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The application research of environment-friendly reactive surfactants in acrylate emulsion pressure sensitive adhesives

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ABSTRACT

In this article acrylate pressure sensitive adhesive (PSA) latexes were synthesized via a pre-emulsion seeded semi-batch emulsion polymerization process with a conventional nonreactive surfactant (CO-436) and two polymerizable surfactants (traditional surfmer SE-10N and environment-friendly surfmer SR-10). The effects of surfactant contents on the particle size, zeta potential, electrolyte stability of the latexes and gel content, sol molecular weight (M_w, M_n), water absorption of the PSA copolymers were investigated. In addition, X-ray photoelectron spectroscopy (XPS) and contact angle measurements were used to characterize the latex films. The results showed that the particle sizes of latexes prepared with surfmers were smaller than their CO-436 containing counterparts. And the latexes prepared with surfmers had a lower storage stability than the one prepared with CO-436. However, surfmers can improve the electrolyte stability of the latex. Furthermore, the water resistances of the latexes prepared with surfmers were better than that of the latex with CO-436, which can be confirmed by water absorption, contact angle and XPS analysis. The results also indicated that the PSA prepared with SR-10 exhibited the highest gel content among the three surfactants. Finally, the effects of surfactants on the adhesive properties of the PSAs were also evaluated.

1. Introduction

Emulsion polymerization is by far one of the most important techniques for producing acrylic PSAs from an industrial point of view. In the emulsion polymerization process monomer is polymerized in an aqueous medium containing surfactant micelles. Surfactants play a significant role in the process. They are added during the polymerization and, in some cases, also after the product has been synthesized. They are very important for the nucleation of the latex particles, emulsification of monomer droplets and/or preformed polymer, and stabilization of polymer particles during polymerization and longer shelf life of the products. However, the use of conventional surfactants such as sodium lauryl sulfate (SLS) in a latex can have adverse effects on the properties of waterborne pressure sensitive adhesives (PSAs). For example, adhesion strength [1], shear strength [2], water resistance [3], and peel strength [4] have been found to be adversely influenced by surfactant. These effects are caused by the fact that surfactants are only physically attached to the polymer particles, thus they can migrate to the surface of a latex coating and can desorb from the latex particle surface under high shear, causing destabilization [5]. When latexes are used as film-forming polymers, the adsorbed surfactant can migrate toward the interfaces, creating a separate phase [6,7] that reduces gloss and adhesion, and can be entrapped in pockets [7] which increases percolation by water and, in general, water sensitivity. Hence, there is a strong correlation between the heterogeneous distribution of surfactant in the depth of the film and resulting adhesive properties [8]. Surfactants have been found at the locus of failure of adhesives [9].

A possible solution to these problems is to covalently link the surfactants to the polymer so that it cannot desorb and migrate during film formation. This is the rationale behind the use of reactive surfactants [7]. These reactive surfactant molecules can be a combination of a part with surface activity and a part with an intrinsic reactivity toward radical reactions without loss of their surface activity. When the reactive surfactant has a polymerizable double bond it is called a surfmer (polymerizable surfactant), and this is the most promising type in emulsion polymerization [10,11]. In 1956 Bistline et al. [12] first obtained surface-active polymers referred to as surfmers. Since then, many anionic surfmers with sulfate or sulfonate headgroups [11,13], cationic surfmers [14], and nonionic surfmers [15] have been synthesized and applied in emulsion polymerizations. Besides, the reactive groups can be of different types, for example, allylics [16], acrylamides

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[13], (meth)acrylates [15], styrenics [17], or maleates [11].

Recently, the behaviors and applications of reactive surfactants in emulsion polymerization have been widely investigated. Zhang et al. [18] compared the properties of pressure sensitive adhesives (PSAs) generated via emulsion polymerization using both conventional and reactive emulsifiers. They found that the binding of surfactant to the adhesive polymer backbone inhibits its movement to film surfaces during film formation, which helps maintain the performance of the adhesive film. Aramendia et al. [7].discovered that both vapor and water permeability were higher for a film cast from a latex stabilized with a conventional nonionic surfactant than for a film obtained from a latex containing a nonionic surfmer.

However, fundamental studies of the applications of environment-friendly surfmers in both emulsion polymerization and acrylic PSAs are still scarce. In the present study, a series of acrylic emulsion PSAs have been synthesized with three different types of surfactants (conventional surfactants CO-436, conventional surfmer SE-10N, environment-friendly surfmer SR-10). The effects of the three surfactants contents on the particle size, zeta potential and electrolyte stability of the latex and the gel content, sol molecular weight (M_w, M_n) and its distribution (M_w/M_n), water absorption and adhesive properties of the PSA copolymer were investigated. In addition, X-ray photoelectron spectroscopy (XPS) and contact angle measurements were used to characterize the latex films.

