



# Preparation and characterization of low gloss aqueous coating via forming self-roughed surface based on waterborne polyurethane acrylate hybrid emulsion

Qiwen Yong<sup>a,b</sup>, Hao Pang<sup>a,\*</sup>, Bing Liao<sup>c</sup>, Wenwei Mo<sup>a,b</sup>, Furen Huang<sup>a,b</sup>, Hao Huang<sup>a,b</sup>, Yangyang Zhao<sup>a,b</sup>

<sup>a</sup> Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China

<sup>b</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> Guangdong Academy of Sciences, Guangzhou 510070, China

## ARTICLE INFO

### Keywords:

Waterborne polyurethane acrylate  
Low gloss effect  
Self-roughed surface  
Hybrid emulsion  
Phase separation  
Film  
Aqueous coating

## ABSTRACT

A series of low gloss waterborne polyurethane acrylate (WPUA) hybrid emulsions with different weight ratios of hard/soft monomers of acrylic monomers were synthesized successfully. Compared with the traditional low gloss coatings that achieve low gloss effects by adding a large number of pigments, fillers or both to roughen the surfaces, the low gloss effect of these WPUA emulsions was achieved through the formation of self-roughed surfaces during film formation with zero loading of extraneous dulling agent. Gloss levels could be as low as 3 units at 60° incident angle. The chemical structures of these WPUA films were characterized by nuclear magnetic resonance carbon spectroscopy (<sup>13</sup>C NMR), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The rough surface topographies of these WPUA films were observed by scanning electron microscopy (SEM). The particle size distributions of these WPUA emulsions were analyzed by DLS measurement. The polymeric phase separation behaviors of these WPUA films were assessed by DSC analysis. In general, the WPUA emulsions that afforded films with good hardness, good adhesion strengths and excellent thermal stabilities, showed a great advantage in applications of low gloss aqueous coating.

## 1. Introduction

In the modern age, even though the high gloss coatings have dominated the coating market all the time, there are a few applications where the low gloss coatings are required for functional or decorative purposes because they are aesthetically preferred. Such as some interior parts of automobiles, housings of electrical/electronic appliances, wood and furniture surfaces, and the like [1–5]. Low gloss coatings are specified for many reasons: the reduced glare of surfaces in schools and hospitals offers less chance of visual distraction and concentration is better in such environments; low gloss coatings are preferred to hide small scratches and imperfections compared to the high gloss coatings; and matt coatings have become more and more fashionable with architects and designers [6,7].

There are several approaches to prepare a low gloss coating. Post process on the coating surfaces with a powdered abrasive or sandpaper is the most ancient method to obtain a low gloss surface. This method is time consuming and inconvenient [8,9]. During the past decade, low gloss is often provided by adding a great number of pigments, fillers or

both in the coating formulation to roughen and therefore reduce surface gloss. Silicon-containing compounds and polymers such as silica, silicate, silane, and wax treated silica are widely used. Fillers such as diatomaceous earth, clays, zeolites and the like are also known to reduce gloss in coatings [10–14]. With addition of these extra additives, the incompatibility between the additives and bulk resins may easily cause brittle, powdery, or many-seeded appearance of coating surfaces [15]. One of the most recently described approaches to create a micro-texture on the coating surface for matting application employs a two-step UV curing process of photosensitive mixtures [16–21]. The first dosage of UV radiation is sufficient to cure the top layer of the coating and to cause a surface wrinkling. The second dosage of UV radiation is at greater energy than the first and is sufficient to completely cure the coating throughout [22,23]. However, the complicated multi-stepped photo curing process and demand for specific photosensitive mixtures limit their extensive application. Therefore, it is of great interest to develop a simple and low-cost method to prepare a low gloss coating.

Combined with the above methods, we can draw a conclusion: In order to achieve a low gloss effect of the film, a rough surface must be

\* Corresponding author.

E-mail address: [panghao@gic.ac.cn](mailto:panghao@gic.ac.cn) (H. Pang).

produced in some way. The common waterborne dispersed polymer latexes are always flat and high glossy after film formation. The fabrication of a low gloss film with rough surface from waterborne polymer latexes is very challenging. This work presents a straightforward approach to produce a low gloss coating by the formation of self-roughed surface during film formation based on the waterborne polyurethane acrylate (WPUA) hybrid emulsion. The low gloss effect of the WPUA film was self-generated by emulsion itself without the addition of any pigments, fillers or both. Also, through varying the weight ratio of hard/soft monomers of acrylic monomers, the rough degrees of the film surfaces could be finely tuned, which made it possible to meet the demands for different glossy coatings. In general, the resulted WPUA emulsions that afforded films with good hardness, good adhesion strengths and excellent thermal stabilities, showed a great advantage in applications of low gloss aqueous coating.

## 2. Experimental

### 2.1. Materials

Methyl methacrylate (MMA, 98%), styrene (ST, 99%), 2-ethylhexyl acrylate (2-EHA, 99%), butyl acrylate (BA, 99%), vinyl sulfonate (SVS, 99%), emulsifier OP-10, potassium persulfate (KPS, 99.99%), isophorone diisocyanate (IPDI, 99%), polytetramethylene ether glycol (PTMEG,  $M_n = 1000 \text{ g mol}^{-1}$ ), dibutyltin dilaurate (DBTDL), dimethylolpropionic acid (DMPA, 98%), hydroxypropyl acrylate (HPA, 80%), triethylamine (TEA, 99%). All these reagents are commercial agents and used as received. Deionized water is used for all the polymerization and treatment processes.

