

Surface and Interfacial FTIR Spectroscopic Studies of Latexes. V. The Effects of Copolymer Composition on Surfactant Exudation

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SYNOPSIS

The influence of copolymer structure on the magnitude of surfactant enrichment to the film-air and film-substrate interfaces of latex films prepared on a polytetrafluoroethylene (PTFE) substrate is investigated. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) is used to elucidate the surfactant enrichment by the comparison of butyl acrylate/methyl methacrylate/methacrylic acid (BA/MMA/MAA) and ethyl acrylate/methacrylic acid (EA/MAA) latex systems prepared with various anionic surfactants. It is found that, in all cases, the magnitude of exudation of the sulfonate-containing surfactants manifested by the presence of S—O bending and scissors modes is reduced in the case of the BA/MMA/MAA latex. Similar behavior is observed when the spectra of films prepared on a liquid mercury substrate are compared. It is believed that this behavior results from the longer aliphatic *n*-butyl groups present in this copolymer that enhances compatibility by providing a greater opportunity for hydrophobic surfactant-copolymer interactions. The butyl groups may also reduce excess interfacial free energy by orienting themselves toward the film interfaces, which, in turn, will reduce the surface tension-induced driving force for surfactant exudation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Extensive research is currently being devoted to polymer latexes and to the use of these materials in thin films and coatings. Factors such as particle size and polydispersity play crucial roles in film formation and other physical properties. Although typical synthetic procedures often result in a polydisperse product, monodisperse latexes with a carefully controlled mean particle size are often sought to obtain the desired properties. Techniques such as seed growth,¹ controlled emulsifier concentration,^{2,3} and combinations of ionic and nonionic surfactants⁴ have been utilized to obtain the desired degree of monodispersity. Examination of latexes by transmission electron microscopy has enabled the assessment of aspects of latex particle behavior in-

cluding interparticle bridge formation,⁵ anomalous particle morphology,⁶ and the presence of small particles that may result from secondary nucleation.⁷

Although particle morphology exerts a significant influence on latex properties, surfactants also play vital roles in latex technology, both in the synthesis of the latex and as postsynthesis additives that serve purposes such as stabilization of the latex or pigments and modification of rheological properties. Despite their utility, these low molecular weight species can also give rise to a host of undesirable properties. If the surfactant is incompatible with the polymer system, it can exudate to the interfaces of the latex film, resulting in optical defects, premature film degradation, or a loss of adhesion. Because of these and other potential problems, a molecular level understanding of the nature of interactions between the surfactant and latex components and the factors governing surfactant exudation are of particular interest.

The utility of several analytical methods, including electron microscopy,⁸ X-ray photoelectron

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spectroscopy (XPS), secondary ion mass spectroscopy (SIMS),⁹ and attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR),¹⁰ in the detection of surfactant exudation has been demonstrated. Despite these efforts, only limited work has been done in regard to addressing the ultimate molecular level interactions that may influence surfactant mobility and exudation.

Evanson and Urban^{11,12} assessed the nature of surfactant/latex interactions in an ethyl acrylate/methacrylic acid (EA/MAA) latex system prepared with sodium dioctyl sulfosuccinate (SDOSS) surfactant. These initial studies showed that the surfactant is involved in hydrogen-bonding interactions with the acid functionality of the copolymer latex through the sulfonate groups. The $\text{SO}_3^- \text{Na}^+ \cdots \text{HOOC}-$ interactions can, however, be eliminated through neutralization of the acid functionality by the addition of aqueous base. It was also demonstrated that residual water left in the latex film after coalescence was also involved in hydrogen bonding with the surfactant.

The influence of surfactant structure on mobility in the EA/MAA latex was examined^{13,14} using a variety of surfactants including sodium dioctyl sulfosuccinate (SDOSS), sodium dodecylbenzene sulfonate (SDBS), sodium nonylphenol ethylene oxide sulfonate (SNP2S), sodium dodecyl sulfate (SDS), and a nonionic nonylphenol ethylene oxide adduct (40 ethylene oxide units; NP). Spectroscopic analysis of the interfaces of coalesced films prepared on a polytetrafluoroethylene (PTFE) substrate using ATR FTIR revealed that all of the anionic surfactants exhibit preferential enrichment to the film-substrate interface of the latex film. The nonionic NP surfactant, on the other hand, was found to be more compatible with the copolymer and, to the best of our knowledge, it remained uniformly distributed across the film thickness.

