

Waterborne UV Curable Polyurethane Dispersions

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Abstract

Two high molecular weight polyurethane dispersions (PUDs) were synthesized by two step reactions. The chemical structure, the photopolymerization characteristics and properties of the cured films were studied by FTIR and standard methods, the results indicated that the PUDs is tack free before UV curing, the properties of the UV cured films are very good, and make them have the potential application in various fields.

Key Words: polyurethane dispersions, UV curing, FTIR, water resistance

Introduction

Due to the demands of environmental regulations against volatile organic chemicals (VOCs) and versatile structure-property relationships of polyurethane (PU), polyurethane dispersions (PUDs) have gained rapid development in coatings, adhesives, textile, etc^[1-3]. PUDs can be UV curable to give so called UV-PUDs which benefits from the advantages of solvent free 100% UV cure formulation. This system has drawn a growing attention by the market recognizing for the high-end performance and strong potential over the last few years^[4-6]. However, the conventional method of preparing UV-PUDs is by capping the polyurethane with single-hydroxyl acrylate^[7-10] or introducing the double bond with hydroxyl terminated polybutadiene[11] or introducing the vinyl groups into the polyurethane chains[12]. The obtained resins couldn't possess high C=C content and high molecular weight at the same time. Therefore, the films are soft, flexible, cannot provide excellent solvent resistance and mechanical properties^[7,13,14].

In this work, we introduced the acrylate groups into the side chain of the polyurethane using epoxy acrylate which contains isocyanate-reactive hydroxyl group and UV-polymerizable C=C double bond. Instead of terminating the polyurethane with the single-hydroxyl acrylate, amine was used as a chain extension agent to increase the molecular weights. As a result, the content of C=C bond and the molecular weight are both high. Therefore, the cured films exhibited excellent solvent resistance and mechanical properties. In addition, high molecular weight of prepolymer also made the films tack-free before cure which allows flooring and rolling operations.

Experimental

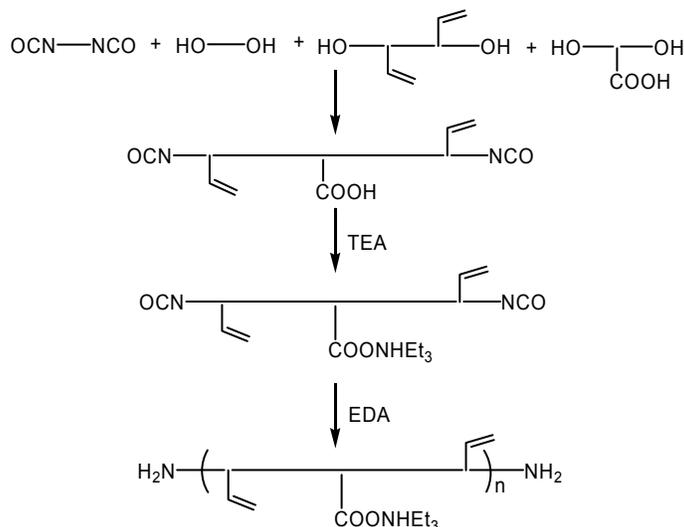
Materials

The following main raw materials were used as received: epoxy acrylate (Sanmu Co.), isophorone diisocyanate (IPDI; Bayer Co.), polyether (Sanmu Co.), dimethylolpropionic acid (DMPA; Perstorp Co.), Irgacure 2959(Ciba Co.), triethylamine (TEA; Tosoh Co.), ethylene diamine, (EDA; Tosoh Co.) etc.

Preparation of polymer

The UV curable waterborne polyurethane dispersions (UV-PUDs) was prepared according to scheme 1: In a 500 mL roundbottom, four-necked separable flask, equipped with a mechanical stirrer, a thermometer, and a condenser with drying tube , IPDI, polyether, epoxy acrylate, DMPA and MEHQ were first added into the reactor with suitable mole ratio. Then the reaction was carried out in a constant temperature oil bath, the prepolymerization of polyurethane was carried out at 80°C for 3h. NCO-terminated prepolymer 1 was synthesized. In order to dilute the prepolymer 1, suitable amount of acetone was added. Then the prepolymers were cooled, and the neutralizing agent was added and stirred for 0.5h.

Dispersion of UV-PUDs was accomplished by adding the mixture of water and ethylene diamine to prepolymer 1 over a period of 20 min under vigorous stirring. And chain extension was continued until NCO peak (2270 cm^{-1}) in the IR spectrum had completely disappeared. All the polyurethane dispersions (40% solid content) were obtained by evaporating acetone and the subsequent addition of an adequate amount of water.



Scheme 1 The synthesis process of the UV-PUDs

Preparation of films

Films were prepared by casting the dispersion onto a Teflon plate at room temperature, followed by drying at 50°C for 5 min. After demolding, the films were stored in a desiccator at room temperature for further studies. Samples were irradiated from one side using an 80W-UV(356 nm) lamp for 1min at room temperature.

Measurements

The viscosity of UV-PUDs was measured with QND-4C at the temperature of 25°C. The molecular weight of UV-PUDs was obtained by GPC (Waters-24).

Water resistance was measured by immersing the films in distilled water to determine the water swell. Water swell was measured by emerging a film into water at room temperature for 300h and swell ratio (%) was calculated by the following equation:

$$\%_{\text{swell}} = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

Where W_0 is the weight of dried film and W is weight after water absorption.

The flexibility was measured according to the Chinese National Standard GB/T1731-1993. The smaller the number was, the better the flexibility was. When the number was 1 mm, the flexibility was the best.

