Surface and Interfacial FTIR Spectroscopic Studies of Latexes. III. The Effects of Substrate Surface Tension and Elongation on Exudation of Surfactants

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SYNOPSIS

This paper focuses on the effect of the substrate surface tension and mechanical elongation of EA/MAA latex films on the ionic and nonionic surfactant mobility. Although the mobility of anionic surfactants is inherently sensitive to the substrate surface tension, nonionic surfactants appear to remain uniformly distributed across the latex film. This behavior is attributed to the enhanced compatibility with the copolymer latex. Mechanical elongation of the latex films enhances surfactant exudation to the surface due to the increased surface energy of the film forcing surfactants to the latex surface.

INTRODUCTION

Polymeric systems are typically complex mixtures of high molecular weight polymer and low molecular weight additives, purposely introduced to the system to chemically or physically modify the polymer. These additives may be plasticizers to lower the glass transition temperature in order to improve the polymer processability, or they may be catalysts to accelerate reactions or crosslinking agents to improve the 3-dimensional polymer network. In synthetic latex polymer systems, surfactants are added to the reaction mixture to emulsify the monomers during polymerization and stabilize the polymer in aqueous environments. Because these additives are usually small, mobile molecules, their behavior and distribution in the latex may lead to undesirable properties, e.g., phase separation due to a limited compatibility or various failure modes. For example, surfactant enrichment at the film–air and film–substrate interfaces may lead to a premature degradation and loss of adhesion. Such phenomena are commonly known in thermoplastics. For example, when bis(2-ethylhexyl) phthalate was used in biocompatible poly(vinyl chloride) (PVC),[1] enrich-

ment at both interfaces of a PVC film was detected. This behavior was attributed to the concentration gradients across the film which provide a driving force to maintain an equilibrium concentration. For these reasons, it is important to understand how such factors as compatibility, mechanical stress, and interfacial surface tension may govern mobility and the distribution of surfactant molecules in latex films.

Using a simplified view, the components of a polymer mixture may be considered compatible if they exhibit similar chemical structures or possess functional groups capable of favorable interaction.[2] Since these features may or may not exist between the copolymer and the surfactant in a latex, the choice of the copolymer and surfactant structures is essential in providing suitable environment for the chemical compatibility of the components. In an effort to determine the relationship of surfactant compatibility and the exudation behavior, Vanderhoff[3] analyzed a series of styrene–butadiene (SBR) latexes with electron microscopy (EM). The compatibility of nonylphenol ethylene oxide surfactants with the nonpolar SBR copolymer was shown to decrease with the increased hydrophilicity (polarity) of the surfactant. In contrast, adsorption studies[4] on the more polar poly(vinyl acetate–butyl acrylate) (PVAc–BA) latexes stabilized by the same nonionic surfactants indicated the increased sur-

factant absorption with the increased hydrophile lipophile balance number (HLB) or hydrophilicity. Apparently, vinyl acetate groups are hydrolyzed to form poly(vinyl alcohol), which provides the OH functional groups that can interact with the ether oxygens in the PEO segments of the surfactant, leading to compatibility enhancement.

Due to the presence of highly polar hydrophilic sulfonate and sulfate groups, one would expect that anionic surfactants have lower compatibility with vinyl and acrylic copolymers. However, depending upon ionic functionality, many anionic surfactants have shown different degrees of compatibility relative to each other.[5] Attenuated total reflectance (ATR) FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS) have been used to analyze the film–air and film–substrate interfaces of latex films prepared from methyl methacrylate–butyl acrylate (MMA–BA) synthesized with two different anionic surfactants, sodium dodecyl sulfate (SDS) and sodium dodecyl diphenyl ether disulfonate (SDED).[6] Although both latexes showed the surfactant enrichment at both the film–air and film–substrate interfaces, revealing a parabolic distribution of surfactant throughout the film, the SDS formed a thick layer at the film–substrate interface described as a weak boundary layer (WBL). The formation of the WBL was attributed to a lower surfactant compatibility with the MMA–BA copolymer. As a result of the WBL formation, the SDS latex films exhibited significantly lower adhesion. The surface enrichment observed in the MMA–BA latex films was attributed to the following processes: (1) enrichment at the film–air interface due to nonadsorbed surfactant in the aqueous phase transported to the surface by the water flux out of the film; (2) long range migration to both interfaces due to surfactant incompatibility; and (3) initial enrichment at both interfaces in order to lower the interfacial free energy. The third process is particularly important since different surfaces exhibit different interfacial free energies which may influence initial surfactant enrichment. Since the nature of the interfaces influences interfacial tension,[7] interfacial surface tension of the polymer–water interface will affect the surfactant adsorption on various polymer surfaces.[8,9] The surface area per molecule of sodium dodecyl sulfate on a latex polymer particle was shown to increase with the increased polarity of the polymer–water interface. Thus, the driving force for the adsorption of surfactant at various polymer–water interfaces is related to the differences in the interaction energy between the surfactant molecules and the surfaces in question.

In an effort to determine the effect of interfacial surface tension on surfactant exudation to the film–substrate interface, the surface morphology of styrene–butadiene copolymer latex films prepared on a variety of substrates such as polytetrafluoroethylene, Mylar polyester, rubber, and mercury.[10] Upon the latex removal from the substrate, the surfaces were analyzed by electron microscopy (EM). Although differences were observed for the film–substrate interfaces of films prepared on different substrates, they were determined to be small and, therefore, of a negligible significance. In fact, the surfactant exudation and film formation behavior at the film–substrate interface were concluded to closely parallel that at the film–air interface.

Based on this brief literature survey, it is clear that, although the initial studies on surfactant exudation in latex films have revealed some insights into the latex interfacial chemistry, only selected surfactants were studied. Hence, it is difficult to assess the forces governing mobility of surfactants. In this paper, the exudation behavior of a series of surfactants in the EA/MAA latex films with the modified copolymer polarity by the addition of a small fraction of acid monomer is investigated and the surface structures that may develop as a result of mobility. In order to establish how surfactant mobility may be modified by the surfactant–copolymer compatibility and the effects of interfacial surface tension of the substrate and mechanical elongation of latex films, the film–air and film–substrate interfaces will be monitored by ATR FT-IR spectroscopy.

