Chapter 20

Latex Film Formation at Surfaces and Interfaces

Spectroscopic Attenuated Total Reflectance and Photoacoustic Fourier Transform IR Approaches

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This chapter explores novel spectroscopic approaches that can be utilized in the analysis of film formation near surfaces and interfaces. Emphasis is given to attenuated total reflectance (ATR) and step-scan photoacoustic (SSPAS) Fourier transform infrared (FT-IR) spectroscopy as both techniques can provide meaningful information from various surface depths of organic films as well as are capable of determining molecular level interactions among film components. This chapter attempts to provide a comprehensive description of internal and external factors that may influence coalescence near the film-air (F-A) and film-substrate (F-S) interfaces of latex films.

In the last few years our efforts focused on understanding mobility and distribution of surfactant molecules during and after latex film formation. Although these studies have led to several findings concerning the influence of a latex chemical makeup and coalescence conditions in relation to the behavior of small molecules in polymer networks, it became quite apparent that there are numerous opportunities for learning more about latex film formation. Our particular interest lies in molecular level understanding of processes near the film-air (F-A) and film-substrate (F-S) interfaces, as these zones of latex films have a significant influence on numerous properties. A particular emphasis will be given to a chemical makeup of latex particles, their size and size distribution, and the presence and behavior of low molecular weight species during coalescence. In a context of the film formation, we will focus on the recent developments in attenuated total reflectance (ATR) and step-scan photoacoustic (SS-PAS) spectroscopies, as utilized to the interfacial and surface studies of latex films. In view of the above considerations, let us first establish the principles governing these measurements.

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ATR FT-IR Spectroscopy

When light passes through two media with different refractive indices, and the media are in contact with each other, the path of the light is distorted. This is schematically illustrated in Figure 1. The majority of light is transmitted at a 90° angle of incidence (θ), and the light is partially reflected at θ < θc. A total reflection will occur at θ > θc. When the angle of incidence θ is greater than θc, and n1 > n2, the light is totally reflected. The critical angle is defined by θc = sin⁻¹n2/n1, and n1 and n2 are the refractive indices of a crystal and a sample, respectively. This is the basis for internal reflection spectroscopy (IRS).

![Schematic diagram of the refractive index changes on the light path as a function of incidence angle.](image)

Figure 1. Schematic diagram of the refractive index changes on the light path as a function of incidence angle.

IRS can be used to measure the optical spectrum of a sample that is in contact with an optically denser and transparent medium. Since there is only one reflection during the measurement, sensitivity is limited. Therefore, this technique was modified by increasing the number of reflections, giving rise to attenuated total reflection spectroscopy (ATR). Experimental setups of the internal reflection technique for single reflection and multi-reflection methods is shown in Figure 2, B and C. For comparison, Figure 2 also shows transmission (A), reflection-absorption (D), diffuse reflectance (E) and photoacoustic (F) setups.

One of the advantages of ATR is that it is possible to conduct depth penetration experiments. The penetration depth, d_p, is expressed by the following equation:
\[ d_p = \frac{\lambda}{2\pi (\sin^2 \theta - n_2^2)^{1/2}} \]

where: \( d_p \) (cm) is the depth penetration into the surface; \( n_1 \) and \( n_2 \) are the refractive index values of an ATR crystal and a sample, respectively; \( \theta \) (degree) is the angle of incidence, and \( \lambda \) (cm\(^{-1}\)) is the wavelength of electromagnetic radiation in medium \( n_1 \).

Figure 2. Schematic diagram of IR techniques: A - transmission; B - single reflection IRS (internal reflection spectroscopy); C - attenuated total reflection (ATR); D - reflection-absorption; E - diffuse reflectance setup; F - photoacoustic setup.

