



Silicylacrylate copolymer core–shell emulsion for humidity coatings



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ABSTRACT

Using silicylacrylate (SPMA: 3-(trimethoxysilyl)propyl methacrylate) and acrylic acid as functional monomers, silicylacrylate copolymer core–shell emulsion (SiA-CSE) was prepared by emulsion polymerization. The relationships between stability of SiA-CSE and contents of SPMA, emulsifier, initiator and copolymerization temperature were investigated. Moreover, the structure of SiA-CSE was characterized by FTIR, TEM and TGA techniques. The SiA-CSE was applied to prepare the silicylacrylate copolymer humidity coatings (SiA-CSE-C) by compositing with pigments and porous fillers. Based on measuring the basic performance of copolymer emulsion film and SiA-CSE coatings, the humidifying function of SiA-CSE coatings was investigated. In conclusion, SPMA could improve the adhesion of SiA-CSE film and water resistance of the coatings. The obtained coatings showed excellent humidity-sensitivity and humidity retention, which could be used as the interior walls coatings in the building.

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1. Introduction

Relative humidity (RH) of air directly affects our perception of temperature. Over high or low RH of environment easily causes physical discomforts, even sicknesses [1]. Therefore, the regulation and controlling of the indoor humidity becomes particularly important [2,3]. Using humidity controlling materials, interior wall coatings can be applied to adjust relative humidity of our living environment. We previously found that amphiphilic acrylate-based copolymers can be applied in the preparation of humidity coatings [4]. Acrylic resins are environment-friendly, showing excellent and resistances against weathering, acid, alkali and corrosion [5,6]. But acrylic usually suffers from poor thermal stability and poor water and stain resistance, etc. [7,8]. In order to improve its properties, some modified acrylate-based copolymers were prepared and applied to coatings [9,10].

Polysiloxanes, the bond energy of Si–O, is up to 450 kJ/mol, which is higher than those of the C–C bond (345 kJ/mol) and the Si–C bond (318 kJ/mol). Therefore, it has excellent properties of heat, oxidation and radiation resistance, etc. [11]. It can improve the properties of water resistance, stain resistance and others. The composite of acrylic and polysiloxanes has the potential to improve the mechanical properties of acrylic, and couple with the

thermal stability and water resistance of silicones, which can overcome the weakness of each other [12]. Core–shell particles have distinct geometry which is composed of a core and a shell and usually prepared by emulsion polymerization [13]. They always exhibit improved physical and chemical properties compared to random copolymer and physical blending, such as excellent film formation, appearance, block resistance and hardness [14]. Polymer shells are frequently used to stabilize pigments in paints. By using core–shell particles, it is possible to lower the minimum film forming temperature and keep the high glass transition temperature (T_g) of copolymer [15], and the contradictions of film-forming and application properties can be solved effectively. Developing organic–inorganic coatings, which is exhibited the good thermal and physico-mechanical properties required in coatings applications [16–18]. Realizing not much work reported humidity coatings prepared by polysiloxanes modified acrylics core–shell particles.

In this article, a typical silicylacrylate monomer, 3-(trimethoxysilyl)propyl methacrylate (SPMA), was used as a functional monomer to prepare acrylate copolymer core–shell emulsion (SiA-CSE). The ratio of cell/shell monomers, temperature of polymerization, and quantities of composite emulsifier and initiator were investigated. The silicylacrylate copolymer humidity coatings (SiA-CSE-C) were prepared by SiA-CSE, pigments, and fillers. With their basic properties measured, the water absorption and humidity-controlling properties of the humidity-sensitive coatings were also investigated.

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2. Experimental

2.1. Materials

Methyl methacrylate (MMA), acrylic acid (AA), butyl acrylate (BA) (Qilu Petrochemical Kaitai Industry Co., China), and hydroxypropyl methacrylate (HPMA) (Wuxi Yangshi Sanlian Chemical Co., China) were washed with 10% sodium hydroxide solution to remove inhibitors and then with deionized water to remove the base residual. 3-(Trimethoxysilyl)propyl methacrylate (SPMA) was obtained from Shanghai Mairuier Chemical Co. China. Potassium persulfate (KPS) (Yixing Secondary Planet Industry Co.), sodium hydrogen carbonate (NaHCO_3) (Hengyang Yuhua Industry Co.), sodium dodecyl sulfate (SDS), and Tween-20 were obtained from commercial sources. Titanium dioxide, talc, montmorillonite, kaolin, bentonite, diatomite (CD02), diatomite (CD05), natural crystalline calcium carbonate and precipitated calcium carbonate were all industrial grades. Dispersant agent DA-01 (Beijing Yakeli Chemical Co., Ltd.), and defoaming agent 3016 (Shanghai Changfeng Chemical Co.) were coatings assistants.

2.2. Preparation of the silicylacrylate core-shell emulsion (SiA-CSE)

The core-shell emulsion was prepared by P (MMA/BA/AA) core and P (MMA/BA/HPMA/SPMA) shell with free-radical copolymerization (Scheme 1). The core-shell emulsion was prepared in two stages, namely core and shell formation.

