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Electrical, Film and Surface Properties of Water-Based Latexes Prepared by Semicontinuous Emulsion Polymerization

*Ayça Kahraman, Ayfer Sarac**

Summary: In this study, the results obtained with latexes prepared by semicontinuous emulsion polymerization with conventional anionic and nonionic emulsifiers and their different mixtures were presented. For this study, vinyl acetate-butyl acrylate latexes with a conventional anionic emulsifier (sodium lauril ether sulfate) and a nonionic emulsifier (30 mole nonyl phenol ethoxylate), of which films can be easily cast, were used. The latex properties in terms of mechanical stability, film-water absorption, and film-emulsifier exudation, and surface and electrical properties were assessed and compared.

Keywords: absorption; initiators; surfaces; surfactants; thin films

Introduction

Emulsion polymerization is one of the most important techniques for preparing polymers from an industrial point of view. In emulsion polymerization, carried out to obtain film forming latexes (useful in waterborne coatings); it is necessary to introduce emulsifiers in the polymerization recipe in order to control both the size of the particles and the stability of the latexes. For many applications of latexes, latex film properties, such as film modulus, tensile strength, % elongation at break, wet strength, and solvent resistance, are very important.[1,2]

Latexes can also be synthesized in the form of stable colloids by using polymeric stabilizers or emulsifiers. In this case, the effect of the emulsifier molecules is that firstly, they provide requirements for the polymerization reaction to proceed via the emulsion or inverse emulsion pathway.[3] Secondly, they lead to an improvement in properties such as conductivity, stability, solubility in organic solvents, and the processibility. Some advantageous are reported for latexes synthesized in the presence of an anionic emulsifier. These advantages are mentioned to be improved stability toward coagulation, better colloidal and thermal stability, improved electrical parameters, morphology that is more compact and reduced particle size latexes. Higher solubility is also announced that had been achieved for some conductive polymer using emulsifier in the synthesis.[3] It was also reported that the mentioned advantages can be achieved only in the case of using anionic emulsifiers and cationic or neutral emulsifiers were reported to be ineffective for same conductive polymer.[3] So far, the anionic emulsifiers in the form of free acid or salt have been the mostly used stabilizers for these purposes. Dodecyl benzene sulfonic acid or its substituted derivatives, sodium dodecyl benzene sulfonate and sodium dodecyl sulfate are among the mostly used emulsifiers in the form of free acid or salts.

Latex particles with diameters of a few hundred nanometers are widely used as binders in coatings in a wide variety of applications including paints and coated papers.[4] Coating technology has long been interested in the preparation of films from water-based and oil-based formulations. In the coatings technology, mechanical

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Yildiz Technical University, Department of Chemistry,
Davutpasa Campus, 34220 Esenler-Istanbul, Turkey
Fax: +90 212 383 41 06;
E-mail: ayfersarac2002@yahoo.com

strength and adhesion in the case of waterborne coatings, wetting of the substrate, will be the main requirements. Such surfaces, as required for film formation from an academic point of view, are far removed from the typical everyday surfaces that the developed end-coatings will typically be used on.[2,5–7] These properties are affected not only by the nature of the polymers, but also by the method of both: a) polymer; and b) film preparation and conditioning. As an example, emulsion polymers typically contain emulsifier, which may not be uniformly dispersed throughout the full thickness of the film or, due to incompatibilities, may exude from the polymer. Films may be amorphous homopolymers or heterogeneous depending on whether they are prepared from a single polymer type or from blended polymers or core-shell-type latex particles. Such heterogeneity may provide uniquely tailored properties, e.g. the dispersion of a softer, lower glass transition temperature (T_g) latex, or soft particle core, into a matrix of harder polymer can act to prevent crack propagation through the system i.e. act as an impact modifier. Fundamental understanding of film formation provides a positive feedback allowing modification to polymerization reactions coating recipes and methods of film formation and the development of better quality films.[6] Although the conventional solvent-based paints are widely used in the paint industry, they are environmentally unfriendly. Water-soluble and water dispersible polymers may also be used in coating systems, but some disadvantages of waterborne systems, in general, it is needed developing extra formulation for this purpose.

