Progress in Organic Coatings 76 (2013) 1522–1526

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis and characterization of siloxane-modified two-component waterborne polyurethane

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ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form 15 April 2013
Accepted 4 June 2013
Available online 11 July 2013

Keywords:
Two-component waterborne polyurethane
Siloxane-modified
Surface properties
Thermal stability
Coating

ABSTRACT

A series of siloxane-modified two-component waterborne polyurethane (2K WPU) was synthesized by the reaction between siloxane-modified hydroxyl-functional polyurethane aqueous dispersion and the hydrophilic-modified polyisocyanate. The siloxane-modified 2K WPUs were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and surface contact angle measurement. The effect of DHPDMS content on the application properties (water and chemical resistance, flexibility, impact resistance, dry time, gloss, hardness and adhesion) of siloxane-modified 2K WPU coatings was also investigated. The results showed that the siloxane-modified 2K WPUs had better thermal stability owing to the forming of Si—O—Si crosslinking network and good surface properties due to the enrichment of siloxane chains on the surface of films compared with conventional 2K WPU. The application properties of the siloxane-modified 2K WPUs are satisfactory for their use in coatings.

1. Introduction

Polyurethane has attracted particular attention in some fields such as plastics, foams, elastomers, coatings, adhesives and sealants, because it is easy to control surface properties of toughness, flexibility, adhesion on substrate, antiabrasion resistance, etc. Waterborne polyurethane has advantages in environmental pollution, fire safety, and soil resistance compared with solvent based polyurethane [1]. Therefore, many researches have been done on waterborne polyurethane due to industrial demand according to intensifying environmental regulation [2–5]. Two-component waterborne polyurethane (2K WPU), which has a high crosslinking density and similar properties with solvent-based polyurethane, has attracted more interest in the world. Most study about 2K WPU was focused on synthesis of its components including water-dispersible hydroxyl-terminated resin [6–9] and polyisocyanate [10–16], preparation and forming mechanism of 2K WPU film [17–20]. But its application was limited because some weakness of 2K WPU such as poor water and chemical resistance compared with traditional solvent-based polyurethane. Moreover, the properties of 2K WPU have been still needed improvement.

Polysiloxane materials which have a lot of interesting properties such as low T_g, low surface energy, good biocompatibility, high thermal and oxidative stability, have been used to modify some properties of polyurethane materials. The siloxane-modified polyurethane obtained by incorporating siloxane units into the chain of polyurethane possesses the properties of polysiloxane and polyurethane. Especially, the siloxane-modified waterborne polyurethane has good water and chemical resistance. There are many papers about the preparation and properties of one-component siloxane-modified waterborne polyurethane [21–26]. But the investigation of siloxane-modified 2K WPU was seldom reported in the publications. Only a researcher described some work about siloxane-modified 2K WPU. Zhang prepared siloxane-modified 2K WPU using a siloxane-modified acrylic emulsion as the hydroxyl component and the results showed the hydroxyl value of the acrylic emulsion and amount of siloxane had an important effect on the properties of 2K WPU [27]. To the best of our knowledge, there is no information presented about the study of siloxane-modified 2K WPU prepared by using siloxane-modified hydroxyl-functional polyurethane aqueous dispersion.

In this work, a series of siloxane-modified 2K WPUs was synthesized by using a self-prepared siloxane-modified hydroxyl-functional polyurethane aqueous dispersion as the hydroxyl component and hydrophilic-modified polyisocyanate as the curing agent. The surface property, thermal stability, water and chemical resistance of the siloxane-modified 2K WPUs were also investigated. Additionally, the application properties (dry time, hardness, impact resistance, dry time, gloss, hardness and adhesion) of siloxane-modified 2K WPU coatings were also studied.

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http://dx.doi.org/10.1016/j.porgcoat.2013.06.007

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), Junsei Chemical Co. Ltd.; dimethylol propionic acid (DMPA), trimethylolpropane (TMP), 1,4-butane diol (BDO), dibutyltindilautrate (DBTDL) triethylamine (TEA) and acetone (AC) were purchased from China Medicine, Shanghai Chemical Reagent Corporation; dihydroxybutyl terminated polydimethylsiloxane (DHDHPDMS), M_n = 2000, C_{OH} = 60 mg KOH/g, Dow Chemical Company; polypropylene glycol (PPG), M_n = 2000, Daicel Chemical Industries, Ltd.; the hydrophilic-modified polyisocyanate was Bayhydur®XP2547 prepared by polyethylene glycol mono-methyl ether and hexamethylene diisocyanate(HDI) trimer, tetramer and other polymer (Bayer) – NCO content, 2.5 ± 0.5%. DMPA, DHPDMS, PPG, TMP 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 siloxane-modified hydroxyl-functional polyurethane aqueous dispersion