2.2.1. Preparation of the core particles

The requisite amounts of NaHCO_3 and KPS were dissolved in water in a 250 mL four-necked round-bottomed flask equipped with a thermometer, a reflux condenser, a mechanical stirrer, and dropping funnels. A mixture of core monomers consisted of AA, MMA, and BA (about 20% of the total monomers) was dropped into the system at 80 °C over a period of 1 h, and then the mixture was allowed to react for a further 1 h. Thereafter, polyacrylate core particles were obtained.

2.2.2. Preparation of the core-shell emulsion

A mixture of shell monomers consisting of HPMA, SPMA, MMA, and BA was placed in a dropping funnel. Simultaneously, KPS was dissolved in water and this solution was placed in another dropping funnel. The KPS solution and shell monomers were dropped into the reaction flask at 80 °C over a period of 2–3 h and the mixture was allowed to react for a further 2 h. The obtained emulsion was cooled to 50 °C. The target pH was adjusted by adding pre-determined amounts of 10% $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the emulsion, which was then filtered through a filter of 100-mesh sieve.

2.3. Preparation of the silicylacrylate copolymer coatings (SiA-CSE-C)

The silicylacrylate copolymer humidity coatings were prepared by SiA-CSE, pigments, porous fillers and distilled water. Firstly, the pigments and fillers were dispersed in water with stirring. Then, the SiA-CSE was added. The mixture was ground for a period of 1 h with an attritor filled with glass balls of 0.3 mm in diameter for a period of 45 min at room temperature, which afforded the humidity coatings (SiA-CSE-C).

2.4. Measurements of the SiA-CSE and SiA-CSE-C

The solid content and the final conversion were measured by the gravimetric method. The solid content (Solid%) and overall

conversion (X), respectively, were calculated by the following formulas (Eqs. (1) and (2)):

$$\text{Solid\%} = \left(\frac{W_{\text{de}}}{W_{\text{e}}} \right) \times 100 \quad (1)$$

$$X = \frac{\left(\left(\frac{\text{Solid\%}}{100} \right) - (W_1 + W_2 + W_3 + W_4) \right)}{W_m} \quad (2)$$

where Solid% is the solid content, W_{de} is the weight of dry emulsion, W_{e} is the weight of emulsion; and W_1 , W_2 , W_3 , W_4 , and W_m are the weight fractions of KPS, NaHCO_3 , compound emulsifier, and initial monomer respectively, in the feed for each sample.

The filterable solids obtained from each run were dried. The coagulum contents were then calculated according to Eq. (3):

$$\text{Coagulation\%} = \frac{M_f}{\text{Solid\%} \times M_s + M_f} \times 100 \quad (3)$$

where M_f and M_s are the weights of dried filterable solids and the filtered emulsion, respectively.

The average particle size and particle size distribution of the emulsion particles were measured by dynamic light scattering (DLS) (Nano Series, Malvern Instruments Ltd., UK) at 25 °C, and the samples were highly diluted (<0.01%) to prevent multiple scattering before tested. The micrographs of the SiA-CSE were observed by JEM-1230 transmission electron microscope (TEM) from JEOL, at 200 kV. For physical and mechanical properties, coatings with a wet thickness of 100 μm were cast on a clean glass and galvanized iron plate at ambient temperature (25 °C) for 48 h. The films of the SiA-CSE were prepared by drying their resins at room temperature. The FT-IR spectra were detected by Digital FTS3000 spectrometer. The TGA was performed with a Pyris Diamond (Perkin Elmer) under the nitrogen atmosphere at a heating rate of 10 °C/min from 20 °C to 750 °C.

3. Results and discussion

The physical, chemical and mechanical properties of copolymer were decided by monomers. In this study, MMA and BA were used as hard and soft monomers, respectively. HPMA was used as cross-linked monomers, and SPMA was used to improve the various properties of acrylate copolymer. The core-shell particles have hard core and soft shell, which were prepared via two-stage emulsion polymerization. The hard core includes hydrophobic (MMA, BA) and hydrophilic species (AA). The extra soft monomers (HPMA) and SPMA in shell can lower the T_g , and improve the performance of film-forming and the hardness, thermal stability and water resistance of the acrylate copolymer. We found that the functions of the silicylacrylate core-shell emulsion and coatings were influenced by monomers, emulsifier, initiator, polymerization temperature and coatings formulation. These influences were investigated as follows.

3.1. Effect of the core/shell monomer composition

The contents of AA in core and SPMA in shell have a strong influence on the coagulum content and particle size of the resultant emulsion. The results are shown in Table 1. It can be seen that the particle size was large (155 nm) and a lot of coagulum was produced (11.3%) when AA is added to the core composition (entry 1). The particle sizes decrease from 155 to 128 nm and coagulum contents decrease from 11.3% to 0.4% by increasing the AA/(MMA + BA) ratios from 0:6 to 2:6 when the SPMA/(MMA + BA + HPMA) ratio is 3:27 (entries 1, 2, 5). The reason for this behavior is likely that the increasing of AA amount will increase the amounts of oligomer and polymer chains with more carboxyl groups. As a result, the increase of carboxyl-enriched oligomer in water phase, just like

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