EXPERIMENTAL

Synthetic acrylic latex copolymers based on ethyl acrylate and methacrylic acid were prepared as described earlier (Part II).[11] The latex films were prepared using the following surfactants: sodium dioctyl-sulfosuccinate (SDOSS; OT-75—75% in EtOH, American Cyanamid Co.), sodium dodecylbenzene sulfonate (SDBS; Witconate K, Witco Corp.), sodium dodecyl sulfate (SDS; BDH Chemicals Ltd.), sodium sulfonate adduct of nonylphenol ethylene oxide-2 units (SNP2S; Triton X-200, Rohm and Haas), and nonylphenol ethylene oxide-40 units (NP, Iconol NP-40, BASF). Table I of Ref. 11 lists the particle diameters of the studied latex systems. The spectral analysis at the film–air and film–substrate interfaces was described previously (Part I).[12]

Latex particle size analysis was performed on a Coulter submicron particle analyzer Model N4-SD using 200 scans at a light angle of 90°, a temperature of 20°C and a refractive index of 1.33 (water).

A JEOL 301 (Jeol Co.) scanning electron microscope (SEM) was used to obtain photographs of the film-air and film-substrate latex interfaces. Pictures were obtained at a magnification of 2000 applying 14 kV with a polaroid camera attached to the scanner.

RESULTS AND DISCUSSION

In order to determine the effect of surface tension on the mobility of surfactants in latex films, various substrates with different surface energies are required. Moreover, the films should be easily removed from the substrate in order to minimize mechanical stresses induced during sample preparation. In an effort to fulfill these requirements, polytetrafluoroethylene (PTFE) and liquid mercury (Hg) substrates were used since their surfaces allow relatively easy removal of the films with a minimal mechanical stress while providing substantial surface tension differences. The films were also cast directly onto the ATR element, with a surface tension close to that of a glass substrate, from which the films are not easily removed. However, such a configuration permits monitoring the film-substrate interface without any mechanical interference to the film.

Substrate Surface Tension Effect

Although the surface tension of the substrate is only one factor which may affect the behavior of surfactants, the chemical structures of the surfactants themselves are also important. For that reason, the latex films were prepared from several latexes synthesized using various surfactants. Although the infrared spectra of the surfactants along with the band assignments and chemical structure of each surfactant were presented in Part II of the series (Fig. 1 and Tables I and II of Ref. 11), the substrate surface tension effect on both the film-air and film-substrate interface compositions will be examined here. The spectra obtained for the film-air interface of latex films deposited on PTFE are presented in Figure 1. Since the EA/MAA copolymer (trace F) has no characteristic absorption bands in the 700-400 cm^{-1} region, this region can be used to identify the presence of surfactant at the latex interfaces. The latex prepared using the SDOSS surfactant (trace
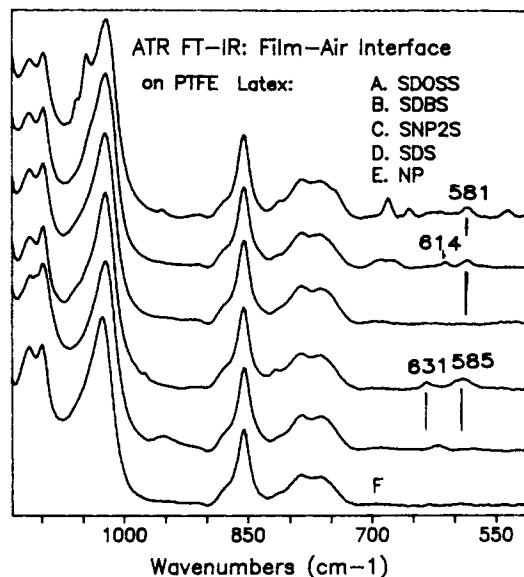

Figure 1 ATR FT-IR spectra in the region from 1150 to 500 cm^{-1} recorded at the film-air interface of latex films prepared on PTFE: (A) SDOSS; (B) SDBS; (C) SNP2S; (D) SDS; (E) NP; (F) EA/MAA copolymer.

A) exhibits the band at 581 cm^{-1} characteristic of the SO$_2$ scissor mode of SDOSS. Similarly, the SDBS latex (trace B), exhibits the band at 614 cm^{-1} characteristic of the S—O bending mode of the SO$_3$ groups in SDBS. Traces D and E show two bands at 631 and 585 cm^{-1} characteristic of the S—O bending of the sulfate group (D) and the band at 947 cm^{-1} assigned to the C—O stretching mode of ether groups in the polyethylene oxide segment of the surfactant (E). In contrast, the SNP2S latex spectrum (trace C) does not exhibit any surfactant bands in the characteristic surfactant region. Since these spectra represent the chemical structures present at the film-air interface, this observation indicates that the SNP2S surfactant does not exude to this interface, most likely, because it is more compatible with the EA/MAA copolymer latex than other surfactants (for example, SDOSS and SDBS). In view of the above results and keeping in mind that the direction of the water flux out of the film is away from the substrate, let us now analyze the film-substrate interface spectra.

