Preparation of Ethylene-Modified Latex Using Ethylene-Acrylic Acid Resin

Jin-Sup Shin, Doug-Youn Lee, Jung-Hyun Kim*

Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Sudaemoon-ku, Seoul 120-749, Korea

SUMMARY: Ethylene-modified latexes were prepared by emulsion polymerization of styrene and n-butyl methacrylate using ethylene-acrylic acid (EAA), [M_n: 18,800, acid number: 140], as a polymeric emulsifier respectively. EAA containing 20% portion of acrylic acid could form aggregates like micelles and the solubilization ability of the aggregates were dependent on the electrolyte concentration above 100% degree of neutralization of EAA. The polystyrene (PS) latexes prepared using EAA showed small particle size and monodispersed particle size distribution in the presence of excess neutralizing agent or relatively high content of electrolyte. The EAA improved the barrier properties of ethylene-modified poly(n-butyl methacrylate) (PBMA) films.

Introduction

It is well known that either amphiphilic polymers which consist of both hydrophobic and hydrophilic groups can stabilize polymer particles or form aggregates, like micelles, due to the intermolecular and/or intramolecular hydrophobic interactions.1) Recently, alkali-soluble resins containing carboxylated random copolymers were used as polymeric surfactants in the emulsion polymerization of polystyrene (PS) and poly(methyl methacrylate) latex particles.2-4) Ethylene-acrylic acid resin (EAA) containing the ethylene group has good water resistance and barrier property similar to low-density polyethylene (LDPE). At high carboxylic levels, there are enough acid groups to be neutralized with alkali in hot water to form a surfactant-free dispersion. This dispersion can be applied as polymeric surfactants in the emulsion polymerization. The present study was undertaken to investigate the role of EAA in the emulsion polymerization of styrene and butyl methacrylate.

Experimental

Preparation of ethylene-modified latexes using ethylene-acrylic acid resin was carried out as follows. In the reactor, EAA and NaOH were dissolved in distilled deionized water, and

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monomer was added. NaOH was added to neutralize the carboxyl groups of EAA and NaCl was used to adjust ionic strength. Batch polymerizations were carried out at 70 °C. The average particle size and particle size distribution of the latex particles were determined using capillary hydrodynamic fractionation (Model CHDF-2000, Matec Applied Sci., USA). The polydispersity index (PDI) was given as D_w/D_n, where D_w is the weight average diameter of latex particles and D_n is the number average diameter. The barrier properties of ethylene-modified polymer films were evaluated by measuring the weight loss of water from bottles made with these materials. The weight loss of water was determined after 14 days at 20 °C.

Results and Discussion

EAA, having both hydrophobic and hydrophilic groups, can form aggregates in aqueous solution providing polymerization loci. In order to find out whether the random copolymer forms aggregates in aqueous solution, pyrene solubility in the EAA solutions was studied.

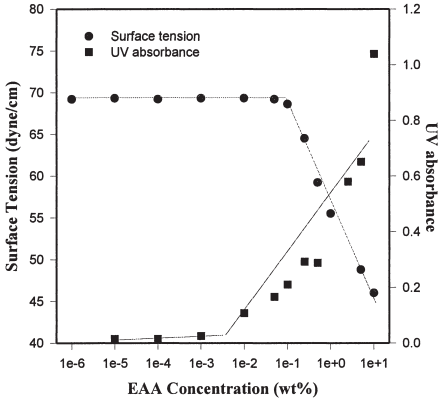

Fig. 1: UV absorbance of pyrene at 360nm and surface tension of EAA solution as a function of EAA concentration (wt% based on total).

Pyrene is an aromatic hydrocarbon exhibiting a very low solubility in pure water ($[Py]_{s,water} \approx 7\times10^{-7}M$). The increase in pyrene absorbance with EAA concentration was observed.(Fig. 1) This indicated the formation of polymer aggregates like micelles in aqueous solution. In the surface tension versus concentration measurement, an equivalent to the critical micelle concentration (cmc) of low-molecular-weight surfactants is missing.(Fig. 1) Our findings are in general agreement with recent work by P. Anton et al.[5)] on the aggregational behavior of polymeric emulsifiers. A particular feature of polymeric emulsifiers seems to be their intramolecular hydrophobic aggregation[6)] which is explained by the close proximity of the surfactant side chains within one macromolecule. Due to the intramolecular aggregation, an equivalent to the cmc of low-molecular-weight surfactants is generally missing.[6)] As shown in pyrene solubility results, however, EAA molecules in aqueous phase seem to form aggregates at low concentration before it starts to transfer to air-water interface.

The particle formation in emulsion polymerization using EAA would be affected by the properties of EAA aggregates which depend on the degree of neutralization of EAA, as well as the content of electrolytes, and the water solubility of monomer. Fig. 2 showed that the PS latex particle size decreased upon increasing the concentration of EAA. This result was similar to that obtained in emulsion polymerization using conventional surfactants.