The nature of the substrate was identified as a significant factor that may influence the exudation of surfactant.^{14,15} As was mentioned above, anionic surfactants can migrate to the film-PTFE interface and this exudation was attributed to the low surface free energy of the substrate (18.5 mN/m). As a result, a high degree of interfacial tension between the substrate and the latex suspension may occur, which provides a driving force for the migration of surfactant to the interface.

In this study, we will further examine the nature of surfactant/copolymer interactions and focus on the influence of copolymer structure on these interactions. For that purpose, latexes with a butyl acrylate/methyl methacrylate/methacrylic acid (BA/

MMA/MAA) monomer system formulated to maintain the same glass transition temperature (T_g) and MAA content as the formulation discussed above will be examined. An ultimate objective of this study is to investigate the effect of the copolymer structure on the migration of surfactants to the film-air (F-A) and film-substrate (F-S) interfaces. Structures of the copolymer latexes and the surfactants employed in this study are illustrated in Figure 1.

EXPERIMENTAL

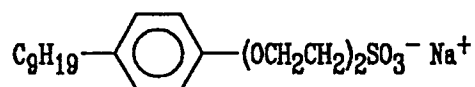
Spectral acquisition and analysis, film preparation, and the synthesis of ethyl acrylate/methacrylic acid (EA/MAA) latexes were performed as described in the previously reported methodologies.¹² BA/MMA/MAA latexes with the same theoretical T_g and MAA content as the EA/MAA formulations were prepared using a recipe consisting of 270.0 g DDI H₂O and a total monomer charge of 180.0 g, which was composed of 66.0 w/w % BA, 30.0 w/w % MMA, and 4.0 w/w % MAA. A synthetic procedure identical to that used for the EA/MAA formulations was employed.¹² The surfactants, sodium dioctyl sulfosuccinate (SDOSS; Aldrich), sodium dodecylbenzene sulfonate (SDBS; Aldrich), and a sodium nonylphenol ethylene oxide adduct with 2 ethylene oxide units (Rohm and Hass; SNP2S) were employed in synthesis at 4.0 w/w % based on total monomer content.

RESULTS AND DISCUSSION

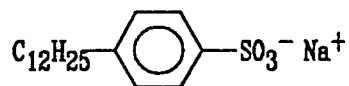
As a starting point for the analysis, let us briefly consider relevant spectral features of EA/MAA and BA/MMA/MAA copolymers. Figure 2 shows ATR FTIR spectra of copolymer films prepared after the latexes were cleaned of SDOSS surfactant through repeated dissolution in acetone and precipitation with water. Characteristic bands of the copolymers and their tentative assignments are summarized in Table I. Figure 2 shows that neither the EA/MAA (trace A) nor BA/MMA/MAA (trace B) copolymer spectra exhibit bands in the 700–500 cm^{-1} region. Since surfactants with the structures shown in Figure 1 reveal absorbances in this region due to S—O bending and scissors modes of the sulfonate groups,¹³ we will use this region for monitoring surfactant exudation.

To analyze the interactions of the surfactants in structurally different polymer environments, it is

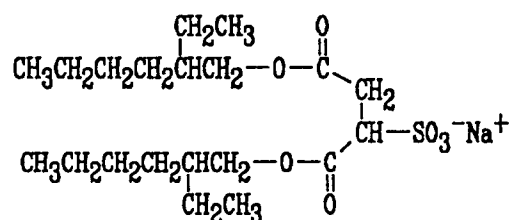
A. Sodium nonylphenol ethylene oxide sulfonate (SNP2S)



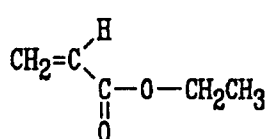
B. Sodium dodecylbenzene sulfonate (SDBS)



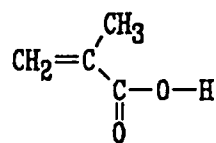
C. Sodium dioctyl sulfosuccinate (SDOSS)



D. Components of ethyl acrylate/methacrylic acid (EA/MAA)

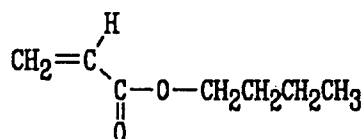


ethyl acrylate (EA)

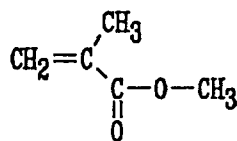


methacrylic acid (MAA)

