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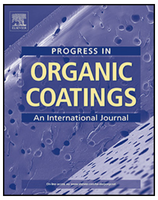

Preparation and characterization of cationic silicone-acrylic latex surface sizing agent

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ABSTRACT

Series of cationic silicone-acrylic latexes used as surface sizing agents were prepared by using the semi-continuous emulsion polymerization of styrene and butyl acrylate in the presence of acrylamide, (2-(methacryloyloxy) ethyl) trimethyl ammonium chloride and vinyltriisopropoxysilane (A-173). The structure and properties of the cationic silicone-acrylic latexes were examined by Fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS) and differential scanning calorimetry (DSC). The latexes were subsequently used as surface sizing agents, and the sizing properties were evaluated using scanning electron microscope (SEM), a video-based contact angle measuring device and a Cobb absorbency tester. It was observed that the cationic silicone-acrylic latexes produced possessed remarkable chemical stability. The surface sizing agent containing this type of cationic silicone-acrylic latex, even in the absence of aluminum salt, was excellent in improving the water resistance and mechanical properties of the corrugated paper. Compared with that of the pure anionic cassava starch sizing agent, the Cobb value of the sizing agent that consisted of 99.6% anionic cassava starch and 0.4% cationic silicone-acrylic latex, in which the dosage of vinyltriisopropoxysilane was 4%, decreased by 40%, and the ring crush index increased by 20%.

1. Introduction

Paper, especially paper that contains hemicellulose, has a strong tendency to absorb water and shows poor mechanical properties. Many types of surface sizing agents such as wax, alkyl ketene dimer (AKD), poly (styrene-acrylic acid) (SAA), styrene-acrylate emulsion (SAE), poly (styrene-maleic anhydride) (SMA), polyurethane (PU), etc., were used to improve the properties of paper [1–12]. Therefore, more and more attention has been paid to the synthesis of surface sizing agents with superior characteristics. Low-priced wax can be unsuitable for improving the water resistance of paper because of the difficulty in paper recycling. Because the water solubility of anionic polymers such as SMA and SAA depends entirely on the dissociation of carboxylate, a large amount of aluminum salts seem necessary if those polymers are used as surface sizing agents. Additionally, their high expense and easy hydrolysis may limit the application of PU and AKD respectively. Compared comprehensively with the above sizing agents, SAE should be the more appropriate candidate for surface sizing agent in the paper coating field.

SAE made by a cationic system has more advantages over those made by an anionic one because of the electronegative of the paper fibers. To obtain cationic SAE with a better surface sizing performance, many efforts were made to modify SAE. Rosin was introduced into an SAE surface sizing agent to improve the water resistance of paper [2,7]. A type of fiber crosslinking cationic latex was synthesized by grafting modified ammonium groups functionalized SAE with epichlorohydrin [12]. Waterborne polyurethane/poly (n-butyl acrylate-styrene) hybrid emulsions were also used as surface sizing agents, and the Cobb values at 30 and 60 s were only 10.23 and 11.89% of the original paper, respectively [13]. The mechanical properties of the PU sizing agents were remarkably improved by incorporating hyper branched polyether or isophorone diisocyanate [4,8]. Apparently, interest in the cationic SAE surface sizing agent has increased in recent years and the majority of the studies focused on enhancing the water resistance and mechanical properties of paper. Nevertheless, most of the surface sizing agents either need the assistance of aluminum salt or improve just one of the water resistance and mechanical properties. To overcome these limitations of existing surface sizing agents, the synthesis of an economical cationic

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surface sizing agent with excellent sizing performance is in urgent need.

Silicon-containing monomers are good alternatives to fluorinated monomers in enhancing the water resistance of some materials. γ-Methacryloxypropyl trimethoxysilane was usually used as the crosslinking agent in the synthesis of SAE [14]. Because of the steric effect of isopropyl, Si–O–R groups in vinyltriisopropoxysilane (A-173) are so stable in water that self-crosslinking rarely occurs in the process of polymerization. After surface sizing, Si–O–R hydrolyzes in the process of drying and the Si–OH generated reacts with the hydroxyl groups on oxidized starch and fibers, to conquer the low bonding strength of starch-containing surface sizing agent.

In this work, a novel cationic silicone-acrylic latex containing A-173 was prepared and the mixture of starch gel and a small amount of the cationic silicone-acrylic latex mentioned above was used as the surface sizing agent. The water resistance and mechanical properties of the sized paper were significantly improved, i.e., the Cobb value decreased by 40%, the contact angle mounted up to 93° from 44.5°, the ring crush index increased by 20% and the tensile strength also improved to some extent, with the surface sizing agent consisting of 99.6% starch and 0.4% cationic silicone-acrylic latex, in which the addition of A-173 was 4%.