This article is presented a study where the effects of concentration and composition of a conventional anionic surfactant (sodium lauryl ether sulfate) and a nonionic surfactant (30 mole nonyl phenol ethoxylate), and initiator on latex and film properties have been investigated. The latex and their film properties in terms of film-water absorption, film-emulsifier exudation, surface and electrical properties were studied.

Experimental Part

Materials

Semi-continuous emulsion copolymerization of vinyl acetate (VAc) and butyl acrylate (BuA) was carried out using oligomeric stabilizator, two thermal initiators and different types emulsifiers which are nonionic and anionic character in 50:50 and 30:70 ratio, respectively. Elsan Fibre Co. (Turkey) VAc and BuA monomers at commercial purification and 85:15 wt % monomer ratio were used. Total emulsifier molar concentration was changed from 1.88×10^{-4} to 2.52×10^{-4}. The copolymerizations were carried out above the critical micelle concentration (CMC) of both emulsifiers.

The emulsifiers were sodium lauryl sulfate ether (SELES 24.5-25.5%, Cognis, Germany) and nonylphenol polyethoxylate with an average of 30 ethylene oxides per molecule (NP 30), $C_9H_{19}{-}C_6H_4{-}O{-}(CH_2CH_2O)_{30}H$, (NP 30%99, Henkel, Turkey). The stock solution of SELES was prepared as 15% by weight from the original chemical for the using in polymerizations. Ammonium persulfate ($(NH_4)_2S_2O_8$, Merck) (APS) and potassium persulfate ($K_2S_2O_8$, Merck) (PPS) were used as thermal initiators. Sodium bicarbonate ($NaHCO_3$, Merck) was used as buffer and oligomeric N-methylol acrylamide as protective colloid. The preparation of oligomeric N-methylol acrylamide was described with all details in previous paper.[8] All substances were used as received. De-ionized water was used throughout the work.

Preparation of the P(VAc-BuA) Latex

Semi-continuous emulsion copolymerization of VAc and BuA was carried out in a 1 L glass reactor fitted with a reflux condenser, teflon anchor stirrer having a constant speed of 300 rpm and a dropping funnel in a total batch period of 3.5 h. Deionized water, buffer, oligomeric N-methylol acrylamide, and emulsifier mixture were initially charged to reactor under atmospheric conditions for half an hour. Only 10% of the total monomer was introduced at the beginning of the reaction at 70°C and the remaining monomer was added drop wise at 71 ± 2°C from dropping funnels during the remaining time. Initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction.

Preparation of Latex Films

Latex films about 1.5 mm thickness were cast in glass petri dishes (covered properly to avoid contamination) and drying for 2–3 days at ambient temperature. The films were all transparent in color.

Results and Discussion

Polymer Characterization

The conversion was determined gravimetrically. According to the calculating results from solid contents as theoretical and practical, conversion changed between 89.6% and 93.7% for 3.5 hours polymerization time for all copolymers.

The surface tensions of the produced latexes were measured after the total solids contents of the samples were adjusted to 40 wt % by diluting. The surface tension measurements were performed on a Sigma 701 model tensiometer (KSV instruments, Helsinki, Finland) equipped with a Pt du Nouy ring at 25 °C, and results were given in Figure 1.