Figure 2 illustrates the ATR FT-IR spectra recorded at the film-substrate interface for the same latex films prepared on a PTFE substrate. Similarly in Figure 1, all spectra exhibit the bands characteristic of their surfactants, but their intensities are different and vary substantially among the surfactants. In the case of the SDOSS latex (trace A),
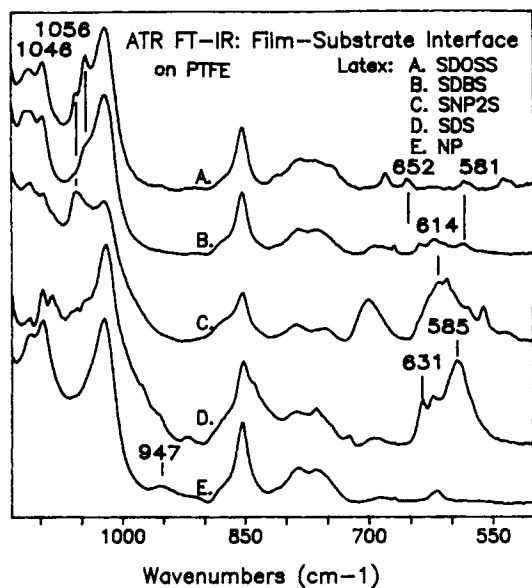
Figure 2 ATR FT-IR spectra in the region from 1150 to 500 cm^{-1} recorded at the film–substrate interface of latex films prepared on PTFE: (A) SDOSS; (B) SDBS; (C) SNP2S; (D) SDS; (E) NP.

both intensities of the surfactant bands in the film–air and film–substrate spectra are the same, indicating similar concentrations of the surfactant at these interfaces. However, the film–substrate interface spectrum of the SDBS latex film (trace B) exhibits the band at 614 cm^{-1} with a significantly greater intensity than that observed for the film–air interface. Similarly, stronger surfactant bands at 614 cm^{-1} (S—O bending) for the SNP2S latex (trace C) and at 631 and 585 cm^{-1} (S—O bending) for the SDS latex (trace D) indicate a greater concentration of these surfactants at the film–substrate interface. In contrast, the spectrum of the NP latex (trace E) shows no apparent intensity differences, and hence the distribution of surfactant at the film–air and the film–substrate interfaces is similar. This is in part related to the fact that nonionic surfactants may adsorb onto the copolymer through interactions between alkyl segments such as van der Waals and London dispersion forces and, due to a strong tendency to form hydrogen bonding[13] between acid groups of the copolymer and ether linkages on the surfactant, compatibility may be promoted, inhibiting phase separation and subsequent exudation to either interface.

Based on these comparative results, it is apparent that the distribution of surfactants in the latex films varies depending upon the surfactant structures, and this distribution is most likely established during

latex coalescence. Because the process of latex film formation parallels evaporation of water, initially, a thin layer coalesces at the surface of the film, followed by a slow film formation towards the substrate. Since the anionic surfactants are highly water-soluble, the surfactant prefers an aqueous environment and will remain in the aqueous phase. As water evaporates at the film–air interface, the surfactant diffuses towards the film–substrate interface. This would explain the higher concentration of the anionic surfactants observed at the film–substrate interface. In view of these considerations, it is also important to consider the effect of the surface tension of the substrate. In general, a liquid will wet a substrate with higher surface energy. In the case of PTFE with an unusually low surface energy (18.5 mN/m),[14] the surfactant may be driven to the film–substrate interface in order to lower the interfacial tension difference between the latex and the substrate. If this is the case, the latex films deposited on substrates with substantially different surface tensions should yield information regarding the effect of surface tension on the surfactant distribution in the latex films.

In an attempt to answer this question, latex films were prepared directly on the ATR element (KRS-5). Such an approach eliminates mechanical effects imparted to the films during film removal. Figure 3 illustrates the film–substrate spectra in the 1135–
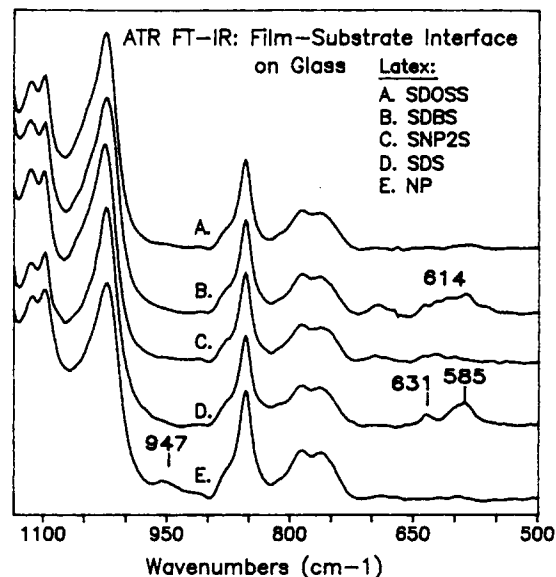

Figure 3 ATR FT-IR spectra in the region from 1150 to 500 cm^{-1} recorded at the film–substrate interface of latex films prepared on glass: (A) SDOSS; (B) SDBS; (C) SNP2S; (D) SDS; (E) NP.

500 cm^{-1} region, recorded for the same series of latexes. The spectra of the SDOSS latex (trace A) as well as the SNP2S latices (trace C) do not exhibit any infrared bands characteristic of the surfactants. Although this observation indicates that there is no surfactant exudation to the film–substrate interface, it appears to be contrary to the solubility effect described above which supposedly promotes migration to this interface. However, for the substrates like KRS-5 with a surface tension of 70 mN/m, the SDOSS surfactant migrates away from or is displaced by the copolymer at the film–substrate interface (Part II).[11] This temporary controversy becomes even more complex if one considers SDBS and SDS surfactants. Although the SDBS spectrum (trace B) has the bands at 614 and 583 cm^{-1} due to the S—O bending and scissor normal vibrational modes, respectively, the SDS spectrum (trace D) exhibits the bands at 631 and 585 cm^{-1}, both due to the S—O bending normal vibrations. Again, the increased intensities indicate exudation of these surfactants to the film–substrate interface. The NP latex film also exhibits a band characteristic of the surfactant at 947 cm^{-1}, previously assigned to the —O—CH$_2$— groups. In this case, however, the intensity changes between the film–air and film–substrate interfaces do not have appreciable differences between spectra obtained for the films prepared on PTFE and glass substrates, indicating that the mobility of the nonionic surfactant is not influenced by the differences in the substrate surface tension of the different substrates.