As shown by eqn. 1, one disadvantage for ATR FT-IR spectroscopy is that the depth of penetration is wavelength dependent. In an effort to eliminate this effect, a new algorithm was developed.\(^{14}\) Furthermore, because eqn. 1 was derived with an assumption that the examined specimens are homogeneous, any composition/concentration variations preclude the use of this useful relationship for quantitative purposes. In an effort to utilize this relationship, especially if one is interested in depth profiling experiments, the approach schematically illustrated in Figure 3 was developed.\(^{14}\) The surface is divided into \( n \) layers with each layer thickness, \( h_j \). At the each boundary layer, \( L_j \), the response of the sample to local evanescent waves is characterized by a complex refractive index defined by \( \tilde{n}_j = n_j - ik_j \), and \( n_j \) is refractive index and \( k_j \) is the absorption index. By applying
developed algorithm to each layer,¹⁴ which is assumed to be homogeneous, eqn. 1 can be utilized. However, the layers among themselves are not homogeneous, and by stacking all layers together, the surface is reconstructed by a step-wise treatment of volumes occupied by each layer. This approach allows quite accurate quantitative analysis of surfaces and its precision is determined by the number of spectra collected at various depths. Based on this principle, quantitative analysis of surfactant concentration near the F-A and F-S interfaces may be examined.

![Figure 3. A schematic diagram of numerically slicing a nonhomogeneous surface to form a stack of parallel thin homogeneous layers.](image)

Furthermore, by incorporating polarized IR light in an ATR experiment, it is possible to determine orientation of the surface species. The diagram of polarized ATR FT-IR experimental setup is schematically illustrated in Figure 4, and transverse electric (TE) and transverse magnetic (TM) are parallel and perpendicular polarized components of electromagnetic radiation.

![Figure 4. A schematic diagram of the polarized ATR FT-IR elements.](image)
Photoacoustic (PA) Fourier Transform Spectroscopy

Photoacoustic spectroscopy is based on the detection of an acoustic signal emitted from a sample due to absorption of modulated radiation. This is schematically illustrated in Figure 5, A. The sample is placed in an acoustically isolated chamber to which a sensitive microphone is attached. On absorption of modulated light, heat is generated within the sample. Its release leads to temperature fluctuations at the sample surface. These temperature fluctuations at the sample surface cause pressure changes in a surrounding gas, which, in turn, generate acoustic waves in the sample chamber. The pressure changes of the gas are detected by a sensitive microphone, and the obtained electrical signal is Fourier-transformed. In the PAS experiment, the absorbed energy is released in a form of heat that is transferred to the sample surface, and the efficiency of the heat transfer is determined by the thermal diffusion coefficient of the sample, $\alpha$, (cm), and the modulation frequency of the incident radiation, $\omega$:  

$$\alpha = \left( \frac{\omega}{2\alpha} \right)^{1/2}$$  

(4)

where: $\alpha$ (cm$^2$/s) is the thermal diffusivity, $\omega$ (s$^{-1}$) is the angular modulation frequency, and equal to $4\pi\nu\omega$ (cm/s) and $\nu$ (cm$^{-1}$), are velocity of mirror and wavenumbers, respectively. The thermal diffusion length $\mu_a$ (cm) is related to the thermal diffusion coefficient $\alpha$, through

$$\mu_a = \frac{1}{\alpha} = \left( \frac{2\alpha}{\omega} \right)^{1/2}$$  

(5)

Based on this relationship, the thermal diffusion length is inversely proportional to the modulation frequency. Therefore, by changing $\omega$, one changes $\mu_a$, which in effect result in changing the depth from which the acoustic signal is generated. Thus, the capability of surface depth profiling is one of the most appealing features of PA FT-IR. Urban et al.$^{14,17}$ have demonstrated several applications of PAS regarding surface depth profiling. However, the major drawback of this approach is that the thermal diffuse length $\mu_a$ also depends on wavenumber. As a result, low wavenumber regions result in deeper penetration depths, and at high wavenumbers, the spectral information comes from shallower depths. In an effort to eliminate the wavenumber dependence, and obtain the penetration depth wavenumber independent spectra, step-scan photoacoustic FT-IR spectroscopy can be employed.$^{18}$