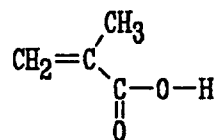
E. Components of butyl acrylate/methyl methacrylate/methacrylic acid (BA/MMA/MAA)



butyl acrylate (BA)



methyl methacrylate (MMA)



methacrylic acid (MAA)

Figure 1 Structures of surfactants used in synthesis: (A) sodium nonylphenol ethylene oxide sulfonate (SNP2S); (B) sodium dodecylbenzene sulfonate (SDBS); (C) sodium dioctyl sulfosuccinate (SDOSS); (D) components of ethyl acrylate/methacrylic acid (EA/MAA) latex; (E) components of butyl acrylate/methyl methacrylate/methacrylic acid (BA/MMA/MAA) latex.

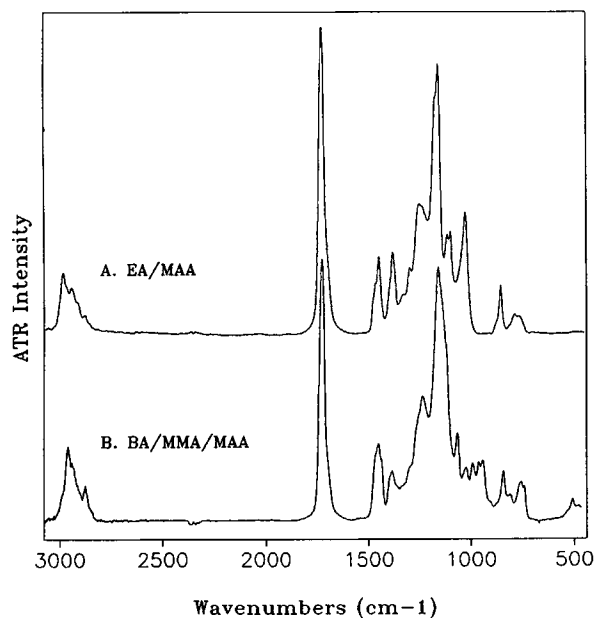
necessary to address the methods of spectral normalization that allow direct qualitative comparison of the spectra. To accomplish this, we have selected the C=O stretching mode as the band of choice for

normalization. In spite of the possibility of hydrogen-bonding interactions, this band seems reasonable because the carbonyl environments are nearly identical in the two copolymers and comparable ex-

Table I A List of the Major Copolymer Bands and Their Tentative Assignments

EA/MAA (from Ref. 13)	BA/MMA/ MAA	Assignments
2981	—	Asym C—H stretch (CH_3)
2960	2958	Asym C—H stretch (CH_3)
2934	2941	Asym C—H stretch (CH_2)
2879	2875	Sym C—H stretch (CH_3)
1735	1727	C=O stretch (ester)
1466	1450	Asym C—H def. (CH_3)
1447	1442	CH_2 scissors
—	1438	Sym C—H def.
1382	1386	Sym C—H def. (C—CH_3)
1299	1301	CH_2 wagging
1252	1237	C—O stretch
1173	1158	Asym C—O—C stretch
1098	1066	Sym C—O—C stretch
1025	1023	C—C—O ester
—	992	Ester skeletal vibration
—	963	Ester skeletal vibration
—	944	Ester skeletal vibration
854	842	Ester skeletal vibration
—	755	CH_2 rocking
—	741	CH_2 rocking

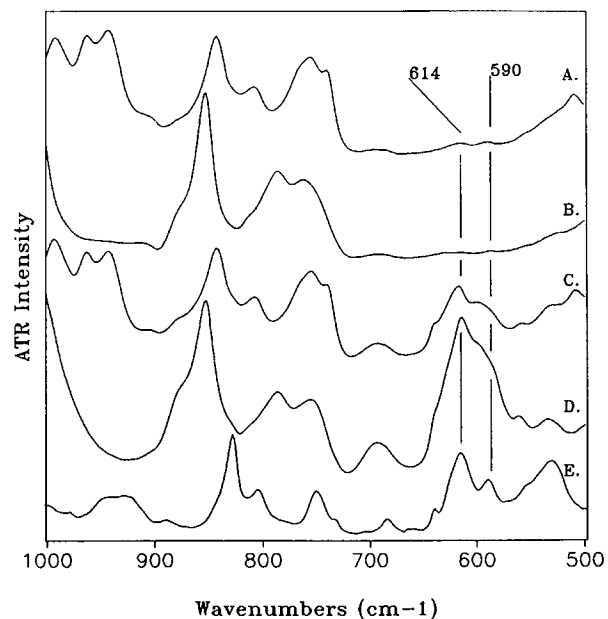
tion coefficients can be anticipated. Additionally, the bulk carbonyl group concentration of the two copolymers is quite similar: 28.2 w/w % for EA/MAA and 24.4 w/w % for BA/MMA/MAA. It

