

Effect of anionic/nonionic surfactant systems on the properties of water-based styrene/acrylic copolymer latexes

B. C. Ayhan¹, D. Şakar^{1*}, E. C. Tarakçı²

¹*Yildiz Technical University, Chemistry Department, 34220 Esenler, Istanbul, Turkey*

²*Hürkimsa Kimya Sanayi, Çayırova, Kocaeli, Turkey*

Accepted: August 07, 2023

The effect of anionic, nonionic and anionic/nonionic surfactants on the reaction during the emulsion copolymerization of styrene and acrylic monomers was investigated. For this purpose, the effect of anionic, nonionic and anionic/nonionic surfactant systems at different ratios on the emulsion copolymerization of styrene with butyl acrylate, acryl amide and acrylic acid in the presence of ammonium persulfate initiator to obtain water-based styrene copolymer-based paint binders was examined and characterized *via* solid substance analysis, FTIR/ATR, DSC and viscosity. Then, after comparing the obtained results, the optimum anionic/nonionic surfactant system was created and water-based emulsion paint binders contributed to the properties such as better bonding of the paint to the surface to be applied and better distribution of the pigment in the system.

Keywords: Paint binder; water-based styrene/acrylic copolymer; surfactant

INTRODUCTION

Emulsion polymerization is an important process that has been used for many years for the industrial production of synthetic polymers and copolymers. Selection of process type (batch, semi-batch, continuous) is important in emulsion polymerization, especially in a copolymerization system with monomers with different reactivity rates and quite different solubility values in water. It determines the homogeneity of the copolymer composition, the molecular, surface and colloidal properties of the copolymer and, accordingly, its physical and mechanical behavior. In the synthesis of St/A latexes, the semi-batch method is commonly used to increase the homogeneity of the copolymer [1-3] When monomers with different water solubility and different reactivity degrees are used in semi-batch emulsion processes, it is assumed that particle nucleation occurs predominantly in the aqueous phase. The fact that the polymerization is devoid of monomer makes the copolymer composition in the particle homogeneous. It has been observed that the latex properties change depending on the difference in the polymerization mechanism. In dispersed media, an important component of the formulation of emulsion polymerization is the surfactant. Anionic surfactants act as strong particle generators and stabilize the latex particles *via* electrostatic repulsion while nonionic surfactants provide entropic repulsion and steric stabilization. To overcome the limited stabilizing effect at high solid content and high water

sensitivity of latexes, stabilization with anionic surfactants or with a mixture of anionic/nonionic surfactant is used in latexes [4-6].

In this study, styrene-acrylate latexes were synthesized *via* semi-batch emulsion polymerization method in the presence of anionic, nonionic and anionic/nonionic surfactant mixture and ammonium persulfate initiator. The characterization of the synthesized latexes was done by FTIR/ATR, DSC, determining solid content percentage, viscosity and minimum film forming temperature.

EXPERIMENTAL

Chemicals and instrumentation

Styrene, butyl acrylate, acrylic acid and acrylamide (monomers), ammonium persulfate (thermal initiator) were purchased from Merck. An anionic emulsifier (AE, ANIODAC 13P 20-27) based on polyethoxy sulfate and a nonionic emulsifier (NE, NONIDAC 11P 30-70), a fatty alcohol polyethylene glycol ether based on ethylene oxide, were taken from SASOL. The active substance ratio of the anionic emulsifier is 30% and the active substance ratio of the nonionic emulsifier is 70%. Ammonia (NH₃) was used as a pH regulator and defoamer, biocide and plasticizer were added in reaction media.

Bruker Instruments ALPHA II FTIR/ATR was used for structural characterization of St/A latexes. Viscosity of latexes was determined on a Brookfield viscosimeter at 25 °C using spindle 3.