The surface tensions of polymer changed almost regularly with the increasing total emulsifier concentration in the polymerization. The presence of the long hydrophobic chain of the emulsifier had a screening effect on the Coulombic forces which prevents the emulsifier adsorption. Consequently, the higher the chain lengths of the hydrophobic part of the emulsifier, the higher the emulsifier adsorption on the polymer.[9] Surface tension depends on free emulsifier amounts in the latex, and the increase in this amount leads to decrease in the tendency of surface tension. However, free emulsifier amount in latex decrease with the adsorption of emulsifier onto surface of polymer particle, thus surface tension increases with increasing adsorption. This activity between water phase surface and organic phase surface in latex depends on emulsifier structure, polarity, and other molecular interactions of organic phase. Polarity differences between water and polymer particles are the main parameter to affect adsorption.[10,11] The increasing hydrophobic character in copolymer composition (by increasing anionic character) causes to increase the emulsifier adsorption onto polymer particles. Thus the increase in free emulsifier concentration in latex by blocking of emulsifier adsorption and the decrease in polarity differences between interfaces cause to increase the surface tension, especially for VAc–BuA copolymer latexes (Figure 1).

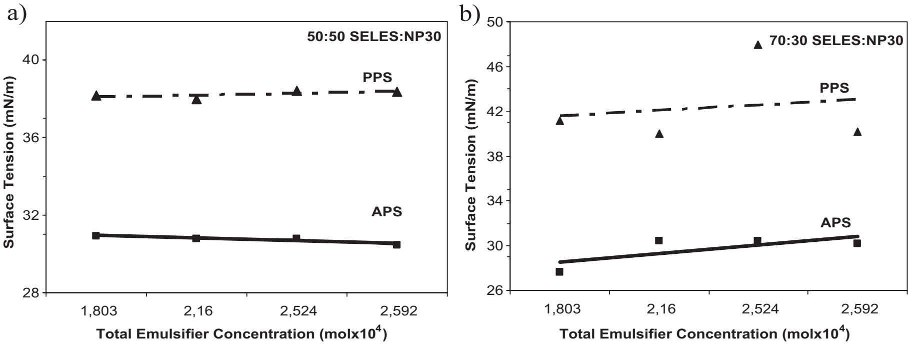

Figure 1.

Surface tension of latexes as a function of total emulsifier concentration and initiator for different anionic and nonionic emulsifier compositions a. 50:50 wt %, b. 70:30 wt % respectively.

On the other hands, surface tension can be used as a measure for the coverage of particles. As can be derived from the surface tension values, the particle surfaces of the latexes are incompletely covered with surfactant molecules because the surface tensions of the latexes lie well above the values of the saturated emulsifier solution. The smaller the particles are, the higher the surface tension is and, therefore, the coverage of the particles with emulsifier increases with decreasing particle size. For polymerization, one starts from large monomer droplets and emulsifier micelles in the water phase. The water-soluble initiator forms oligoradicals from slightly water-soluble monomer units. These oligoradicals then enter the micelles and start to form particles. During polymerization, monomer diffuses through the water phase to the micelles in order to sustain polymer particle growth. Due to the increase in the interfacial area, the surface tension of a latex increases with polymerization.[12]

Characterization of Latex Film Properties

Water contact angles were determined by using a CAM 200 model goniometer (KSV instruments, Helsinki, Finland) and deionized water on thin films cast on a glass substrate. Volume of each water droplet was about 5 µl. Each contact angle value given in Figure 2a and Figure 2b represents an average of five readings.

Saturated water absorption (A_w) of the films was measured as method below: put a piece of the film (about 1 g) into 50 g of water for 14 days at 40 °C, then it was dried again. Comparing the weight of the film before drying (w_1) and after drying (w_2), the absorption ratio was calculated.[13]

$$A_w\,(\%) = ((w_1 - w_2)\,/\,w_2) \times 100$$

The surface resistances of latex films were measured using a Keithley 6517 B model electrometer by standard text fixture having sample putting circle with 5.1 cm. The film samples were prepared by casting the latex solution onto a glass petri dishes and subsequently drying the film in an oven at room temperature for 2 days. The thickness of all films after drying was maintained to be around 1.5 mm. Latex film conductivities were measured on the glass surface at 100 volt 20 µA. The conductivity, r of copolymer film was calculated by the equation, $\sigma = 1/R$ where σ is the conductivity in S/cm, and R is the surface resistance in Ω.

