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Investigation of Water-Based Emulsions: Surface and Film-Forming Properties

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Summary: In the present study, reaction components such as emulsifiers, emulsifier combinations, and initiators were used for the particle stabilization of water-borne vinyl acetate - butyl acrylate copolymer latexes. The effects of these parameters on the colloidal film-forming properties of the vinyl acetate-*co*-butyl acrylate latex colloidal, physicochemical, surface, and film forming properties were investigated, in particular the aspect of their surface coating applications.

Keywords: coatings; differential scanning calorimetry (DSC); films; transparency; water-soluble polymers

Introduction

Copolymer dispersions of vinyl acetate (VAc) are a widely used type of synthetic latexes in paint, adhesive and coating industries. Copolymers of acrylics and VAc have many specific properties such as good film formation, transparency, and mechanical properties, and the corresponding products have been widely used as coatings, adhesives, paints. However, a high percentage of hydrophilic monomers and nonionic emulsifier, poor water resistance and low temperature resistance limit their application.[1–4]

It may be anticipated that the range of applications of latex polymers will continue increasing in the next years beyond their current uses in paints, adhesives, binders, paper coatings, textile finishes, pharmaceuticals including sustained and controlled release formulations, floor polishes, printing inks, etc. because of the reduced volatile organic compound emissions afforded by these water-based systems. In most applications emulsifier mixtures rather than pure materials are used. Electrosterically stabilized polymer particles can be prepared not only with a emulsion polymerization stabilized by the mixture of ionic and nonionic emulsifiers, but also by sterically stabilized emulsion polymerization initiated with peroxodisulfate where the electric double layer is generated during the polymerization. The mixed micelles composed of both nonionic and ionic emulsifier are interesting because of the strong interaction that accompanies their formation; they are also advantageous for the preparation of stable polymer dispersions.[5]

Latex particles with diameters of a few hundreds of nanometers are widely used as binders in coatings in a wide variety of applications including paints and coated papers.[6] The coating technology has long been interesting in the preparation of films from water-based and oil-based formulations. In the coating technology, mechanical strength and adhesion in the case of water-borne coatings, wetting of the substrate, are the main requirements. Such surfaces as required for film formation from an academic point of view are far from the typical everyday surfaces that the developed final coatings are typically used on.[5,7–9] These properties are affected not only by the nature of the polymers, but also by film preparation and conditioning. As an example, emulsion polymers typically contain an emulsifier, which may not be uniformly dispersed throughout the full

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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 soft, lower-glass transition-temperature (T_g) latex or soft particle core into a matrix of hard 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 of coating recipes, methods of film formation and the development of better-quality films.[5] Although the conventional solvent-based paints are widely used in the painting industry, they are environmentally unfriendly. Water-soluble and water-dispersible polymers may also be used in coating systems, but due to some disadvantages of water-borne systems in general, it is needed to develop extra formulation for this purpose.

This paper presents various results, concerning the influence of the emulsifier concentration, composition, and varying the ethylene oxide chain in the emulsifier mixture on the properties of the polymer dispersion, their film formation, and film and surface properties. Film-forming is an important area of research since a large proportion of the commercially produced latex polymers are typically utilized in casting into films or as binders. Some of the most important properties of a latex and its film, such as viscosity, particle size, surface tension and contact angle with water depend very much on a proper choice of the emulsifier which can be nonionic or a nonionic and ionic emulsifier mixture.

Experimental Part

Materials

The basic recipe for VAc - butyl acrylate (BuA) (85:15 wt.%) emulsions is given in Table 1. Ethoxylated nonylphenols with degrees of ethoxylation varying from 10 to 40 mol of ethylene oxide units per mol of the phenol were used as nonionic emulsifiers. The latexes were synthesized by combining nonylphenol with various amounts of ethylene oxide (EO) and sodium dodecylbenzenesulfonate (SDBS) as anionic emulsifier in different compositions, and in the presence of different thermal initiators.

Table 1.
Basic recipe for the preparation of VAc/BuA latexes.

Emulsifiers	33 wt.% nonionic emulsifier, NP 10 34–70 wt.% nonionic emulsifier, NP 30 50–70 wt.% nonionic emulsifier, NP 40 50–70 wt.% anionic emulsifier, SDBS
Protective colloid	PVOH
Initiators	APS, PPS

Two series of experiments were carried out. In the first, the amount of the nonylphenol with 30 mol EO per mol of the phenol (NP 30) was varied from 30 to 70% relative to the amount of emulsifier. In the second series, the influence of the degree of ethoxylation was studied: relative to a concentration of 50 parts by weight of the non-ionic emulsifier NP 30 or NP 40, weight equivalents of the anionic emulsifier with 50-70 were used. The compositions of polymerization mixtures are summarized in Table 1.