Based upon these results, it is apparent that the low surface energy of PTFE induces surfactant enrichment at the film–substrate interface in order to lower the interfacial tension that exists after film application. On the other hand, the glass substrate, with a higher surface energy ($\sim$70 mN/m), gives a significantly lower concentration or no surfactant enrichment at the film–substrate interface for all the anionic surfactant latex films. Since the polymer has the surface tension of approx. 30 mN/m, it will wet the glass substrate during coalescence, thereby significantly lowering the driving force for surfactant exudation to this interface. Thus, it is the interfacial surface tension at the film–substrate interface which provides a driving force for the surfactant exudation to this interface and not necessarily the solubility of the surfactants in water. Therefore, the copolymer will be able to more efficiently wet the substrates with much higher surface energy than glass and thus lower the driving force for surfactant exudation to this interface.

In an effort to determine the effect of high surface energy substrates on surfactant exudation, the latex films were prepared on liquid mercury with a reported surface tension of 416 mN/m.[15] The ATR FT-IR spectra recorded at the film–substrate interface are presented in Figure 4. Surprisingly, a significant surfactant exudation is detected to the film–substrate interface, as evidenced by the presence of strong bands characteristic of the respective surfactants. The SDOSS latex film (trace A) exhibits characteristic surfactant bands at 1046 and 1056 cm^{-1}, previously assigned to the symmetric S—O stretch of the surfactant sulfonate groups, as well as the bands at 653 and 581 cm^{-1}, assigned to the S—O bending and S—O scissor vibrations of the sulfonate groups. The enhanced intensity of these bands indicates that the surfactant exudation is significantly greater for the SDOSS latex films prepared on Hg than that on glass or PTFE. In addition, several new bands not present in the previous spectra of SDOSS latex films are observed in this region. The SDBS latex film (trace B) also exhibits increased surfactant exudation to the film–substrate interface, characterized by the enhanced intensities of the previously assigned bands at 614, 581, and 691 cm^{-1}. The SDS latex film spectrum (trace D) exhibits similar trends with the bands at 829 cm^{-1} as well as 631 and 585 cm^{-1}.

The SNP2S latex film spectrum (trace C) exhibits similar features, with the 614 cm^{-1} band in the spectra of the SNP2S latex film prepared on Hg [Fig. 4(C)], than that on glass [Fib. 3(C)]. Interestingly enough, the 614 cm^{-1} band is significantly stronger in the spectra of the film prepared on PTFE [Fig. 2(C)], indicating that, for this surfactant, the direction of exudation is the same, but its magnitude is inhibited when Hg is a substrate. Moreover, the spectroscopic data is supported by the visual assessment after a removal of the SNP2S latex film from mercury; apparently, a thin cloudy film was noted on the substrate. Upon dissolving the film in water, subsequent characterization by transmission FT-IR revealed almost exclusively SNP2S surfactant, indicating a greater degree of surfactant enrichment at the film-mercury interface than that detected in the ATR spectrum [Fig. 4(C)]. In addition, the surface morphology of the film–substrate interface was substantially different as compared to the film–air and film–substrate interfaces of the other latex films. In an attempt to further understand and explain the exudation behavior of the SNP2S surfactant in latex films prepared on mercury, electron microscopy was used to analyze the
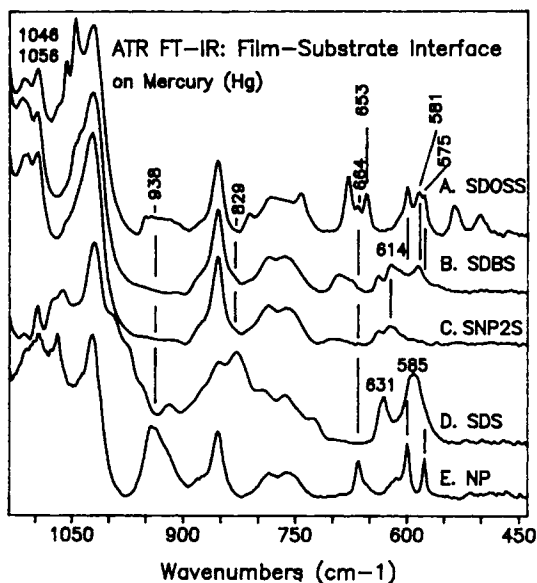
Figure 4 ATR FT-IR spectra in the region from 1150 to 500 cm⁻¹ recorded at the film–substrate interface of latex films prepared on Mercury: (A) SDOSS; (B) SDBS; (C) SNP2S; (D) SDS; (E) NP.

film–air and film–substrate interfaces of the SNP2S latex films. Figure 5 illustrates the electron micrographs of the film–air (A) and film–substrate (B) obtained at a magnification of ×2000. Although the film–air interface exhibits a smooth continuous morphology of a coalesced latex, the film–substrate interface clearly shows noncontinuous, agglomerated latex particles which did not coalesce. Since there is an excess of surfactant at the latex–mercury interface, the surfactant will inhibit the latex particle coalescence by acting as a barrier which prevents latex particle coalescence. As shown in Figure 5(B), this is clearly the case.