* To whom all correspondence should be sent:
E-mail: dsakar@yildiz.edu.tr

DSC Q20 TGA was used to determine glass transition temperature of St/A latex films under N₂ atmosphere (10 °C/min heating rate). Mettler Toledo pH meter was used to determine pH of St/A latexes. Rhopoint minimum film forming temperature (MFFT) 90 equipment was used to determine MFF temperature of St/A latex films and measurements were done between -10°C and 90°C.

Determination of the solid content of the latexes

To measure the solids of the synthesized St/A copolymers, a certain amount of polymer was weighed into the tared aluminum foil container. The weighed copolymers were heated up to 120°C in the device used for solids determination. Thus, all the water in the polymer was evaporated and the solid material of the polymer was read from the device.

This process was performed 3 times for each synthesized polymer, and the solid matter content of the polymer was determined according to the following equation by taking the average of the results.

$$\% \text{ Solid content} = 100[(w_3-w_1)/(w_2-w_1)] \quad (1)$$

where w_1 is the weight of the empty container (g); w_2 is the mass of latex weighed initially (g); w_3 is the mass of solid polymer weighed after drying in an oven at 120°C for 30 minutes (g).

Synthesis of water-based styrene/acrylic copolymer paint binders

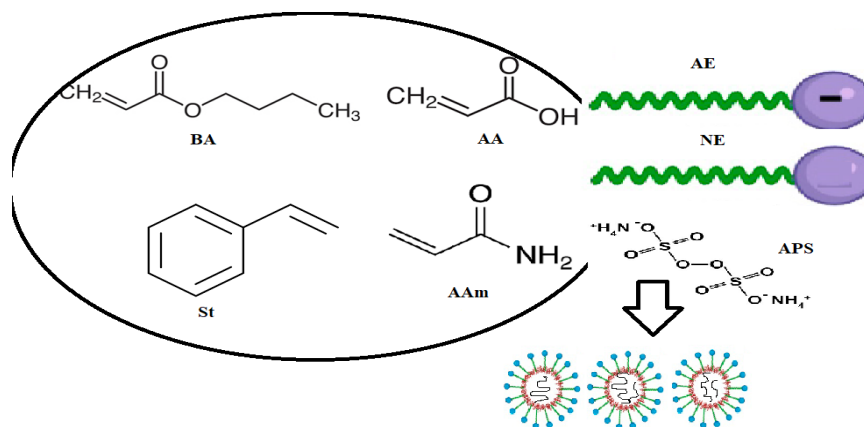
St/BA/ AAm /AA latexes were synthesized *via* semi-batch emulsion polymerization method. Firstly, the emulsifier was dissolved in water and defoamer was added to the glass reactor (5L) and the temperature was brought to 80-85 °C at a mixing rate of 200-250 rpm. Monomers, namely styrene, butyl acrylate, acrylamide and acrylic acid were mixed in a 2L balloon. Meanwhile, the APS solution was prepared and poured into a dropping funnel. Monomer mixture and APS solution were fed to the reaction phase with the help of an electric pump in 3 hours (Table 1). When all of the initiator and emulsion phase was added, the reaction mixture was stirred for 1 hour. *Tert*-butyl hydroperoxide (70%)

and sodium formaldehyde sulfoxylate (100%) were added to the polymer when the temperature of the reaction mixture reaction fell below 75 °C. Plasticizer was added to the reaction mixture cooled below 50°C, and ammonia was added below 40°C. Finally, when the reaction temperature reached below 25 °C, the reaction was terminated and the latex was separated by filtration.

