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## The Role of Sodium Lauryl Sulfate on the Film Properties of Styrene-Butyl Acrylate-Acrylic Acid Copolymer Latex

Bilge EREN<sup>\*1</sup>, Yasemin SOLMAZ<sup>2</sup>

### Abstract

In this study, the concentration effect of sodium lauryl sulfate (SLS) as a surfactant in the synthesis of styrene/acrylic acid/butyl acrylate copolymer (SAC) latex particles via seeded emulsion polymerization technique was investigated. Scanning electron microscopy (SEM), minimum film-forming temperature (MFFT), differential scanning calorimetry (DSC), dynamic light scattering (DLS), and thermal gravimetric analysis (TGA) techniques were used to explain the change on physicochemical properties and morphology. The main goal is to determine an optimal surfactant concentration to obtain latexes with low MFFT. DLS studies showed that the particle size decreases 118.30 to 75.18 nm with the increase of SLS concentration. MFFT of latexes decreased with increasing SLS concentration. From the TGA curves, it was found that all the SAC latex particles exhibit a three-step decomposition process. The observed single  $T_g$  values for SAC particles showed that the latexes were prepared successfully.

**Keywords:** Latex, Emulsion polymer, Acrylate, Styrene.

### 1. INTRODUCTION

In the last decade, there has been an increase in the number of studies aimed at the development of high performance, easy to apply, low cost, and environmentally friendly binders used in the coating industry. Styrene acrylate copolymer (SAC) latexes are one of the most preferred binders due to their properties such as good dispersion in water, strong bonding with

substrates, low film-forming temperature, mechanical and chemical stability. In addition to binder applications, SAC latexes have a wide range of work in industrial applications like paint, coating, ink and adhesive [1-5]. Due to the wide range of applications of SAC latexes, there has been an increase in the number of studies focused on improving the chemical properties of SAC latexes in recent years [6-12].

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SAC latexes having a minimum film-forming temperature above the application temperature show surface defects after coating [13,14]. Therefore, in practical applications, the MFFT value of the SAC latex is reduced by adding volatile aliphatic or aromatic compounds. However, many countries have regulations regarding the amount of volatile organic compounds (VOCs) that can be found in a product. For this purpose, it is necessary to develop SAC latexes containing low VOC with appropriate MFFT [15-19].

Anionic surfactants contain an anionic group attached to a long hydrophobic backbone. The negatively charged group of the surfactant used in the emulsion polymerization reaction affects the latex stability, while the hydrophobic group affects the critical micelle concentration (CMC) value, the interface tension between water and the monomer. Anionic surfactants are often used to adjust the particle size of SAC latexes and give them particle stability [20-23].

Amaly [24] found that the particle size decreased with the increased amount of surfactant and particle stability reached a maximum value. Also, the author indicated that the water adsorption and the stability of films were changed considerably with increasing surfactant amount. Zhang et al. [25] investigated the effect of surfactant amount and surfactant types on the physical properties of latex particles. They indicated that when SLS and p-octyl polyethylene glycol phenyl ether (OP) mixed surfactants were added, at the amount of 3%, and a ratio of SLS/OP of 4/6, the latex showed lower coagulum. Chanra et al. [26] showed that monomer conversion rate (> 99%) increased with the increasing amount of water-soluble surfactant SDS from 2.0 to 4.0 wt%, but particle size increased from 80 to 102 nm [26].

Surfactants behave as “solubilizing” non-polar substances like organic monomers above their CMC. The stability of latex during and after production is important issue in latex production. The amount of surfactant has an effect on overall latex stability. Thus, the concentration of surfactant is an important consideration when designing a latex formulation. Also, the amount of surfactant used in emulsion polymerization has

a strong effect on particle size and distribution, thermal characteristics, and film formation. The goal of present study is to examine the role of anionic surfactant on the styrene-acrylic emulsion polymerization. For this purpose, the concentration effect of SLS on the physicochemical characteristics of SAC particle properties have been studied in detail. The physical and chemical properties of SAC particles were elucidated by SEM, MFFT, DSC, TGA and DLS techniques.

## 2. MATERIALS AND METHODS

Styrene (Sty), butyl acrylate (BA), acrylic acid (AAc) and SLS, ammonium persulfate (APS, initiator), NaHCO<sub>3</sub> and ammonia were all obtained from Merck. All reagents were all of analytical grades and used without further purification.

The thermal gravimetric analysis (TGA) studies were made using EXSTAR SII TGA/DTA 7200 TG/DTG apparatus. Perkin Elmer DSC 6000 apparatus were used to obtain  $T_g$  values of the latex films under N<sub>2</sub> atmosphere (10°C/min heating rate). Morphology of SAC particles were studied using a ZEISS Supra 40 VP model field emission scanning electron microscopy (SEM). Particle size of latexes was determined using MALVERN Nano-ZS Zeta Potentiometer. MFFT of the latex particles were determined by Rhopoint MFFT 90 device.

