Surface and Interfacial FTIR Spectroscopic Studies of Latexes. X. The Effect of Coalescence on Surfactant Exudation in Polystyrene and Poly(n-butyl acrylate) Latex Films

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SYNOPSIS

In an effort to establish to what extent transient effects prior to coalescence may influence mobility, distribution, and orientation of surfactant molecules after coalescence, poly(n-butyl acrylate) (n-BA) and polystyrene (Sty) were polymerized independently and mixed in a 5 : 1 ratio. It appears that if a mixture of the n-BA and Sty latex particles is allowed to stabilize prior to coalescence, the time of stabilization may have a significant effect not only on the distribution of SDOSS surfactant molecules across the coalesced film, but also on their orientation changes depending upon the stage of coalescence and the water front moving toward the surface. The coalescence of latex films was conducted under gaseous nitrogen and at 60% relative humidity. While the water front moves from the film-substrate upward, during this process, various segments of the surfactant molecule change their orientation. Near the F–A interface, hydrophobic segments are being reoriented from parallel to perpendicular, whereas preferentially parallel orientation exhibit hydrophylic SO_3^- Na^+ segments. When water molecules, however, diffuse out of the film, the surfactant molecules have no preferred orientation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In previous studies, we identified numerous factors that affect the distribution of surfactants in latex films.[1-11] Among several factors that influence surfactant mobility, and therefore their local concentration, the major ones are the distribution of water during coalescence, surface tension of the substrate, and surfactant/latex copolymer compatibility. Although we realize that there are other factors, such as a partial water-vapor pressure above the latex surface during coalescence, surfactant structure, solubility, compatibility with other latex components, and external forces imposed on the latex films,

perhaps of primary significance are the dynamics and transient effects prior to and during coalescence.

In view of the above discussion, let us consider the events prior to coalescence which may affect latex suspension stability. If, e.g., latex particles are allowed to flocculate prior to coalescence, the surfactant molecules may be displaced from the particle surface as a result of two particles coming into contact. In this case, the surfactant molecules may be expelled into the aqueous phase and thus become readily available for migration during coalescence. Although one would argue that during coalescence the particles also come into contact and surfactant molecules can also be expelled, the situation in latex suspension is different because of a significantly higher water content. As a matter of fact, our previous studies[9] showed that there is a significant difference in surfactant behavior when flocculation and

coalescence are compared. Coalescence does not seem to yield the same extent of surfactant exudation that is detected for flocculated suspensions prior to coalescence. The situation becomes even more complex when the latex suspension is composed of particles having different copolymer compositions. An example of such a situation is when poly(n-butyl acrylate) and polystyrene latex particles are mixed together and are allowed to coalesce. In this case, the core–shell situation which would occur if monomers were copolymerized is avoided.

When two monomers are polymerized in two separate batches to form two latex dispersions, and such latex dispersions are mixed together, the individual properties of each latex and their concentrations will determine the film properties after coalescence. For example, if a mixture of latex polymer particles consists of low and high glass transition temperature polymers, the free volume of a coalesced latex along with other properties will be affected by their relative concentrations. For that reason, we prepared a 5 : 1 % w/w mixture of soft poly(butyl acrylate) ($T_g = -54°C$) and hard polystyrene ($T_g = 100°C$) latex particles. Such a choice of particles, and their relative concentration ratio in the latex mixture, will ensure a relatively low glass transition temperature ($T_g = -37°C$), while maintaining desired film properties. Due to hydrophobicity differences of the latex components and their transient effects with respect to the dispersion stability after latex synthesis, the size and the degree of aggregation may not only alter film properties, but may also influence distribution and mobility of low molecular weight surfactants across the film. With this in mind, we will attempt to consider how surfactant–copolymer compatibility, aggregate formation, and surfactant concentration at the F–A and F–S interfaces may be affected by the suspension stability.

