



Synthesis and characterization of polyacrylate modified by polysiloxane latexes and films



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ABSTRACT

In this paper, a new method was designed to prepare polyacrylate modified by polysiloxane latex particles, with methyl methacrylate (MMA) and butyl acrylate (BA) as main monomers, vinyltriethoxysilane (A-151) as functional monomer and octamethylcyclotetrasiloxane (D₄) as grafting agent. The chemical structure and morphology of the latexes were characterized by FTIR, TEM, and particle size analyzer. The properties of the films were tested in terms of static contact angle, water absorption and TGA. The results showed that uniform spherical structure and narrow particle size distribution could be obtained in the latexes. Furthermore, the hydrophobicity, low surface free energy and thermal stability were also noticeably increased with the content of polysiloxane. The mechanism of ring opening polymerization between D₄ and A-151 was also discussed; it turned out that it was quite important to control the pH under faintly acid conditions.

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1. Introduction

Recently, polyacrylate (PA) has aroused the interests of numerous researchers owing to its wide range of applications and excellent properties such as good cohesiveness, high-gloss, transparency, and excellent film forming property. PA can be applied into coating, adhesives, impact-resistance plastics, and strengthening rubber [1]. But the chemical structure and high sensitivity to temperature make it lack of strong waterproof and weather-resistance ability, which causes a series of problems when it is used as coatings in exterior walls of buildings [2]. Compared with polyacrylate, polysiloxane has various special properties such as great abilities of water repellency and weather resistance, low surface free energy, high flexibility, as well as excellent thermal stability [3]. Therefore, it is of vital importance to synthesize polysiloxane/polyacrylate polymers by combining the extraordinary properties of both polymers, namely, polysiloxane and polyacrylate [4,5].

Different methods of grafting polysiloxane onto polyacrylate by emulsion polymerization have been reported. One of which is free radical polymerization between silane coupling agent containing double bond with acrylate monomers [6]. But silane coupling agent is inclined to hydrolyze and crosslink, so the siloxane grafted on the polyacrylate is quite limited. Besides, this method also has a

negative influence on the stability of the emulsion and can lead a higher coagulation. Another method is to utilize condensation polymerization between polysiloxane containing active groups, such as hydroxyl, double bond and acrylic resin [7–10]. The octamethylcyclotetrasiloxane (D₄) is frequently used as the grafting agent to synthesize special polymer with core-shell structure [11,12]. The way to synthesize polyacrylate latex with high content of polysiloxane is quite useful. The last method is sol-gel method used to synthesize organic-inorganic hybrid materials. It has attracted great attention because the organic-inorganic hybrid materials can combine the properties of the inorganic particles, such as mechanical strength and thermal stability, with the process ability and the flexibility of the organic polymer matrix [13–15]. The researchers usually synthesize the copolymers which have special microcosmic pentablock or core-shell structures [11,12,16]. These copolymers have special characteristics owing to the different properties of the core and shell. However, the polymerization processes are extremely complex in all these methods mentioned above. Besides, long reaction time is necessary for multistage emulsion. Therefore, it is far from satisfying to manufacture coating made of polyacrylate siloxane hybrid latex via the above-mentioned methods.

In this paper, a novel and relatively more convenient method to prepare polyacrylate modified by polysiloxane latex via semi-continuous seeded emulsion polymerization was designed. The radical polymerization of acrylate and the ring opening polycondensation of D₄ were designed in the same procedure under faintly acid conditions. It turned out that a high content of silicon was brought into while the reaction time and procedures were reduced.

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The results were characterized by FTIR, TEM, TGA, particle size analyzer, static contact angles and water absorption, and it showed that the emulsions and films were provided with excellent properties. This method provided a promising approach to manufacture polyacrylate modified by polysiloxane emulsion as protective coating.

2. Experimental

2.1. Materials

Materials including methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA), were purified by 5 wt% aqueous solution of sodium hydroxide, deionized water until the pH was 7.0, and then distilled under reduced pressure and stored in refrigerator at -5°C . Vinyltriethoxysilane (A-151), octamethylcyclotetrasiloxane (D_4), ammonium persulfate (APS Aldrich), sodium bicarbonate (NaHCO_3), sodium dodecyl benzene sulfonate (SDBS), polyoxyethyleneoctylphenyl-10 (op-10) and dodecylbenzene sulfonic acid (DBSA) were all used as received. Deionized water was used throughout the whole experimental process.

2.2. Synthesis of polyacrylate modified by polysiloxane latex

In all polymerizations, the amount of monomers controlled in the solid content of the final latex was 45 wt% with completely monomer conversion. The preparation of polyacrylate modified by polysiloxane latex involved three steps: preparation of pre-emulsion, synthesis of seed latex and polyacrylate siloxane hybrid latex.

