

Short communication

Water resistance of the membranes for UV curable waterborne polyurethane dispersions

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Abstract

The water absorption of the membranes made from UV curable waterborne polyurethane dispersions (UV-PUDs) was investigated systematically and correlated with the nature of the polymer and its gel content after curing. It was found that the water absorption of the membranes was reduced significantly by using polyester polyols, reducing the COOH content and increasing the gel content through a higher C=C level. In particular, the membranes made from polyurethanes having hydroxyl-terminated polybutadiene (HTPB) or modified with dihydroxybutyl-terminated polydimethylsiloxane (PDMS) presented a superior water resistance. The results showed a linear relationship between the water absorption and the surface tension of the membrane.

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1. Introduction

In recent years, significant emphasis has been placed on the use of waterborne coating systems such as ultraviolet (UV) curable waterborne polyurethane dispersions (PUDs) due to their rapid curing features and environmental safety [1–5]. These environmental friendly products are used to reduce the volatile organic compounds (VOC) released to the atmosphere by solvent-borne systems and are expected to exhibit the same performance as that of conventional solvent-borne systems. Polyurethane dispersions can be tailored to various applications by varying the preparation method and chemical structures of the polyurethane. Typically the UV curable waterborne PUD UV-PUDs is formed by incorporating the groups into polyurethane chains, and a polyol having hydrophilic group is used to incorporate carboxylic functionality into the prepolymer backbone [6,7]. The prepolymer is then dispersed in water using a tertiary amine to ionic centers, thus stabilizing the polymer particles. Because of their fast curing features and environmental friendliness, UV-PUDs are now one of the most

rapidly developing and active branches of PU chemistry and technology.

However, many of the patents [8] and journal articles [9] on UV-PUDs in the literature appear to focus almost exclusively on the application of these interesting systems. There are relatively little reported systematic studies on UV-PUDs to generate basic data aimed at providing fundamental insights into the relationships among the polymer structure, water resistance and coating performance under conditions that the UV-PUDs are likely to encounter during use. By systematically varying the COOH weight content, polyhydric alcohol species and the gel content, our long-rang research will shed light on how to control the water resistance of the UV-PUDs membranes. It is hoped that the present study will provide a quantitative and qualitative experimental basis for any future theory development of the relatively new UV-PUDs and the prediction of their water resistance.

Many PUDs including UV curable and non-UV curable systems are known to exhibit poor water resistance. Water resistance of PUDs is of both practical importance and theoretical interest. Therefore it is essential to understand the influencing factor of the water resistance of the PUDs membranes so that they can be prepared and used in a controlled reproducible manner. In this article we explore the UV-PUDs systems as functions of COOH weight content, polyhydric alcohol species and the gel

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content. It is expected that the water resistance of UV-PUDs can be controlled by changing the experimental parameters used here, providing a fundamental basis for optimizing their applications.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co. Ltd.) was vacuum distilled before use. Polycarbonic acid ester glycol (PCD1000, $M_n = 1000$), polycaprolactone glycol (PCL1000, $M_n = 1000$; PCL2000, $M_n = 2000$), polytetramethylene glycol (PTMG1000, $M_n = 1000$; PTMG2000, $M_n = 2000$), and poly(propylene glycol) (PPG1000, $M_n = 1000$) were all from Daicel Chemical Industries, Ltd. and were desiccated at 110 °C before use. Hydroxyl-terminated polybutadiene (HTPB, $M_n = 1200$, Qilong reagent, zibo Co. China) were desiccated at 80 °C under vacuum pressure before use. Dihydroxybutyl-terminated polydimethylsiloxane (PDMS, $C_{OH} = 60$ mgKOH/g, Dow Chemical Co.) were desiccated at 110 °C before use. Pentaerythritol triacrylate (PETA, Aldrich Chemical Co.) was dissociated by chromatographic column using benzene as solvent. Dimethylpropionic acid (DMPA, Aldrich Chemical Co.), trimethylolpropane monoethylene ether (TMPME, Perstorp Polyols, Inc.) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Darocur2959, Ciba Geigy Co.) were all used as received. Triethyl amine (TEA,) and dibutyltin dilaurate (DBT, as catalyst) were used as received from Shanghai Reagent Co. China.