In a step-scan interferometry, a mirror of a Fourier transform interferometer is moved incrementally, and the spectra are acquired while the retardation is constant. As a result, the Fourier frequency dependence is eliminated and the photoacoustic sampling depth is constant across the spectrum. Furthermore, using a two-phase lock-in amplifier, in-phase (I) and in-quadrature (Q) components of the signal can be simultaneously acquired, and used to obtain the signal phase. A schematic diagram of a PAS cell is illustrated in Figure 5, A, and a detection of (I) and (Q) spectra are presented in Figure 5, B. While amplitude modulation of the PA signal is accomplished by a chopper to generate PA signal, in the phase modulation the
retardation is sinusoidally varied by dithering the mirror at a fixed frequency. The disadvantage for amplitude modulation is that it produces a signal containing a large DC component, placing phase modulation in advantage over the amplitude modulation. The reason behind is that the use of PM rather than AM for a signal generation increases the step-scan signal-to-noise ratio (SNR) by a factor of 2. Secondly, the amplitude of the PM can be used to select the wavelength region most efficiently modulated. Thus, the step-scan mode, particularly in conjunction with PM, provides a constant frequency modulation for all wavelengths.

In this chapter, Fourier transform infrared spectroscopy, especially ATR and step-scan photoacoustic FT-IR will be employed to the analysis of latex film formation at the film-air and film-substrate interfaces. The distribution of surfactant molecules at the interfaces will be followed during the film formation and the structural features, such as orientation of surfactant molecules near the film-air and film-substrate interfaces will be examined. Our particular interest is understanding of molecular level interactions resulting from coalescence conditions, chemical makeup of latex particles, surfactant/copolymer interactions, and their effect on macroscopic film properties.

Figure 5. A - Schematic diagram of step-scan photoacoustic cell; B - Schematic diagram of two components of in-phase (I) and in-quadrature (Q) in step-scan phase analysis.
Homopolymer Latex Blends

Let us examine a series of ATR FT-IR spectra obtained from the F-A interface of a 50/50 mixture of polystyrene (p-Sty) and poly(n-butyl acrylate) (p-BA) latex homopolymers. Figure 6, Traces A through E, illustrate the spectra recorded from the same specimen using TM polarized light, obtained at the angles of incidence between 60 and 40°. Such choice of the incidence angles was dictated by the fact that such a range allows us to vary the depth of penetration of light into the film from 1.3 to 2.3 μm. Therefore, molecular level information from different depths can be obtained.

![Figure 6. ATR FT-IR spectra in the 950-1150 cm\(^{-1}\) region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under ambient conditions, at various angles of incidence: A - 1.3 μm, B - 1.4 μm, C - 1.6 μm, D - 1.9 μm, E - 2.3 μm.](image)

Analysis of the spectra shown in Figure 6 shows that, while going from 1.3 to 2.3 μm depths into the F-A interface, the intensity of the S-O stretching bands, resulting from the presence of the SO\(_2\)Na\(^+\) entities associated with H\(_2\)O and acid groups at 1046 and 1056 cm\(^{-1}\) decreases with depth. At 1.6 μm (Trace C), the 1056 cm\(^{-1}\) band is not detected, and the 1046 cm\(^{-1}\) band continues to decrease at a greater depth (Traces D, E). At the same time, the intensity of the 700 cm\(^{-1}\) band changes in such a way that the band reaches its maximum around 1.6 μm from the top surface layer (Figure 7, Trace C). What is even more interesting is that, for the spectra recorded using TE polarization (Figure 7, Traces A-E), the strongest intensity of the
700 cm$^{-1}$ band is also detected around 1.5 μm, and the band is more pronounced in the TE polarization.

![Graph showing ATR FT-IR spectra](image)

Figure 7. ATR FT-IR spectra in the 650-750 cm$^{-1}$ region, recorded at the F-A interface (TM polarization) of a 50/50 p-Sty/p-BA latex film coalesced under ambient conditions, at various angles of incidence: (A) 1.3 μm, (B) 1.4 μm, (C) 1.6 μm, (D) 1.9 μm, (E) 2.3 μm.

Considering the fact that the 700 cm$^{-1}$ band is due to the aromatic out-of-plane C-H normal deformation modes in p-Sty, these experiments indicate that styrene rings as a well as the SO$_3$Na$^+$ hydrophilic groups exhibit preferential orientation near the surface. Whereas the SO$_3$Na$^+$ groups are parallel near the surface, styrene rings of the p-Sty phase appear to be also parallel, at the depths around 1.6 μm from the surface. This is schematically shown in Figure 8, A.