EXPERIMENTAL

Latex Preparation

n-Butyl acrylate (n-BA) and Styrene (Sty) monomers were individually copolymerized using a semi-continuous emulsion polymerization process in a glass four-neck breakaway reaction vessel equipped with a mechanical stirrer, addition funnel, thermometer, condenser, and a nitrogen inlet tube. In a typical recipe for the polymerization of the BA/methacrylic acid copolymer, the formulation included double-deionized (DDI) water, 59.1 w/w %; BA, 38.1 w/w % (96.5% based on total monomer

weight); methacrylic acid, 1.35 w/w % (3.5% based on total monomer weight); sodium dioctylsulfosuccinate (SDOSS, Aerosol OT; American Cyanamide), 1.4 w/w % (3.5% based on total monomer weight); and ammonium persulfate (Aldrich Chemical Co.), 0.22 w/w % (0.55% based on total monomer weight). A typical recipe for the polymerization of the Sty/methacrylic acid copolymer, also based upon a total monomer formulation weight, included DDI water, 58.5 w/w %; Sty, 37.6 w/w % (95.8% based on total monomer weight); methacrylic acid, 1.6 w/w % (4.2% based on total monomer weight); SDOSS, 1.7 w/w % (4.3% based on total monomer weight); and ammonium persulfate, 0.26 w/w % (0.65% based on total monomer weight).

Respective monomers were placed in the addition funnel and the reaction vessel was purged with nitrogen for 20 min. Water, SDOSS, and the initiator were added and allowed to stir for 10 min while heating. At 50°C, 30% of the monomer was slowly added while stirring over a 5 min period. The temperature was raised to 70°C for 30 min. A white, milky emulsion was obtained. The remaining monomer was added slowly over a period of 3 h. The temperature was raised to 85°C and held at that level for 3 h, or until no further monomer odor could be detected. Prepared in such a way, latex suspensions had a particle size of 70–75 μm.

Film Preparation

Prepared in a separate synthesis, poly(BA) and polySty homopolymer suspensions were mixed in a 5 : 1 w/w % ratio, stirred, and allowed to store at ambient conditions for 3 to 36 days. Such latex mixtures were deposited on polytetrafluoroethylene (PTFE) to maintain a film thickness between 100 and 150 μm and allowed to coalesce for 72 h under a nitrogen atmosphere or at ambient conditions.

Spectroscopic Analysis

ATR FTIR spectra were recorded on a Digilab FTS-20 equipped with a variable angle rectangular ATR attachment (Spectra Tech). Typically, 200 coadded sample scans were acquired at a resolution of 4 cm^{-1} and then ratioed against the same number of scans of a single-beam spectrum of our empty ATR cell. Polarization of the IR radiation was accomplished using a Specac 12000 IR polarizer that was placed directly in the beam path and adjusted to the desired polarization. All spectra were corrected for optical distortions using recently developed algorithms al-

lowing simultaneous corrections for optical effects of strong and weak bonds.[12,13]

RESULTS AND DISCUSSION

Figure 1 illustrates a series of polarized ATR FTIR spectra recorded from the Sty/n-BA latex colloidal dispersion that was 3 days in storage after individually polymerized n-BA and Sty suspensions were mixed. The film, after depositing it on a substrate, was allowed to coalesce for 3 days under nitrogen. The primary reason for using a water-vapor-free atmosphere above the latex surface was to accelerate water evaporation from the film while monitoring the surfactant content at the F–A and F–S interfaces. Traces A and C show the transverse magnetic (TM) polarized FTIR spectra recorded from the F–A and F–S interfaces, respectively. While the majority of the spectral features are the same at both interfaces, the most pronounced difference is the presence of the bands at 880, 1046, and 1088 cm^{-1} in the F–S interface spectrum. Since these bands are due to normal modes of the SO$_3^-$ groups in SDOSS,[4] these data indicate that there is an excess of surfactant molecules at the F–S interface. The bands at 880, 1046, and 1088 cm^{-1} are attributed to

the CH$_2$ out-of-plane deformation modes (880 cm^{-1}), the S — O stretching modes (1046 cm^{-1}) of the SO$_3^-$ groups of SDOSS, and the symmetric O — C — S stretching of the SDOSS backbone (1088 cm^{-1}). When the polarization of the infrared incident beam is changed to a transverse electric (TE) polarization, the changes become even more pronounced. This is illustrated in traces B and D of Figure 1, which represent the TE-polarized ATR spectra obtained from the F–A and F–S interfaces, respectively. These results indicate that when water molecules are removed fast from the F–A interface the SDOSS surfactant is not capable of migrating at the same rate, and, therefore, it is not detected at the F–A interface. Instead, it is trapped at the F–S interface.