2.2. Synthesis of UV-PUDs

In this work we give two preparation methods for UV-PUDs, one is the conventional preparation method, incorporating the C=C bond into the end of the polyurethane [6], and the synthesis process was showed in the Fig. 1(a); the other method is introducing the C=C bond into the side and the end of the polyurethane, which is a new method to raise the C=C content [10], and the synthesis process was shown in Fig. 1(b). And the detailed preparation process for the new method was as follows:

First the polyol, IPDI and DMPA were added into the reactor according to a suitable mole ratio. The polymerization was carried out at a certain temperature until the NCO content reached the theoretical value. The content of NCO was determined by the standard dibutylamine titration method. In order to dilute the prepolymer, suitable amount of acetone was added. Then dihydric alcohol monomer TMPME containing C=C bond was added into the reactor to react at a certain temperature in N_2 atmosphere until the NCO content reached the theoretical value and at the same time suitable inhibitor was added. At last, single-hydroxyl acrylate monomer PETA was added to terminate the polyurethane until the NCO groups were reacted completely. As neutralization agent, TEA was added into the reaction mixture to react with carboxylic group in the side chain of polymer. The stoichiometric proportion of reaction between TEA and

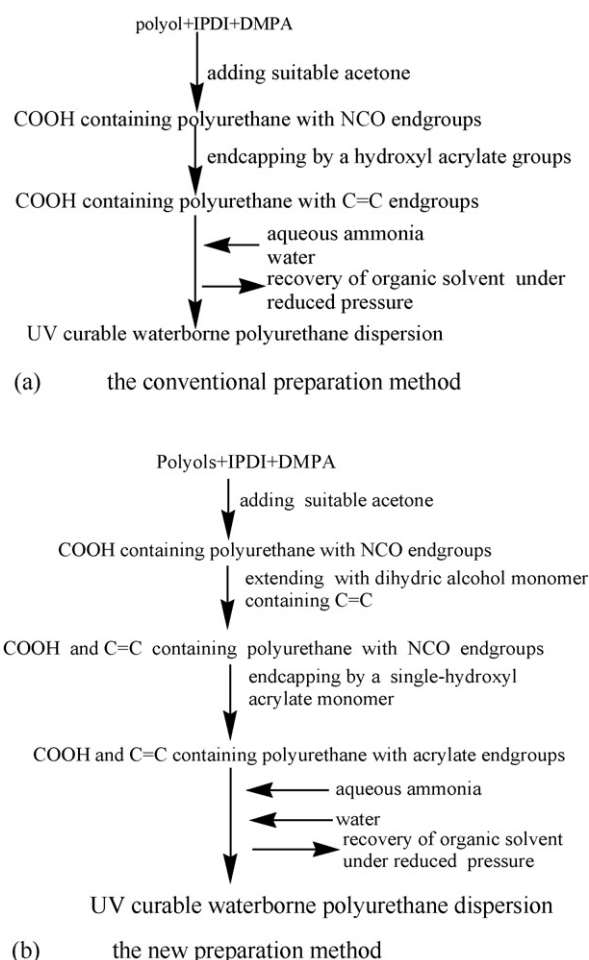


Fig. 1. Synthesis routes of UV-PUD of the conventional method and the new method.

DMPA was 1.1:1. Finally high speed shearing (1200 r/min) was used to emulsify the solution after suitable deionized water was added into the reaction system. Then UV-PUD was obtained after removal of the acetone from the emulsion by rotary vacuum evaporation at 45 °C.

2.3. Preparation of UV-PUD membranes

The UV-PUD membranes were formed by casting the formulated dispersions with suitable photo-initiator Darocur 2959 based on the resins onto a glass plate at room temperature and then followed by drying the membrane at 60 °C until reaching a constant weight then by radiated under medium pressure mercury lamp (the UV dose was 125 mw/cm^2). The thickness of the membranes was 60 μm .

2.4. Measurement of water resistance

The water resistance of the membranes was characterized by the water absorption of the membranes. The procedures were described as follows: the UV-PUD membranes were cut into 3 cm \times 1 cm and dried in a vacuum oven for 24 h to determine their dry weight (W_d). Water absorption was measured by

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