

PREPARATION AND PROPERTIES OF SILICONE-ACRYLATE COPOLYMER LATEX

Mu-jie Yang* and Wei Zhang

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Abstract Silicone-acrylate copolymer latex was prepared through three different polymerization processes, *i.e.*, the batch process, preemulsified monomer addition and the monomer addition process. The results revealed that the monomer addition process is a desirable approach to produce narrow particle size distribution latex with higher polymerization conversion and less amount of coagulum. The effect of silicone content on the glossiness and water absorption of latex film was investigated and the results showed that the glossiness of latex film is improved up to a silicone content of 10% of total monomers, but becomes impaired thereafter, whereas water absorption is reduced accordingly.

Keywords Silicone-acrylate latex, Polymerization conversion, Latex film properties, Water absorption

INTRODUCTION

Owing to their outstanding properties such as film-forming, gloss and transparency, acrylic latexes have been widely used in paints, coatings^[1–3], textiles, adhesives, and other applications for many years^[4–5]. However, acrylic latexes have relatively poor water resistance and unsatisfactory weather resistance, which limit their practical application in many fields, especially when they are used in construction and building materials for outdoor purposes. In contrast, polysiloxane has low glass-transition temperature and surface tension, good water repellency and thermal stability. Thus it is considered as an effective approach to modify acrylic latex with silicone to improve a variety of physical or chemical properties of acrylic latex, and this silicone-acrylate copolymer latex would possess the desirable advantages of both silicone and acrylate resin.

Many reports concerning the preparation of silicone-acrylate copolymer latex have been published in the past^[6–9]. Kong *et al.*^[7] prepared stable silicone-acrylate copolymer latex by simultaneous free-radical and cationic copolymerization of [3-(methacryloyloxy)propyl]trimethoxysilane (MATS) with octamethyl cyclotetrasiloxane (D₄) as silicone monomer. In order to improve the glossiness of coated paper, Wu *et al.*^[8] synthesized silicone-modified styrene-butyl acrylate copolymer latex using MATS, D₄, styrene, and butyl acrylate (BA) as raw materials. However, methyltriethoxysilane (MTS) was rarely employed to prepare silicone-acrylate latex in previous work.

In this paper, we synthesized silicone-acrylate latexes with MATS and MTS as silicone monomers. The copolymerization process was investigated and the properties of corresponding latex films were characterized.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), BA, methacrylic acid (MAA) (Shanghai Chemical Reagent Plant) and hydroxyethyl methacrylate (HEMA) (Sigma Chemical Co.) were distilled before use. Silicone monomers including MATS and MTS were available from Nanjing Shuguang Chemical Plant and purified before use.

*Corresponding author: Mu-jie Yang (杨慕杰), E-mail: yangmj@cmsce.zju.edu.cn

Received January 3, 2003; Revised February 24, 2003; Accepted February 27, 2003

Ammonium persulfate (APS), di-*n*-butyltin dilaurate (DBTDL, catalyst for MTS condensation reaction), sodium dodecyl sulfate (SDS), ethoxylated nonyl phenol containing 10 U of ethylene oxide (OP-10), Na₂CO₃, deionized water and ammonia water (NH₃ • H₂O) were of reagent grade and used as supplied.

Emulsion Polymerization

Copolymerization was performed in a 500 mL reactor in a thermostated water bath, and the latex was neutralized with ammonia water at 60°C after polymerization. Finally, the reaction mixture was filtered, and the amount of coagulum was weighed. A typical recipe is: MMA, 40 g; BA, 44 g; MAA, 1.0 g; HEMA, 1.0 g; APS, 0.2 g and DBTDL, 0.4 g; OP-10, 1.0 g; SDS, 0.8 g; Na₂CO₃, 0.2 g; deionized water, 120 g; weight ratio of MATS: MTS, 6.5:1. In certain recipes, the content of silicone was changeable, while the solid content of the final latex remained about 40 wt%.

Emulsion copolymerization was carried out using three different processes: (1) Batch process (Method I): Water, emulsifier, Na₂CO₃, DBTDL and all monomers were poured into the reactor at 60°C, and then the temperature was raised to 80°C with stirring. The aqueous solution of APS was added into the reactor and the polymerization was continued for 4 h. (2) Preemulsified monomer addition process (Method II): Water, 60 percent of emulsifiers, DBTDL and all monomers were mixed at room temperature and emulsified for 30 min by stirring. The obtained monomer emulsion was then charged successively for 2 h into the reactor containing the residual water, 40% of emulsifiers, Na₂CO₃ and APS solution at 80°C. After that the polymerization continued for 2 h. (3) Monomer addition process (Method III): Water, emulsifier, Na₂CO₃, DBTDL and 10% of monomers were placed into the reactor. When the temperature of the system was raised to 80°C, APS solution was added. 10 min later, the residual monomers were continuously introduced dropwise into the reactor for 2 h. The polymerization was terminated after continuing for 2 h.