A comparison of the TE and TM spectra also indicates that the band enhancement in the TE-polarized spectrum recorded from the F–S interface is induced by the orientation of the surfactant molecules. In this experiment, the TE wave is defined as having its electric vector parallel to the crystal plane (or perpendicular to the plane of incidence), and the TM wave has its electric vector perpendicular to the crystal plane. Pictorial definitions of the TE and TM polarizations, and the orientation at the electric vector of the incident beam with respect
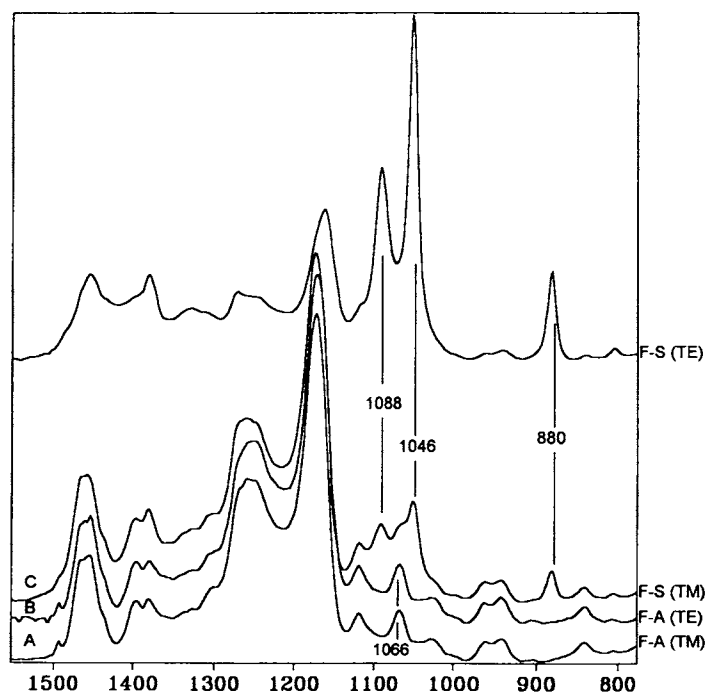

Figure 1   ATR FT–IR spectra of a 5 : 1 n-BA/Sty latex mixture stored for 3 days and coalesced under dry nitrogen: (A) F/A interface; TM Polarization; (B) F/A interface; TE polarization; (C) F/S interface; TM polarization; (D) F/S interface; TE Polarization.
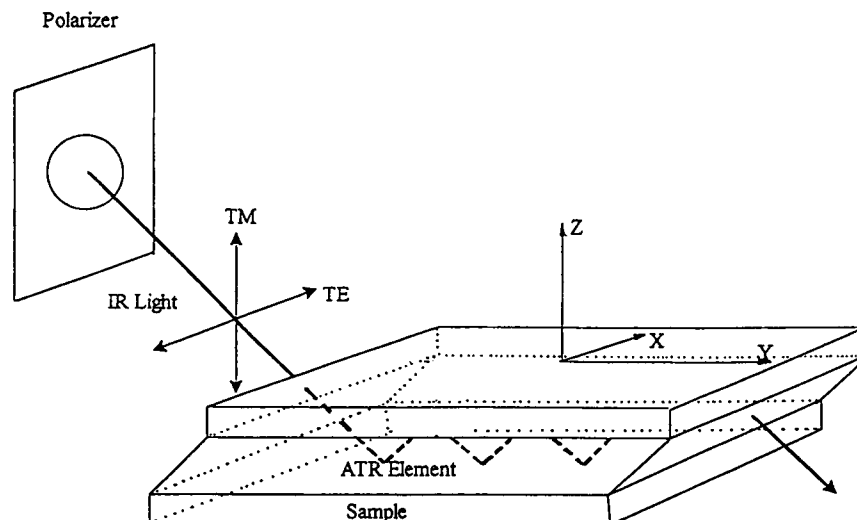
Figure 2 Schematic diagram of an ATR FTIR experimental setup.

to the film surface at the ATR crystal, are shown in Figure 2. Using the above definitions, if a given bond has a specific orientation, changing orientation of the polarized light will result in the intensity changes of those bands that are attributed to the species having specific orientation. In contrast, for randomly distributed species, no intensity changes with the polarization changes are anticipated.

