



Synthesis and characterization of low-temperature self-crosslinkable acrylic emulsion for PE film ink



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ABSTRACT

A low-temperature self-crosslinkable acrylic emulsion was synthesized by semi-continuous emulsion polymerization technology using methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA) and diacetone acrylamide (DAAM) as monomers and adipic dihydrazide (ADH) as crosslinker. Transmission electron microscope (TEM) micrograph disclosed spherical emulsion particles possess core-shell structure. Fourier transform infrared (FTIR) spectrogram showed that crosslinking reaction between —CO— groups of DAAM and —NHNH_2 groups of ADH can occur during coating film formation at low temperature, even at room temperature. Differential scanning calorimeter (DSC) analysis indicated that glass transition temperature (T_g) of the crosslinked film is increased by 5°C . Thermogravimetric analysis (TGA) curves demonstrated that self-crosslinking reaction improves thermal stability of film. As DAAM content increased from 0% to 2%, water absorption ratio of film decreased from 26.2% to 7.4%, adhesion ratio on the PE thin film increased from 0% to 97%. While the $n(\text{ADH})/n(\text{DAAM})$ ratio increased from 0:1 to 0.8:1, crosslinking density of films was increased from 0% to 88%, water absorption ratio decreased from 36.5% to 7.4% and adhesion ratio on the PE thin film increased from 0% to 97%. The optimal DAAM content and $n(\text{ADH})/n(\text{DAAM})$ ratio was 2% and 0.8:1 in this experiment. The emulsion has good potential application in water-based ink for PE film.

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1. Introduction

Acrylic emulsion is widely used in preparation of high-performance coatings, inks and adhesives [1,2]. However, acrylic emulsion is difficult to be applied in PE thin film ink because of its weak adhesion and wet friction resistance, due to low polarity and low surface tension of PE thin film [3]. One solution to improve these performances of acrylic emulsion is to introduce crosslinkable groups into acrylate polymer. Some crosslinkable monomers, such as N-methylol acrylamide (NMA) [4] and glycidyl methacrylate (GMA) [5] are often used to copolymerize with acrylate monomers and form self-crosslinkable acrylate polymer. However, crosslinking reactions of these crosslinkable monomers need higher reaction temperature over 100°C and are not suitable for ink resin of PE thin film with lower softening temperature.

Ketone-hydrazide crosslinking reaction which can occur at lower temperature, even at room temperature, was often introduced to prepare low-temperature self-crosslinkable resin [6–8]. The reaction between carbonyl group of ketone and

hydrazine group can easily occur at low temperature as volatile alkali moving away during film formation [9], while it cannot occur when storing at alkalinity condition. Guo et al. [10] studied the effect of carboxyl group on ambient self-crosslinkable polyacrylate emulsion with diacetone acrylamide (DAAM) as functional monomer and adipic dihydrazide (ADH) as curing agent. Kan et al. [11] observed morphologies of the p(styrene-butyl acrylate-acrylic acid-DAAM) emulsion particles of different preparation methods and DAAM amount. Nakayama [12] discussed the technologies which enhance the latent capacities of ketone-hydrazide crosslinking reaction. Wang et al. [13] prepared an acrylate-based copolymer emulsion containing keto-carbonyl, amide and carboxyl groups, which was used in interior wall coatings with good humidity-sensitivity and humidity-retention. Yoshihiro et al. [14] prepared urethane/acrylic composite polymer emulsion through the reaction between carbonyl group of DAAM in polyacrylate and carbohydrazide of ADH in polyurethane, which was applied in floor coatings, laminating adhesives and paper and textile finishes. Lai et al. [15] synthesized a kind of water-borne polyurethane modified with 3-aminopropyltriethoxysilane and using trimethylol propane as internal crosslinker, ADH as post-crosslinker, which has good gloss, high hardness and water resistance. Luo et al. [16] synthesized self-crosslinkable acrylic

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emulsion by introducing DAAM–ADH system for wood coating with sealed function. However, there has been no report of using ketone-hydrazide crosslinking reaction to synthesize low-temperature self-crosslinkable emulsion for PE thin film ink.

In this paper, ketone-hydrazide crosslinking reaction was introduced into acrylic emulsion using for ink resin on PE thin film. The acrylic emulsion with low-temperature self-crosslinkable groups was prepared by semi-continuous emulsion polymerization technology, using DAAM as crosslinkable monomer copolymerized with methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA), adding ADH as crosslinker. Fourier transform infrared (FT-IR), transmission electron microscope (TEM), thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) analyses were employed to investigate the structures and curing properties of the emulsion.

2. Experimental

2.1. Materials

MMA, BA, AA, DAAM, and ADH were supplied by Guangdong Chengfang chemical Co Ltd (China). Ammonium persulfate (APS), alkylidiphenyloxide disulfonate (DowFax2A-1) and nonyl phenyl polyoxyethylene ether-10 (OP-10) were purchased from Shanghai Outer Trade Co Ltd (China). Ammonia water (25%) was supplied by Guangzhou Chemical Co. Ammonium persulfate (APS) and sodium bicarbonate (NaHCO_3) were purchased from Shanghai Chemistry Reagent Co (China). Distilled water was self-made.