Measurements

Polymerization conversion was measured by gravimetric method. Polymerization stability was measured with weight percentage of coagulum formed in the polymerization process to the total amount of monomers.

Particle morphology and particle diameter were determined by using a transmission electron microscope (TEM-1200 EX) and an LS Particle Size Analyzer (Coulter), respectively.

Water absorption is defined as $(W_2 - W_1)/W_1 \times 100\%$, where W_1 and W_2 are the weight of the latex film before and after immersion. The latex films were immersed in deionized water for 48 h.

A Specular Gloss Tester was used to measure the glossiness of latex film according to Chinese Standard Testing Method GB 8941.3. Glossiness is an indication of the degree to which the coated surface simulates a perfect mirror in its capacity to reflect incident light. The angle used in the determination is 75°.

RESULTS AND DISCUSSION

Effect of Polymerization Process on Silicone-Acrylate Latex

The effects of different polymerization processes on polymerization conversion and coagulum in copolymerization are shown in Table 1. Generally, polyacrylics are prepared by free-radical polymerization, while polysiloxane is synthesized by polycondensation. In this paper, polysiloxane was obtained by hydrolytic condensation between MATS and MTS during the emulsion polymerization with DBTDL as catalyst. Thus, there existed a competitive relation between free-radical polymerization and hydrolytic condensation. In method I, all monomers, initiator and catalyst were poured into the reactor, and free-radical polymerization and hydrolytic condensation proceeded simultaneously. Because the reaction speed of hydrolytic condensation is fast, crosslinking often occurred among silicone monomers, which resulted in the production of a larger amount of coagulum and in the lowering of polymerization conversion in method I.

In Methods II and III, the reaction system had a high concentration of APS at the beginning of polymerization, and the free-radical polymerization had superiority over hydrolytic condensation, which increased the possibility of copolymerization between vinyl monomers and polysiloxane. Once MATS copolymerized with acrylate, the hydrolytic condensation between MATS and MTS could hardly produce

coagulum. Thus a high polymerization conversion and low yield of coagulum were obtained. Furthermore, it can be seen from Table 1 that the yield of coagulum based on Method III is lower than that in Method II. This may be due to the fact that polysiloxane is difficult to emulsify.

Table 1. Effect of different polymerization processes on the yield of coagulum^a

Process	Polymerization conversion (wt%)	Coagulum (wt%)
Method I	72.4	3.6
Method II	83.6	1.5
Method III	94.1	0.9

^a Silicone content was 8 wt%.

The particle diameter of latex was also affected by the polymerization process. In Method I, the free-radical reaction was of violent intensity because all the initiator and monomer were present together in the reactor during the early stage of polymerization. The monomer with high reactivity ratio polymerized rapidly, while other monomers may not convert when initiator was lacking as the polymerization process proceeded, which easily led to a wide range of distribution in latex particles. However, in the other two methods monomers were added dropwise into the reactor, which reduced the effect of reactivity ratio of monomers, especially in Method III. Thus the latex particle tended to form a relatively narrow distribution with an average diameter of 60 nm (Fig. 1). The latex particle morphology prepared by Method III is shown in Fig. 2. In addition, there is no coagulum in the latex formed by using Method III after 2 months' storage, which indicates that the latex is relatively stable.

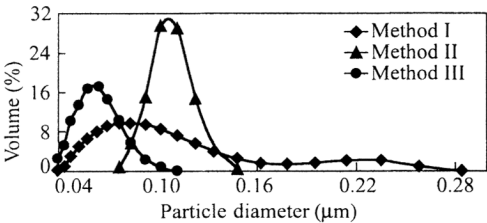


Fig. 1 The effect of polymerization process on latex particle distribution

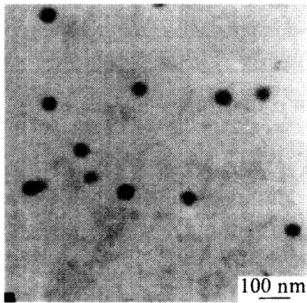


Fig. 2 Transmission electron micrographs of silicone-acrylate prepared by Method III

Effect of Silicone Content on Latex Properties

Properties of silicone-acrylate latex are affected greatly by the content of silicone in monomers. However, excess silicone would result in lowering of the monomer conversion and an increased amount of coagulum. The influence of silicone content on polymerization is shown in Table 2. It was found obviously that the amount of coagulum increases and the polymerization conversion decreases with increasing silicone content. The polymerization conversion was only 50.3% when silicone content attained 25%. In order to study the effect of silicone content on latex properties, experiments were performed within a certain range of silicone content.