Sty, BA, and AAc ratios were 44/54/2 wt%, respectively. Polymerization was conducted according to our previous study about seeded emulsion polymerization [27]. Latex particle compositions are given in Table 1. The feeding and agitation speed rate were 0.1 ml/min and 200 rpm, respectively. After 10 min of seed latex particles formation, the emulsion feed was started. The SLS concentration was changed from 0.5 to 3 % of total monomers. Samples containing surfactant as 0.5, 0.9, 1.5, and 3 % of total monomer mass were designated as SAC-1, SAC-2, SAC-3, and SAC-4, respectively.

Table 1  
Copolymer formulation

Components	Reactor Charge (g)	Feeding (g)
Sty	-	39.60
BA	-	48.60
AAc	0.90	0.90
APS	0.36	
Water	88.30	14.80
SLS	0.45-2.70	0.45-2.70
NaHCO <sub>3</sub>	0.72	0.27

### 3. RESULTS AND DISCUSSION

The effects of the change in surfactant concentration on the thermal behavior of latex films are shown in Figure 1. TGA measurements indicated a shift in maximum decomposition temperature ( $T_{max}$ ) with increasing of surfactant concentration due to partial penetration of the polymer surface by SLS. As given in Table 1, it was found that all the SAC latex particles exhibit a three-step decomposition process. The first step about 100 °C is related to the loss of the absorbed water. The second step, between 330 °C and 420 °C, can be assigned to the decomposition of the copolymer main chain, the breakage of the ester bonds. [27,28]. The third step, between 600-800 °C, the copolymer decomposes collectively and carbonization (charcoal formation) followed by oxidation takes place [29]. The second maximum decomposition temperature ( $T_{max2}$ ) for SAC samples was observed the temperature range of 383-405 °C. This means that the latex thermal stability changed with the increased SLS concentration. Also, the decomposition rate at second step increased from 15.37 to 19.85 %/min with increasing SLS concentration (Table 2). This result means that the decomposition of latex catalyzed by sulfonic acid moiety on SLS as a weak acid.

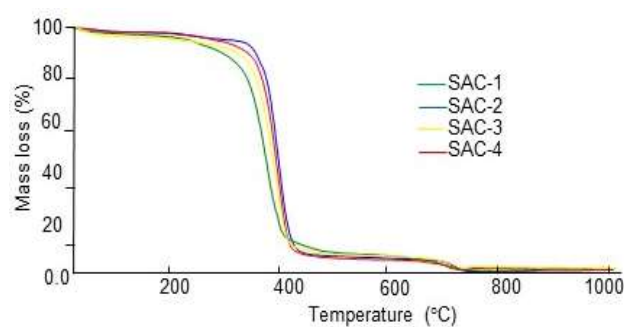


Figure 1 TG curves of the latex films recorded in nitrogen atmosphere depending on the amount of surfactant

Table 2

The effect of the amount of surfactant on the decomposition temperatures and thermal stability of latex films

Latex	$T_{max}$ (°C)	Decomposition Rate (%/min)	$T_{%10}$ (°C)	$T_{%50}$ (°C)
SAC-1	48	0.67		
	383	15.37	277	377
	705	1.08		
SAC-2	71	0.32		
	405	18.66	332	384
	716	0.72		
SAC-3	54	0.85		
	392	16.31	306	384
	718	1.1		
SAC-4	80	0.34		
	403	19.85	327	383
	719	1.4		

The DSC curves of the prepared SAC latex films depending on the amount of SLS are given comparatively in Figure 2. The latex particles showed only a single  $T_g$ , indicating that the latex is a kind of random copolymer. The  $T_g$  values of SAC latexes decreased with increasing amount of SLS (Table 3). When the SLS amount was adjusted to be 0.5, 0.9, 1.5 and 3% of the total monomer mass, the  $T_g$  values of SAC latexes were determined to be 8.6, 7.5, -0.8 and -9.7°C, respectively. This indicates that SLS emulsifies monomers into small droplets and forms more micelles that provide the polymerization zone

[30]. When the amount of SLS is low, a sufficient amount of micelle cannot be formed, causing the monomers to not be fully emulsified. Low  $T_g$  values obtained as the amount of SLS increases means that it is difficult for Sty monomers to enter SLS micelles, and more reactive centers are encouraged for BA monomers.

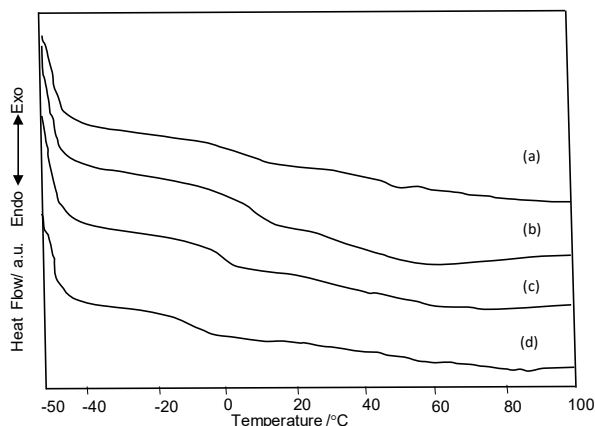


Figure 2 DSC figures of the SAC particles; SAC-1 (a), SAC-2 (b), SAC-3 (c) and SAC-4 (d)

MFFT values fluctuated with the increased amount of SLS (Table 3). This could be due to the plasticizing influence of water and SLS present in the latex during particle coalescence. However, it can be said that MFFT of latexes decreased with the decrease in  $T_g$  value as expected.