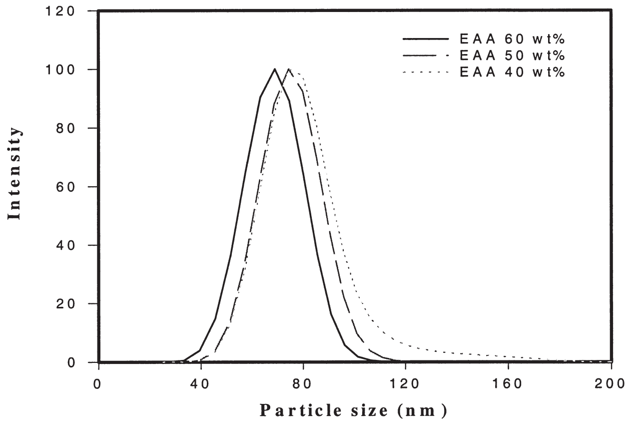

Fig. 2: Particle size and size distribution of ethylene-modified PS with different EAA concentration at 140% degree of neutralization of EAA.

The PS latexes prepared using 100% degree of neutralization of EAA showed broad particle size distribution (PSD) and large particle size.(Table 1) However PS latexes prepared using excess neutralizing agent, NaOH, showed small particle size (ca. 70 nm) compared to that observed for conventional emulsion polymers.

Table 1. Particle Size Analyses of Ethylene-Modified PS Latexes Prepared Using Ethylene-acrylic Acid Resin

EAA[a]	Degree of Neutralization	D_n (nm)	D_w (nm)	PDI (D_w/D_n)
40	100	115	235	2.04
40	140	82	101	1.23
40	180	70	76	1.09

PDI : polydispersity index, D_n : number average diameter, D_w : weight average diameter

a) wt% based on monomer

Fig. 3 shows the particle size and PSD of ethylene-modified PS latexes with different amounts of electrolyte, NaCl, added to the solution of the 100% degree of neutralization of EAA. With increasing the content of added electrolyte, the PSD of ethylene-modified PS latexes becomes narrow and particle size becomes small. Added electrolyte plays a role in increasing the ionic strength of aqueous phase. That is, in aqueous phase, electrolyte results in the screening of the electrostatic repulsion7) between charges along the EAA chain and brings about the more effective aggregation of the EAA chains. Thus, electrolyte promotes aggregate formation of EAA in the aqueous solution and these effective aggregations of the EAA chains would result in narrow PSD and small particle of ethylene-modified PS latexes. These results indicated that the excess neutralization agent used plays a role as an electrolyte in aqueous phase, which resulted in same trend of the particle size.(Table 1)

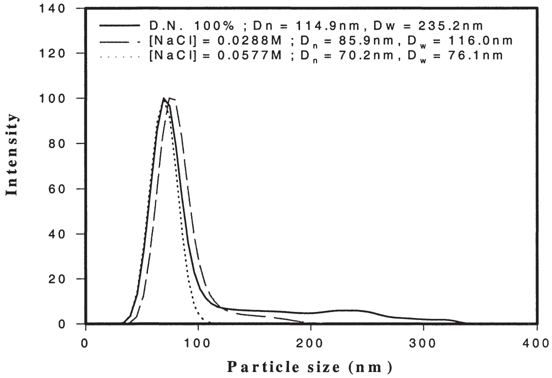

Fig. 3. Particle size and size distribution of ethylene-modified PS using 40wt% EAA based on PS with added electrolyte, NaCl, at 100% degree of neutralization of EAA.

From Table 2, it is clear that the ethylene-modified poly(butyl methacrylate) (PBMA) films lead to lower the water permeability compared to pure PBMA film. Indeed, the permeability decreases with increasing EAA concentration in the PBMA latex films. The improvement in the water resistance is assigned to the ethylene groups in the EAA.

Table 2. Permeability of PBMA latex, ethylene-modified PBMA latexes, and pure EAA films

	Permeability [a] **(g mm/m^2 day)**		**Permeability** [a] **(g mm/m^2 day)**
Pure PBMA film	8.1267	PBMA-EAA 20[b] film	4.2276
Pure EAA film	0.2275	PBMA-EAA 40[b] film	3.9046
		PBMA-EAA 60[b] film	3.5568

a) measured at 20°C and 90% RH.

b) % based on n-butyl methacrylate monomer.

Conclusion

The EAA containing a large number of carboxyl groups formed aggregates like micelles. The size and size distribution of ethylene-modified PS latex particles were investigated using different EAA concentrations, degree of neutralizations of EAA, and electrolyte contents. The PS latexes prepared using EAA showed very small particle size (ca. 70 nm) compared to that observed for conventional emulsion polymers. The size of ethylene-modified PS latex particles decreased with increase of EAA as a polymeric emulsifier. This result was similar to conventional emulsifier. The polydispersity of latex particles was influenced by both the EAA concentration and the electrolyte content in latex. The water permeability of ethylene-modified PBMA films decreased with increase of EAA concentration. The low water permeability was caused by the water resistance of ethylene group of EAA.

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