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A Study on the Vinyl Acetate-*co*-Butyl Acrylate Latexes in the Presence of *N*-Methylol Acrylamide and Mixed Type Emulsifiers

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Summary: The properties of copolymer latexes depend on the copolymer composition, polymer morphology, initiator, polymerization medium and colloidal characteristics of copolymer particles. Poly(vinyl acetate-co-butyl acrylate) latexes with N-metylol acrylamide were prepared by applying semicontinuous emulsion polymerization. The systems studied were (a) the mixture of anionic sodium lauryl sulfate ether (SELES) with nonionic 30 moles ethoxylated nonyl phenol (NP 30) (50:50), (b) the mixture of anionic sodium lauryl sulfate ether (SELES) with nonionic 30 moles ethoxylated nonyl phenol (NP 30) (70:30), and (c) anionic sodium lauryl sulfate ether (SELES) (100%). The effects of the emulsifier and emulsifier composition on the physicochemical properties of obtained vinyl acetate-co-butyl acrylate latex properties in the presence of N-methylol acrylamide initiated by ammonium persulfate were investigated.

Keywords: emulsion polymerization; lattices; stabilization; surfactants

Introduction

Emulsion polymerization is a unique chemical process widely used to produce waterborne latexes with various colloidal and physicochemical properties. This heterogeneous free radical polymerization process involves emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water-insoluble initiator or an oil-soluble initiator. Typical monomers used in emulsion polymerization include especially butadiene, styrene, acrylate ester and methacrylate ester monomers, vinyl acetate (VAc), and vinyl chloride. An extremely large oil–water interfacial area is generated as the particle nuclei form and grow in size with the progress of the polymerization.[1,2] The environmentally friendly latexes comprise a large population of polymer particles dispersed in the continuous aqueous phase. These emulsion polymers find a wide range of applications such as synthetic rubbers, thermoplastics, coatings, adhesives, binders, rheological modifiers, plastic pigments, standards for the calibration of instruments, polymeric supports for the purification of proteins and drug delivery system, etc.

Mixed anionic and non-ionic surfactants have been widely used in industry to manufacture latex particles. Anionic surfactants can provide repulsive force between two similarly charged electric double layers to the latex particles. By contrast, non-ionic surfactants can impart two approaching particles with the steric stabilization mechanism. In addition, non-ionic surfactants can improve the chemical and freeze–thaw stability of latex products.

The hydrophilic–hydrophobic nature of polymeric surfactants has a significant influence on the properties of micelles. In contrast to small surfactants, polymeric surfac-

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tant molecules exhibit rather restricted mobility in the heterogeneous polymerization system and this characteristic feature may have an impact on the polymerization mechanisms and kinetics. In general, latex products stabilized by polymeric surfactants show better water resistance than those stabilized by conventional surfactants. Among various polymeric stabilizers used in industry, amphiphilic block or graft copolymers are the most effective in stabilizing emulsion polymerization. Nevertheless, some water-soluble polymers such as polyvinyl alcohol (PVOH) and hydroxyethyl cellulose (HEC) are commonly, N-methylol acrylamide[3,4] is rarely used as the protective colloid in stabilizing the vinyl acetate-based emulsion polymerizations. The grafting reaction of the hydrophobic polyvinyl acetate (PVAc) chains onto the water-soluble polymer chain results in an amphiphilic graft copolymer chain in situ, which can be used to stabilize particle nuclei generated in the continuous aqueous phase. However, the contribution of adsorption of water-soluble polymer molecules on the particle surface to the colloidal stability during polymerization cannot be ruled out. These vinyl acetate-based latex products find applications in laminating adhesives and interior architecture coatings.[1]

There has been published the numbers of studies regarding with the influence of the emulsifier molecular structure and concentration on the polymerization kinetics, latex stability, and particle size distribution for semibatch emulsion copolymerization of VAc and butyl acrylate (BuA).[1,5–9] Most of time sodium dodecyl sulfate has been used as anionic emulsifier in emulsifier mixtures in these studies.

In the present study, N-methylol acrylamide (Amol) was employed as protective colloid with anionic or the mixture of anionic + nonionic emulsifiers for the particle stabilization of water-borne VAc- co-BuA latexes. The effects of the emulsifier and emulsifier composition on the emulsion copolymerization of vinyl acetate and butyl acrylate in the presence of N-methylol acrylamide initiated by ammonium persulfate were investigated.

Experimental Part

Materials

The butyl acrylate (BuA) and vinyl acetate (VAc) were supplied by Argon Chemistry Inc., and used at commercial purification and monomer ratio was 85:15. The initiator, ammonium persulfate (APS) (Merck), the anionic emulsifier, sodium lauryl sulfate ether (SELES) and the nonionic emulsifier 30 moles ethoxylated nonyl phenol (NP 30) were obtained from Turkish-Henkel Chemicals Industry Co., and were used as received. Sodium bicarbonate was obtained from Merck and used as a buffer. Nopco-1497 was obtained from Turkish-Henkel Chemicals Industry Co. and used as an antifoam agent. All substances were used without further purification. De-ionized water was used in all studies.