Influence of the Emulsifier Concentration and Emulsifier Composition on the Colloidal and Film Properties of Latexes

As shown in Figure 1a and Figure 1b, surface tension of copolymer latexes increased with initiator, emulsifier concentration and the percentage of anionic emulsifier in total emulsifier mixture. This can be explained by taking into account that

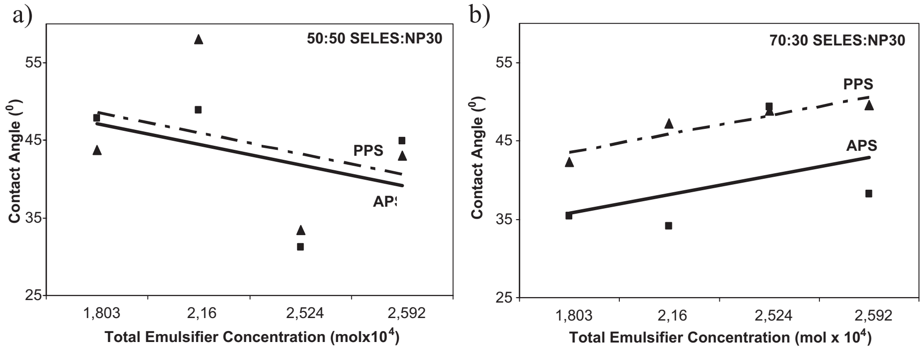

Figure 2.

Water contact angle of latex films as a function of total emulsifier concentration and initiator for different anionic and nonionic emulsifier compositions a. 50:50 wt %, b. 70:30 wt % respectively.

the surface area stabilized by the emulsifier increases with an increase of the concentration of the emulsifier resulting in smaller particles due to mass balance considerations. On the other hand the ethoxylated 30 moles nonyl phenol used here are wax-like compound; it is likely that they act as internal plasticizers. However, it cannot be ruled out unambiguously that the stronger effects observed with the VAc/BuA copolymers may partially be due to a slightly higher built-in of ethylene during the polymerization. Moreover, it is known that the emulsifiers affect the way the initiator or the thermal systems are decomposed. These results in a change of the polymerization rate, which in turn influences the amount of ethylene incorporated in the copolymers.[14]

Water contact angles of all the samples are summarized against the initiator, emulsifier composition and emulsifier concentration as shown in Figure 2a and Figure 2b. The water contact angle is not increased much by increasing amount (composition) of anionic emulsifier at the same concentration up to 14°. Almost regular decrease is observed for PPS depending on increasing anionic emulsifier percentage at the same emulsifier concentration. The contact angle results are the combined effects of chemical properties and surface morphology.[15] Addition of only 20 wt % of the NP 30 into emulsion recipe copolymer latex results in the obvious increase of the water contact angle for both initiators because protective colloid with VAc tended to migrate to the air surface of the latex films due to its low surface energy in spite of the chemical linkage and influence of the emulsifiers used in the emulsion polymerization. Water contact angles of polymer films prepared with APS or PPS reflect the differences of solubility between APS and PPS. The surfaces of the polymer films have different character (hydrophilic for APS, hydrophobic for PPS), and can be understand that either surface tension or water contact angles data. Contact angle values increased with emulsifier concentration increased for 70:30 wt % anionic and nonionic emulsifier composition, but same parameter decreased for 50:50 wt % emulsifier composition. Anionic characters increased in the emulsifier composition lead to hydrophobicity of the latex films, due to increasing molar concentration of anionic emulsifier in the per unit of volume.