Table 2. Influence of silicone content on polymerization^a

Silicone contents (wt%)	4	8	12	16	20	25
Conversion (wt%)	96.9	94.1	91.0	85.2	68.7	50.3
Coagulum (wt%)	0.4	0.9	2.5	5.5	6.4	12.7

^a The silicone-acrylate latex was prepared based on Method III.

The glossiness of latex can be improved usually by increasing the amount of hard monomers, but a serious drawback of this approach is that the latex film tends to crack into pieces if hard monomers with high T_g exceed a given level. In our experiment, the effect of silicone content on glossiness of the film is illustrated in Fig. 3, and the result is similar to the description in the literature^[8]. The glossiness increases with the increase of silicone

content, but decreases when silicone content exceeds 10%. The result could be understood as follows: silicone segments within the copolymer can lower the polymer-air interfacial tension, and tend to migrate to the surface of film and to form a uniform coating, or in other words increase the glossiness. However, with the increase of silicone content, the polymerization conversion decreases, so self- and homo polycondensation takes place and the silicone formed with low surface tension will float on the film surface and change its regularity; accordingly, the glossiness is reduced.

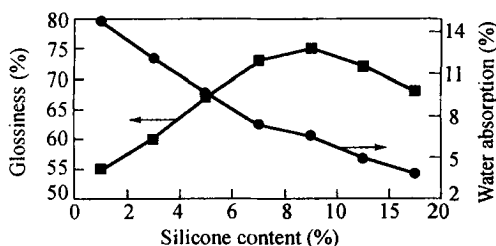


Fig. 3 Effect of silicone content on glossiness and water absorption of silicone-acrylate latex film
 ■ Glossiness; ● Water absorption

The effect of silicone content on water absorption of the latex film is also illustrated in Fig. 3. Obviously, water absorption decreases with the increase of silicone content, which can be attributed to two factors: (1) silicone segments with functional Si—OH groups served as a crosslinking agent and tends to form polymer networks during the film formation, which prevents the permeation of water; (2) silicone segments have low surface energy because of their flexible Si—O bonds, and easily forms a hydrophobic surface.

CONCLUSIONS

The yield of coagulum and the latex particle diameter were significantly influenced by the polymerization process. Compared with monomer preemulsion addition and the batch process, the monomer addition process can be used to prepare narrow particle distribution latex with higher polymerization conversion and lower coagulum yield.

The effect of silicone content on glossiness and water absorption of latex film was different. With the increase of silicone content, the glossiness of latex film is improved up to 10%, but becomes impaired when the silicone content exceeds this level, whereas water absorption of the film is reduced accordingly.

REFERENCES

- 1 Kozakiewicz, J., Rosciszewski, P., Rokicki, G., Koldonski, G., Skarzynski, J. and Koncka-Foland, A., *Surf. Coat. Inter.* (Part B), 2001, 84: 243
- 2 Park, H.S., Yang, I.M., Wu, J.P., Kim, M.S., Hahm, H.S., Kim, S.K. and Rhee, H.W., *J. Appl. Polym. Sci.*, 2001, 81: 1614
- 3 Harui, N. and Agawa, T., *J. Coatings Technol.*, 1998, 70(880): 73
- 4 Mazurek, M., Kinning, D.J. and Kinoshita, T., *J. Appl. Polym. Sci.*, 2001, 80: 159
- 5 Li, S.Q., Xia, Y.Z., Shi, S.X. and Jiao, S.K., *J. Beijing. Univ. Chem. Technol.* (in Chinese), 2002, 29 (3): 32
- 6 Kokko, B.J., *J. Appl. Polym. Sci.*, 1993, 47: 1309
- 7 Kong, X.Z., Kan, C.Y., Luo, D. and Yuan, Q., *Chem. J. Chin. Univ.*, 1995, 16: 1810
- 8 Wu, Y., Duan, H.D., Yu, Y.Q. and Zhang, C.G., *J. Appl. Polym. Sci.*, 2001, 79: 333
- 9 Kan, C.Y., Liu, D.S., Kong, X.Z. and Zhu, X.L., *J. Appl. Polym. Sci.*, 2001, 82: 3194