The results of latex coalescence under a gaseous nitrogen atmosphere indicate that the intensity changes observed in Figure 1 are due to the fact that no surfactant molecules are detected at the F–A interface (traces A and B of Fig. 1) and hydrophilic SO_3^- groups as well as acid groups have a preferential surface orientation at the F–S interface. While the first assessment is quite obvious, it appears that the bands at 880, 1046, and 1088 cm^{-1} are significantly enhanced when going from the TM to TE polarization. As we recall from our experimental setup for the TE polarization shown in Figure 2, the enhanced band intensities are anticipated if the species of interest are parallel to the surface. In view of these considerations, after 3 days when both latex suspensions were mixed, the SO_3^- groups along with the acid functionalities form H-bonded entities that are preferentially aligned parallel to the F–S interface. These results agree with our previous findings[8] and are depicted in Figure 3(A). Because there are no detectable intensity changes for other surfactant bands due to hydrophobic groups, it is assumed that the hydrophobic tails are random.

As illustrated in Figure 1, we have been primarily concerned with the changes occurring at the F–S interface, because, essentially, no surfactant exu-

dation was detected at the F–A interface. However, when the latex films are allowed to stabilize as an aqueous colloidal dispersion for 11 days, the changes began to be detected at the F–A interface. Again, the latex films were allowed to coalesce under a dry nitrogen flow. Figure 4, traces A and C, show TM-polarized ATR spectra recorded from the F–A and F–S interfaces for these specimens. The 1046 and 1056 cm^{-1} bands are detected only at the F–A interface for the TM and TE polarizations (traces A and B). In addition to these bands, the TM-polarized spectra exhibit the bands at 1207, 1233, 1261, 1288, 1453, 1465, and 1493 cm^{-1} (trace A).

The results presented in Figure 4 are somewhat surprising. First of all, enhancement of the 880 and 1046 cm^{-1} bands is not detected in the spectra recorded at the F–S interface for both the TM and TE polarizations. The major changes are, in fact, detected at the F–A interface. In addition to the 1046 and 1056 cm^{-1} bands, the bands at 1207, 1233, 1261, and 1288 cm^{-1} are affected by polarization changes. Postponing temporarily the discussion of the intensity changes resulting from the polarization experiments, one needs to establish the origin of the spectral features. First, let us return to the IR spectrum of pure SDOSS and point out the two spectral features attributed to the $SO_3^-Na^+$ groups: symmetric and asymmetric S — O stretching bands are detected at 1050 (sym) and 1216 (asym) cm^{-1}. According to the group theory, the local environment of the $SO_3^-Na^+$ group gives C_{3v} symmetry. Using group theory formalism, one can show that the C_{3v} point group leads to $2A_1$ and $2E$ normal vibrations. The A_1 modes are the symmetric once, giving one
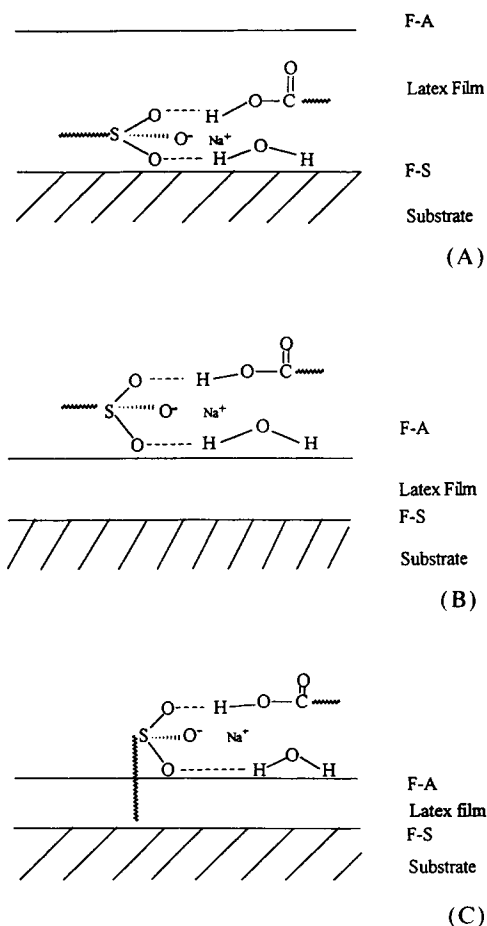
Figure 3 Schematic representation and location of SDOSS in n-BA/Sty latex film: (A) SDOSS is primarily present at the F/S interface; $SO_3^-Na^+$ Na^+ parallel; (B) SDOSS is detected at the F/A interface and takes preferentially parallel orientation; (C) $SO_3^-Na^+$ groups are parallel, whereas hydrophobic tails are perpendicular.

