane was confirmed by FTIR. The crosslinking reaction occurrence in the waterborne siloxane–polyurethane film dealt with UV lamp was testified by ATR and gel fraction measurement. The kinetics of the UV crosslinking reaction of the novel WPU was also investigated. In

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addition, the water contact angle, water absorption and TG of the UV crosslinking waterborne siloxane–polyurethane were also measured.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), Junsei Chemical Co. Ltd.; dimethylol propionic acid (DMPA), 1,4-butane diol (BDO), dibutyltindilautrate (DBTDL) triethylamine (TEA) and acetone (AC) were purchased from China Medicine, Shanghai Chemical Reagent Corporation. Dihydroxybutyl terminated polydimethylsiloxane (DHPDMS), Mn = 2000, C_{OH} = 60mg KOH/g, Dow Chemical Company; glycidyl azide polymer (GAP), Mn = 3380, C_{OH} = 36.17mg KOH/g, China Liming Chemical Institution; Polytetramethylene glycol (PTMG), Mn = 2000, C_{OH} = 60mg KOH/g, Daicel Chemical Industries were also received. DMPA, DHPDMS, GAP, PTMG and BDO were vacuum desiccated and IPDI was vacuum distilled before using. All the materials above mentioned were used without further purification unless otherwise specified.

2.2. Synthesis of UV crosslinking waterborne siloxane–polyurethane

IPDI (27 g), PTMG (10.8 g), GAP (22.7 g) and DHPDMS (17.5 g) were first introduced into a three-necked flask reactor fitted with a mechanical stirrer, a thermometer and a reflux condenser and reacted at 90 °C for 4 h under N_2 atmosphere. After the system temperature was dropped to room temperature, DMPA (4.6 g), BDO (4.3 g), DTBDL (0.1 g) and AC (20 g) successively were added and then reacted at 80 °C for 3 h until the NCO content reached the theoretical value. The measurement of NCO content was carried out according to the standard titration method (ASTM D1638). Furthermore, TEA (the same mole content as DMPA) was added and stirred for 20 min to neutralize the system. Then deionized water was added into the reaction system and high speed shearing (1500 rpm) was used to emulsify the solution. Finally, a UV crosslinking waterborne siloxane–polyurethane (UV-WPU) with a solid content of 20 wt% was obtained after removal of AC by a rotary evaporator under reduced pressure. The ratio of NCO and OH for the reactant was 1.2 in the reaction. The responding films of UV-WPU for FTIR and ATR analysis were obtained by standing at room temperature for 5d.

2.3. The WPU films obtained by thermal curing and UV curing

The thermal curing films of UV-WPU were obtained by coating UV-WPU onto glass piece or polyester cotton at 60 °C for 6 h. The UV curing films of UV-WPU were obtained as follows. UV-WPUs were coated onto glass piece or the polyester cotton was soaked in UV-WPU. Then the glass piece or the polyester cotton coated with UV-WPU was exposure directly at a distance of 5 cm using UV lamp (2000 W) for 120 s.

2.4. Measurements

Fourier transform infrared spectroscopy (FTIR) and ATR spectra were obtained on a Bruker Equinox 55 FTIR spectrometer in the 4 cm^{-1} resolution mode. Sixteen scans and ninety six scans were averaged for IR and ATR in the range of 4000–500 cm^{-1}, respectively. The UV-WPU film irradiated by UV was measured for FTIR by using KBr disk technique. The prepared UV-WPU film for ATR analysis was measured directly at intervals.

The thermal stability of UV-WPU films were carried out using a Shimadzu TGA-50H thermogravimetric analyzer from 30 °C to 600 °C at 10 °C/min heating rates with N_2 protection. The sample weights are 4–5 mg in all cases.

Water contact angle on the film was measured at 25 °C by the sessile-drop method using a contact angle goniometer (OCA20, Dataphysics Company, Germany). 5–10 μL distilled water was pumped from a microsyringe onto the surface of the films; the image was then captured using a telescope fitted with a video camera. All the results were expressed as the average value of at least five independent measurements.

The water absorption was determined as follows. The polyurethane films were cut into 3 cm × 3 cm pieces and dried in a vacuum oven for 24 h at 40 °C to determine their dry weight (W_d). Then the film was immersed in distilled water for 24 h at room temperature, followed by wiping off the surface water with a piece of filter paper to determine their weight (W_t). The water absorption (W%) was then calculated by the formula:

$$W(\%) = \frac{W_t - W_d}{W_d} \times 100$$

The gel fraction of UV-WPU films was evaluated by solvent extraction. The films were weighted (G_0) and repeatedly reflux extracted in tertrahydrofuran (THF) for 4 h by soxhlet extractor. The undissolved films were taken out, rinsed by tertrahydrofuran, and then dried in a vacuum oven for 24 h at 40 °C. The dried insoluble films were weighted (G_1). The gel fraction (G%) was then calculated by the formula:

$$G(\%) = \frac{G_1}{G_0} \times 100$$

3. Results and discussion

3.1. FTIR characterization

The FTIR spectrum of UV-WPU is shown in Fig. 1. In the spectrum of UV-WPU, the characteristic peaks of PU are observed. All typical absorption peaks of polyurethane such as those at 3330 cm^{-1} (NH stretching vibration), 1710 cm^{-1} (C=O stretching vibration) and 1108 cm^{-1} (C–O–C stretching vibration) for urethane are displayed clearly, showing the existence of urethane in synthesized UV-WPU. The absence of two peaks of NCO group (2270 cm^{-1}) and OH group (3470 cm^{-1}) in the spectrum confirmed that all

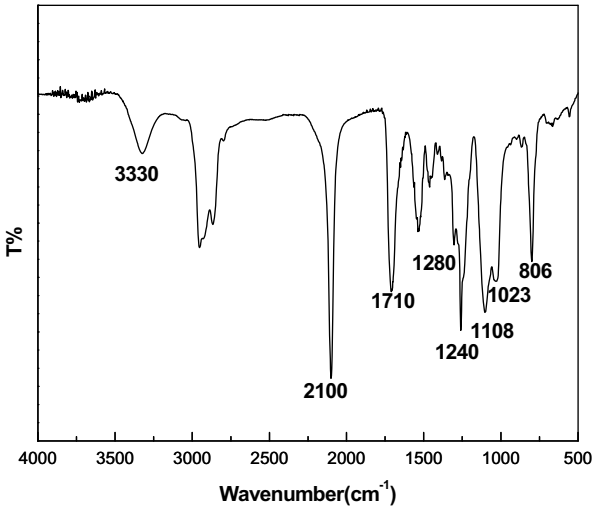

Fig. 1. FTIR spectrum of UV-WPU.