Latex films with anionic and nonionic emulsifier mixture (50:50 wt %) based on VAc-co-BuA had conductivities of 4.2×10^{-8} S/cm for APS and resulted in conductivity of 1.75×10^{-8} S/cm for PPS at the same emulsifier composition for 2.52×10^{-4} molar total emulsifier concentration. The conductivity of the water-base films decrease with a higher anionic emulsifier ratio in total emulsifier mixture. When low amount of NP 30 was added during the polymerization of VAc and BuA, it can be seen that the conductivities increased when the total emulsifier weight percentage increased from 1.88×10^{-4} to 2.52×10^{-4} but decreased when the anionic emulsifier load was increased from 50 to 70 wt % in total emulsifier mixture using APS initiator. PPS latexes give lower conductivities comparing with conductivities APS containing latexes having emulsifier molar concentration from 1.88×10^{-4} to 2.52×10^{-4} for anionic and nonionic emulsifier mixture in 50:50 wt % compositions.

The VAc-co-BuA latex is one of the main formulation components of the waterborne paints, coatings and the water resistance of the waterborne coatings was mostly determined by the latex polymer hydrophobicity. The water absorption ratio and water contact angles of the latex films is two important parameters for characterization of the hydrophobicity.[13] As shown in Figure 3a and Figure 3b, the water absorption ratio was greatly influenced by the emulsifier molar concentration and initiator content of the VAc-co-BuA latex. With the increase of total emulsifier concentration, the water absorption ratio of the latex films decreased for both initiators, which can be contributed to the hydrophobicity of anionic emulsifier; but slightly decreased all of the total emulsifier concentrations for PPS, which could be correlated to the phase

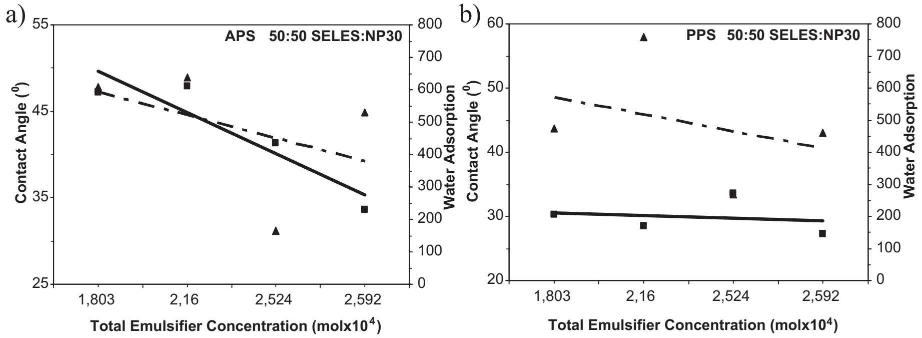

Figure 3.
Water contact angle and water adsorption of latex films as a function of total emulsifier concentration for 50:50 wt % anionic and nonionic emulsifier compositions for different initiator a. APS, and b. PPS respectively.

separation and the formation of high anionic emulsifier concentration and could give a negative affection on the water contact angle of latex film (see Figure 3b). It can also seen that in Figure 3a and Figure 3b, the water absorption ratio was influenced higher by emulsifier concentration and initiator in the latex but we still could make a conclusion that higher emulsifier concentrations would give better water resistance for APS in Figure 3a. However, as shown also in related figures, the water absorption ratio decreases slightly as latex surface tension decreased versus total emulsifier concentration increased. This may also due to the occurrence of large domain of the dispersed latexes.

Conclusion

In this work, VAc-co-BuA lattices were prepared in the presence of ammonium persulfate or potassium persulfate initiators, oligomeric N-methylol acrylamide, anionic and nonionic type emulsifiers SELES/NP30 = 70/30 and 50/50 (wt/wt), and different concentration of emulsifiers by applying semi-continuous emulsion polymerization. The surface tension of copolymer latex decreases with the increasing of the emulsifier concentrations, meanwhile it changed between limited data for both initiators, and followed different trend for APS and PPS. It was also found that the composition of mixed emulsifiers and emulsifier concentration were sensitive to such parameters as surface tension, water contact angle, conductivity, and water adsorption.

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