Technical grade monomers were used. The emulsifiers were sodium dodecylbenzenesulfonate (SDBS), 10 mole nonylphenol ethoxylate (NP 10, 99%), 30 mole nonylphenol ethoxylate (NP 30, 99%), and 40 mole nonylphenol ethoxylate (NP 40, 99%). All emulsifiers were purchased from Turkish-Henkel Chemicals Industry Co., Turkey. Ammonium persulfate, $(NH_4)_2S_2O_8$ (APS; Merck), and potassium persulfate, $K_2S_2O_8$ (PPS; Merck) were used as thermal initiators. Sodium hydrogencarbonate ($NaHCO_3$, Merck) was used as buffer, poly(vinyl alcohol) (PVOH) as protective colloid. All substances were used as received. Deionized water was used throughout the work. Total emulsifier concentration was kept constant in all polymerizations at 3.7 wt.%.

Polymerizations were carried out in a 500-mL glass reactor fitted with a reflux condenser, a teflon anchor stirrer having a constant speed of 300 rpm and a dropping funnel. Only 10% of the total monomer was introduced at the beginning of the reaction at 70 °C and the rest was added dropwise at 71 ± 2 °C during the remaining time. The initiator was dissolved in a small amount of water and these freshly prepared initiator portions were added at 30 minute intervals throughout the reaction.

Results and Discussion

Characterization of Latex

Monomer conversion was measured by the gravimetric method. The particle size of the latex was determined with a Malvern Zetasizer Nano ZS model instrument. The viscosity of the copolymer latexes (solids content *ca.* 48.69 wt.%) was determined with a Brookfield Programmable DV-II model viscometer with spindle number 4 at 20.6 °C at 50 rpm after dilution to a solid content of 45 wt.% for all samples. The surface tension measurements were performed on a Sigma 701 model tensiometer (KSV instruments, Helsinki, Finland) equipped with a Pt du Nouy ring at 22 °C using latexes adjusted to the solid content 45 wt.%.

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

The increase in the nonylphenol composition from 33 to 70 wt.%, and the ethoxylation degree of the nonionic emulsifier from 10 to 40 results in a decrease in the particle size and in narrow particle size distribution. The viscosity of the emulsions at different emulsifier compositions and the degree of ethoxylation of the nonionic emulsifier increase drastically in the presence of APS (Figure 1).

Similar results were obtained at the same emulsifier composition but at different degrees of ethoxylation of the nonionic emulsifiers in the presence of PPS (Figure 2); an increase in the EO chain length leads to latices with smaller particles and higher viscosities.

Brookfield viscosity and particle size results of all the synthesized latexes in different emulsifier, and emulsifier composition for two initiators were given in Table 2.

As shown in Figure 3 and Figure 4, surface tension of copolymer latexes increased with the ethoxylation degree of

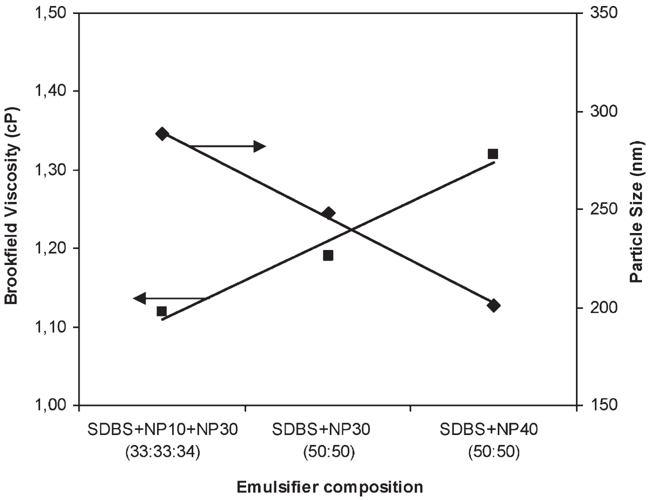

Figure 1.
Brookfield viscosity and particle size as function of emulsifier composition for APS.