![Schematic diagrams](image)

Figure 8. Stratification of p-Sty and orientation changes of surfactant molecules near the F-A and F-S interfaces: A - 40 % humidity; B - 100 % humidity.
In view of the above observations, and considering our previous data pertaining to the behavior of the $\text{SO}_3\text{Na}^+$ groups of SDOSS, one of the puzzling issues is the intensity changes of the 700 cm$^{-1}$ band. Since this band can serve as a probe for p-Sty behavior, let us examine if there are changes in the p-Sty content as a function of the coalescence time at various surface depths. For that reason, we followed the intensity changes of the 700 cm$^{-1}$ band over a period of time at various angles of incidence. Figure 9 illustrates Sty intensity changes as a function of depth from the surface from 24 to 72 hours. After 24 hours, the p-Sty intensity increases at greater depths. After 40 hours, at the shallower depths, ranging from 1.3 to 1.6 $\mu$m, the 700 cm$^{-1}$ band further increases. The 700 cm$^{-1}$ band reaches its maximum at 1.6 $\mu$m from the F-A interface after 56 hours, and at depths beyond 1.6 $\mu$m continues to decrease with the increasing penetration depths. The same trend is found in the F-A interface spectra recorded 72 hours after coalescence. However, when the penetration depth reaches approximately 2 $\mu$m (corresponding to 43° angle of incidence), the band intensities converge for both polarizations. Although from the latex film formation point of view, it is apparent that there are changes in the latex composition across the film, at this point, one should realize that the effect of critical angle needs to be addressed. The question arises if the presented results are not affected by the optical distortions resulting from a proximity of the critical angle. For that reason we measured the refractive index of the latex films in the non-absorbing region. It appears that the refractive index is 1.53 ± 0.01. This value of refractive index gives a critical angle of 40°, and solving over the spectral range of interest, gives critical angles between 39.6° and 40.5°. Thus, the data convergence at 43° is not affected by the proximity of the critical angle, and results from coalescence. In contrast, the 700 cm$^{-1}$ band showed no
intensity changes at the F-S interface for either the TM or TE polarizations, indicating that stratification of p-Sty occurs only near the F-A interface.

Although based on the presented data it is quite apparent that there is a preferential phase separation near the F-A interface, let us utilize dynamic mechanical thermal analysis (DMTA) and examine the tan δ values as a function of temperature, as their maximum represent a glass transition temperature (Tg) of a polymer. Analysis of the DMTA tan δ curves for the 50/50 p-Sty/p-BA latex mixture showed the presence of two Tg’s at -52°C and at 98°C, indicating the presence of two separate phases within the latex film. While the Tg of -52°C is due to the p-BA latex component in a mixture, the 98°C Tg is that of p-Sty. These observations indicate that, at this stage of coalescence, the two latex homopolymers in the mixture do not coalesce into a uniform network, and although DMTA data indicates that the separation occurs, these, and for that matter any other measurements, are unable to distinguish which portion of the film is phase separated. In contrast, ATR FT-IR surface depth profiling experiments near the F-A interfaces clearly demonstrate non-homogeneity in the direction perpendicular to the film plane. Thus, the presence of two separate Tg’s results from stratification near the F-A interface. It should be noted that there were numerous studies dealing with the phase separation in polymers and polymer blends, to our best knowledge, this is the first approach actually showing where, in respect to the rest of the film, the phase separation occurs.

The above data demonstrate that the 50/50 p-BA/p-Sty latex film is a non-uniform composite of soft and hard particles near the F-A interface, and hydrophobic and hydrophilic particles of the composite latex will facilitate different interactions of the individual components. Therefore, the ability of water uptake can be used as a means of altering these interactions. A comparison of the results for the latex exposed to 100% RH (not shown), with the data shown in Figure 9 (40% RH) indicated that, upon exposure to humidity, the bands of 1046 and 1056 cm⁻¹, characteristic of SDOSS, are not detected. Furthermore, the band due to p-Sty at 700 cm⁻¹ is significantly weaker, and reaches its maximum intensity at approximately 2.3 μm from the F-A interface. As we recall, a maximum intensity at 40% RH was detected near 1.6 μm for the F-A interface.