Semicontinuous Emulsion Copolymerization of VAc and BuA

Polymerization was performed in a conventional 1L glass emulsion polymerization reactor equipped with a a condenser, a thermometer, two dropping funnels, and a mechanical stirrer in a total batch period of 3 h. Initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction. The polymerization reactions were carried out at the required temperature with an automatically controlled water circulation bath. All experiments were run with mechanical stirring at 300 rpm. This speed is in the range where the agitation has no noticeable effect on the rate of polymerization. Emulsion copolymerizations were carried out under atmospheric conditions according to the recipe, which is given in previous study.[3]

Measurements

Copolymer latexes were characterized by measuring Brookfield viscosity, particle size, and surface tension of copolymer latexes to air.

Conversion was monitored gravimetrically. The viscosities of the copolymer latexes were determined by Brookfield Programmable DV-II model viscometer with spindle number 4 at 28 °C after diluting 40% (wt.) solid content of all samples. The particle size of the latexes was determined by Malvern Zetasizer Nano ZS model instrument. The surface tensions of the produced latexes were measured after the total solids contents of the samples were adjusted to 25 wt% by diluting. The surface tension measurements were done with ring-detachment method by torsion tensiometer and a platinium ring at 24 °C.

Results and Discussion

The copolymer latex properties were investigated depending on weight ratio of emulsifier and emulsifier type with the using of N-methylol acrylamide as protective colloid.

The total emulsifier amount was used in a constant weight ratio (3.0%) in the polymerization recipe, and anionic emulsifier percentage in emulsifier mixture was varied. A regular latex viscosity increase is seen with an increase anionic SELES percentage in the polymerization in Figure 1.

The effect of the mixed surfactant SELES/NP 30 on the formation of VAc-co-BuA particles is dramatic. It is found that adding a certain amount of the anionic surfactant SELES into the polymerization system can dramatically increase the number of latex particles and also reduce the particle size of the latex product. The increasing concentration anionic emulsifier in the mixed emulsifier system (SELES/NP-30) can greatly improve the latex stability via the synergetic effects provided by both the electrostatic and steric stabilization mechanisms and, thereby, retard the extent of the limited flocculation process. This action then can increase the number of latex particles significantly and reduce the particle size of the final semi-continuous latexes can be seen in Figure 2.

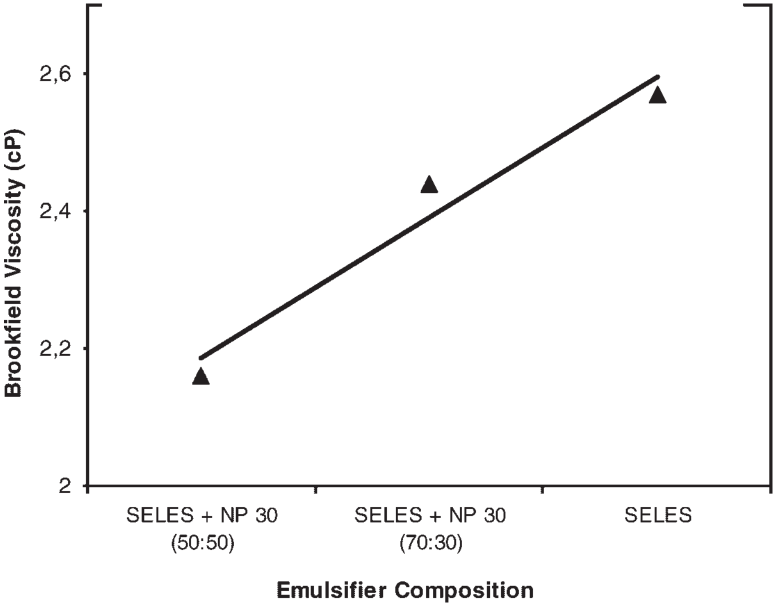

Figure 1.
Brookfield viscosity of copolymer latexes as a function of anionic emulsifier concentration: SELES + NP30 = 50:50 (% wt), SELES + NP30 = 70:30 (%wt), and 100% SELES.