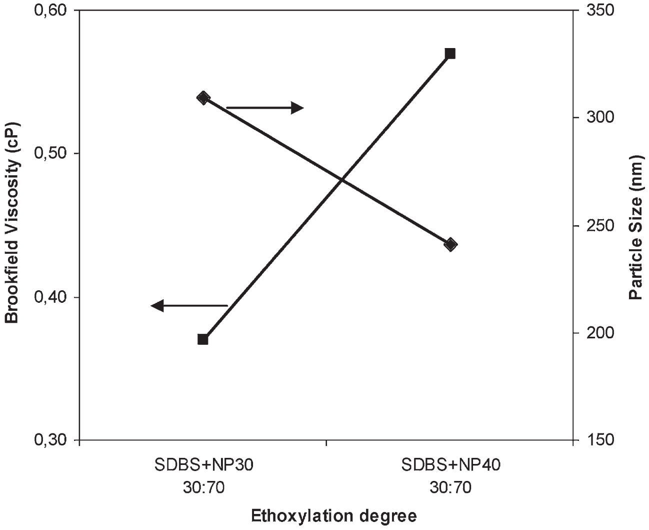

Figure 2.
Brookfield viscosity and particle size as function of ethoxylation degree of PPS.

nonionic emulsifier or emulsifier mixture. This can be explained by taking into account that the surface area stabilized by the emulsifier increases with an increase in the surfactant concentration resulting in smaller particles mass balance considerations. Dispersion with a large number of small particles exhibits a higher viscosity than with a small number of large particles.

The glass transition temperature (T_g) of the VAc/BuA copolymers decreases with an increase in the ethoxylation degree of the nonionic emulsifier (Figure 3). This effect is even more pronounced for the VAc/BuA copolymers where an increase in the content of the nonionic emulsifier long chain (NP 30) by 70% results in a depression of the glass temperature by 1 °C.

The same trend is observed if the EO chain is longer (from 30 to 40 EO units) (Figure 4). Since the ethoxylated (30 units) nonylphenol used here are wax-like compounds, it is likely that they act as internal plasticizers. However, it can not be ruled out unambiguously that the stronger effects observed with the VAc/BuA copolymers may partially be due to a slightly higher content of ethylene. Moreover, it is well known that the emulsifiers affect the way the initiator or the thermal systems are

Table 2.
Viscosity and particle size of synthesized latexes.

APS					
	SDBS-NP10-NP30 33:33:34	SDBS-NP30 30:70	SDBS-NP30 50:50	SDBS-NP40 30:70	SDBS-NP40 50:50
Brookfield viscosity (cP)	1.12	0.75	1.19	0.94	1.32
Particle size (nm)	288.2	329.6	248	244.5	201.3

PPS					
	SDBS-NP10-NP30 33:33:34	SDBS-NP30 30:70	SDBS-NP30 50:50	SDBS-NP40 30:70	SDBS-NP40 50:50
Brookfield viscosity (cP)	0.65	0.37	0.42	0.57	0.75
Particle size (nm)	280.1	309.1	238.9	241	198.7

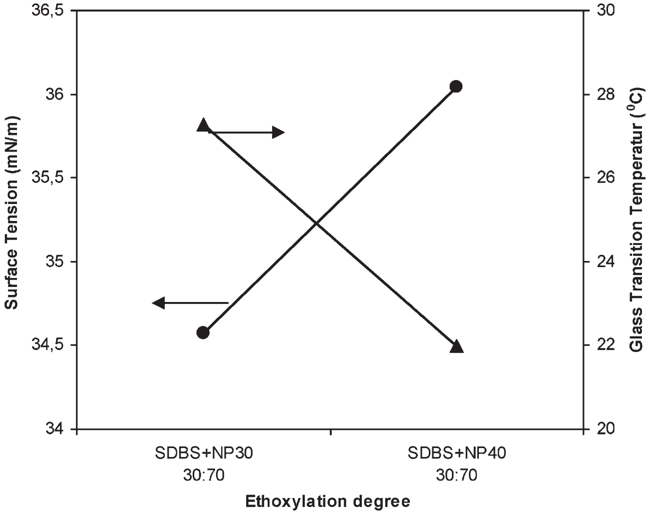

Figure 3.
Dependence of surface tension and T_g of the copolymers on the ethoxylation degree of nonionic emulsifier for PPS.

decomposed. This results in a change of the polymerization rate, which in turn influences the amount of ethylene incorporated in the copolymers.[1] On the other hand, polymerizations stabilized by NP 40 alone showed the largest particle sizes along with the broadest particle size distributions. This was attributed to the long particle nucleation period and/or limited particle flocculation.[10]

Characterization of Latex Film

Latex films (about 1.5 mm thickness) were cast in a glass mold at ambient temperature.