Based on these experiments, it is obvious that when the latex films are exposed to 100% humidity, water uptake occurs. Furthermore, since surfactant molecules are water soluble, their removal from the surface is attributed to the fact that water penetrates the network, thus allowing SDOSS molecules to diffuse into it. This process is facilitated by an excess of the free volume at the temperature of experiment (27°C), as the Tg of the p-BA phase is -52°C, as oppose to the p-Sty phase which exhibits the Tg of 98°C. Thus, p-BA has substantially accessive amount of the free volume and represents a good medium for water uptake and subsequent diffusion of SDOSS molecules. While this behavior of SDOSS under given conditions is anticipated, the diminished intensity of the 700 cm⁻¹ band due to the p-Sty phase is somewhat surprising. However, when water diffuses into the film, the top p-BA surface layer can be plasticized by water, which results in swelling it. Thus, the effective thickness of the p-BA layer increases due to water intake, and this phenomenon is believed to be responsible for the hydrophobic p-Sty phase being detected at greater depths. While Figure 8-A schematically depicts a stratification of
the p-Sty phase near the F-A interface, Figure 8, B illustrates the case of the top p-BA layer being swelled by H2O. When such a latex film is exposed to 100% RH, the top layer becomes thicker. This is shown in Figure 8, B.

At this point it is appropriate to mention that, in contrast to our previous studies on 50/50 p-Sty/p-BA copolymer,\textsuperscript{12} not a mixture of homopolymers, there was no stratification of polystyrene near the F-A interface. Furthermore, there were no intensity changes of the 700 cm\textsuperscript{-1} band for the TM and TE polarizations, and no intensity differences between various penetration depths. As one would anticipate, the DMTA data showed the presence of a single \textit{T}\textsubscript{g} at 16°C. Thus, the results on the p-Sty/p-BA copolymer indicated no phase separation, which was also accompanied by no preferential orientation of the polystyrene rings near the surface. In addition, only the 1046 cm\textsuperscript{-1} band characteristic of the SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+}-H\textsubscript{2}O interactions near the F-A interface was detected. However, the 1056 cm\textsuperscript{-1} band was not present,\textsuperscript{12} indicating that the SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+}-HOOC latex interactions are not detected. Thus, there are significant differences in the latex surface and interfacial properties, depending upon the original latex makeup. When latex particles are made up of a copolymer, the latex particles are able to coalesce, thus giving a single phase latex film. In a latex film composed of homopolymers, the hard p-Sty and soft p-BA particles display a phase separation, but the separation occurs near the F-A interface, and stratification of the p-Sty layers are detected. The phase separation between the homopolymers during the film formation also influences the mobility and orientation changes of SDOSS within the latex film.

**Latex Particle Composition**

In an effort to determine how the monomer composition of the latex films influences the surfactant concentration and its orientation throughout the film, the following latex copolymers were prepared: 50% Sty/50% n-BA, 30% Sty/70% n-BA, and 10% Sty/90% n-BA. Traces A, B, C, D, and E of Figure 10a illustrate ATR FT-IR spectra of the 50% Sty/50% n-BA latex copolymer. The spectra were recorded using parallel (TE) polarization. For reference purposes, the spectrum of neat SDOSS surfactant is shown in trace F. The presence of the 1046 cm\textsuperscript{-1} and 1056 cm\textsuperscript{-1} bands indicates that there is a significant amount of water and hydrogen-bonded acid groups associated with the SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+} surfactant groups near this interface.\textsuperscript{4} Based on the analysis of the spectra shown in Figure 10a, it appears that there is a decrease in the surfactant concentration of the SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+} groups associated with water and acid entities when going from approximately 1.35 to 2.30 μm. This is demonstrated by the decrease of the 1046 cm\textsuperscript{-1} and 1056 cm\textsuperscript{-1} band intensities. However, when the perpendicular (TM) polarization spectra are examined, the situation changes. Instead of the 1046 cm\textsuperscript{-1} and 1056 cm\textsuperscript{-1} bands, the 1050 cm\textsuperscript{-1} S-O stretching band is detected for the penetration depths ranging from 1.35 to 1.48 μm. This is illustrated by traces E and D, Figure 10b. As the penetration depth increases, the 1046 cm\textsuperscript{-1} and 1056 cm\textsuperscript{-1} bands become more pronounced (traces C, B, and A, Figure 10b).