Table 3

The effect of surfactant amount on the  $T_g$  and MFFT values of the SAC latexes

Latex	$T_g$ (°C)	MFFT (°C)
SAC-1	8.6	1
SAC-2	7.5	5.0
SAC-3	-0.8	0.3
SAC-4	-9.7	0.7

Morphological structures, average particle size and size distributions of prepared latexes were determined by SEM and DLS techniques. As seen in Figure 3, SEM images obtained can be observed quite stably, even approximately 6 months after their preparation. Figure 3 shows the role of surfactant amount on the average particle size of SAC latexes obtained using DLS technique. Average particle size obtained by both techniques are compatible with each other. As

seen in Table 3, the average particle size of prepared latexes are between 75-118 nm according to DLS data and are compatible with SEM data. According to DLS measurements, the particle size increased from 75.25 to 118.30 nm with 0.9 % SLS addition, and decreased to 75.18 nm with further increase of SLS concentration to 3.0%. It is known that the latex particles are formed by homogeneous nucleation mechanism at SLS concentration below critic micelle concentration [31]. According to this mechanism, SLS retained on monomer droplets can leave the droplet surface and then adsorb on the growing particle surface. The amount of the SLS molecules increases gradually on the surface with increasing SLS concentration in the reaction medium. It results in more suppression of growing the particles in the expanding step. Thus, the particle size becomes smaller due to higher surface charges in case of higher concentration of SLS used. The experimental particle size data of the present investigation are comparable with reported values. Amalvy [24] reported that the particle size in acrylate emulsion was decreased from 110 to 80 nm after increasing the amount of SLS from 1% to 4%. Zhang et al. [25] have found that the particle size of BA/MMA/AA copolymer was decreased from 145 to 122 nm when the surfactant concentration increased from 1.5% to 4%. Chanra et al. [26] calculated that the particle size for poly-(St-co-BA-co-MMA) decreased from 156 to 80 nm as the SDS concentration increased from 0.50 to 4.00 %.

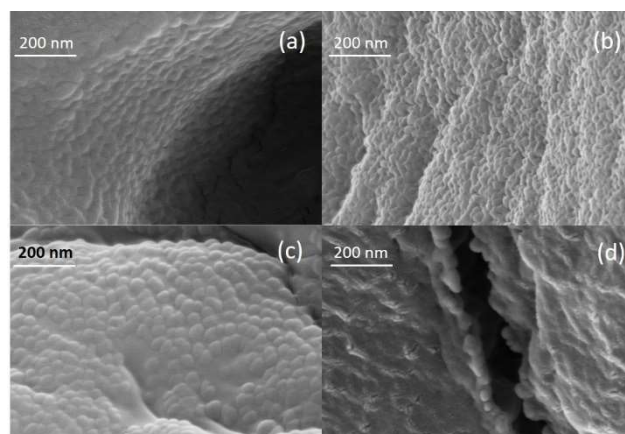


Figure 3 SEM images of the SAC particles; SAC-1 (a), SAC-2 (b), SAC-3 (c) and SAC-4 (d)

Table 4  
The effect of surfactant amount on the average particle size values of the SAC latexes

Latex	Average Particle Size (nm)		PDI
	SEM	DLS	
SAC-1	87	78.25	0.014
SAC-2	110	118.30	0.150
SAC-3	83	85.16	0.073
SAC-4	72	75.18	0.236

#### 4. CONCLUSION

In this study, optimization of process parameters was studied in detail in the preparation of SAC latexes. All prepared SAC latex particles have a single  $T_g$  value. This showed that all monomers were involved in the polymerization to form latex and copolymer formed during polymerization. It has been determined that all particles are homogeneous and the particle size and size distributions are sufficient for practical applications. The thermal stability of SAC latexes changed with the increasing amount of SLS. When the SLS amount is 0.9 %, latex is the highest of thermal stability. It was observed that  $T_g$  values of SAC latexes increased in parallel with the hard monomer ratio. MFFT values were also found to be suitable for practical coating applications. Optimization studies have shown that the thermal stability,  $T_g$ , MFFT and particle size values expected from binding acrylic latexes in industry applications are best provided by SAC-2 latex. The amount of SLS in the pre-emulsion and reactor loading stages is 0.9 % of the total monomer mass.

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#### *The Declaration of Conflict of Interest/ Common Interest*

No conflict of interest or common interest has been declared by the authors.

#### *Authors' Contribution*

B.E. planned and supervised the project. Y.S. carried out the experiments and performed the thermal analysis of samples. B.E. analyzed the results and wrote the manuscript.

#### *The Declaration of Ethics Committee Approval*

The authors declare that this document does not require an ethics committee approval or any special permission.

#### *The Declaration of Research and Publication Ethics*

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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