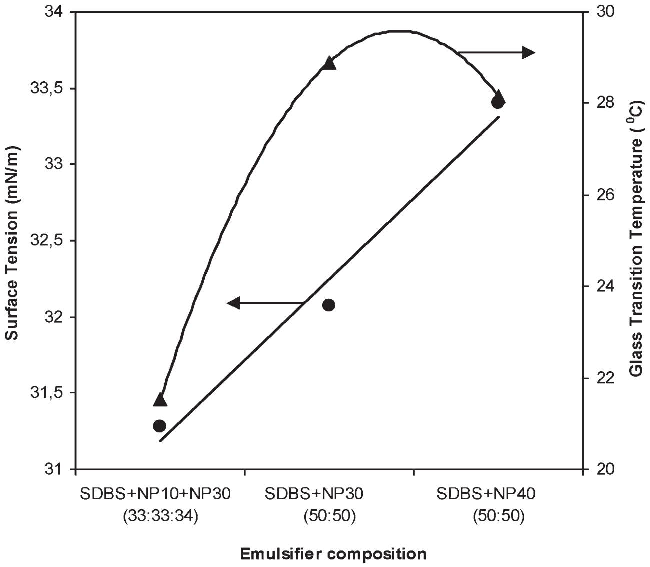

Figure 4.
Dependence surface tension and T_g of the copolymers on the emulsifier composition for APS.

A Perkin Elmer Pyris 6 type differential scanning calorimeter was used to measure the T_g of the copolymers. The scan was performed at a heating rate of 10 °C/min under N_2. Water contact angles on thin films were determined using CAM 200 model goniometer (KSV instruments, Helsinki, Finland). Contact angles were measured immediately from dropping of droplets. The volume of each water droplet was about 5 μl. The values of contact angles given in Table 3 are averages of five readings.

The high heat of evaporation of water leads to long drying times such that commercial volatile co-solvents have been used to reduce this problem and to aid plasticization of high-T_g polymers. Current trends are to choose more acceptable co-solvents or to eliminate them. When lower-T_g polymers are chosen at the outset, their film surfaces tend to be tacky. Low-T_g and high-T_g copolymeres can overcome this problem especially when core-shell morphologies are employed. The high surface tension of water leads to wetting problems which could be overcome by the use of co-solvents albeit with the above mentioned disadvantages or by the use of emulsifiers with the disadvantages of foam stabilization and possible entrapment of air bubbles into films. The high freezing point of water compared with organic solvents may require addition of a commercial antifreeze or the problem may be overcome by the use of strong steric stabilization. The latter copolymer particles of smaller diameters were intended to occupy the voids between the larger hard particles. Despite the hard particles do not deform, transparent films could be obtained by air drying. They depend on a critical volume fraction 40–50% and therefore, to a certain extent, the diameter of soft copolymer particles. Transparency was independent of the copolymer's T_g though tested for T_g values below the film formation temperature.[5]

Table 3.
Water contact angles (°) of copolymers prepared with various emulsifiers and initiators.

Emulsifier	APS	PPS
SDBS-NP10-NP30 33:33:34	51.34	59.96
SDBS-NP30 30:70	57.69	41.07
SDBS-NP30 50:50	58.60	–
SDBS-NP40 30:70	61.13	33.42
SDBS-NP40 50:50	64.05	16.57

Water contact angles of all the copolymers are summarized along with the initiator, emulsifier and emulsifier composition in Table 3. The water contact angle does not increase much with increasing chain length of nonionic emulsifiers at the same composition up to 10^0 for APS. Regular decrease is observed for PPS depending on increasing ethoxylation degree at the same emulsifier composition. However, due to the increased viscosity of the emulsion, the roughness was increased at the same time. The contact angle results are the combined effects of chemical properties and surface morphology.[11] Addition of only 16 wt.% of the NP 30 to copolymer latex results in an increase in the water contact angle because ungrafted PVOH 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 the influence of the emulsifiers used in the emulsion polymerization. The water contact angles of polymer films prepared with APS or PPS initiators reflect the differences in solubility between APS and PPS. The surfaces of the polymer films have different characters (hydrophilic for APS, hydrophobic for PPS), and can be understand in terms of surface tension or water contact angles data.

Conclusion

The influence of nonionic emulsifiers on the properties of VAc/BuA copolymer emulsions and films has been studied. It was observed that an increase in the nonionic emulsifier concentration and its ethoxylation degree lead to dispersions with smaller particles and higher viscosities as well as to films with higher surface tensions and lower glass transition temperatures.

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