Preparation and Performance in Paper Coating of Silicone-Modified Styrene–Butyl Acrylate Copolymer Latex

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ABSTRACT: Silicone-modified styrene-butyl acrylate copolymer latex was synthesized by emulsion copolymerization by using octamethylcyclotetrasiloxane (D_4), styrene, and butyl acrylate as raw materials, potassium persulfate as initiator and propylmethacrylate triethoxysilane (KH-570) as crosslinking agent. The infrared spectra studies showed that the vinyl monomers were completely copolymerized with D_4 . The prepared silicone-modified copolymer latex with the interpenetrating polymer networks tended to have higher stability, and better toluene and water resistance than styrene-butyl acrylate latex. The glossiness of coated paper was improved with silicone-modified copolymer latex, and it was at a maximum when D_4 was about 3% of total monomers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 333–336, 2001

Key words: silicone; styrene; butyl acrylate; coated paper; latex

INTRODUCTION

Large amounts of styrene (ST)-acrylate and STbutadiene latex are used in the paper industry as binders in paper coatings. Although the binder is used in small amounts in the final coating, the film-forming ability, as well as the physical and mechanical properties of the binder, are of great importance to the performance of the coating.^{1,2} These latexes are able to improve the surface strength, the glossiness, the water resistance, and the printing adaptability of the coated paper.³

Recently, major breakthroughs in synthesis and applied performance of silicone-modified acrylate latex have been reported. $^{4-6}$ The siliconemodified latex appears to possess the advantages of both silicone and acrylate resin in overcoming the high cost of silicone or the poor performance of acrylate resin in thermal stability and resisting water. It is well known that interpenetrating polymer networks (IPN) are a special type of polymer mixture with three dimensions consisting of two or more different polymer networks synthesized and/or crosslinked independently within each other, and the IPNs have several advantages over blends.⁷ Therefore, the modified latex has more comprehensive performance with the formation of IPN,⁸⁻¹¹ and can be successfully applied in the leather and coating industry.^{6,12} So far, silicone-modified latexes have not been applied in the coated paper industries. Dominating the market for coated papers, ST-butyl acrylate (BA) and ST-butadiene copolymer latexes offer low cost and

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easy operation, but with the rapid development of the coated paper and printing industry, these single varieties of latex have not satisfied the needs of the paper market. To improve performances of latexes¹³ and the glossiness of coated paper, we have satisfactorily prepared silicone-modified ST–BA latexes with emulsion copolymerization techniques.

EXPERIMENTAL

Materials

Ethoxylated nonyl phenol containing 10 U of ethylene oxide (OP10), sodium dodecyl sulfate, potassium persulfate, and ammonia water (NH₃ · H₂O) were chemically pure. Octamethylcyclotetrasiloxane (D₄), ST, BA, and propylmethacrylate triethoxysilane (KH-570) crosslinking agent were industrial grade.

Preparation of Latexes

Copolymerization was performed in a stirred 500-mL reactor fitted with an overhead condenser and two feed funnels. The temperature of the reactor contents was maintained at 40-80°C by partially immersing the reactor in a thermostated water bath. The starting materials, including monomers (D₄, KH-570, and 1/4 mixed monomers of BA and ST) mixed with surfactants (OP10 and sodium dodecyl sulfate) and deionized water, were stirred for 0.5 h and the temperature was set at 40°C. Then the starting materials were heated to 80° C; potassium persulfate and the other 3/4mixed monomers were fed from two funnels simultaneously for 2 h. After the total addition, the reaction mixture was heated for an additional 2 h at 80°C for complete conversion. While stirring, the temperature was lowered to 55°C, and the mixture neutralized to pH value 8-9 by NH_3 . H_2O . Finally, the reaction mixture was filtered at 40°C.

Measurements of Latexes

The infrared (IR) spectra in this research were determined by a HITACHI 275-50 IR spectrophotometer after drying the latex for 4 h at 80°C in vacuum and grinding it into a powder. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum.

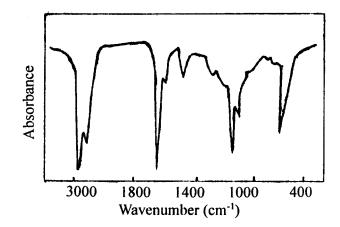


Figure 1 IR spectra of unmodified ST–BA copolymer.