The film–substrate spectrum of the NP latex prepared on mercury is illustrated in Figure 4, trace E. The characteristic surfactant band at 947 cm⁻¹ is not observed. Instead, a broad band centered at 938 cm⁻¹ assigned to the OH···OC out-of-plane deformation vibrations of the carboxylic acid groups are detected. Along with this band, the bands at 664, 600, and 575 cm⁻¹ due to the O—CO in-plane vibration of α-branched aliphatic carboxylic acid groups are observed. As illustrated in Figure 4, these
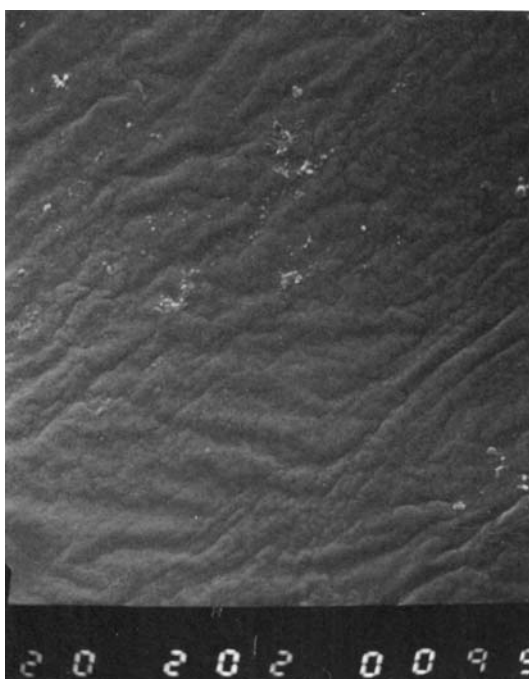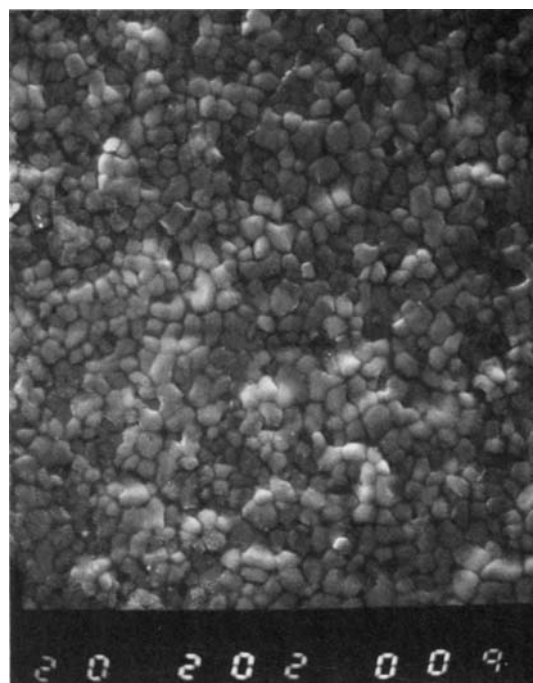
Figure 5 Electron micrographs of the surface morphology of the SNP2S latex film prepared on mercury: (A) film–air interface; (B) film–substrate interface.

Film-Air Interface

Surfactant

Latex Film

Film-Substrate
Interface

Glass

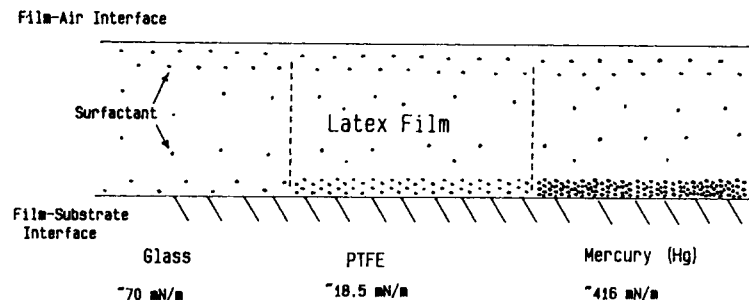PTFE

Mercury (Hg)

⁻70 mN/m

⁻18.5 mN/m

⁻416 mN/m

Figure 6 Schematic representation of the substrate effect on the distribution of surfactant across the latex films prepared on glass, PTFE, and mercury.

spectral features are also observed in the spectra of the SDOSS latex film (trace A). The appearance of these bands indicates that there is a driving force for the acid groups to migrate to the film–substrate interface. Based on these data, the effect of the substrate surface tension on surfactant mobility can be proposed.

Figure 6 depicts the ionic surfactant behavior on the three substrates. Although latex films prepared on PTFE exhibit moderate exudation of surfactants to the film–substrate interface in order to lower the interfacial surface tension between the copolymer and the PTFE, the films prepared on glass (KRS-5) exhibit minimal or no exudation to the film–substrate interface. This is because copolymer is able to wet the substrate, thus lowering the driving force for surfactant exudation to this interface. In the case of the latex films prepared on mercury, the enhancement of surfactant exudation to the film–substrate interface is attributed to the fact that a liquid will only wet a surface of higher surface energy. Therefore, if the latex is deposited on a liquid Hg substrate, there are two liquids in contact with each other. Initial surfactant enrichment may occur to lower the surface tension at the liquid–liquid interface. As the coalescence progresses, water evaporates, leaving the copolymer film in contact with the mercury, and forming a solid (latex film)–liquid (Hg) interface. Because mercury has a high surface energy, a high interfacial surface tension exists at this interface, providing a sufficient driving force for the surfactant to exudate to this interface.

So far, we were concerned with the critical surface tension of the PTFE, KRS-5, and mercury. However, it should be remembered that upon latex deposition on the substrate, the critical surface tension becomes an interfacial surface tension. The interfacial surface tension can be described as a sum of the critical surface tensions minus the geometric

mean of the dispersion components for each interface.[16] The relationship governing the surface tension changes at the interface is expressed by the following equation:

$$\gamma_{int} = \gamma_{sub} + \gamma_{film} - 2(\gamma_{sub}^{d}\gamma_{film}^{d})^{1/2} \qquad (1)$$

where γ_{int} is the interfacial surface tension and γ_{sub} and γ_{film} are critical surface tensions of the substrate and the film, respectively. Similarly, γ_{sub}^{d} and γ_{film}^{d} describe the dispersion interfacial components of the substrate and film, respectively.