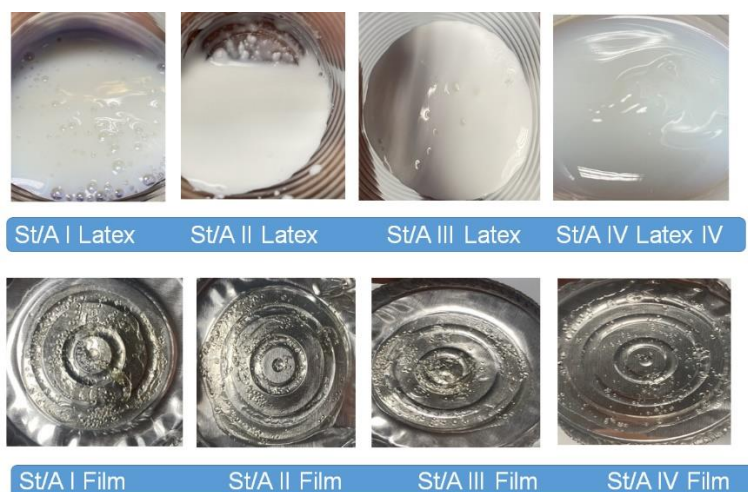
Looking at the four syntheses, polymerization occurred when anionic emulsifiers were used alone in the system, as seen in St/A copolymer I. However, when nonionic emulsifier with the same active substance was used in St/A copolymer II, it was seen that no polymerization occurred. While the negatively charged part in anionic emulsifiers affects the stabilization of the formed polymer, namely the latex, the hydrophobic chain part provides the critical micellar concentration (CMC) and lowers the surface tension between monomer/water [7]. However, nonionic emulsifiers are mostly used for freezing of latex, etc. Polymerization took place because the critical micellar concentration was achieved and the surface tension between monomer/water decreased even when only anionic emulsifier was used. However, since micelles did not form at the desired level in nonionic emulsifiers, polymerization did not occur in Synthesis 2. Starting from Synthesis 2, the amount of nonionic emulsifier was increased in Synthesis 3 with a view to bring it to the required level for CMC. It was observed that a lot of pollution was formed during the experiment. It has been observed that when nonionic emulsifiers were used alone, problems occurred in polymerization and pollution increased. In Synthesis 4, an anionic/nonionic emulsifier system was created. While preparing the emulsion phase, both anionic and nonionic emulsifiers were added according to the ratios given in Table 1 and polymerization was realized. No problems were observed during the polymerization, and no pollution was encountered in the reactor. St/A I, III and IV latexes were successfully synthesized (Scheme 1). The pictures of St/A I, III and IV latexes and films are given in Scheme 2.

Table 1. Formulations of St/BA/ AAm /AA latexes

St/A	St (%)	BA (%)	AA (%)	AAm (%)	AE (%)	NE (%)	APS (%)	Others (%)
I	23.60	23.50	0.78	0.82	3.10	-	0.3	47.9
II	23.60	23.50	0.78	0.82	-	1.5	0.3	49.5
III	23.60	23.50	0.78	0.82	-	2.2	0.3	48.8
IV	23.60	23.50	0.78	0.82	1.3	0.8	0.3	48.9



Scheme 1. Synthesis of St/A latexes



Scheme 2 St/A I, III and IV latexes and films

RESULTS AND DISCUSSION

To examine the effect of anionic/nonionic emulsifier systems on various properties of water-based styrene/acrylic copolymer paint binders, St/BA/AAm/AA latexes were synthesized and structural characterization of St/A copolymers was done by FTIR/ATR. The spectra are given in Figures 1, 2 and 3. The FTIR/ATR spectra of St/BA/AAm/AA latex films showed that monomers participated in the copolymerization reaction. In the FTIR/ATR spectra, the -OH vibration band belonging to the -COOH group was not observed in the 3200-3500 cm^{-1} region. The absence of -OH vibration band indicated the presence of a -COO- group in the environment. Aromatic C-H stretch of polystyrene was 3000 cm^{-1} , aliphatic C-H stretches were 2925, 2928, 2924 cm^{-1} , aromatic C=C stretches of 1451, 1452, 1453 cm^{-1} peaks were observed. Stretching vibrations of AAc (1705 cm^{-1}) and BA (~1730 cm^{-1}) -COO- carbonyl groups coincided and were observed as a sharp band at 1727, 1726 cm^{-1} . Polyacrylamide was observed at C=O ~1650 cm^{-1}

and CN ~1400 cm^{-1} . The DSC curves of the St/A latex films depending on the AE and NE are given in Figures 4, 5 and 6.