IR and one Raman active band, while the E mode is doubly degenerated asymmetric mode which is also IR active.

With these considerations in mind, the 1050 cm^{-1} band of the pure surfactant is an IR active A_1 mode, whereas the 1216 cm^{-1} band is an asymmetric mode. However, when the surfactant hydrophilic $SO_3^-Na^+$ group is placed in the Sty/n-BA environment, also present in the coalesced film, the $SO_3^-Na^+$ environment changes due to $SO_3^-Na^+$ interactions with various latex components. Our previous studies have shown that these interactions are reflected by a splitting of the 1050 cm^{-1} symmetric S — O stretching mode into two bands at 1046 and 1056 cm^{-1}.[3] The 1056 cm^{-1} band is attributed to the H-bonding associations of $SO_3^-Na^+$ with acid groups, whereas the 1046 cm^{-1} band is due to interactions

with water. These are also the associations that disturb the local $SO_3^-Na^+$ symmetry and result in the splitting of the 1241 and 1216 cm^{-1} asymmetric bands into four bands at 1288, 1261, 1233, and 1207 cm^{-1}. They result from the splitting of the 1216 cm^{-1} band due to S — O mode stretching vibrations to 1207 and 1261 cm^{-1} bands and the splitting of the C — O stretching of the surfactant backbone band at 1241 cm^{-1} to 1233 and 1288 cm^{-1} bands. This is illustrated in Figure 4, traces A and B.

This information, along with the observations of the intensity changes under different polarization conditions, leads us to two conclusions: (1) the surfactant molecules detected at the F–S interface, when a latex suspension is allowed to age for 3 days (Fig. 1), have now shifted to the F–A interface when the latex suspension is in storage for 11 days before coalescence, and (2) hydrophilic SO_3^- groups and the C — O surfactant entities are preferentially parallel near the F–A interface. This is schematically depicted in Figure 3(B).

Having identified structural and orientational features at both interfaces for latex films coalesced under nitrogen, let us focus on the transient effects prior to coalescence for the films coalesced under approximately 60% relative humidity. This approach slows down diffusion of water to the F–A interface. Figure 5 illustrates a series of the TM-polarized ATR FTIR spectra recorded from the F–A interface of the latex films allowed to be in a form of the colloidal dispersion for 3, 6, 12, 15, and 18 days after mixing polySty and poly(n-BA) suspensions (traces A, B, C, D, and E, respectively). It appears that after 15 days the band intensities of 1207, 1233, 1261, and 1288 cm^{-1} began to increase (trace D), which parallels the appearance of the 1046 and 1056 cm^{-1} bands. Interestingly enough, changing polarization from TM and TE generates the intensity changes of the bands at 1261 and 1207 cm^{-1}, which again parallels the appearance of the 1046 and 1056 cm^{-1} bands. This is illustrated in Figure 6. In contrast to the results illustrated in Figure 5, the bands at 1233 and 1288 cm^{-1} in the TM polarization (Fig. 5, trace D) are not detected with the polarization changes.