In an effort to establish how the interfacial surface tension may affect surfactant mobility, the interfacial surface tension values were estimated using eq. (1) and taking approximate critical surface tension and dispersion values.[16] Based on these calculations listed in Table I, it is apparent that the surfactant exudation is driven by an initially high

Table I Estimated Interfacial Surface Tensions

	Interfacial Surface Tensions[a] (mN/m)	
	γ_{int} (water)	γ_{int} (film)
Substrate		
Mercury	424	351
PTFE	50	1.25
KRS-5	60	0.5

[a] Calculations are based on eq. (1) and the following values for critical and dispersive elements of the surface tensions were used:

	γ_c (mN/m)	γ^d (mN/m)
Mercury	484	200
PTFE	18.5	19.5
KRS-5	70	78
H_2O	72.8	21.8

interfacial (water–substrate) surface tension difference. For example, due to extremely high interfacial surface tension at the latex–mercury interface (> 350 mN/m), the surfactant is driven to this interface in order to compensate the interfacial surface tension difference. On the other hand, upon coalescence on the KRS-5 substrate, the surfactant may be displayed by the copolymer due to a relatively low interfacial surface tension (< 0.5 mN/m). This is why in the case of SDOSS, this surfactant preferentially exudes to the film–air interface. In spite of the fact that these values are only rough estimations and, hence, may suffer a significant error, it is interesting to note that for the PTFE–water and PTFE–latex the γ_{int} values are similar to that determined for KRS-5, but their magnitude is larger. This is because fluorocarbons are known to exhibit higher interfacial surface tension values, attributed to the disparity in size of the CF_2 groups acting at the interface which are larger than CH_2.

As mentioned earlier, the acid groups of the copolymer latex diffuse to the film–substrate interface when SDOSS and NP surfactants are used in the synthesis of the EA/MAA latex. In an effort to further understand the behavior and function of the —COOH latex groups on surfactant mobility, the carbonyl region of the film–air and film–substrate interface of the SDOSS latex film prepared on Hg will be examined. As illustrated in Figure 7(a), the
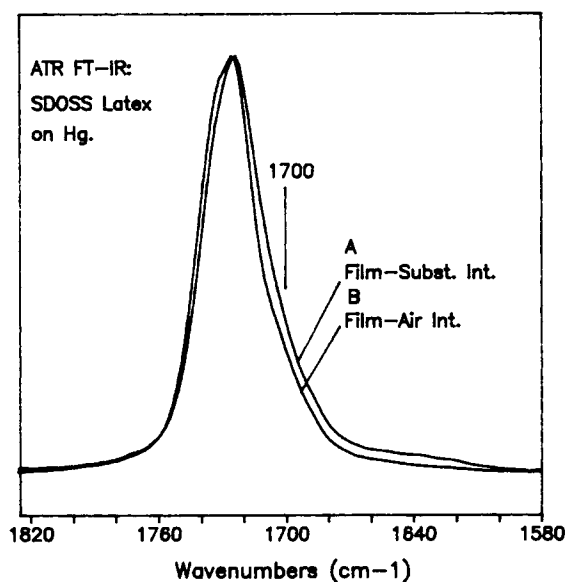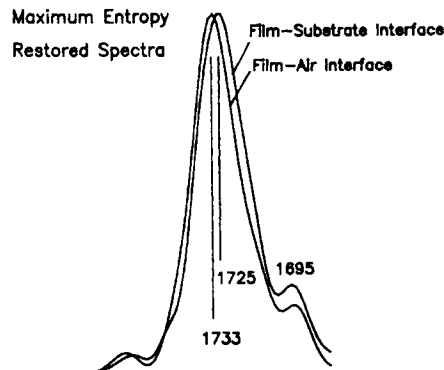

Figure 7(b) Maximum entropy restored spectra in the region from 1820 to 1620 cm⁻¹ for SDOSS latex films prepared on Hg: (A) film–substrate interface; (B) film–air interface.

Figure 7(a) ATR FT-IR spectra in the region from 1820 to 1580 cm⁻¹ of a SDOSS latex film prepared on Hg: (A) film–substrate interface; (B) film–air interface.

band at approximately 1700 cm⁻¹ assigned to the hydrogen-bonded carboxylic acid groups becomes broader at the lower frequency, indicating that, at the film–substrate interface, a greater concentration of the hydrogen bonded carboxylic acid groups is present. This is further exemplified by using a maximum entropy restoration algorithm to resolve the heavily overlaying bands in this region. As shown in Figure 7(b), the band at 1695 cm⁻¹ due to the hydrogen bonded carboxylic acid groups is resolved and its intensity is greater at the film–substrate interface. It is also apparent to note that the carbonyl band at 1725 cm⁻¹ at the film–substrate interface is detected at lower wavenumber than that at 1733 cm⁻¹ for the film–air interface. This observation is not surprising, since a fraction of the interfacial carboxylic acid species may be hydrogen-bonded to the surfactant sulfonate groups. Consequently, the increased intensity of the 1725 cm⁻¹ band is observed and is due to the greater amount of free carbonyl groups of the carboxylic acids.

With these observations, we are in a position to address the issue as to why carboxylic acid groups diffuse to the film–mercury interface of the SDOSS and NP latex films. As stated earlier, mercury will wet a surface of a higher surface energy. Since the copolymer latex has a much lower surface energy, the copolymer may respond by reorientation of the carboxylic acid groups towards the mercury substrate. Such a configuration of acid groups will produce the polymer surface of the highest surface energy due to much greater polarity of the acid groups with respect to the alkyl and ester copolymer groups of the latex. The reorientation effect also provides a rationale for why such behavior is observed for

the NP latex films at the film–substrate interface when the low polarity and exudation behavior of the surfactant are detected. This is the reorientation effect that provides a surface of higher surface energy, more conducive to wetting by the mercury.

In an attempt to elucidate the mobility differences among surfactants used in this study, in addition to the substrate surface tension contributions, structural differences between surfactants should be considered. Although the exudation behavior of the anionic surfactants follows similar trends for the substrates with substantially different surface tension, the nonionic surfactant (NP) exhibits no exudation to either interface. This behavior is most likely attributed to the large size of the molecule decreasing its mobility in the polymer matrix, as well as the ability of the ethylene oxide groups to form hydrogen bonds with carboxylic acid groups of the copolymer.[17] Therefore, the surfactant may anchor in the copolymer matrix.