T_g values of PS, PBA, PAA and PAAm homopolymers are 105, -54, 106 and 165 $^{\circ}\text{C}$, respectively. The latex particles showed only a single T_g , indicating that a copolymer was formed as a result of polymerization [7]. When a low amount of emulsifier was used, insufficient micelles were formed where monomers could emulsify. As the amount of emulsifier increased, the particle size of the micelles decreased. Therefore, while styrene monomers had difficulty penetrating the micelles, butyl acrylate monomers bound more easily with the reactive sites. Thus, an increase in the amount of soft monomer in the polymer and a decrease in T_g value was observed (Table 2)

Analysis results such as solid matter, pH, viscosity, glass transition temperature and minimum film forming temperature (MFFT) of the synthesized St/A latexes are given in Table 2.

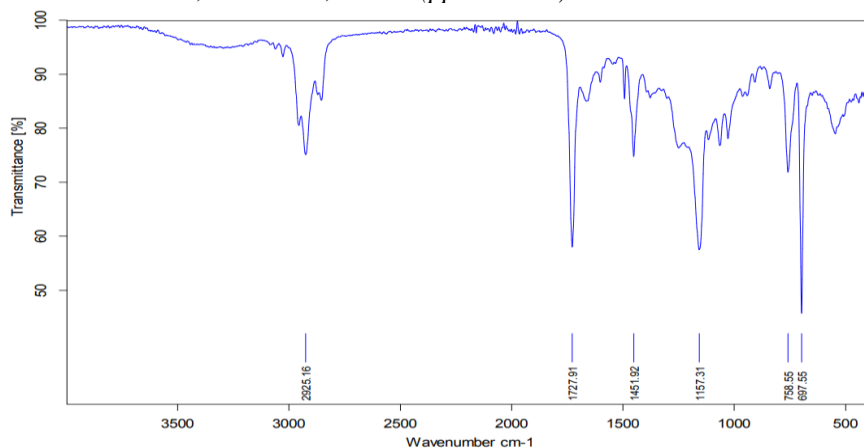


Figure 1. FTIR/ATR spectrum of St /A I latex film

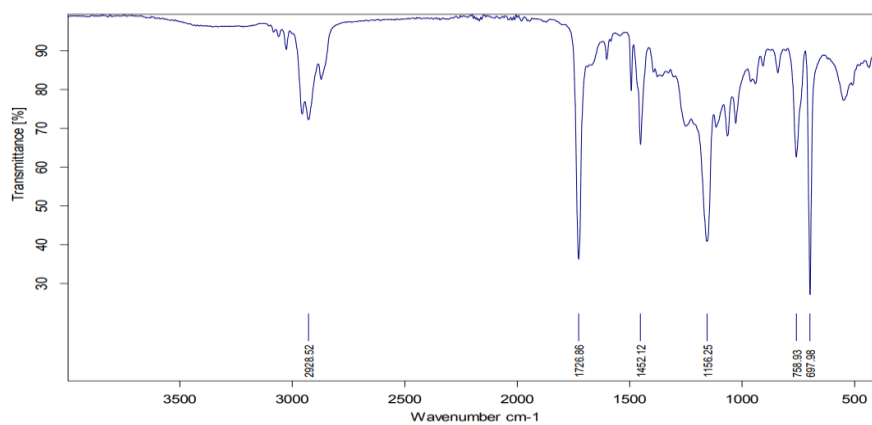


Figure 2. FTIR/ATR spectrum of St /A III latex film

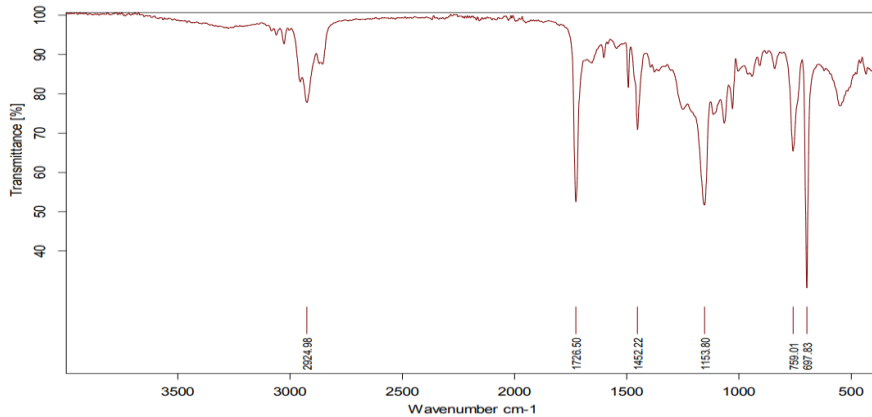


Figure 3. FTIR/ATR Spectrum of St /A IV latex film

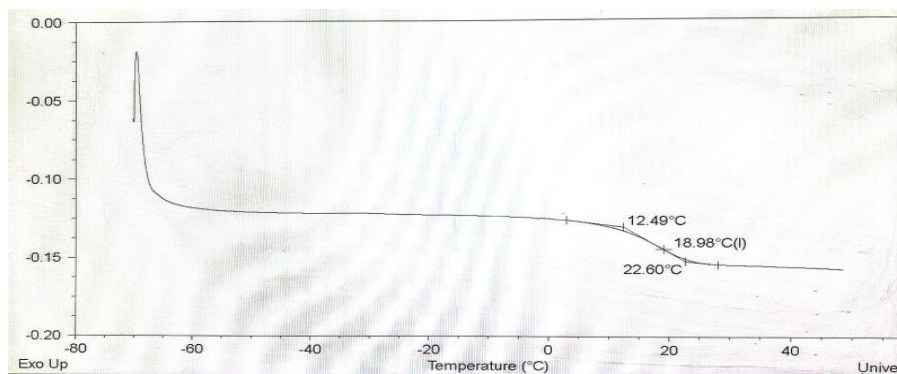


Figure 4. DSC thermogram of St/A I latex

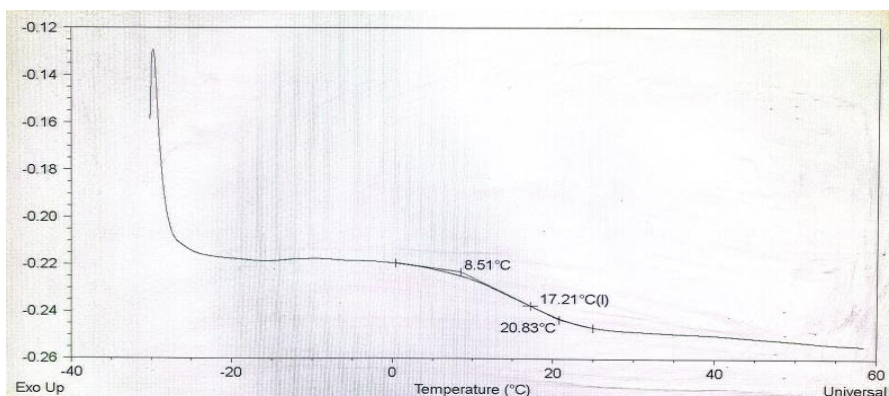


Figure 5. DSC thermogram of St/A III latex

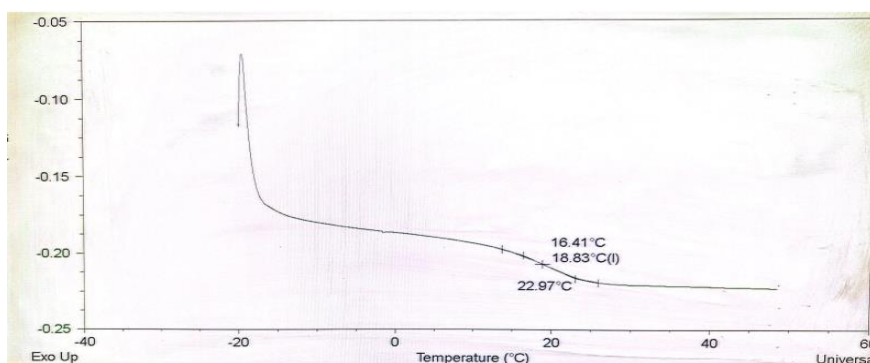


Figure 6. DSC thermogram of St/A IV latex

Table 2. Solid matter percentage, pH, viscosity, glass transition temperature and minimum film forming temperature (MFFT) of the synthesized St/A latexes

St/A	Solid matter (%)	pH	Viscosity (cP)	T _g (°C)	MFFT (°C)
