

## **Synthesis of Vinyl Acetate-Co-Butyl Acrylate Latexes: Investigation of the Effects of Polymerization Temperature on the Latex Properties**

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**Abstract:** In this study, poly(vinyl acetate-co-butyl acrylate) latexes were synthesized by applying semicontinuous emulsion polymerization method. Copolymerizations were carried out keeping constant monomer ratio of vinyl acetate (VAc): butyl acrylate (BuA) as 85:15 at four different temperatures (55 °C, 60 °C, 65 °C and 70 °C) and constant stirring rate (350 rpm) with the using of N-methylol acrylamide as protective colloid, ammonium persulfate potassium persulfate as thermal initiators, and 30 mole ethoxylated nonyl phenol as nonionic emulsifier. The characterization of synthesized latexes were done by determining solid content, conversion, Brookfield viscosity, particle size, the particle size distribution, surface tension and surface charges of latexes.

**Keywords:** Emulsion polymerization, Latex, Polymerization temperature, Vinyl acetate-butyl acrylate copolymer,

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### **I. Introduction**

Bulk, solution, suspension and emulsion polymerization are the main polymerization processes which are used for manufacturing industrial polymers. Emulsion polymerization is the complex process which radicals are added into the heterogeneous polymerization systems. This process is very similar to suspension polymerization but there are small differences in reaction characteristic and mechanisms. Emulsion polymerization contains mainly four ingredients: initiator, monomer, emulsifier and reaction medium[2]. Emulsifier which is used in emulsion polymerization may be anionic, cationic, nonionic, amphoteric or polymeric. Emulsion polymerization has three stages. Nucleation is the first stage and in this stage micelles are occurred. In the second stage of emulsion polymerization, monomers which are nucleated in the aqueous phase, are diffused into the micelles and polymerization starts. The speed of this stage is very slow. Final stage of the polymerization, long chain radicals which have all the monomers in them are occurred. All the micelles have the same length so microspheres have also same dimensions. For this reason, distribution of the particle size is very narrow in the emulsion polymerization. Emulsion polymerization has a lot of advantages than other polymerization techniques [1].

In the emulsion polymerization products, poly(vinyl acetate) emulsion homopolymer and vinyl acetate based emulsion copolymers have a great importance in industrial aspect as well as scientific aspect [3]. In 2002, Sarac and Yildirim investigated the effect of the initiator and nonionic emulsifier ethoxylation degree on the vinyl acetate-co-butyl acrylate copolymer latex properties. They used VAc:BuA as monomers, sodium dodecyl sulfonate and nonyl phenol ethoxylate whose ethoxylate number is changed between 0 and 40 are used for emulsifier. In this study they investigated how the effect viscosity, molecular weight and distribution by using ammonium persulfate (APS) and potassium persulfate (PPS) as initiators. They observed APS has a linear relationship with the viscosity but PPS has an inverse relationship with the viscosity. They also found that number average molecule distribution increases with the increasing ethoxylation number [4]. In 2006, Sarac and et all. investigated the effect of the protective colloid, monomer rate and initiator on the VAc-BuA copolymerization in the semi-continuous process [5]. In 2012, Ovando-Medina and et all. investigated the effect of the emulsifier concentration, monomer additions into the system and latex properties. They found that low particle size is related to high copolymer contents and it has also high polymerization rate. They found that average particle size is between 36 and 55 nm [6]. In this study, poly(vinyl acetate-co-butyl acrylate) latexes were synthesized by applying semicontinuous emulsion polymerization method. Copolymerizations were carried out keeping constant monomer ratio of vinyl acetate (VAc): butyl acrylate (BuA) as 85:15 at four different temperatures (55 °C, 60 °C, 65 °C and 70 °C) and constant stirring rate (350 rpm) with the using of N-methylol acrylamide as protective colloid, ammonium persulfate, potassium persulfate as thermal initiators, and 30 mole ethoxylated nonyl phenol as nonionic emulsifier. The characterization of synthesized latexes were done by determining solid content, conversion, Brookfield viscosity, particle size, the particle size distribution, surface tension and surface charges of latexes.