2. Experimental

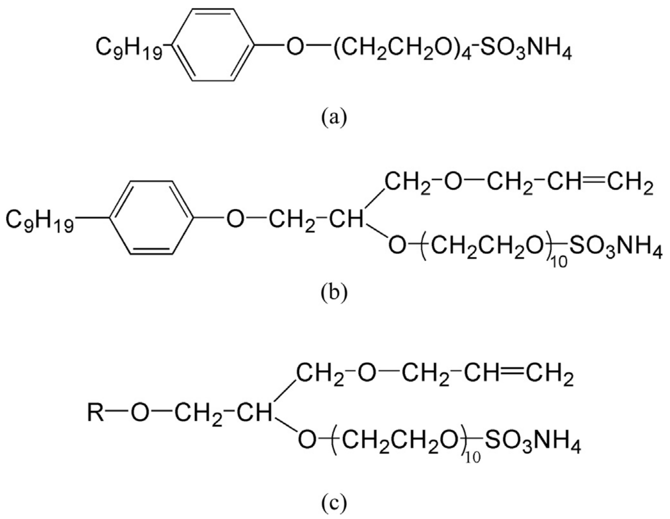
2.1. Materials

Butyl acrylate (BA; technical grade, Shanghai Huayi Acrylic, China), methyl methacrylate (MMA; Reagent grade, Shanghai Lingfeng Chemical, China), acrylic acid (AA; reagent grade, Shanghai Lingfeng Chemical, China), 2-hydroxy ethyl acrylate (HEA, technical grade, Shanghai Huayi Acrylic, China), ammonium persulfate (APS; technical grade, Shanghai Aijian Modern Reagent Factory, China) and sodium bicarbonate ($NaHCO_3$; reagent grade, Shanghai Lingfeng Chemical, China); the latter two used as the initiator and the buffer agent, respectively. All these materials were used without further purification. The conventional ammonium nonyl phenol ethoxylate sulfate surfactant (Rhodapex CO-436), which contains 4 poly(ethylene oxide) (PEO) groups, was supplied by Shanghai Honesty Fine Chemical (China). The traditional polymerizable ammonium allyloxtmethylate nonyl phenol ethoxylate sulfate surfactant (ADEKA SE-10N) and environment-friendly polymerizable ammonium allyloxtmethylate alkyl alcohol ethoxylate sulfate surfactant (ADEKA SR-10), which both contain 10 PEO groups, were both purchased commercially and used as received. The molecular structures of CO-436, SE-10N and SR-10 are shown in Scheme 1. Distilled deionized water (DI-H_2O) was used throughout the study. Ammonia (25 wt% in H_2O) was obtained from Nanjing Chemical Reagent Co. The solvent used in the polymer characterization such as tetrahydrofuran (THF, HPLC grade, Shanghai Lingfeng Chemical) was also used as supplied by the manufacturer.

2.2. Emulsion polymerization

The recipes for water-based PSA latexes synthesized with different types and contents of surfactants are shown in Table 1. 25 g deionized water and all the required amount of surfactant were added to a 500 mL four-neck round-bottom flask and stirred rapidly to allow sufficient dissolution of the emulsifier. The monomer mixtures were then slowly added into the water-emulsifier mixture through a constant pressure funnel over a period of 20 min. The pre-emulsion was then stirred for a further 30 min.

Polymerization was carried out by a pre-emulsion seeded semi-batch emulsion polymerization process in a 500 mL four-neck round-bottom flask equipped with an electromotive stirrer, thermometer, two separated addition funnels, and a reflux condenser. Stirring speed was maintained at 270 rpm throughout the experiments. First, a homogeneous aqueous solution containing 50 g DI-H_2O and 0.2 g $NaHCO_3$ was charged into the reactor. When the temperature reached 78 °C, 6 g pre-emulsion and an initiator solution containing 0.15 g APS and 5 g water were charged to the flask to form the seed latex. The temperature was then raised to 83 ± 2 °C and the seed polymerization was continued for an additional 30 min. Subsequently, the pre-emulsion and initiator solution containing 0.35 g APS and 25 g water were added slowly to the reactor using two separate constant pressure funnels. The feeding times for the pre-emulsion and the initiator solutions were 3.5 and 4.0 h, respectively. After the feed was completed, the reaction was allowed to proceed for an additional 1 h to increase monomer conversion. The latex was then cooled to room temperature and poured into a glass bottle and used for further characterization.



Scheme 1. The molecular structures of (a) CO-436, (b) SE-10N, (c) SR-10.

Table 1
Experimental design and latex properties (BA/MMA/AA/HEA weight ratio: 87/10/1/2).

Latex ID	CO-436 (phm)	SE-10N (phm)	SR-10 (phm)	Conversion (wt%)	Particle size (nm)	PDI
1	1	0	0	92.15	259	0.041
2	2	0	0	94.73	192	0.031
3	3	0	0	95.30	161	0.011
4	0	1	0	95.22	253	0.037
5	0	2	0	95.20	187	0.023
6	0	3	0	95.94	154	0.011
7	0	0	1	94.19	255	0.044
8	0	0	2	96.06	185	0.011
9	0	0	3	96.30	157	0.011

Note: “phm” is the abbreviation for “parts per hundred parts monomer”.

2.3. Characterization

2.3.1. Particle size and zeta potential

Particle size and zeta potential values of latexes were measured using a Dynamic Light Scattering (DLS) instrument (Malvern NanoS Zetasizer). The analyses were carried out at 25 °C, with each result being an average of three parallel measurements. The latex was diluted until the solid content was about 1%. The reported diameter is an intensity-weighted average particle size.

2.3.2. Electrolyte stability

Latex stability against electrolytes was determined by adding 10 mL of an electrolyte solution to 10 g of latex. After 24 h, the particle size was measured again, and the amount of coagulum, if any, was weighed.