As indicated before, the SDOSS latex films also show diffusion of acid groups as well as surfactant exudation. The structure of the surfactant, that is, two alkyl tails, may prevent orientation of the surfactant at the interface and lower the efficiency to reduce the interfacial surface tension. Although the same phenomenon may explain the presence of carboxylic acid groups at the film–substrate interface for the films prepared on mercury, additional data is needed in order to make conclusive assessments.

and 11, respectively. The SDOSS latex films illustrated in Figure 8 exhibit the previously discussed[11] characteristic surfactant bands at 1056, 1046, 652, and 581 cm^{-1}. Initially, at 10% elongation (trace A), these bands are weak, indicating only a slight exudation of the surfactant to the surface. However, as the films are further elongated to 30% and 50% (traces B and C, respectively), a significant increase of the intensities is observed. Similar results are detected for the SDBS and SNP2S latex films, illustrated in Figures 9 and 10, respectively, indicating enhanced exudation of surfactants as a result of elongation. The SDS latex films (Fig. 11) also exhibit the same behavior; however, the band at 921 cm^{-1}, attributed to bisulfate ion, appears in the spectrum of the film elongated up to 50%. Interestingly enough, this band is not characteristic of either the surfactant or copolymer. Considering the chemical structure of SDS, it is known that during the emulsion polymerization, SDS may hydrolyze to form dodecanol and sodium bisulfate.[18] Therefore, it is not surprising to find sodium bisulfate present in the latex films. Although a portion of the surfactant may hydrolyze and, in this form, exude to the surface, the analysis of the $C-H$ stretching region shown in Figure 12, further illustrates that it is predominantly the SDS surfactant exuding in the latex films. Since the sodium bisulfate has no alkyl tail, the increase of the 2956, 2919, and 2852 cm^{-1} band intensities with elongation indicates the exudation

Elongation Effect

During the course of this study, the effect of mechanical elongation of the latex films which often occurs during removal of the films from a substrate was noted to influence the surfactant distribution at either the film–air or the film–substrate interfaces. Initial observations indicated inconsistency of the results among the same latex films prepared on PTFE. Since identical procedures and substrates were used in preparing the latex films, the effect of mechanical elongation was responsible for these inconsistencies. In an attempt to address the issue of film elongation on surfactant exudation, the latex film surfaces were washed with $MeOH/H_2O$[12] to remove the surfactant that exuded during the film formation or subsequent removal from the substrate. The films were then elongated (10, 30, and 50%) for 5 min and then allowed to relax. The effect of elongation on the spectra of SDOSS, SDBS, SNP2S, and SDS latex films is presented in Figures 8, 9, 10,

Figure 8   ATR FT-IR spectra in the region from 1135 to 500 cm^{-1} of the SDOSS latex films recorded as a function of % elongation: (A) 10%; (B) 30%; (C) 50%.
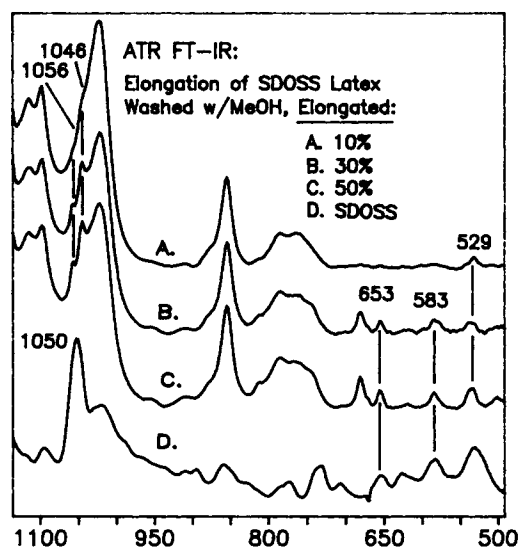
Figure 9 ATR FT-IR spectra in the region from 1135 to 500 cm⁻¹ of the SDBS latex films recorded as a function of % elongation: (A) 10%; (B) 30%; (C) 50%.