Solvent resistance to methyl ethyl ketone (MEK) was determined by brushing the films with MEK. Fourier transform infrared spectra (FTIR) were obtained on a Nicolet 5700 instrument (Thermo Electron Corporation, Madison, WI, USA). Series RTIR was used to determine the conversion of double bonds. The mixture of dispersions and initiator was casted onto KBr pellets. UV photopolymerization was carried out at room temperature with a 300-500nm spot light source and the light intensity was 30mW/cm² (Honle UV meter, Germany). Real time FTIR were collected with resolution 4cm⁻¹ and 0.3985 second sampling interval. The absorbance change of the =C-H peak area from 796 to 817 cm⁻¹ was correlated to the extent of polymerization. For each sample, the series RTIR runs were repeated three times.

Results and discussion

Properties of UV-PUDs

Table1 Properties of UV-PUDs

Dispersion	Viscosity(s-1)	PH	Mn
UV-PADs_1	16	7.8	97273
UV-PADs_2	14	7.8	17911

The characteristics of the UV-PUDs were shown in Table1. It could be seen that the molecular weight of the prepolymer was very high and the film of prepolymer was tack-free before UV curing which allows good sandability and stackability. The viscosity of dispersion was very low. In addition, in order to study the storage stability, acceleration test had been preceded, the dispersions were reserving at 50°C for 1 month. The results showed that the dispersions were still homogeneous and had no deposits or oily floaters after the test.

FT-IR analysis of UV-PUDs

The structure of the UV-PUDs was confirmed by FTIR spectroscopy and as an example for UV-PUDs_1 sample was shown in Fig1. The spectrum showed that the absorption peaks of typical polyurethane at 3330-3360 cm^{-1} (NH, hydrogen bond), 2855-2955 cm^{-1} (CH₂ and CH₃), 1722 cm^{-1} (C=O), respectively.

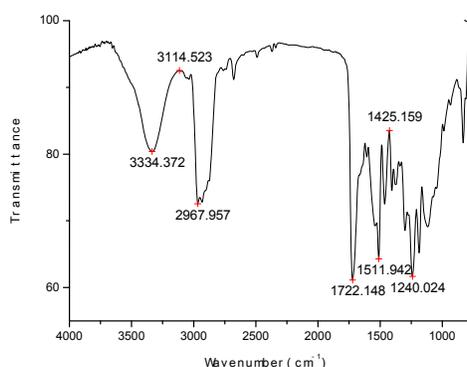


Fig. 1 FTIR spectroscopy of UV-PUDs_1 sample

UV curing kinetics

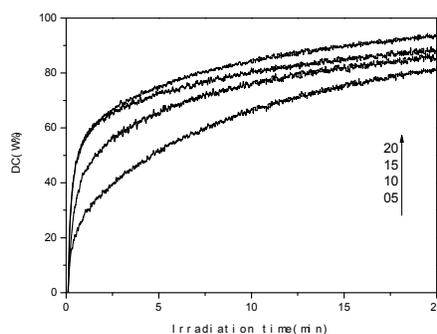


Fig. 2 Effect of concentration of 2959 on the photopolymerization of UV-PUDs_1

The properties of UV-PUDs strongly depend on the final C=C conversion achieved after UV irradiation. In this study, 2959 was chosen to study the effect of concentration of initiator on the photopolymerization of UV-PUDs. As shown in Fig.2, When the concentration of 2959 increased from

0.5% to 2.0%, the final double bond conversion increased from 70% to 90% (UV-PUDs_1). However, the sample of the UV-PUDs films were very thin and not protected by nitrogen, oxygen inhibit was noticeable, therefore, the rate of photopolymerization was slow.

Properties of UV-cured coatings

Table 2 showed some physical properties of the UV-PUDs films. It can be seen that the uncured films exhibited excellent adhesion and flexibility. When the films were cured with UV light, the films became harder and better MEK resistant. Therefore, these UV-PUDs should be useful for various applications in which excellent overall properties are required, such as wood lacquers and plastic coatings.

Table 2 Properties of UV-cured coatings

	Hardness		Flexibility (mm)		Adhesion to PVC (grade)		MEK resistant (times)	
	Before UV cured	After UV cured	Before UV cured	After UV cured	Before UV cured	After UV cured	Before UV cured	After UV cured
UV-PUDs_1	HB	3H	1	1	1	1	120	200
UV-PUDs_2	HB	3H	1	1	1	1	80	180

Water absorption of UV-PUDs

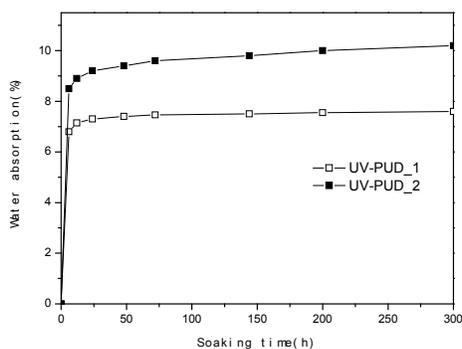


Fig.3 Water absorption of UV-PUDs

Fig.3 showed the relationship between the water absorption and the soaking time. UV-PUDs_1 shows better water absorption than UV-PUDs_2. This was ascribed to the higher molecular weight of UV-PUDs_1.

Conclusions

Two novel waterborne UV curable polyurethane dispersions were synthesized. The content of C=C bond and the molecular weight are both high. High molecular weight of dispersion made the films tack-free before cure. When the films were cured with UV light, the films showed excellent properties and make them have potential applications in various fields.

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