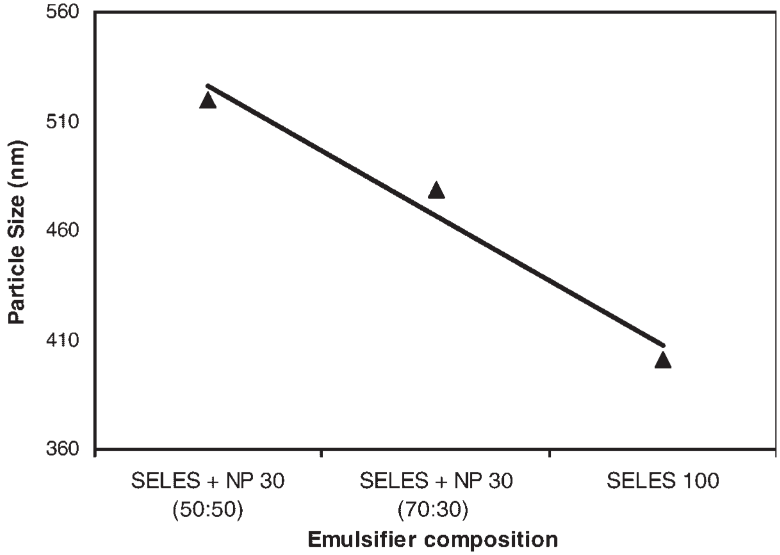

Figure 2.
Particle size of copolymer latexes as a function of anionic emulsifier concentration: SELES + NP30 = 50:50 (% wt), SELES + NP30 = 70:30 (%wt), and 100% SELES.

Anionic emulsifiers are used to produce finer particles, and the mixture of anionic and nonionic emulsifiers contributes balanced properties. The emulsifier adsorption onto the particle surface decreases with increasing polarity of the polymer surface. Depending on the extent of the dispersion, polar, orientation, and hydrogen bonding interactions, the emulsifier molecules adsorbed onto the polymer phase-liquid interface may acquire a nonvertical orientation, they may be arranged with greater planarity the higher the interaction on the polar part of the emulsifier molecule. Therefore,

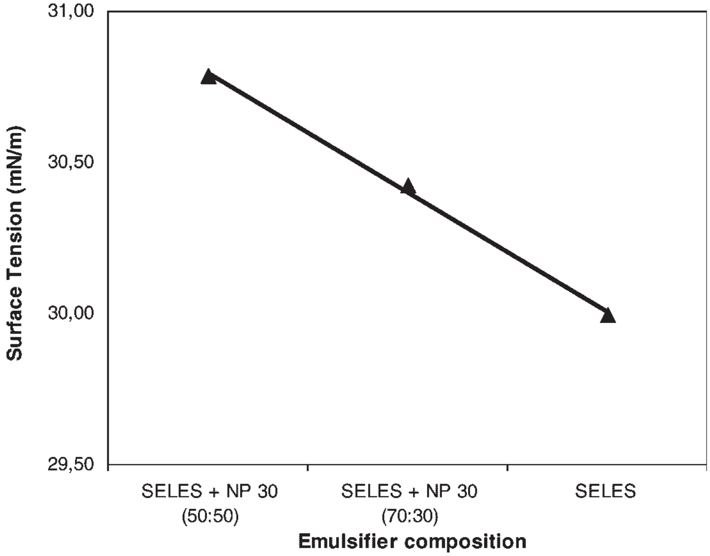

Figure 3.
Surface tension of copolymer latexes as a function of anionic emulsifier concentration: SELES + NP30 = 50:50 (% wt), SELES + NP30 = 70:30 (%wt), and 100% SELES.

less emulsifier may be consumed for the formation of a given PVAc surface, which helps the increase of the overall surface area and the decrease in particle size. The above arguments were also confirmed by literature.[8–11]

The surface tensions of polymer changed regularly with the increasing anionic emulsifier percentage in the polymerization. Surface tension depends on free emulsifier amounts in the latex, and the raising of this amount leads to the tendency of surface tension to decrease. But emulsifier adsorption onto polymer particles cause to decrease free emulsifier concentration in latex, the increasing adsorption cause to increase surface tension of latexes. The increasing hydrophobic character into polymer causes to increasing emulsifier adsorption onto polymer particles. Thus the increasing of free emulsifier concentration in latex by blocking of emulsifier adsorption and the decreasing of polarity differences between interfaces cause to decrease the surface tension, especially for VAc latexes. It was determined that increase of the anionic emulsifier percentage in the copolymerization of VAc and BuA initiated by a persulfate does not affect the surface tension of the final latex very seriously, but small changes were seen in Figure 3.

Conclusion

In this work, VAc-co-BuA lattices were prepared in the presence of potassium persulfate initiator, new polymeric surfactant by applying semicontinuous emulsion polymerizations. It was determined that when the weight ratio of the anionic emulsifier in the recipe was increased the resulting latex viscosity increases, and particle size of final latex decreases. The surface tension of copolymer latex decreases with the increasing of the anionic character in total emulsifier mixture, meanwhile it does not changed very seriously.

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