Figure 11 ATR FT-IR spectra in the region from 1135 to 500 cm⁻¹ of the SDS latex films recorded as a function of % elongation: (A) 10%; (B) 30%; (C) 50%.
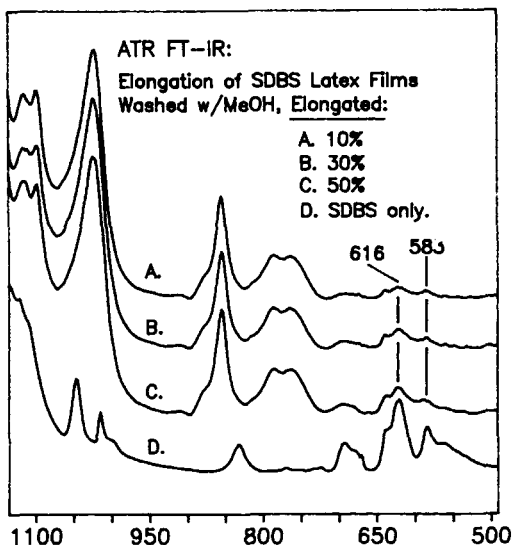
of unhydrolyzed surfactant. In contrast to the ionic surfactants, the nonionic surfactant (NP) latex films do not exhibit any spectral changes as a result of elongation, indicating that the surfactant is not forced out of the film. As was established before,[12] this is attributed to the increased compatibility of the surfactant with the copolymer.
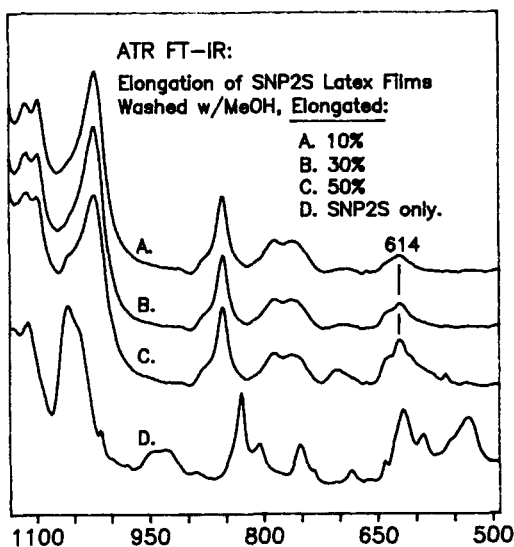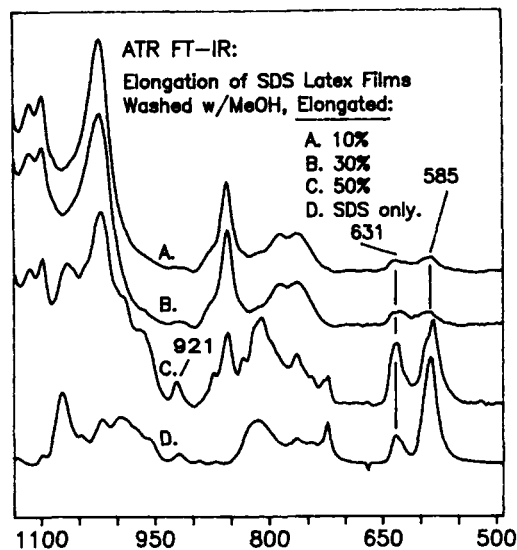
The spectral changes observed as a result of elongation of the anionic surfactant latex films along with the previously reported compatibility studies[12] suggest that the surfactant may be trapped in interstices existing between incompletely coalesced
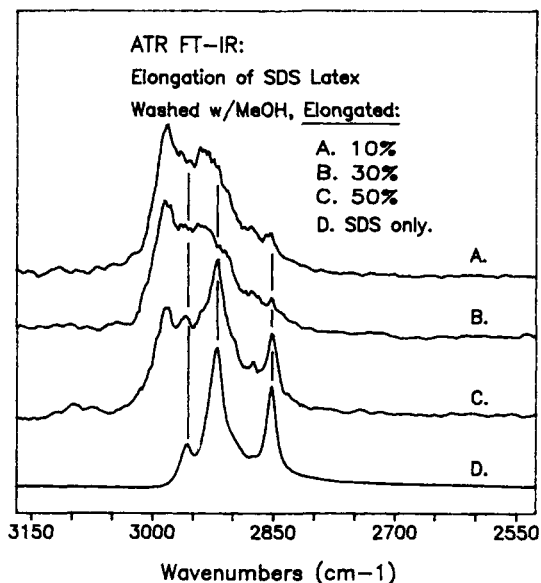

Figure 10 ATR FT-IR spectra in the region from 1135 to 500 cm⁻¹ of the SNP2S latex films recorded as a function of % elongation: (A) 10%; (B) 30%; (C) 50%.

Figure 12 ATR FT-IR spectra in the region from 3150 to 2550 cm⁻¹ of the SDS latex films recorded as a function of % elongation: (A) 10%; (B) 30%; (C) 50%; (D) SDS only.
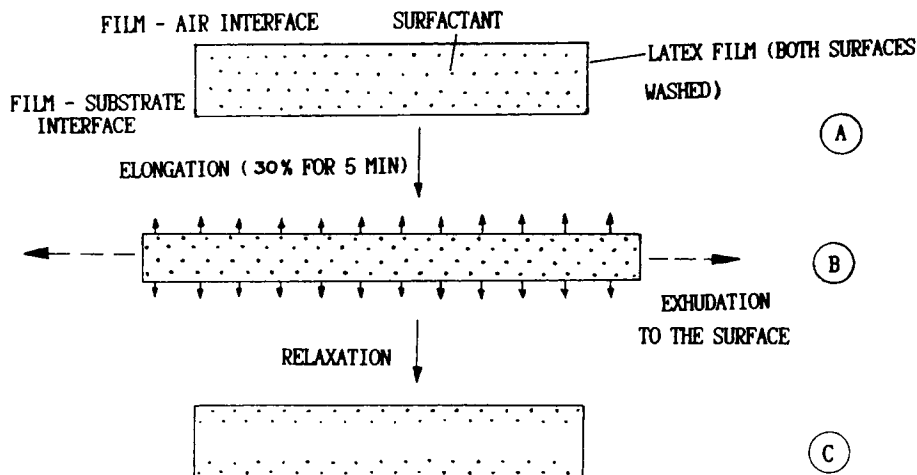
Figure 13 Schematic diagram of the surfactant exudation process in latex films as a result of mechanical elongation.

latex particles. If one visualizes the latex film as a partially nonuniform polymer medium, such as that schematically illustrated in Figure 13, the interstices of incompletely coalesced particles will have excess of surfactant (A). One can draw the analogy between a latex/surfactant system and a sponge saturated with water. The sponge, upon elongation, will expel water present in the capillaries. During the elongation process of a latex film, the surfactant located in the capillary interstices near the film surface (B) will be forced to the surface (C) in a way similar to stretching the sponge saturated with water.

The same phenomenon may be expressed in terms of the surface tension changes resulting from elongation. Since surface tension is the amount of surface energy per unit area, elongation of the latex film increases the total surface area of the latex film, leading to the increased total surface energy of the latex film. As a result, the additional surface energy brought on by elongation increases the surface tension. This increased surface tension is a driving force for the surfactant exudation to the surface in an effort to minimize the increased surface tension.

CONCLUSIONS

The extent of surfactant exudation on glass, PTFE, and mercury varies according to the magnitude of the interfacial surface tension of the substrate. Since the copolymer is able to wet the glass substrate, virtually no surfactant exudation is detected at the film–substrate interface. However, the low surface energy of PTFE induces surfactant enrichment in order to lower the interfacial surface tension that exists between the copolymer and the PTFE. The solid–liquid interface that exists after coalescence of latex films prepared on mercury provides a high interfacial surface tension environment which results in a greater surfactant enrichment at this interface. The anionic surfactants are sensitive to the effect of the substrate surface tension, whereas the nonionic surfactant NP due to its large size and greater compatibility with the copolymer remains in the latex network. Mechanical elongation of latex films induces surfactant exudation to the surface due to the increased surface energy of the film forcing surfactants from interstices to the latex surface.

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