The data presented in Figures 10a and 10b indicate that the SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+} hydrophilic groups of SDOSS are present in three forms: non-associated (1050 cm\textsuperscript{-1}),
Figure 10a. Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/n-BA latex cast on PTFE: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.

Figure 10b. Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/n-BA latex cast on PTFE: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.
associated with H$_2$O (1046 cm$^{-1}$), and associated with COOH groups (1056 cm$^{-1}$). Furthermore, while non-associated SO$_3$Na$^+$ groups are perpendicular at shallow depths from the surface, the SO$_3$Na$^+$ associations with H$_2$O and COOH groups are preferentially parallel. Going deeper into the F-A interface, the SO$_3$Na$^+$ are preferentially parallel, and no free SO$_3$Na$^+$ groups are detected. Although at this point it is too early to assess the origin of the free SDOSS near the surface, the presence of the hydrophobic styrene groups near the F-A interface may repel water, acid groups or other hydrophilic entities, therefore leaving surfactant groups in a non-associated form.

With these data in mind let us examine the same latex films at the F-S interface. For the 50% Sty/50% n-BA latex films cast on PTFE, SDOSS is present at significantly lower concentration levels than that detected at the F-A interface. As shown in Figures 11a and 11b, for both parallel (TE) and perpendicular (TM) polarizations, respectively, the 1050 cm$^{-1}$ band is detected at the penetration depths ranging from 1.35 to 1.48 µm. Furthermore, the band shifts to 1046 cm$^{-1}$, when penetration depth approaches 1.65 µm. Thus, based on this analysis, it is apparent that not only the concentration of SDOSS is much smaller near the F-S interface, but its environment also changes. This behavior is attributed to the fact that the PTFE surface is hydrophobic, and repels water molecules present near the F-S interface. Therefore, only small fractions of SDOSS are detected as not associated with water molecules. However, when the distance from the PTFE substrate increases, the hydrophobic effect of the PTFE substrate diminishes, making it easier for the surfactant molecules to become associated with water.

Let us now consider the effect of substrate surface tension on the distribution and/or orientation of SDOSS across the 50%/50% Copolymer Sty/n-BA latex films. For that reason latex films were deposited on a liquid Hg, which exhibits a surface tension significantly higher than that of PTFE (approximately 420 mN/m). Figure 12a illustrates ATR FT-IR spectra recorded from the F-A interface using parallel (TE) polarization. It appears that the 1046 cm$^{-1}$ and 1056 cm$^{-1}$ bands are strong, indicating that a high concentration of SDOSS hydrophilic surfactant groups is present at this interface. Furthermore, SO$_3$Na$^+$ surfactant groups associated with water and acid groups are preferentially parallel to the surface and, as observed in Figure 12a, decrease, while penetrating deeper into the film (traces E through A). When, however, TM polarization is employed, the situation changes again. Figure 12b depicts a series of the ATR FT-IR spectra recorded from the F-A interface using perpendicular (TM) polarization. As shown in Figure 12b (traces E through A), an increase of the 1046 cm$^{-1}$ and 1056 cm$^{-1}$ bands is observed up to 1.65 µm into the surface. However, 1.89 µm below the surface, the 1046 cm$^{-1}$ band dominates this spectral region. These data indicate that these are not only orientation changes of the SO$_3$Na$^+$ groups, but there are significantly different environments at various depths. Furthermore, a comparison of traces A and E in Figures 10b and 12b also indicates that there is a significant effect of the substrate on the distribution and environment of the SO$_3$Na$^+$ groups. For example, at approximately 1.35 µm depth (trace E in Figure 10b) near the F-A interface, the SDOSS in a non-associated form is present when PTFE is used as a substrate. However, on a liquid Hg, the SDOSS is detected, but its concentration levels are significantly smaller and moreover, the SO$_3$Na$^+$ environment contains water and acid groups (Figure 12b).
Figure 11a Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/n-BA latex cast on PTFE: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.

