



# The influence of monobutyl itaconate and $\beta$ -carboxyethyl acrylate on acrylic latex pressure sensitive adhesives



Cheng Fang\*, Qiming Yan, Zhuangzhuang Liu, Yifeng Lu, Zhongxiang Lin

College of Chemical Engineering, Nanjing Forestry University, Nanjing, 210037, People's Republic of China

## ARTICLE INFO

### Keywords:

Monobutyl itaconate  
 $\beta$ -carboxyethyl acrylate  
 Acrylic pressure sensitive adhesive  
 Emulsion polymerization  
 Adhesive property

## ABSTRACT

The application of two different kinds of carboxylic monomers, monobutyl itaconate (MBI) and  $\beta$ -carboxyethyl acrylate ( $\beta$ -CEA), in acrylic pressure sensitive adhesive (PSA) latexes is presented in this article. The hydrophilic-lipophilic balance (HLB) values of carboxylic monomers were calculated to determine their water solubility, which was further confirmed by their partition coefficients between organic and water phases. Influences of the functional monomers on particle size and zeta potential of the latexes, as well as on water resistance, thermal stability, gel content, sol molecular weight ( $M_w$ ,  $M_n$ ) and adhesive properties of the polymer were investigated in this work. In addition, the application of commonly used methacrylic acid (MAA) was also determined as a benchmark. The results indicated that for equiweight amounts of acid comonomer, latex particle sizes fall in the order: MBI > MAA >  $\beta$ -CEA, depending on water solubility of the corresponding monomer. Besides, the latex film prepared with MBI showed the best water resistance when compared with other two counterparts. Results also indicated that the PSA prepared with  $\beta$ -CEA exhibited the highest gel content among the three acid monomers. Moreover, the thermal stability of the three carboxylated polymers follow the order P(n-BA + MAA) > P(n-BA +  $\beta$ -CEA) > P(n-BA + MBI). Finally, the effects of carboxylic monomers on the adhesive properties of the PSAs were also evaluated.

## 1. Introduction

Functionalized latexes are often synthesized by emulsion polymerization via the addition of a small amount of functional carboxylic acids into the comonomer mixture. These latexes are typically used in the production of paper coatings, textile coatings, and adhesives [1,2]. The application of unsaturated carboxylic acids as functional comonomers at low concentrations (usually < 20 wt% of the total monomer) in emulsion polymerization can enhance the colloidal and freeze-thaw stability, improve adhesion to various substrates, improve compatibility with pigments and allow the introduction of reactive groups on the particle surface for posterior reactions of chemical modification [3,4]. The most frequently studied carboxylic acid monomers used in emulsion polymerization are itaconic acid (IA) [5,6], acrylic acid (AA) [7,8], methacrylic acid (MAA) [9,10], and fumaric acid (FA) [5], listed in order of increasing hydrophobic nature. Oliveira [5] and coworkers discussed the effect of IA and FA in the emulsion copolymerization of methyl methacrylate (MMA) with n-butyl acrylate (BA) and found that IA and FA were distributed differently throughout the three phases of the emulsion, with these differences depending on the solubility of the corresponding monomer. Koh et al. [9] reported the influence of

copolymerization with methacrylic acid on poly(butyl acrylate) film properties. They found that the presence of small amounts of MAA enhanced the tensile and adhesive properties of the film, and the distribution of the MAA in the latexes was predominantly inside the particles regardless of the polymerization temperatures.

In this article, we employed two unsaturated carboxylic acids, monobutyl itaconate (MBI) and  $\beta$ -carboxyethyl acrylate ( $\beta$ -CEA), instead of those traditional acid monomers, into the application of emulsion polymerization. Itaconic acid esters are obtained by introducing one or two ester groups into the molecular structure of itaconic acid. Moreover, the monoesters were found more active in polymerization than corresponding itaconic acid and diesters and therefore play a significant role in the production of a series of polymers and copolymers with free carboxyl groups that offer excellent properties as adhesives, cleaning media, surfactants, and plastic additives, etc [11]. Hence, monoitaconate esters, especially monobutyl itaconate (MBI), which contains both ester and carboxylic groups, are in high market demand. An important achievement obtained by copolymerizing monoitaconates is a possibility of balancing hydrophilic/hydrophobic properties at different pH levels [12]. Lu et al. [13] discussed the function of three different carboxylic monomers in acrylate emulsion

\* Corresponding author.

E-mail address: [fangcheng533@163.com](mailto:fangcheng533@163.com) (C. Fang).

copolymerization, where they found that the latex prepared with MBI has better water resistance than latex with AA.  $\beta$ -CEA is a carboxylic monomer of the acrylic or methacrylic acid type. A significant difference of  $\beta$ -CEA compared to common carboxylic acids is the greater separation of the carboxylic acid functional group from the unsaturated vinyl functionality in the molecule. It can be polymerized in solution or emulsion to produce acrylic, vinyl-acrylic or styrenic-acrylic polymers with improved adhesive properties. Other major characteristics of  $\beta$ -CEA monomer are: (1) it promotes flexibility in the copolymers owing to the relative low glass transition temperature ( $T_g$ ) of its homopolymers ( $< 30^\circ\text{C}$ ). (2) It provides improved adhesion and stability in the emulsion polymers, due to its -COOH groups being more available than those in the conventional carboxylic acids. (3)  $\beta$ -CEA can be incorporated into the copolymer at high levels over a wide pH range, due to its more reactive salt form compared to AA. (4)  $\beta$ -CEA is more compatible with other monomers, hence reducing polymerization in the aqueous phase and producing more uniform copolymers because of its long chain [14].

