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Preparation and characterization of a novel low gloss waterborne polyurethane resin

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ABSTRACT

A novel waterborne polyurethane (WPU) resin with low gloss and micro-roughness was synthesized by the prepolymer and self-emulsification method. It was achieved by introducing multi-hydroxyl castor oil and reactive bisphenol A-type epoxy E-44 or E-51 resin to polyurethane prepolymer to form a cross-linking network structural waterborne polyurethane emulsion, which demonstrated the distinctive characteristic of the shear-thinning pseudoplastic fluid with a yield stress. The chemical structures and rough surface morphologies of the WPU films were characterized by FTIR-ATR, LCRS, AFM, SPMS and SEM, respectively. The specular gloss values at 20°, 60° and 85° incident angles were measured, and the values of different kinds of roughness parameters were obtained. The relationship between the gloss and the castor oil content was also discussed in detail. In general, this WPU resin endowed the film with micro-roughness, moderate hardness and good adhesive strength, making it very prospective in substitution for the traditional low gloss coatings.

1. Introduction

It is a truth universally acknowledged that waterborne polyurethane or aqueous polyurethane, or water-based polyurethane is composed of soft segments and hard segments, and both segments have extensive material resources [1,2]. So, it is quite easy to design the molecular structure of waterborne polyurethane through changing the type and content of the soft and hard segments. Currently, waterborne polyurethane has been widely used in many occasions due to the good impact resistance, chemical resistance, heat resistance, mechanical strength and processability as well as the beautiful appearance characteristic [3–7]. Compared with oil-based polyurethane resin, Waterborne polyurethane also emits less volatile organic compounds (VOC), which makes it very suitable for use as coating in various fields, such as parts of automobiles, housings of electrical or electronic appliances, wood or leather surfaces, and the like [8–10]. However, most of waterborne polyurethane resins show the typical characteristics of high glossy and plastic feeling after film formation [11–13]. With the change of people's aesthetic perception, there is an increased demand for waterborne polyurethane resin having the characteristics of both low gloss and soft-touch feeling [14].

In previous studies, a great deal of effort has been devoted to developing techniques in preparation of low gloss coatings. Adding a certain amount of matting agent into the bulk resin, such as silicon-containing compounds and polymers [15,16] (e.g. silica, silicate, silane, wax treated silica) and fillers (e.g. diatomaceous earth, clays, zeolites), is the most common method over the past few decades [17,18]. However, in order to avoid the precipitation problem caused by incompatibility between the resin and the matting agent, the selection of suitable matting agent for different kinds of bulk resins is of great importance [19]. Post-treatment on coating surfaces, such as etching or polishing, is another traditional method to create a low gloss surface [20,21]. However, it is very time-consuming and costly. One of the new developed approaches to create a micro-rough surface for matting application employs a two-step UV curing process of photosensitive mixtures [22–24]. The first dosage of UV radiation is only sufficient to cure the surface layer of the coating and to cause a surface wrinkling. The second dosage of UV radiation is at higher energy than the first and is sufficient to cure the coating throughout [25,26]. However, the complicated physical process, the demand for specially designed equipment and the limitation on photosensitive monomers hinder the wide application in coatings. D. Chandra et al. [27] demonstrated a novel mechanism of self-wrinkling in UV-cured polymer films through the use of UV-light and oxygen simultaneously. Marta Palacios-Cuesta et al. [28] reported a versatile approach for the fabrication of functional wrinkled polymer surfaces through the simultaneous heating and

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irradiation with UV light of a photosensitive monomer solution confined between two substrates. And then, J. Ou et al. [29] provided an acrylic-polyurethane hybrid emulsion in extinction electrophoresis based on the phase separation within the resin. However, these techniques are exceedingly complex, which makes them difficult to be applied for mass industrial production. Based on above considerations, we initially prepared a novel bulk-matte waterborne polyurethane resin [30]. A great number of micron-level emulsion particles were aggregated on the film surface, leading to a micro-rough surface morphology for matting purpose. However, the large emulsion particles would result in the precipitation problem, and the process of synthesizing large emulsion particles is difficult to control.