The latex stability was determined by using the procedure outlined in previously. $^{12}\,$

Toluene resistance of the latex film was measured as follows: 10-mL latex was coated on a piece of 12×12 cm glass plate and dried at ambient temperature, forming the film. The film was dipped into toluene for 1 h, and the swelling ratio of the latex film was measured after weighing.

Water absorption of the latex film was measured according to the following procedure. The weighed latex film was immersed in deionized water for 48 h, and the water absorption was calculated by drying the surface water of the film and weighing.

Glossiness of the coated paper was tested according to Chinese Standard GB8941.3 by a Specular Gloss Tester. 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°. The higher the specular gloss, the higher is the microsmoothness and the glossiness.

RESULTS AND DISCUSSION

Figures 1 and 2 show the IR spectra of unmodified and silicone-modified ST–BA copolymers, respectively. The bands are identified as follows: the band at 1060 cm⁻¹ is attributed to the Si—O stretching modes, whereas the band at 1450 cm⁻¹ is due to the Si—CH₃ rocking normal vibrations. The bands at 2950, 700, and 1725 cm⁻¹ result from C—H stretching vibrations, benzene wagging modes, and C=O stretching vibrations, respectively. Figure 2 demonstrates that vinyl

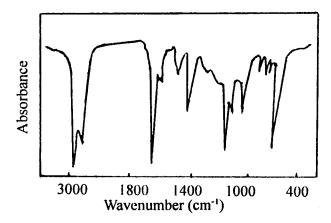
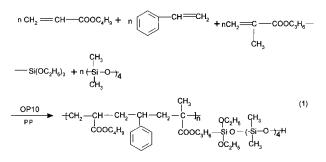


Figure 2 IR spectra of silicone-modified ST–BA copolymer.

monomers (including KH-570) have reacted completely because there are no bands at 1800-1860 cm⁻¹, which belong to the C=C bond.

The silicone-modified latex offers higher stability than the ST-BA latex, i.e., longer storage life and fewer separated solids. The modified latex can be stored for a period of 60 weeks without any performance change, whereas the unmodified latex only has a storage life of 38 weeks. Filtration suggests that the separated solid retained on a filter cloth of the silicone-modified latex is lower than that of ST–BA latex. The authors offer the following two reasons for the stability of the modified latex. First, because the Si-O bond energy is higher than that of the C—O bond, it acts as an excellent stabilizer by itself. Correspondingly, the latex stability is improved by silicone modification. Second, D₄, ST, and BA can be copolymerized into an IPN by crosslinking, as shown in the eq. (1), which obviously improves chemical stabilities of Si-O, C-C, and C-O bonds. At the same time, the IPN may exhibit comprehensive chemical properties of silicone and ST–BA copolymer, and appears to increase the chemical stability of silicone-modified ST-BA latex.



The trend toward silicone-modified ST–BA latex film with smoothness and uniformity has im-

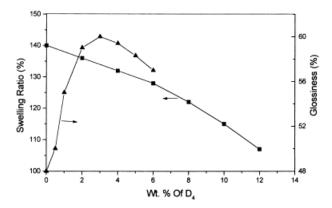


Figure 3 Swelling ratio (toluene) and glossiness as functions of wt % of D_4 (temperature, 25°C). \blacktriangle , Swelling ratio; \blacksquare , glossiness.

proved many physical properties such as toluene resistance and water resistance. Figure 3 shows that the swelling ratio of latex film may diminish with increasing D_4 feed, i.e., the toluene resistance appears to rise. It is the unique solvent resistance of silicone that improves such a performance of silicone-modified latex film. The silicone-containing materials are noted for their high surface activity and low surface energy, thus the silicone segments within copolymers tend to migrate to the air-polymer interface so as to form a solvent-resistant surface.¹⁴ In addition, the silicone-modified copolymers can also have a hydrophobic surface. Table I provides the effect of D_4 dosage on water absorption of the film. Our studies indicate that the presence of silicone in copolymer may play a significant role in the obvious increase in water resistance of latex.

From another point of view, the above results of toluene resistance and water resistance indicate that the silicone segments have been crosslinked into the IPN of the ST–BA copolymer, and the performances of the copolymer latex are improved.