**Figure 2** ATR FTIR spectra in the 3100–500 cm^{-1} region of surfactant-free copolymer films: (A) EA/MAA copolymer; (B) BA/MMA/MAA copolymer.

should be realized that some error may be induced by these assumptions and, furthermore, by the additional variables imposed by using ATR as the analytical method.^{16,17} Because of these factors, we will not attempt quantitative assessments of the magnitude of surfactant exudation, but rather the discussion will be restricted to qualitative differences. These differences, as we shall see, will adequately allow us to assess the influences of copolymer structure on surfactant behavior.

Let us first consider the behavior for SNP2S. As shown in Figure 3, neither film exhibits a measurable degree of enrichment at the film–air (F–A) interfaces (traces A and B). In contrast to these results, the spectra of the film–substrate (F–S) interfaces reveal significant exudation, which is shown by the strong surfactant bands at 614 cm^{-1} (S—O bending mode) and 589 cm^{-1} (SO_2 scissors). A comparison of the normalized spectra clearly reveals that the magnitude of the surfactant enrichment is much greater in the case of the EA/MAA latex.

Similar results are observed for SDBS. Figure 4 shows the ATR FTIR spectra recorded at the interfaces of BA/MMA/MAA and EA/MAA latex films prepared on a PTFE substrate. At the F–A interfaces (traces A and B), hardly any detectable

**Figure 3** ATR FTIR spectra in the 1000–500 cm^{-1} region recorded at the interfaces of films of BA/MMA/MAA and EA/MAA latexes prepared with SNP2S surfactant: (A) BA/MMA/MAA F–A interface; (B) EA/MAA F–A interface; (C) BA/MMA/MAA F–S interface; (D) EA/MAA F–S interface; (E) SNP2S surfactant only.

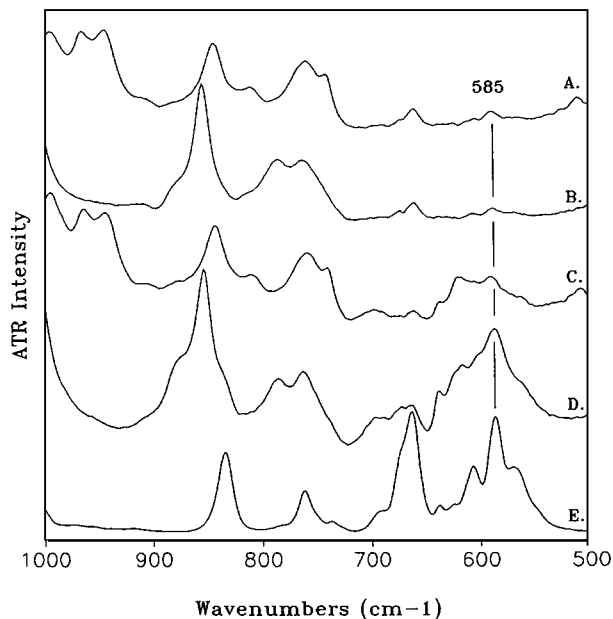


Figure 4 ATR FTIR spectra in the 1000–500 cm^{-1} region recorded at the interfaces of films of BA/MMA/MAA and EA/MAA latexes prepared with SDBS surfactant: (A) BA/MMA/MAA F–A interface; (B) EA/MAA F–A interface; (C) BA/MMA/MAA F–S interface; (D) EA/MAA F–S interface; (E) SDBS surfactant only.

traces of surfactant are observed and the concentration levels in both cases appear to be quite similar. However, significantly greater surfactant concentration is detected at the F–S interfaces. Although the BA/MMA/MAA film (trace C) does show some enrichment to this interface, as evidenced by the characteristic surfactant bands, it is apparent that the degree of enrichment is substantially greater in the case of the EA/MAA latex (trace D).