In this study, we developed a novel waterborne polyurethane (WPU) resin with low gloss and micro-roughness, which was achieved by introducing the multi-hydroxyl castor oil and reactive bisphenol A-type epoxy E-44 or E-51 resin to the polyurethane prepolymer. The resultant WPU resin showed a distinctive characteristic of shear-thinning pseudoplastic fluid having a yield stress, which can make the WPU resin form a micro-rough surface after film formation. The surface morphology, rheological behavior, surface roughness and chemical structure of the low gloss WPU resin were characterized by scanning electron microscopy (SEM), surface profile measurement station (SPMS), advanced rotational rheometer (ARR), atomic force microscopy (AFM), Fourier-transform infrared attenuated total reflectance spectrometer (FTIR-ATR) and laser confocal Raman spectroscopy (LCRS), respectively. Moreover, the effect of the different incident light angles on the specular gloss, and the relationship between the castor oil content and the specular gloss were discussed.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, 99%), dimethylol propionic acid (DMPA, 98%), triethyl amine (TEA, ≥ 99.5%), ethylene diamine (EDA, ≥ 99.5%), dibutyltin dilaurate (DBTDL, 95%) and castor oil (Chemical pure, hydroxyl value = 175–185 mg KOH g^{-1}) were purchased from Shanghai Aladdin Reagent Co., China. Polypropylene glycol (PPG, Chemical pure, M_n = 2000 g mol^{-1}, Shanghai Energy Chemical Co., China) was dried at 60 °C in a vacuum oven for 5 h before use. Bisphenol A-type epoxy E-44 resin and bisphenol A-type epoxy E-51 resin (Chemical pure, epoxy value = 0.44 and 0.51, respectively) were purchased from Star Chemical New Material Co., China. All these reagents were of analytical grade and were used as received if not specially stated.

2.2. Synthesis of self-rough WPU with low gloss

PPG in combination with castor oil was first added into a vessel and oil-bathed for 30 min at 80 °C. Prepolymerization was carried out at 80–90 °C by adding IPDI under nitrogen atmosphere for 2 h in the presence of DBTDL as the catalyst. Afterwards, DMPA either without or containing bisphenol A-type epoxy resin dissolved in acetone solution was added to the reactor. The reaction lasted for 3 h under the loop of nitrogen. TEA was added to neutralize the carboxylic groups of the DMPA at 45 °C for 30 min. Finally, the resulted prepolymer was dropwise added into a new vessel filled with EDA and a great amount of deionized water under vigorous stirring. This manipulated step was key to obtain the stabled WPU resin, as it could avoid gelation and coagulation compared to the traditional dispersive method. The stoichiometric ratio of IPDI/PPG/DMPA/TEA/EDA was 3.95:1:1.43:1.43:1.35. Film-forming emulsions were rolled onto a 10 × 10 cm Teflon plate, followed by drying in an oven at 40 °C for 24 h and 60 °C for 48 h [31]. After that, films were peeled off from the Teflon plate and stored in a closed desiccator (Table 1).

Table 1
Designations of WPU resin with low gloss and micro-roughness.

Designation	Castor oil (wt%)	E-44 (wt%)	E-51 (wt%)
WPU1	3.44	9.23	0
WPU2	3.44	0	0
WPU3	3.44	0	7.96

2.3. Characterization

2.3.1. AFM

3D-AFM measurements were carried out at room temperature using a Bruker Multimode 8-HR atomic force microscope with 125 × 125 μm scan size and 10 μm vertical range. All images were obtained under ScanAsyst® mode with a pixel resolution of 512 × 512. The resulted images were further analyzed with NanoScope Analysis 1.8 software. The surface roughness parameters, including the arithmetic average height S_a, root mean square height S_q, maximum peak height S_p, maximum valley height S_v, and the maximum height S_z were obtained. S_a is the Average Roughness evaluated over the complete 3D surface: [32]

$$S_a = \iint_a |Z(x,y)|\, d(x)dy$$

S_q is the Root Mean Square roughness evaluated over the complete 3D surface:

$$S_q = \iint_a (Z(x,y))^2 d(x)dy$$

S_p, the Maximum Peak Height, is the height of the highest point.
S_v, the Maximum Valley Depth, is the depth of the lowest point.
S_z, the Maximum Height of the Surface; $S_z = S_p - S_v$.

2.3.2. SEM

Film morphologies were captured using a Hitachi S-3400N scanning electron microscopy at ambient temperature in vacuum. The accelerating voltage was 15 kV. Prior to the SEM analysis the dried films were stained on a copper with conductive adhesive tape and then were sprayed with a thin layer of gold powder.

2.3.3. SPMS

The configuration includes a precise measurement stand with granite bridge, translation XY-stages, a confocal chromatic sensor and a system controller. The lateral resolution is better than 1 μm and vertical resolution is approximately 1 nm. The images were obtained at 5 × 5 mm areas with an array of 751 × 751 measured heights.

2.3.4. ARR

Rheological properties were performed on an ARES-G2 rheometer (TA-Instruments, USA) using parallel-plate geometry with two different measuring procedures: steady-state shear and dynamic-state frequency sweep at 25 °C.

2.3.5. FTIR-ATR

FTIR-ATR measurements were carried out on a Bruker Tensor 27 FTIR spectrometer with an ATR sampling accessory under N2 purging. Each sample was scanned 16 times over the frequency range of 4000–600 cm^{-1}.

2.3.6. LCRS

Raman spectra were acquired using a HORIBA LabRAM HR800 Laser confocal Raman spectrometer equipped with a 532-nm laser with a spot size of 2.0 μm. Each spectrum was collected at room temperature by scanning a sample 10 times at 10 s intervals. The frequency range was 4000–100 cm^{-1}.