## II. Experimental

### 2.1 Chemicals and instrumentation

Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and sodium bicarbonate (NaHCO<sub>3</sub>) were purchased from Merck. Ammonium and potassium persulfate were used for thermal initiators. Sodium bicarbonate was used as a pH regulative. Vinyl acetate (VAc), butyl acrylate (BuA) and protective colloid were purchased from Elsan Fiber Corporation without any further purification. Vinyl acetate and butyl acrylate were used as monomers. Oligomeric N-methylol acrylamide (NMA) was a protective colloid. 30 ethoxylated nonyl phenol (NP30) was a emulsifier and it was bought from Turkish Henkel Chemicals Industry and Trade Corporation. Nopco V 1497 was a defoamers and was purchased from Boysan Corporation without any purification. Brookfield viscometer which was programmed with DV II model was used for measuring latexes original viscosity at 25 °C. Brookhaven 90 Plus model zeta sizer was used for measuring latexes particle sizes and surface charges at room temperature. KSV brand 701 model du Nouy tensiometer with platinum ring was used for measuring latexes surface tensions at 25 °C.

### 2.2 Synthesis of vinyl acetate-co-butyl acrylate latexes

First 1,5 g NMA which is known as protective colloid, 0,12 g NaHCO<sub>3</sub>, 3 g emulsifier which is begun to dissolve at 40±2 °C, two or three droplet defoamers and 37,5 mL distilled water are added in reactor and then blend begin to mingle with stable mixing speed (350 rpm) and heat (55 °C, 60 °C, 65 °C and 70 °C). 37,5 g Vac and 6,56 g BuA are weighed in the covered erlenmeyer. Monomer mixture is divided into fiive equal portion and pour into the reactor each 15 minutes with 0,04 g initiator (APS) which is dissolved with 2 mL distilled water. At the end of the adding monomer mixture, 0,02 g APS solution is also added the reactor and heat the mixture 15-20 °C up. The experimental setup is shown in Fig 1.



Fig. 1 The picture of the the experimental setup

## III. Results and Discussions

### 3.1 Determination of the solid amount of the latexes

1 g latex sample was measured in the aluminum container for determinating pratic solid amount (m<sub>1</sub>). These containers were waited in the oven at 90±2 °C for 210 minutes. And then containers were measured again (m<sub>2</sub>). The solid amount of the latexes were found by using below equation:

$$\% \text{ Practical solid particle (PSP)} = 100 \times (m_2/m_1) \quad (\text{Eq. 1})$$

m<sub>1</sub> = Initial latex mass

m<sub>2</sub> = Latex mass after drying

The % solid particle was used in % transformation calculation which is given in the below:

$$\text{Theoretical solid particle (TSP)} = \% \text{ Monomer} + \% \text{ Protective colloid amount} \times 0,95\% + \% \text{ Emulsifier amount} \times 0,76\% + \% \text{ Initiator} + \% \text{ NaHCO}_3 \quad (\text{Eq. 2})$$

$$\% \text{ Transformation} = (\text{PSP}/\text{TSP}) \quad (\text{Eq. 3})$$

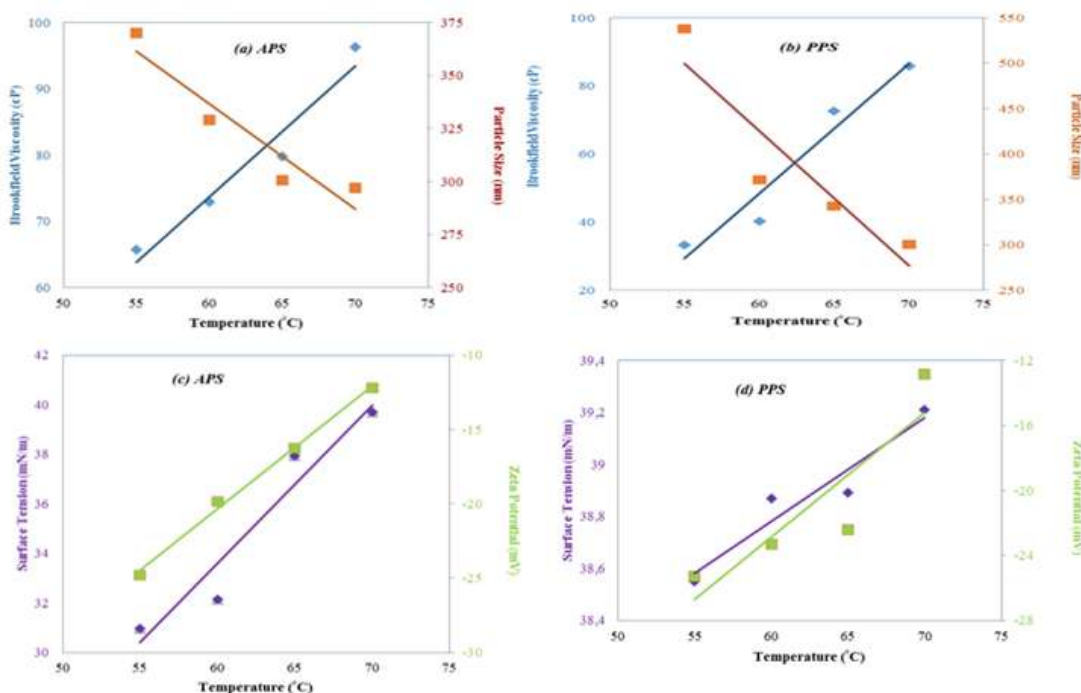
Amount of theoretical solid substance was calculated as 47,88%. Amount of practical solid substance changed between 29,97% and 45,75% for APS initiator and 27,93% and 45,63% for PPS initiator with the stable stirring speed (350 rpm), 3% stable emulsifier concentration in 105 minutes. At the same experimental conditions, % transformation was found between 89,71% and 95,56 % for APS initiator and 89,43% and 95,32 % for PPS initiator.