In the first place, emulsifier (op-10, SDBS) and NaHCO_3 were dissolved into water at room temperature to obtain solution (I), after which three-fourths of the solution (I) was transferred into a round-bottom flask, and A-151, D_4 with all the acrylate monomer were added by a dropping funnel in 0.5 h and emulsified 1 h by strong stirring to obtain emulsion (II). Then, one-fifth of the emulsion (II) and residual emulsifier solution (I) were transferred into four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel and inlet for nitrogen gas. When the flask temperature was heated to 85°C , APS aqueous solution was added in to prepare the seed latex for 0.5 h. After that, the residual monomer emulsion was continuously dropped into the flask in 2 h, with the residual APS aqueous solution added three times, followed by continuous polymerization for 3 h. Finally, when the reaction finished, the temperature was dropped to 40°C , and the pH was around 5.0. At this stage, saturated NaHCO_3 aqueous solution was added to adjust pH to 7.0 in order to maintain emulsion stability.

2.3. Characterization

Monomer conversion was measured by the gravimetric method. Two to three grams of emulsion and two drops of hydroquinone were cast onto a glass plate which began to be dried at $70\text{--}85^{\circ}\text{C}$ until the weight remained constant. The solids content (S) and final conversion (C), respectively, were determined by the following equations:

$$S(\text{wt}\%) = \frac{w_2 - w_0}{w_1 - w_0} \times 100\%$$

where w_0 was the weight of the glass plate, and w_1 and w_2 were the weights of emulsion before and after dried.

$$C(\text{wt}\%) = \frac{S(\text{wt}\%) \times (w_3 - w_4)}{w_5} \times 100\%$$

where w_3 was the total weight of all constituents put in the flask before polymerization, w_4 was the weight of constituents that could

Table 1

Different contents of siloxane and properties of latex for the prepared samples.

Sample	A-151 (%)	D_4 (%)	Solid content (%)	Conversion (%)	Film	Stability
1	0	0	44.3	98	Glassy	Good
2	4	0	42.6	94	Glassy	Good
3	4	2	43.9	97	Glassy	Good
4	4	4	43	95	Even	Good
5	4	6	42.7	94.4	Even	Good
6	4	8	42.2	93.3	Whitish	Good

^a The mass ratio of A-151 and D_4 to total monomer.

not volatilize during the drying period, and w_5 was the total weight of the monomers.

The films were prepared by coating the latex onto the surface of the clean glass and dried firstly at room temperature and then in a vacuum oven at 70°C for 6 h. The films were transparent and their thicknesses were about $200\ \mu\text{m}$. The films were peeled off from the glass and immersed in water for 72 h. During this time, water absorption was measured by the following equation:

$$\delta = \frac{w_2 - w_1}{w_1} \times 100\%$$

where w_1 was the weight of films before immersed in water, and w_2 was the weight after immersed in water. The films ought to be weighed immediately when the water attached to the surface was wiped off.

FITP spectra test was recorded on NICOLET 5700 spectrophotometer with a distinguish ability spectral width of $500\text{--}4000\ \text{cm}^{-1}$ by the KBr pellet method.

TEM of the polyacrylate particles was taken with Tecnai 12 transmission electron microscope (Philips Company, Holland) with an acceleration voltage of 120 kV. The latexes were diluted with water at a ratio of 1:9 and dyed with phosphotungstic acid staining solution ($\text{H}_3\text{PO}_4\text{W}_{12}\cdot x\text{H}_2\text{O}$, pH=2) at a ratio of 1:1 for 30 min.

TGA was carried out on a Perkin Elmer TGA 4000 under nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}\ \text{min}^{-1}$ from 30°C to 550°C .

The particle size of the prepared polyacrylate and polyacrylate/polysiloxane were measured by NanoZS ZEN3600 (Malvern UK) particle size analyzer and the latexes were highly diluted ($C < 0.01\ \text{wt}\%$) before testing to prevent multiple scattering.

Static contact angles of deionized water at film–air surface and film–glass surface were performed with JC2000XP contact angles goniometer (Zhongcheng, Shanghai). In the process of testing, $5\ \mu\text{L}$ water was dropped on the surface of films.

3. Results and discussion

The solid contents and conversions of the samples were summarized in Table 1. The content of A-151 was constant at 4% with D_4 increasing from 0 to 8%. The solid contents of the samples were about 44 wt%, which were identical with the theoretical values. When radical polymerization was performed, the hydrolysis of $\text{Si}(\text{OCH}_2\text{CH}_3)_3$ group in A-151 forming $\text{Si}(\text{OH})_3$ would proceed at the same time [17]. It was quite easy for the Si–OH group to form Si–O–Si group which had three-dimensional reticular structure. As a result, the conversion was very low in sample 2. When there was D_4 in the solution, ring opening polymerization would take place between Si–OH group and D_4 . These reactions could inhibit crosslinking between Si–OH groups. But the low reactivity and compatibility between D_4 and A-151 made the conversion decrease with the increase of D_4 in other samples. The results in Table 1 also showed that the appearance of the films changed from glassy to whitish with the increase of D_4 and the stability of the latex was not influenced by the content of D_4 .

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