2. Experimental

2.1. Materials

Cetyl trimethyl ammonium bromide (CTAB, 99%), (2-(methacryloyloxy) ethyl) trimethyl ammonium chloride solution (DMC, 75%), a molecular sieve (2–3 mm, used as drier) and 2, 2′-azobis (2-amidinopropane) dihydrochloride (AIBA, 99%) were purchased from Aladdin Industrial Corporation. Vinyltriisopropoxysilane (A-173, 98%) was supplied by Longkom Chemical Co., Ltd (Guangzhou, China). Styrene (St, 99%), butyl acrylate (BA, 98%), acetic acid (HOAc, 99.8%), acrylamide (AM, 98%), tetrahydrofuran (THF, 99%) and other reagents were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). St and BA were passed through a basic alumina column to remove the inhibitor and dried by the molecular sieve. The other reagents were used as received. Deionized water prepared in our lab was used for all of the emulsion polymerization experiments. The starch used was anionic cassava starch. Corrugated paper with basis weight of 86 g/m^2 was obtained commercially by Hangzhou Baist Industrial Co., Ltd.

2.2. Preparation of cationic silicone-acrylic latex

Table 1
Recipe for preparing cationic silicone-acrylic latexes.[a]

Ingredients	Quantity
H_2O	70 g
CTAB	0.9 g
St	15 g
BA	15 g
AIBA	0.33%
HOAc	1 g
DMC	0–4%
AM	0–4%
A-173	0–6%

[a] The percentage composition of DMC, AM and A-173 is relative to the mixture of St and BA. The percentage composition of AIBA is relative to the total monomers.

The semi-continuous emulsion polymerizations were conducted in a 500 ml four-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser. The recipe used in the polymerization is given in Table 1. Prior to the polymerization, 85% of the total CTAB, 1 g HOAc and 28% of the total water were introduced in a round-bottom flask and stirred at 800 rpm for 10 min. The mixture of St and BA was then added under stirring and kept agitated for another 15 min to make the primary pre-emulsion. At the same time, hydrophilic monomers (HM) DMC and AM were dissolved in 65% of the total water. Next, 25% of the total primary pre-emulsion and the solution of hydrophilic monomers were introduced into the four-necked flask loaded with 15% of the total CTAB and stirred at 300 rpm in a thermostatically controlled oil bath. The mixture of A-173 and glycol was added in the residual primary pre-emulsion and agitated for 5 min to obtain the final pre-emulsion. The total AIBA was also dissolved in 7% of the total water prior to the polymerization. A third part of the initiator solution was introduced into the reactor to start the polymerization and the stirring rate was decreased to 200 rpm when the reaction system reached 70 °C. Twenty minutes later, the rest of the final pre-emulsion and initiator solution were added at an appropriate rate over 3.5 h. After the adding all of the monomers, the reaction system was heated to 75 °C and maintained at this temperature for another 1 h to chase the rest of the monomers. The latexes were finally filtered to remove the gel after being cooled.

2.3. Characterization of cationic silicone-acrylic latex

2.3.1. FT-IR analysis

The latexes were demulsified by ethanol and sodium chloride and then washed three times by water at 60 °C. After drying, the polymers were dissolved in THF to form polymer solutions. Samples were prepared by depositing the solutions on a KBr pellet several times and detected by a Jasco IR-700 infrared spectrophotometer.

2.3.2. Particle size and its distribution

The hydrodynamic diameter and size distribution were measured by dynamic light scattering (Zetasizer 3000, Malvern Instruments) three times to give the average.

2.3.3. Zeta potential

Zeta potential measurements were carried on dynamic light scattering (Nano ZS 90, Malvern, UK) at 0.1% solid content.

2.3.4. Apparent viscosity

Previous to detection, the latexes were heated to 25 °C by a water bath. The apparent viscosity of the latexes was determined by a rotational viscometer (NDJ-5S, Shanghai Geological Instrument Research Institute, China).

2.3.5. Differential scanning calorimetry

The latexes were demulsified by ethanol and sodium chloride and then washed three times by water at 60 °C. The samples were dried at 100 °C for 1 h before detection. The glass transition temperature was determined by a differential scanning calorimeter (TA-Q200, USA) at a rate of 10 °C/min from −60 to 80 °C.

2.3.6. Transmission electron microscopy

Particles of cationic silicone-acrylic latex were observed by transmission electron microscopy (Hitachi, JEM-1200EX). A highly diluted dispersion of the sample was cast onto a carbon-coated copper grid and dried in air.

2.4. Sizing formulation preparation and surface sizing of the corrugated paper

A certain amount of starch was cooked with water at 95 °C. The above system was cooled to 75 °C and the concentration of