Considering the band assignments and the intensity changes at the F–A interface illustrated in Figures 5 and 6, the enhancement of the 1288 and 1233 bands in the TM detection indicates that the surfactant backbone now changes its orientation from random to perpendicular to the surface. In contrast, changing polarization to TE (Fig. 6) enhances the 1261 and 1207 cm^{-1} bands due to the SO_3^- hydrophilic groups, indicating again their preferential parallel orientation. These results indicate that
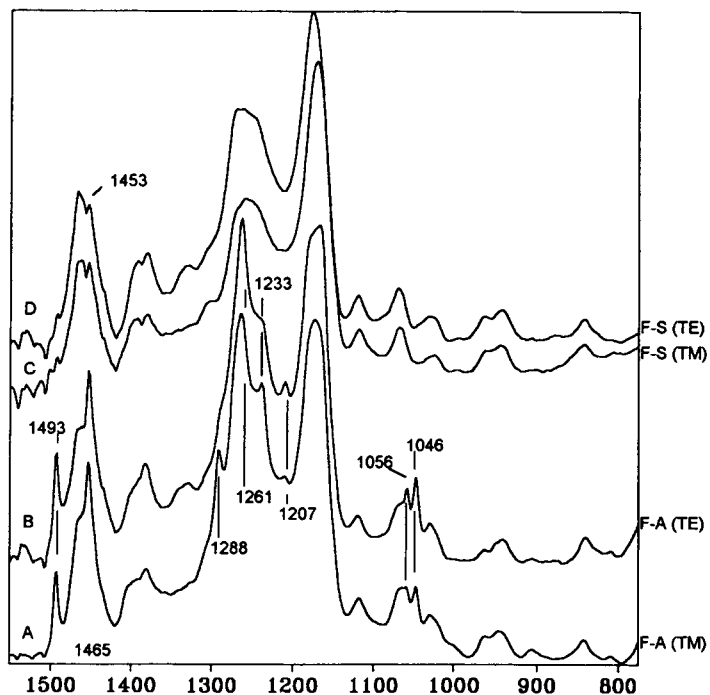
Figure 4   ATR FTIR spectra of 5 : 1 *n*-BA/Sty latex mixture stored for 11 days and coalesced under dry nitrogen: (A) F/A interface, TM polarization; (B) F/A interface, TE polarization; (C) F/S interface, TM polarization; (D) F/S interface, TE polarization.
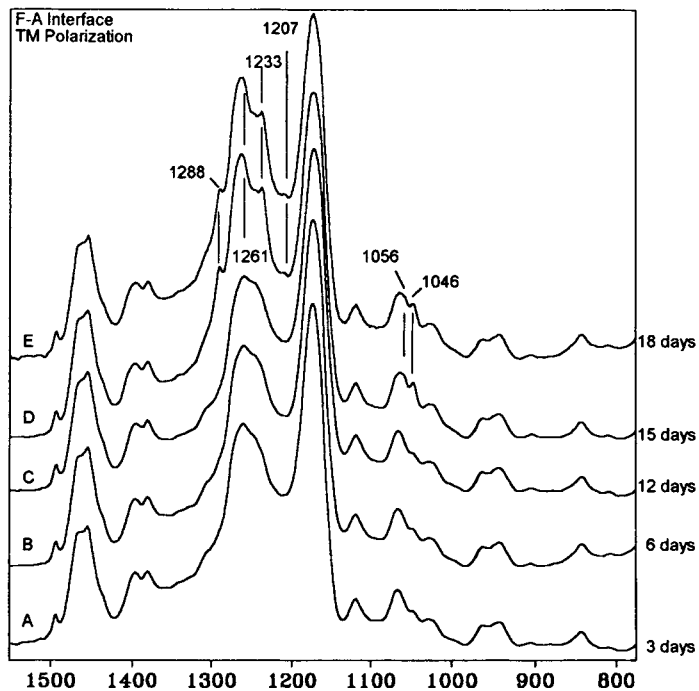

