



Synthesis of UV-curing waterborne polyurethane-acrylate coating and its photopolymerization kinetics using FT-IR and photo-DSC methods

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ABSTRACT

Environmentally friendly waterborne polyurethane-acrylate (WPUA) oligomers and ultraviolet curing WPUA films (UV-WPUA) were prepared. The thermal stability, solvent-resistance and mechanical properties of the films were investigated. FT-IR and photo-DSC methods were used to investigate the photopolymerization kinetics of the UV-WPUA films. The results showed that UV-curing films offered the optimum combination of properties when the polyether polyol (NJ-330), isophorone diisocyanate (IPDI), hydroxyethyl methyl acrylate (HEMA) and dimethylolbutanoic acid (DMBA) were used as the raw materials and the mass ratio of oligomer: monomer butyl acrylate (BA): photoinitiator was fixed at 66:30:4. Reaction kinetics of different photoinitiators systems were calculated by Kissinger equation and Crane equation, thus providing a theoretical guidance for the optimization of diluent and photoinitiator in UV-curing coating industry.

1. Introduction

Waterborne polyurethane coatings are an appealing choice on account of their lack of VOCs [1], flexibility, and durability [2], and high adhesive force [3]. As important green materials, UV-curing materials are advantageous compared to conventional thermosetting solvent resin due to its high efficiency [4], lower energy consumption, being environmentally friendly [5] and shorter curing film time [6]. UV-curing coatings have an edge on toughness, abrasion scrape and chemical resistance compared to traditional coatings because of its cross-linking structure and strong hydrogen bonding. Therefore, the physical or chemical performance of waterborne polyurethane was improved by UV-curing technique [7]. Acrylate is one of typical UV-curing matrix resins and acrylate coating possesses many advantages and of which the most distinct characteristic is its high reactivity. Generally, the mono or multifunctional acrylate monomer performs as a reactive diluent to regulate the viscosity. Furthermore, the resin performance could be improved with addition of acrylate monomers, thus meeting the demand for specific application.

UV-curing technology has been widely used in resins or adhesives. More importantly, the photopolymerization kinetics of the UV-curing systems are worth studying in industrial production and academic research [8]. Even so, few reports have been given about investigations of

the photopolymerization kinetics. Furthermore, it is of immense importance to investigate the effect of photoinitiators on the curing reaction and curing kinetics to take into practical application of UV-WPUA. Therefore, the accurate kinetics analysis could allow a quantitative analysis of the cure behaviors of different photoinitiators systems and be also of some significance in the design and control of the preparation techniques for polyurethane applications [9].

In this work, three kinds of waterborne polyurethane-acrylate prepolymers were prepared by using different molecular weight polyether polyols, isophorone diisocyanate (IPDI), hydroxyethyl methyl acrylate (HEMA) and dimethylolbutanoic acid (DMBA) as main raw materials. Furthermore, the physical properties including particle size, viscosity and surface tension of the prepolymers were studied. Series of UV-WPUA films were obtained by using oligomers, different photoinitiators and butyl acrylate (BA) content. The thermal stability, solvent-resistance and mechanical properties of the films were also investigated. Moreover, the photopolymerization kinetics were studied by FT-IR and photo-DSC methods, which provided a theoretical guidance for the optimization of UV-curing products.

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2. Experimental

2.1. Materials

The polyether polyol (NJ-210, NJ-220 and NJ-330, 99%) were provided by Ningwu Chemical Co., Ltd. Isophorone diisocyanate (IPDI, 99%) was industrial product from Rongrong Chemical Ltd. 2-hydroxyethyl methacrylate (HEMA, 99%) was obtained from Ruipu New Material Co., Ltd. The photo initiators (2-Hydroxy-2-methyl-phenyl-propane-1-one (Darocur 1173, 99%), 1-Hydroxycyclohexyl phenyl ketone (Darocur 184, 99%) and Benzil dimethyl ketal (Darocur 651, 99%) were provided from Mingda Macromolecule Science and Technology Co., Ltd. Dimethylolbutanoic acid (DMBA, 98%), *N*-methyl-2-pyrrolidone (NMP, 99.5%), ethanol (99%), butyl acrylate (BA, 99%), triethylamine (TEA, 99%) and dibutylbis (lauryloxy) tin (DBTL, 98%) were all purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Fabrication of WPUA oligomer

A stoichiometric amount of polyether polyol (NJ-210 or NJ-220 or NJ-330) was slowly added into a 500 mL four-necked round bottomed flask together with IPDI, which was equipped with an electric mechanical agitator, thermometer and condenser. Then, a few drops of DBTL as a catalyst was dropwise added into the mixture. After that, the mixture was allowed to react for 2 h at 60 °C with constant stirring to reach the theoretical –NCO content. Subsequently, a calculated amount of DMBA was dissolved into the NMP and DMBA solution was reacted with the prepolymer above for several hours at 80 °C until the reaction endpoint. Then, FT-IR spectra of mixture were collected to judge the –NCO content. If the characteristic absorption peak (–NCO) disappeared at 2275 cm⁻¹, it could be proved that –NCO content was zero [10]. After the above process, HEMA was added into the mixture for 5 h at 60 °C to prepare HEMA-capped polyurethane oligomer. After that, the carboxylic groups were neutralized with TEA for 30 min when polyurethane oligomer was cooled down to 40 °C. Finally, a suitable amount of the deionized water was dispersed into the polymer under the high-speed shearing for 30 min at 25 °C, and then WPUA oligomer was acquired. The basic recipes are given in Table 1.