Although these two carboxylic acid monomers have so many benefits, only a few fundamental studies have been carried out concerning the behavior of MBI [13,15] and  $\beta$ -CEA [16] in both emulsion polymerization and acrylic PSAs. The partitioning behavior of MBI and  $\beta$ -CEA between organic and water phases was studied in our previous work [17]. In the present study, carboxylated acrylic emulsion PSAs have been synthesized with various vinyl acids. HLB values of different carboxylic monomers were calculated to determine their water solubility, which was further confirmed by their partition coefficients between organic and water phases. Besides, the effect of the functional comonomers on the particle size and zeta potential of the latexes, as well as on the water resistance, thermal stability, gel content, sol molecular weight ( $M_w$ ,  $M_n$ ) and adhesive properties of the polymer films were investigated. Results were compared with those obtained when using methacrylic acid (MAA).

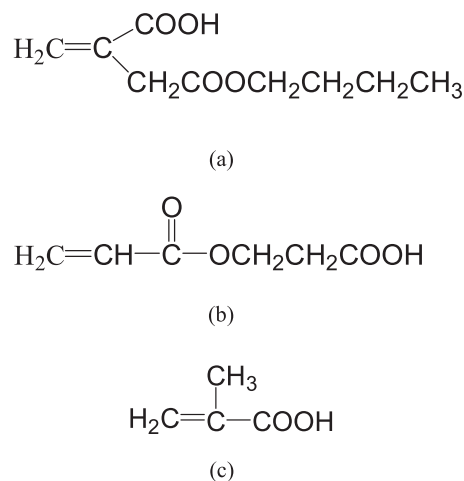
## 2. Experimental

### 2.1. Materials

Butyl acrylate (BA; technical grade, Shanghai Huayi Acrylic, China), methyl methacrylate (MMA; reagent grade, Shanghai Lingfeng Chemical, China), methacrylic acid (MAA; reagent grade, Shanghai Lingfeng Chemical, China), monobutyl itaconate (MBI; technical grade, Qingxin Hanerchem, China),  $\beta$ -carboxy ethyl acrylate ( $\beta$ -CEA; technical grade, Rhodia, France), 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 ( $\text{NaHCO}_3$ ; reagent grade, Shanghai Lingfeng Chemical, China) were 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) and used as received. Distilled deionized water (DI- $\text{H}_2\text{O}$ ) was used throughout the study. Ammonia (25 wt% in  $\text{H}_2\text{O}$ ) was obtained from Nanjing Chemical Reagent Co. The solvent used in the polymer characterization, tetrahydrofuran (THF, HPLC grade, Shanghai Lingfeng Chemical) was also used as supplied by the manufacturer. The molecular structures of MBI,  $\beta$ -CEA and MAA are shown in Scheme 1.

### 2.2. Emulsion polymerization

The recipes for water-based PSA latexes synthesized with different carboxylic monomers are described in Table 1. 25 g deionized water and 2.0 g CO-436 were added to a 500 mL four-neck round-bottom flask and were stirred rapidly to aid dissolution of the emulsifier. The monomer mixtures were then slowly added into the water-emulsifier



**Scheme 1.** The molecular structures of (a) MBI, (b)  $\beta$ -CEA and (c) MAA.

**Table 1**

Emulsion polymerization pressure sensitive adhesive recipe.

| Component             |                    | Amount (g) |
|-----------------------|--------------------|------------|
| Monomers <sup>a</sup> | BA                 | 91         |
|                       | MMA                | 5          |
|                       | carboxylic monomer | 2          |
|                       | HEA                | 2          |
| CO-436                |                    | 2.1        |
| APS                   |                    | 0.5        |
| $\text{NaHCO}_3$      |                    | 0.2        |
| Deionized water       |                    | 102        |

<sup>a</sup> The total monomer weight was set 100 g.

mixture through a constant pressure funnel over a period of 20 min. After that, the pre-emulsion was stirred for a further 30 min.

The polymerization was carried out by a monomer seeded semi-continuous 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. The stirring speed was maintained at 270 rpm throughout the experiments. First, a homogeneous aqueous solution containing 47 g DI- $\text{H}_2\text{O}$ , 0.1 g CO-436, and 0.2 g  $\text{NaHCO}_3$  was charged into the reactor. When the temperature reached  $78^\circ\text{C}$ , a monomer mixture containing 5.69 g BA and 0.31 g MMA 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  $83 \pm 2^\circ\text{C}$  and the seed polymerization was continued for an additional 30 min. Subsequently, the pre-emulsion and initiator solutions 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 to be used for further characterization.

### 2.3. Characterization

#### 2.3.1. HLB value calculation

Griffin's method [18–20]:  $\text{HLB} = 20 \times (M_h/M)$ .

$M_h$  = molecular weight of hydrophilic groups,  $M$  = molecular weight of the whole molecule.

An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 corresponds to a completely hydrophilic molecule.

The HLB value can be used to predict the properties of a molecule: A value  $< 10$ : Lipid soluble, A value  $> 10$ : Water soluble.

Download English Version:

<https://daneshyari.com/en/article/7170923>

Download Persian Version:

<https://daneshyari.com/article/7170923>

[Daneshyari.com](https://daneshyari.com)