Figure 5   ATR FTIR spectra of 5 : 1 *n*-BA/Sty latex mixture at the F/A interface, TM polarization, coalesced under ambient conditions and stored for (A) 3 days, (B) 6 days, (C) 12 days, (D) 15 days, and (E) 18 days.
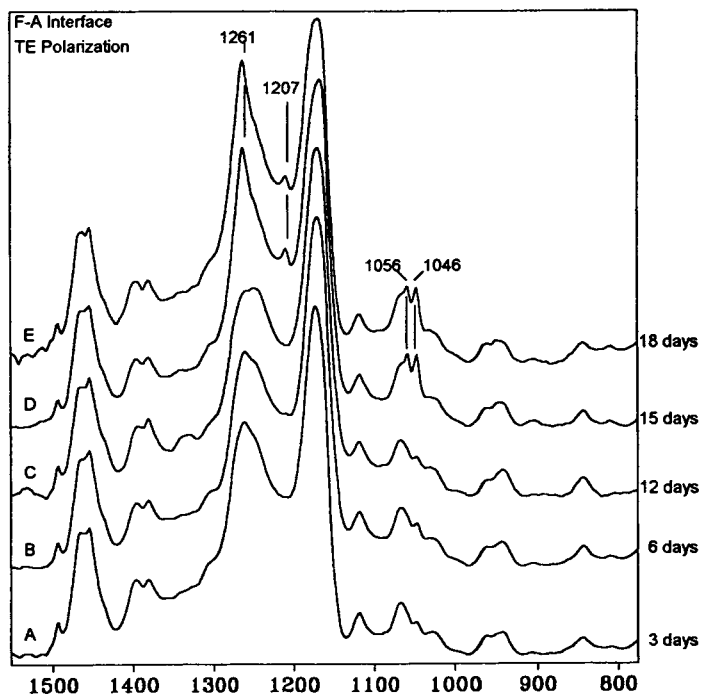
Figure 6 ATR FTIR spectra of 5 : 1 n-BA/Sty latex mixture at the F/A interface, TE polarization, coalesced under ambient conditions and stored for (A) 3 days, (B) 6 days, (C) 12 days, (D) 15 days, and (E) 18 days.
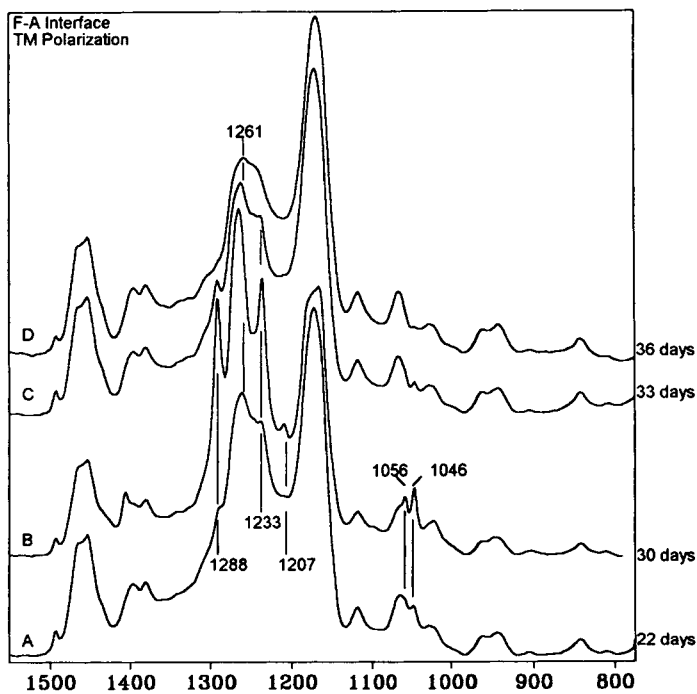

Figure 7 ATR FTIR spectra of 5 : 1 n-BA/Sty latex mixture at the F/A interface, TM polarization, coalesced under ambient conditions and stored for (A) 22 days, (B) 30 days, (C) 33 days, and (D) 36 days.
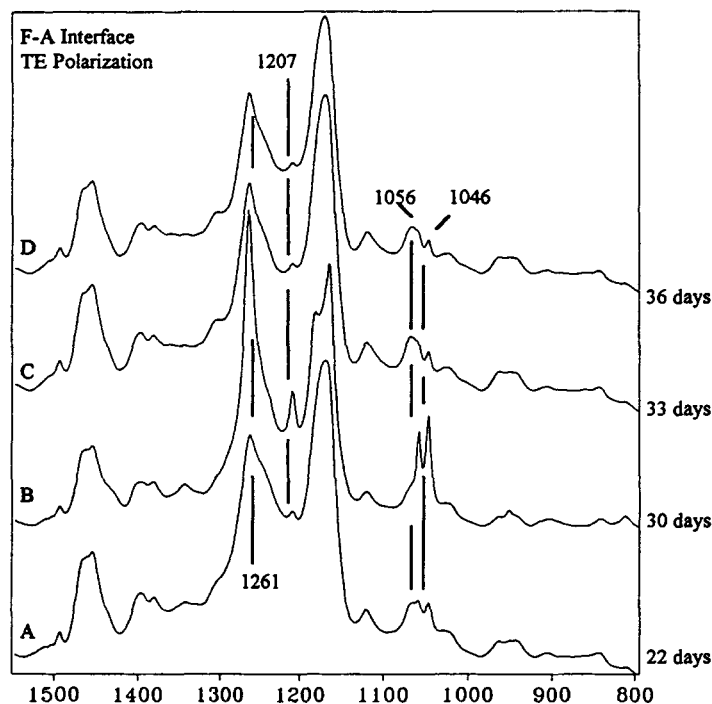
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Figure 8 ATR FTIR spectra of 5 : 1 *n*-BA/Sty latex mixture at the F/A interface, TE polarization, coalesced under ambient conditions and stored for (A) 22 days, (B) 30 days, (C) 33 days, and (D) 36 days.

when water is still present in the system the surfactant molecules take such preferential orientation as that depicted in Figure 3(C). Whereas the $SO_3^-Na^+$ groups interact with the acid groups, a preferred vertical position of the hydrophobic surfactant tail minimizes the "cross section" to allow water molecules to migrate to the surface and diffuse out of the film.