Somewhat different behavior is observed for the SDOSS latexes. As evidenced by the weak bands at the F–S interfaces illustrated in Figure 5, traces C and D, the degree of enrichment is quite small for both latexes, and no significant preferential enrichment, observed for the other surfactants, is detected. It is worthwhile to note that, as with the other surfactants, the total amount of enrichment to the film interfaces is smaller for the BA/MMA/MAA latex than that observed for EA/MAA. As seen in Figure 5, neither the F–A interface of the BA/MMA/MAA latex (trace A) nor the F–S interface (trace C) reveal appreciable amounts of surfactant enrichment. In contrast, however, both the F–A and F–S interfaces of the EA/MAA latex (traces B and D, respectively) reveal a slight degree of enrichment, as shown by the enhanced intensities of the bands at 652 cm^{-1}

(S–O bending mode), 581 cm^{-1} (SO_2 scissors), and 529 cm^{-1} (alkyl chain vibrations).

Although the general trend of reduced enrichment for the BA/MMA/MAA system is followed here, two questions should be imposed. First, why the magnitude of enrichment is smaller for both copolymers, and, second, why there is not a pronounced preferential enrichment in the direction of the F–S interface, as was observed for the other surfactants. To address these issues, two factors, that is, the copolymer–surfactant compatibility and polymer–substrate interfacial tension, should be considered. As shown in Figure 1, SNP2S (A) and SDBS (B) are both aromatic sulfonate salts with long linear aliphatic “tails,” whereas SDOSS (C) is a diester with shorter, branched hydrophobic segments. This structural difference may, first of all, lead to enhanced compatibility with the structurally similar acrylic esters (D and E) that make up the bulk of the copolymers. Additionally, it is possible that the short, branched aliphatic “tails” of SDOSS may not be able to efficiently assemble at the F–S interface and alleviate the interfacial tension present there.

The evidence of this behavior was shown for EA/MAA previously,¹⁵ where it was found that the ATR FTIR spectra collected at the F–S interface of

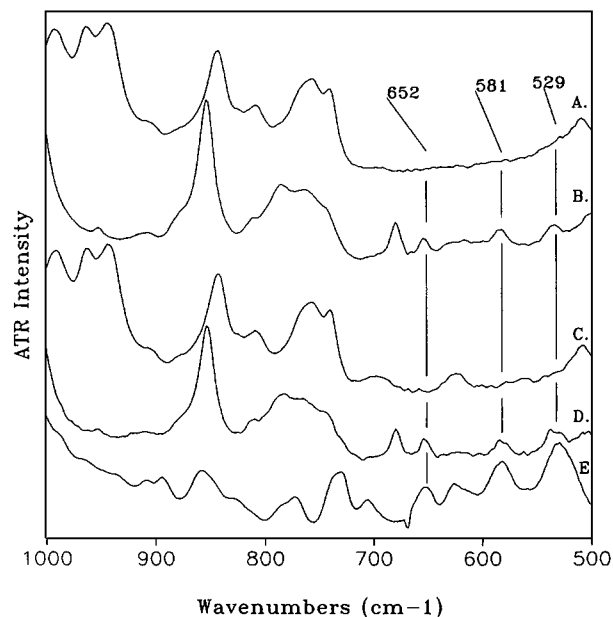


Figure 5 ATR FTIR spectra in the 1000–500 cm^{-1} region recorded at the interfaces of films of BA/MMA/MAA and EA/MAA latexes prepared with SDOSS surfactant: (A) BA/MMA/MAA F–A interface; (B) EA/MAA F–A interface; (C) BA/MMA/MAA F–S interface; (D) EA/MAA F–S interface; (E) SDOSS surfactant only.

SDOSS latex films prepared on liquid mercury revealed the presence of a significant concentration of acid dimer functionality. These species had assembled at the F-S interface and were accompanied by exuded surfactant molecules. Although the films of SDBS and SNP2S latexes prepared on liquid mercury reveal the same qualitative behavior as was observed for PTFE, it is instructive to examine the results obtained for SDOSS latex films prepared on this substrate. As shown in Figure 6, while the BA/MMA/MAA latex (trace A) does not reveal any of the characteristic surfactant bands, a slight degree of enrichment is detected in the spectrum of the EA/MAA latex (trace B). This is shown by the presence of weak bands at 652 cm^{-1} (S—O bending) and 581 cm^{-1} (SO_2 scissors) vibrational modes. In both cases, however, we do observe a significant concentration of acid-functional species demonstrated by the broad band at 938 cm^{-1} (OH \cdots OC out-of-plane deformation) and the bands at 598 and 575 cm^{-1} . The latter are attributed to the O—CO in-plane vibration of the carboxylic acid species. Apparently, as was observed for EA/MAA, the inability of the surfactant to adequately alleviate the