I	49.91	9.13	1675	18.98	19.4
III	46.30	6.77	40	17.21	18.7
IV	49.86	8.34	9235	18.83	16.2

As the total concentration of anionic and nonionic emulsifiers increased in the latexes, the viscosity of the latex increased from 1675 to 9235. As the number of micelles acting on the CMC increased with the increasing emulsifier ratio, the size of the micelles decreased and the viscosity increased. The stability of emulsions with high viscosity also increased.

The minimum film forming temperature (MFFT) indicates the lowest temperature at which a paint or coating can form a film on the surface. Since both the MFFT value and the T_g value of a polymer are affected by the same morphological properties of the polymer, they usually have close values. When the emulsifier used in the emulsion is selected in accordance with the polymer, it shows plasticizer properties and plasticizers can soften the polymer and decrease the T_g and MFFT values [8].

Therefore, since the anionic/nonionic emulsifier system used in St/A IV latex was in the most suitable structure with the synthesized polymer and optimized the particle size, it acted as a plasticizer to the polymer and reduced the MFFT value (Table 2).

CONCLUSION

In the present study styrene/acrylic copolymers were synthesized in 4 different formulations by semi-batch emulsion polymerization using different emulsifier systems. Styrene and butyl acrylate were used as the main monomers in the synthesis, and acryl amide and acrylic acid were used as functional monomers. The observed single T_g values for St/A latexes showed that the latexes were successfully prepared. The ideal result for synthesis was obtained for St/A IV latex, where anionic and nonionic emulsifiers were used together, with a glass