In an effort to further understand the effect of water evaporation on the orientation changes of SDOSS near the F–A interface, the latex mixture was stored from 22 to 36 days. Figure 7 shows the spectral changes detected between 22 and 36 days. It appears that the intensities of the surfactant bands at 1046 and 1056 cm^{-1} continue to increase, which is also accompanied by the increasing intensities of the bands at 1233, and 1288 cm^{-1}. Interestingly enough, the bands reach their maximum intensity after 30 days, and after that time, the bands begin to diminish to a minimum (Fig. 7, traces C and D). The same latex films recorded in the TE mode indicate that the surfactant bands at 1046 and 1056 cm^{-1} along with their asymmetric counterparts at 1207 and 1261 cm^{-1} reach a maximum intensity after 30 days. This is illustrated in Figure 8. After 30 days, however, there is no distinction between TE and TM polarization recorded spectra, suggest-

ing a lack of any orientation feature. The results presented in Figure 7 and 8 indicate that the surfactant molecules maintain the orientation depicted in Figure 3(C) up to 30 days, and after that time, they take on a random orientation.

At this point, let us go back and compare the results for coalescence conditions under nitrogen and 60% relative humidity. The analysis of the F–A and F–S interfaces for latex films coalesced under nitrogen and 60% relative humidity indicate that there are no surfactant molecules at any interface unless there is a sufficient amount of water. Therefore, if we consider coalescence conditions under N_2, it is quite apparent that a low water content near the F–A interface causes surfactant molecules to diffuse to the F–S interface. When a sufficient amount of surfactant is expelled from the latex surface, SDOSS migrates with the water flux to the F–A interface. In view of the above considerations, one could propose a scenario depicted in Figure 9(A), in which the water content decreases first near the F–A interface and moves down closer to the F–S interface. This situation certainly favors surfactant molecules to stay closer to the F–S interface where the water content is high. However, when water evaporates slower, which can be controlled by a relative humidity above the latex surface, the surfac-
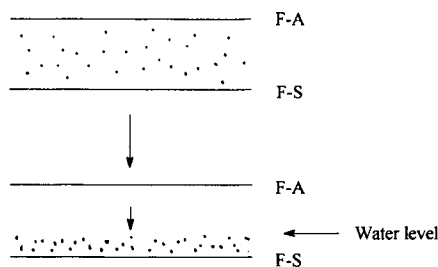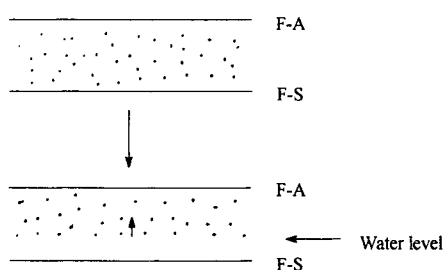
Figure 9.A

Figure 9 Schematic representation of water front changes: (A) latex film coalesced under dry N_2, (B) latex coalesced under 60% relative humidity.

tant molecules, if expelled from the interfacial regions, will follow much slower diffusion of H_2O. Therefore, the water front will move upward to the F–A interface, such as depicted in Figure 9(B). In this case, the SDOSS tails are preferentially oriented perpendicular to the surface in order to accommodate water molecules to reach the surface and eventually to get out of the latex film and evaporate. This is schematically depicted in Figure 3(C). When H_2O is removed from the latex, the SDOSS tails take on a random orientation.

CONCLUSIONS

These studies illustrate that the transient effects prior to coalescence and relative humidity have a

significant effect on the distribution of SDOSS surfactant molecules across the film. The surfactant molecules may change their orientation depending upon coalescence conditions and the latex dispersion stability. It appears that water plays a significant role in the distribution and orientation of surfactant molecules at the latex F–A or F–S interfaces, thus effectively influencing film formation. This study also confirms our previous findings that, if properly used, ATR FT–IR spectroscopy is a powerful tool not only in detecting surfactant distribution at F–A and F–S interfaces, but also in understanding orientation changes during coalescence.

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