### 2.2. Preparation of waterborne polyurethane dispersion

Synthesis of waterborne polyurethane (WPU) dispersion was carried out in a 500 ml round-bottom flask equipped with a mechanical stirrer, a thermometer, a condenser with a drying tube and an inlet for high pure  $\text{N}_2$ . 100 mmol of IPDI and 40 mmol of PTMEG in the presence of catalyst DBTDL (0.05 wt% based on total solids) were added to the flask and maintained at 60 °C for 2 h with a constant stirring speed of 250  $\text{r min}^{-1}$ . The temperature was quickly raised to 75 °C, 19.4 mmol of DMPA and 0.05 wt% of DBTDL were added into the reactor, and the reaction proceeded for 3 h. After that, the reactive system was cooled to 65 °C, 92.3 mmol of HPA was added into the reactor for a further 2 h. 19.4 mmol of TEA was added to neutralize the carboxylic groups of DMPA at 45 °C for 30 min with a stirring speed of 400  $\text{r min}^{-1}$ . Finally, deionized water was added to the reactive system for 1 h with a stirring rate of 600  $\text{r min}^{-1}$ . The WPU dispersion with the Z-average particle size around 90 nm and solid content about 28% was successfully prepared.

### 2.3. Synthesis of waterborne polyurethane acrylate hybrid emulsions

A 500 ml round-bottom flask equipped with a mechanical stirrer, a thermometer, a condenser and an inlet for high pure  $\text{N}_2$  atmosphere, was charged with the stoichiometric amount of the above WPU dispersion, emulsifier and a certain amount of deionized water. The flask was first heated to 45 °C and stirred at a speed of 250  $\text{r min}^{-1}$  to mix the reactants uniformly. Subsequently, the acrylic monomers (AC) with different weight ratios of soft monomers ( $\text{wt}\%_{2\text{-EHA}}:\text{wt}\%_{\text{BA}} = 1:2$ ) and rigid monomers ( $\text{wt}\%_{\text{ST}}:\text{wt}\%_{\text{MMA}} = 0.35:0.65$ ) were added to the reactor. The reactive temperature was raised to 75 °C. The initiator KPS dissolved in a certain amount of deionized water was pumped into the flask over the period of 2.5 h. Finally, the reactive system was incubated at 75 °C for a further 1 h to complete the reaction. In Table 1, the WPUA samples were designated as the weight ratio of the total amount of acrylic monomers.

**Table 1**  
Sample designation of WPUA hybrid emulsions.

Sample	WPU/AC (wt%)	Emulsifier		Hard monomer ST + MMA (wt%)	Soft monomer 2-EHA + BA (wt%)	KPS (wt%)
		SVS + OP-10 (wt%)				
WPUA1	50/50	1.2	0.8	40%	60%	0.6
WPUA2	50/50	1.2	0.8	50%	50%	0.6
WPUA3	50/50	1.2	0.8	60%	40%	0.6

### 2.4. Preparation of low gloss WPUA films with rough surface

The low gloss WPUA films were prepared by casting a certain amount of WPUA emulsions into a mold. The thickness of the wet films was about 150  $\mu\text{m}$ . The mold with a 10 cm  $\times$  5 cm flattened groove was made up of common glass plate and was free to the air on the top. The mold casted with the WPUA emulsions was dried at room temperature for 24 h and at 50 °C in vacuum for another 24 h. The rough patterned surface of the WPUA films was self-generated during film formation. After being peeled off from the mold, the low gloss WPUA films were stored in desiccator at ambient temperature for further analysis.

### 2.5. Characterization

#### 2.5.1. Nuclear magnetic carbon resonance ( $^{13}\text{C}$ NMR)

$^{13}\text{C}$ NMR spectra of the WPU and low gloss WPUA films were recorded on a Bruker DRX-400 spectrometer.  $\text{CDCl}_3$  reagent was used as solvent to dissolve the films. Tetramethylsilane was used for the internal reference.

#### 2.5.2. X-ray photoelectron spectroscopy (XPS)

XPS (Thermo Scientific ESCALAB 250Xi) was used to investigate the chemical states of the WPU and low gloss WPUA films. The spectra were recorded with monochromatic Al  $\text{K}\alpha$  radiation (1486.6 eV) which was used as excitation source. The pass energy and energy step size were 100 eV and 1 eV for survey spectra, and were 30 eV and 0.1 eV for high resolution spectra, respectively. All the peaks were calibrated using  $\text{C}_{1s}$  at 284.60 eV as the reference [24].

#### 2.5.3. Scanning electron microscopy (SEM)

Surface morphologies of the WPU and low gloss WPUA films were observed using SEM (JSM-6360LV) equipment. The dried films were stained on a copper grid with conductive adhesive. Prior to analysis, the gold was sprayed on the films to further enhance the conductivity.

#### 2.5.4. Dynamic light scattering (DLS)

Prior to measurement, the WPU and WPUA emulsions were diluted with deionized water to a concentration of 3000 ppm. The particle size distribution was measured with a laser diffraction size analyzer (Malvern Nano ZS90) in dynamic light scattering mode. The analyzed results were obtained using a cumulant method.

#### 2.5.5. Gas chromatography (GC)

The contents of unreacted monomers were analyzed by GC-2010 Plus gas chromatography (Shimadzu LabSolutions) with a flame ionization detector (FID). The column model was DM-1. The WPUA emulsions were separately extracted with toluene. The upper extracted liquid was transferred into a volumetric flask. The samples for analysis were gained by mixing the upper extracted liquid and the acrylic monomers with known concentrations (standard solution), and the toluene to the flask mark.

#### 2.5.6. Differential scanning calorimetry (DSC)

DSC analysis was carried out in TA-Q200 instrument. Film samples

Download English Version:

<https://daneshyari.com/en/article/7106158>

Download Persian Version:

<https://daneshyari.com/article/7106158>

[Daneshyari.com](https://daneshyari.com)