2.3. Preparation of UV-WPUA coating films

The preparation of UV-WPUA coatings could be divided into two parts, including water flash-off process and UV-curing process. In the water flash-off process, the physical cross-linking caused by the strong intermolecular interaction and the hydrogen bond formation occurred when the emulsion converted into the film. In the UV-curing process, the chemical cross-linking in the polymer network structure occurred, caused by a radical polymerization reaction between activated photo initiators and acrylate double bonds.

UV-WPUA coating films could be fabricated by dumping as-prepared emulsion onto a circular poly (tetrafluoroethylene) vessel at ambient temperature until the coating surface almost did not flow (about 10 h). Then the circular poly (tetrafluoroethylene) vessel was transferred into a UV-curing instrument equipped with a medium pressure mercury lamp, of which had a main wavelength of 365 nm, UV energy of 1000 J/s. The vessel was placed at 15 cm distance from the

center of the mercury lamp, and the irradiating time was 30 s to excite free radicals. Therefore, UV-WPUA coating films with cross-linking structure could be achieved. The basic recipes are listed in Table 2. In addition, the total synthetic routes are shown in Fig. 1.

2.4. The properties of WPUA oligomer

WPUA oligomer was placed at –20 °C for 18 h and then was moved to 25 °C for 12 h. This cycle was repeated five times. The freeze thawing stability of all samples was evaluated by observing whether the sample was precipitated. WPUA oligomer was diluted until the solid content was 20 ± 0.2%, and then placed into a constant temperature oven (about 60 °C) for 72 h. Similarly, the temperature stability could be evaluated by observing the appearance changes. The surface tension measurement of WPUA oligomer was carried out on a DCAT 11 dynamic contact angle measuring device/tensiometer (DataPhysics Instruments, Germany) and the results was analyzed by the software SCAT31. The apparent viscosity of WPUA oligomer was measured by an NDJ-9S numerical viscometer (Shanghai Precision and Scientific Instrument Co., Ltd., China). The particle size and distribution were tested by a BI-9000 laser particle size analyzer (Brookhaven Instrument, USA). The measurements should be repeated at least three times on each sample and taken an average value.

A given mass of WPUA oligomer was put down a vessel and then transferred into an oven for 48 h at 120 °C. After that, the vessel was placed into a desiccator to cool down. It was weighed for several times until a constant weigh. The solid content (ω_1) of WPUA oligomer can be calculated by Eq. (1).

$$\omega_1 = \frac{W_2}{W_1} \times 100(\%) \quad (1)$$

where W_1 is the mass of WPUA oligomer and vessel before being placed in the oven and W_2 is the mass after being taken out from the oven.

2.5. The properties of UV-curing films

The chemical components of UV-WPUA films were characterized by an AVATAR 360 FT-IR spectrometer (Nicolet, USA). The hardness of UV-WPUA films was performed on a KYLX-A sclerometer (Jiangdu Kaiyuan Test Machine Co., Ltd., China) and the measurement was repeated at least three times to obtain the average value. Tensile strength and elongation at break of UV-WPUA films were tested by a KY-8000A tensile tester (Jiangdu Kaiyuan Test Machine Co., Ltd., China) at a speed of 50 mm/min at ambient temperature. A square film (3 cm × 3 cm, m_1) was put into deionized water or 3.0% HCl for 24 h at 25 °C. Then the film was taken out and the surface solution drops was carefully wiped with dust-free paper. Subsequently, the mass of the film was recorded again (m_2). The water absorption or swelling degree (ω_2) can be calculated by Eq. (2).

$$\omega_2 = \frac{m_2 - m_1}{m_1} \times 100(\%) \quad (2)$$

where m_1 and m_2 are the mass of UV-WPUA films before and after soaked in the solution, respectively.

The square film (2 cm × 2 cm) was soaked into toluene for 48 h and dried at 30 °C to obtain gel content (G). G can be calculated by Eq. (3).

Table 1
The basic recipes of WPUA oligomers.

Sample	Polyether polyol (g)			IPDI (g)	DMBA (g)	HEMA (g)	TEA (g)	NMP (g)	Deionized water (g)
	NJ-210	NJ-220	NJ-330						
WPUA-210	13.74	0	0	10.00	1.52	5.85	1.03	10	75
WPUA-220	0	19.54	0	10.00	1.88	5.85	1.29	10	90
WPUA-330	0	0	19.54	10.00	1.88	5.85	1.29	10	90

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