### 3.2 Determination of Brookfield viscosity and particle size

Brookfield viscometer which is programmed with DV II model was used for measuring latexes original viscosity at 25 °C. Brookhaven 90 Plus model zeta sizer was used for measuring latexes particle sizes. Brookfield viscosity and particle sizes data are given in the Table 1. From the Fig 2, Brookfield viscosity value increases with the ascending temperature whereas particle size decreases with the increasing temperature. When average particle size decreases for the latexes, the surface area of polymer particle increases. This situation causes to increase the viscosity and obtain determined latexes [7]. The particle size of VAc homopolymer and copolymer which are synthesized only nonionic emulsifier presence are smaller than 300 nm and they have large particle size distribution [8].

**Table 1** Brookfield viscosity of the latexes, particle size, Zeta potential and surface tension

Reaction Temperature (°C)	Initiator	Brookfield Viscosity (cP)	Particle Size (nm)	Zeta Potential (mV)	Surface Tension (mN/m)
55	APS	65,7	370,1	-24,78	30,98
	PPS	33,2	538,2	-25,28	38,55
60	APS	72,9	328,9	-19,84	32,16
	PPS	40,2	371,6	-23,33	38,87
65	APS	79,8	300,7	-16,25	37,93
	PPS	72,7	342,3	-22,43	38,89
70	APS	96,3	297,0	-12,22	39,71
	PPS	85,8	300,8	-12,82	39,21



**Fig. 2** a) Temperature effect on the viscosity and particle size for APS, b) Temperature effect on the viscosity and particle size for PPS, c) Temperature effect on the surface tension and surface charge for APS, d) Temperature effect on the surface tension and surface charge for PPS

### 3.3 Determination of surface charges and surface tensions

Brookhaven 90 Plus model zeta sizer was used for measuring latexes surface charges at room temperature. KSV brand 701 model du Nouy tensiometer with platinum ring was used for measuring latexes surface tensions at 25 °C. Surface charges and surface tensions data are given in the Table 1. With the increasing polymerization temperature, surface charge decreases and latexes are be more stable. Surface tension values change with the increasing temperature. Surface tension depends on free emulsifier amount that is in latex and if

the amount of free emulsifier increases, surface tension decreases. Surface tension of latex explains interaction magnitude between particle surfaces and aqueous phase which is surrounded particle by using thermodynamic equilibrium principle. Surface tension depends on emulsifier amount and if emulsifier amount increases, surface tension decreases. But emulsifier adsorption on the polymer particles decreases the free emulsifier amount and surface tension increases with the increasing adsorption [9].

#### IV. Conclusions

In this study, solid particle amount and % transformation with APS initiator are more effective than with PPS initiator. While viscosity and surface tension of latexes increasing with the increasing temperature, particle size and surface charge of latexes decreasing. Latexes with APS initiator are very stable and have high viscosity. Particle size of latexes with APS initiator are smaller than with PPS initiator. Stability, viscosity and surface area of latexes increase with adding NP30 emulsifier but particle size decreases. Latexes are stable and latexes with APS initiator are more stable than with PPS initiator. In this study, we found that the latexes with APS initiator are better than with PPS initiator.

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