IPDI, PPG and DHPDMS were first introduced into a three-necked flask reactor fitted with a mechanical stirrer, a thermometer and a reflux condenser according to certain proportion and reacted at 90 °C for 4 h under N_2 atmosphere. After the system temperature was dropped to room temperature, DMPA, BDO, DTBDL, TMP and AC successively were added and then reacted at 80 °C for 2 h until the OH content reached the theoretical value. The measurement of OH content was carried out according to the standard titration method (ISO 4629). The change in the NCO value during the reaction was determined using the standard dibutylamine back-titration method (ASTM D1638). Furthermore, TEA (the same mole content as DMPA) was added and stirred for 30 min to neutralize the system. Then deionized water was added into the reaction system and high speed shearing (1150–1200 rpm) was used to emulsify the solution. Finally, a siloxane-modified hydroxyl-functional polyurethane aqueous dispersion (Si-HPUA) with a solid content of 35 wt% was obtained after removal of AC by a rotary evaporator under reduced pressure. A series of Si-HPUAs with different DHPDMS content was synthesized by regulating the feed ratio of DHPDMS (0%, 1%, 3%, 5%, 9% and 12%, mass percent) in the total amount of original materials with reducing PPG content. The samples were named as Si-HPUA-0, Si-HPUA-1, Si-HPUA-3, Si-HPUA-5, Si-HPUA-9 and Si-HPUA-12, respectively. The ratio of NCO and OH for the reactant was 0.8 in all reaction. Fig. 1 shows a schematic diagram for the synthesis of Si-HPUA.

2.3. Synthesis of siloxane-modified two-component waterborne polyurethane

The siloxane-modified hydroxyl-functional polyurethane aqueous dispersion weighted was added into a beaker, and Bayhydur®XP2547 with the calculated amount was also added to the beaker and stirred with high speed for 10 min. Finally, the product was dealt under vacuum condition in a vacuum dried oven until all the bubble of the product escaped. The formulated siloxane-modified 2K WPUs were casted onto clean glass panels at room temperature and dried at 60 °C for 48 h. The obtained thickness of the films was 100 μm, and then the properties of the siloxane-modified 2K WPU films were measured. A series of two-component waterborne polyurethane was prepared using Si-HPUAs with different DHPDMS content and Bayhydur®XP2547 at same —NCO/OH ratio.

2.4. Measurements

Infrared spectra were obtained on a Bruker Equinox 55 FTIR spectrometer in the 4 cm^{-1} resolution mode. Sixteen scans were averaged for each sample in the range of 4000–500 cm^{-1}. Each prepared Si-HPUA and 2K WPU film for infrared analysis was prepared by the coating of a thin film onto a NaCl window from 5 wt% AC solution, and then the solvent was removed by putting the sample in an oven at 50 °C and finally under vacuum.

The thermal stability of 2K WPU films was carried out using a Shimadzu TGA-50H thermogravimetric analyzer from room temperature to 700 °C at 10 °C/min heating rates with N_2 protection. The sample weights are 6–10 mg in all cases.

Water–air contact angle measurements were used as a measure of the hydrophilicity of the material surface. Water contact angle on the cast film was measured at 25 °C by the sessile-drop method using a contact angle goniometer (JC2000C1, Shanghai Zhongchen Digital Technical Equipment Ltd., China). 5–10 μL distilled water was pumped from a microsyringe onto the surface of the PU film, 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. Additionally, the contact angle of 2K WPU films with *n*-octane was also measured according to the same procedure as water–air contact angle measurements in order to calculate the surface tension of the 2K WPU films by the geometric-mean method.

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 50 °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 chemical resistance was evaluated by spot tests. The film was exposed to droplets of different test liquids for 24 h at room temperature in a closed box kept in equilibrium with the solvent vapor. The drops were then removed by wiping, and chemical resistance was visually determined by evaluating the change.

Other application properties of 2K WPU film coatings were measured as follows: the dry times were determined using an automatic drying time recorder on the glass panel (ASTM D711); the hardness was tested with a pencil having a different hardness on a glass panel (ASTM D2197); the gloss was read directly at 60° on the glass panel using a glossmeter (ISO 2813); the pendulum hardness was tested on a pendulum hardness tester (GB-T1730-1993); the adhesion was tested using the cross-hatch method at a distance of 1 mm on tinplate (ISO 2409); the flexibility was tested with a T-bend tester (ISO 1519); and impact resistance was measured with an impact tester on tinplate (ISO 6272).

3. Results and discussion

3.1. FTIR characterization

The FTIR spectra of Si-HPUA-5 and the siloxane-modified 2K WPU were prepared from Si-HPUA-5 and Bayhydur®XP2547 with [NCO]/[OH] = 1.4 are shown in Fig. 2. In the spectrum of Si-HPUA-5, the band at 3472 cm^{-1} attributes to the OH group stretching vibration; the absorption band at 1108 cm^{-1} originates from C—O—C group. There are characteristic peaks of N—H (3305 cm^{-1}) and C═O (1700–1730 cm^{-1}) in the spectrum of Si-HPUA-5. It can be seen from Fig. 2(A) that the asymmetric stretching vibration of NCO group at 2270 cm^{-1} disappears, which illustrates that there