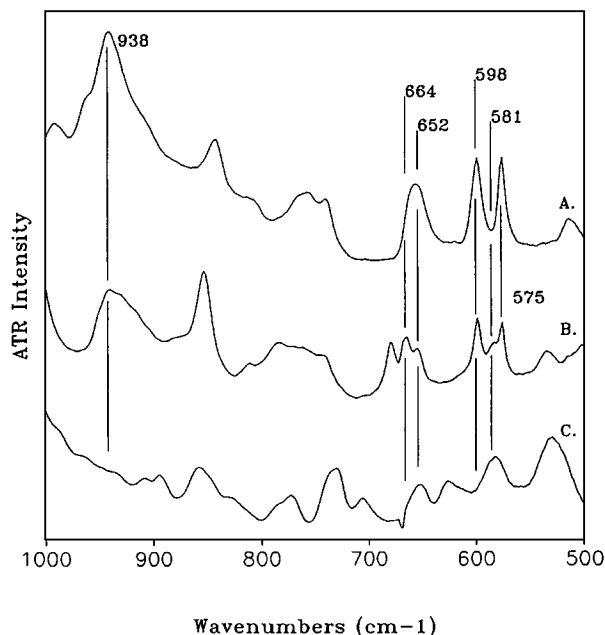


Figure 6 ATR FTIR spectra in the $1000\text{--}500\text{ cm}^{-1}$ region recorded at the film-substrate interface of films of BA/MMA/MAA and EA/MAA latexes prepared with SDOSS surfactant on a mercury substrate: (A) BA/MMA/MAA F-S interface; (B) EA/MAA F-S interface; (C) SDOSS surfactant only.

interfacial tension induces the migration of these species to the interface. Significantly, the degree of acid group enrichment appears to be related to the magnitude of surfactant exudation to the interface; for BA/MMA/MAA, where the magnitude of surfactant exudation is reduced, the acid group concentration is enhanced. These assessments point toward compatibility as being one of the major factors that influences surfactant exudation. If compatibility between BA/MMA/MAA and SDOSS is greater than detected for EA/MAA, reduced surfactant exudation and, in turn, enhanced acid group migration, would be anticipated.

At this point, it is appropriate to address the factors that may be responsible for the reduced magnitude of exudation observed for the BA/MMA/MAA copolymer system. Although free volume effects may be expected to exert significant influence on the diffusion and migration of small molecules within a polymer matrix, these effects will be minimized by comparing copolymer systems with the same T_g , such as in this study. We are therefore able to make qualitative assessments in terms of the ultimate chemical environment of the copolymer. Similarly to the previous studies,¹³ let us consider the behavior of EA/MAA latexes with the neutralized acid functionality by an addition of aqueous base. Neutralization of the acid groups of the EA/MAA copolymer results in swelling of the latex particles and extension of the hydrophobic copolymer segments into the aqueous phase. This chain extension facilitates a greater degree of hydrophobic interactions between the copolymer-surfactant pairs and, as a result, compatibility is increased. In analogy with this approach, one can postulate that the longer pendant hydrophobic segments present in BA/MMA/MAA copolymer (*n*-butyl as opposed to ethyl) are potentially more accessible to the surfactant molecules, even in the nonneutralized latex. These longer aliphatic groups serve to increase the potential for hydrophobic interactions between the copolymer and the surfactant, thus enhancing compatibility.

The possibility that the *n*-butyl groups present in the BA/MMA/MAA system may also serve to reduce interfacial tension is another factor that may also reduce exudation by reducing the driving force for the migration of surfactant to the film interfaces. Relative to the EA/MAA system, the longer pendant groups in the BA/MMA/MAA copolymer can be expected to more effectively orient toward the interfaces of the film, thus reducing the magnitude of the surface or interfacial free energy.

CONCLUSIONS

These studies show that ATR FTIR spectroscopy can be used for qualitative assessments of the surfactant enrichment at the F-A and F-S interfaces. The magnitude of surfactant enrichment to the F-S interfaces of latex films prepared on a PTFE substrate is reduced for BA/MMA/MAA latex systems. As opposed to the EA/MAA latex, the reduced exudation is observed and attributed to the enhanced surfactant-copolymer interactions facilitated by the presence of longer aliphatic *n*-butyl groups. Additionally, it is possible that these groups may serve to alleviate excess surface free energy via orientation toward the latex film interfaces. This, in turn, reduces the driving force for surfactant migration.

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