transition temperature of approximately 20°C and a solids ratio of approximately 50% (w/w). At the end of all the studies, the ideal polymerization process was realized when the anionic/nonionic emulsifier system was used in the emulsion polymerization. In addition, the analyses showed that considering the St/A IV latex synthesized with an anionic/nonionic emulsifier system, the most stable and pollution-free dye binder latexes will be obtained.

Acknowledgement: This study was supported by TUBITAK BİDEB 2209-B (1139B412201959).

REFERENCES

1. G. Marinangelo, W. H. Hirota, R. Giudici, *Chemical Engineering Science*, **66** (23), 5875 (2011). <https://doi.org/10.1016/j.ces.2011.08.006>.
2. V. I. Eliseeva, S. S. Ivanchev, S. I. Kuchanov, A. V. Lebedev, Emulsion polymerization and its applications in industry, Plenum Publishing Corporation, New York, 1981.
3. A. V. Herk, Chemistry and technology of emulsion polymerization, 1st edn., Blackwell Publishing Ltd., Oxford, 2005.
4. J. F. Richard, Chemistry and technology of surfactants, 1st edn., Blackwell Publishing, Oxford, 2006.
5. S. C. Berasategui, Emulsion and miniemulsion polymerization stabilized with oligomeric surfactants (ASRs), Polymat, 2015.
6. J. I. Amalvy, *Pigment & Resin Technology*, **27**, 20 (1998).
7. B. Eren, Y. Solmaz, *Sakarya University Journal of Science*, **24**(5), 1074 (2020).
8. P. A. Steward, J. Hearn, M. C. Wilkinson, An Overview of polymer latex film formation and properties, Elsevier Journal, 2000, p. 200.