2.2. Synthesis of low-temperature self-crosslinkable acrylic emulsion

The synthetic route of low-temperature self-crosslinkable acrylic emulsion was depicted in Fig. 1. Polymerization was performed in a 250 ml, 4-neck flask equipped with a mechanical stirrer (fitted with a crescent Teflon blade), a temperature control system, an inlet for feeding pre-emulsion, an inlet for feeding initiator solution and a reflux condenser. The kettle was charged with 0.5 g NaHCO_3 , 35 g distilled water, 0.36 g DowFax2A-1 and 0.18 g OP-10. 8.0 g MMA, 4.0 g BA, 0.28 g DowFax2A-1, 0.14 g OP-10 with 4.8 g distilled water were placed in a graduated beaker and stirred with a magnetic stirrer to get white core pre-emulsion. The shell pre-emulsion with 19.0 g MMA, 17.5 g BA, 1.5 g AA, DAAM (the mass of DAAM varied from 0 g to 2.5 g), 0.88 g DowFax2A-1, 0.44 g OP-10 with 15.2 g distilled water was prepared by the same method. To make the core emulsion, the kettle contents were heated to 80 °C, and then the core pre-emulsion and the initiator solution (0.1 g of APS dissolved in 5 ml water) were added in 30 min. After the addition was completed, the reaction was maintained for another 30 min at 80 °C, and then the shell pre-emulsion and initiator solution (0.2 g of APS dissolved in 10 ml water) were added in 180 min throughout the process. The reactor was maintained at 85 °C for 120 min after the addition was finished. Then the emulsion in the kettle was cooled to about 40 °C and adjusted the pH value in the range of 7–8 by ammonia. ADH was added according $n(\text{ADH})/n(\text{DAAM})$ ratio from 0:1 to 1.5:1.

2.3. Preparation of ink films

The above-mentioned emulsion was mixed with aqueous color paste (Foshan mangrove water-based coating material Co., LTD) at a mass ratio of 7:3 under a stirring rate of 300 rpm for 15 min, then coated on the surface of PE thin film by an ink proofer (JQ, Shanghai Yinze Equipment Co., LTD, China) and placed at room temperature for 9 h.

2.4. Characterization

Fourier transformation infrared (FTIR) spectroscopy (Nicolet 380, US) was performed in the 400–4000 cm^{-1} region. The transmission electron microscopy (TEM) image was observed using a transmission electron microscope (TEM, JEM-100CXII, Japan) with an acceleration voltage of 200 kV. The sample was stained with 2% phosphotungstic acid solution. Thermogravimetric-differential scanning calorimetry (TG-DSC, Netzsch STA 449 F1 Jupiter, Germany) measurements were carried out in the temperature range of –60 °C to 650 °C. Film samples about 5 mg were placed in a platinum sample pan under N_2 atmosphere, at a heating rate of 10 °C/min. The films were obtained by casting the emulsion onto teflon surfaces and allowing them to dry at room temperature for 7 days.

The water absorption ratio measurement was performed according to the following method. A dried emulsion film (approximately 1 cm × 1 cm, W_0 of weight) was immersed into water for 24 h, and then taken out from the water, removed the water on the surface with filter papers, and weighed immediately the weight (W_1). The water absorption ratio of the films were calculated as follows:

$$\text{Water absorption ratio(\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

Three runs were made for each sample and average values were taken.

The crosslinking density was measured through a typical process. A dried emulsion film (W_0 of weight) was placed in a Soxhlet extractor and extracted with methylbenzene under reflux for 7 days. After extraction, linear polymer was dissolved away by methylbenzene, while crosslinked polymer was remained and weighed (W_1) after dried for 72 h at 30 °C. The crosslinking density of the coatings were calculated as follows:

$$\text{Crosslinking density(\%)} = \frac{W_1}{W_0} \times 100$$

Three runs were made for each sample and average values were taken.

A dried ink film on the PE thin film (approximately 20 cm × 5 cm) was fixed on millimeter grid paper (grid: 1 mm × 1 mm), and a scotch tape (3M, width of 1.5 cm) was pasted onto the ink film tightly. The number of grids covered by tape was recorded as A_0 . Then the tape was pulled off transiently and quickly with the angle of 180°, and the number of grids covered by deciduous ink film was recorded as A . The adhesion ratio of ink film was calculated as follows:

$$\text{Adhesion ratio(\%)} = \frac{A_0 - A}{A_0} \times 100$$

Three runs were made for each specimen and average values were taken.

3. Results and discussion

3.1. FTIR analysis

As ammonia volatilizing away during film formation, emulsion system is becoming weak acidic and the active carbonyl group can condense with hydrazine group of ADH. The crosslinking reaction scheme is showed in Fig. 1.

Fig. 2 shows the FT-IR spectras of films with (curve b) and without crosslinking reaction (curve a) in which ADH is not added. The stretching vibration peak of C=O group at 1735 cm^{-1} , the characteristic stretching peaks of $-\text{CH}_3$ and $-\text{CH}_2$ groups at 2958 cm^{-1} , 2868 cm^{-1} , 1381 cm^{-1} and 1461 cm^{-1} , the stretching vibrations of

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