Table IThe Effect of D_4 Feed on the WaterAbsorption of Latex Films

Sample No.	D_4 Feed (wt %)	Water Absorption (%; 25°C)
1	0	16.1
2	0.5	13.8
3	1	12.2
4	2	11.2
5	4	10.5
6	6	8.6

Until now, improving the glossiness of coated paper has proved to be a difficult task for the traditional ST–BA latex.¹⁵ The glossiness can be increased in the presence of hard monomers (ST, methyl methacrylate, etc.), but a serious drawback of this approach is that the latex film tends to crack into pieces if hard monomers exceed a given level,¹⁶ resulting in poor performance of the coated paper. Fortunately, coated paper can exhibit higher glossiness by the addition of D_4 . As shown in Figure 3, however, the glossiness decreases at high D₄ values. The maximum glossiness occurs when D_4 is about 3% of total monomers. The behavior of the curve may be described as follows: according to the above results and the literature,¹¹ silicone-modified ST-BA copolymer forms an IPN parallel to the directional arrangement of side-chain methyl in silicones, and the silicone segments within copolymers tend to migrate to the air-polymer interface. Therefore, the reflection of light by the copolymer film tends to be more regular, because of the formation of a uniform coating,³ and the corresponding coated paper will exhibit higher glossiness. However, it is reasonable to assume that D_4 may partially be polymerized to silicones by accumulating near the film–air interfaces, and it is found that a part of the silicone floats on the emulsion surface in the synthesis experiment if excess D_4 is added. The auto-polymerization of D_4 is shown in eq. (2). This means that a fraction of the silicone has not entered into the IPN, leading to irregularity of the side-chain methyl groups and the copolymer diminishing the glossiness but which is still higher than that of the D_4 -free latex.

$$\begin{array}{cccc}
 CH_{3} & CH_{3} \\
 | & OP10 & | \\
 n & \overleftarrow{(-Si-O)_{4}} & \overrightarrow{OP10} & (-Si-O)_{4n} \\
 | & PP & | \\
 CH_{3} & CH_{3}
\end{array}$$
(2)

CONCLUSIONS

IR spectra and latex performance studies show that silicone-modified ST–BA copolymerization is feasible involving complete reaction of vinyl monomers. By feeding D_4 into the reaction emulsion in polymerization, silicone is crosslinked with ST–BA copolymer to form an IPN by KH-570. Some performance criteria such as stability, toluene resistance, and water resistance of the copolymer latex, have been improved. Correspondingly, silicone-modified ST–BA copolymer latex facilitates the formation of a uniform coating, and the glossiness of coated paper increases. The glossiness reaches its maximum when the D_4 dosage of total monomers is about 3%.

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REFERENCES

- Karlsson, O.; Hassander, H.; Wesslén, B. J Appl Polym Sci 1997, 63, 1543.
- Chu, F. X.; Graillat, C.; Guyot, A. J Appl Polym Sci 1998, 70, 2667.
- Duan, H. D.; Zhao, C. S.; Wu, Y. M. Polym Adv Technol 1999, 10, 78.
- Huang, G. S.; Li, K. Y. Chin Synthetic Rubber Ind 1994, 17, 288.
- Huang, G. S.; Li, K. Y. Chin Synthetic Rubber Ind 1994, 17, 224.
- Satoh, K.; Urban, M. W. Progress in Organic Coating 1996, 29, 195.
- Samui, A. B.; Suryavanshi, U. G.; Patri, M.; Chakraborty, B. C.; Deb, P. C. J Appl Polym Sci 1998, 68, 255.
- Ali, S. A. M.; Hourston, D. J.; Manzoor, K.; Williams, D. F. J Appl Polym Sci 1995, 55, 733.
- 9. Sperling, L. H. J Appl Polym Sci 1969, 7, 425.
- Huang, Y.; Jones, F. N. Prog Org Coat 1996, 28, 133.
- Fan, Q. H.; Huang, Y. Chin Synthetic Rubber Ind 1995, 18, 276.
- 12. Xu, M. Chin Leather 1995, 22, 21.
- 13. Guo, Z. C. Fine Chem 1997, 14, 52.
- Chiang, W. Y.; Shu, W. J. J Appl Polym Sci 1988, 36, 1889.
- 15. Li, D. X. Guangdong Paper 1995, 2, 34.
- 16. Chen J. H.; Wang, L. J Funct Polym 1995, 8, 220.