Figure 11b Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/n-BA latex cast on PTFE: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.
Figure 12a  Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/BA latex cast on Hg: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.

Figure 12b  Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-A interface of the 50/50 Sty/BA latex cast on Hg: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.
When liquid latex is cast on a solid PTFE substrate, the surface tension differential between the liquid latex and the solid substrate influences the migration and orientation of SO$_3$Na$^+$ hydrophilic surfactant groups at both F-A and F-S interfaces. This surface tension differential is present during coalescence, but it diminishes as the latex becomes a solid film on a solid PTFE surface. The situation is different for the latex cast on a liquid Hg surface: the liquid latex film is deposited on a liquid substrate, therefore creating a surface tension differential as coalescence occurs, and after the solid latex film is formed. For the latex cast on Hg surface, the surface tension differential is present during coalescence, and it increases as the latex becomes a solid film cast on a liquid Hg surface. The surface tension differential effect is illustrated in Figures 10b and 12b for the F-A interface and Figures 11b and 12b for the F-S interface of the 50/50 Sty/n-BA latex films. As seen, the 1046 cm$^{-1}$ and 1056 cm$^{-1}$ bands increase substantially while going deeper into the interfaces for the latex films cast on liquid Hg. This observation indicates that the SO$_3$Na$^+$ surfactant groups are greatly influenced by the surface tension differential between the solid latex film and the liquid Hg substrate.

Figure 13a, traces E through A, illustrate ATR FT-IR data recorded from the F-S interface of the 50% Sty/50% n-BA latex films cast on Hg. The spectra were recorded using parallel (TE) polarization. Although traces of surfactant are present at the F-S interface, in essence, the surfactant present is mostly associated with water. The situation changes, however, when the F-S interface is examined using perpendicular (TM) polarization. Figure 13b illustrates that the intensity of the 1046 cm$^{-1}$ band increases dramatically when penetrating deeper into the latex film (trace A). Again, the 1056 cm$^{-1}$ band is not detected at this interface, indicating that, at this depth, the acid groups are not present. The presence of the 1046 cm$^{-1}$ band results from the presence of residual water molecules trapped between the latex film and the substrate.

A comparison of the data for a 50% Sty/50% n-BA latex films cast on PTFE (Figures 10b and 11b) and on liquid Hg (Figures 12b and 13b) indicates that the surface tension of the substrate greatly influences the migration and orientation of the SDOSS surfactant in a latex film. Although this observation may not be very surprising, the effect is so pronounced that it requires further considerations. When the latex film is deposited on a liquid Hg, the concentration of the SO$_3$Na$^+$ groups associated with water near the F-S interface increases. In addition, the spectra recorded from the F-S interface using perpendicular (TM) polarization show a significant intensity increase of the 1046 cm$^{-1}$ band while penetrating deeper into the tension of Hg causes the surfactant migration toward the F-S interface, and the hydrophilic SO$_3$Na$^+$ surfactant groups are preferentially perpendicular to the surface. This behavior results from the fact that SDOSS lowers the surface tension of the latex, and the latex film, after being deposited on Hg with a high surface tension, film for the film cast on Hg. These observations suggest that the higher surface attracts the surfactant to the F-S interface, in an attempt to lower the surface tension difference between Hg and the latex copolymer. Liquid Hg has also an effect on the F-A interface, as shown by a comparison of the spectra shown in Figures 10b and 12b. The 1050 cm$^{-1}$ band due to non-associated SO$_3$Na$^+$ surfactant groups is not detected when the latex films cast on Hg substrate. Furthermore, the concentration of
Figure 13a Parallel (TE) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/n-BA latex cast on Hg: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.

Figure 13b Perpendicular (TM) polarized ATR FT-IR spectra, recorded at various depths of penetration from the F-S interface of the 50/50 Sty/n-BA latex cast on Hg: (trace A) 2.30 μm, (trace B) 1.89 μm, (trace C) 1.65 μm, (trace D) 1.48 μm, (trace E) 1.35 μm, and (trace F) transmission spectrum of SDOSS surfactant.

the SO3Na" surfactant groups increases while going deeper from the F-A interface inot the latex film deposited of the Hg substrate.

One of the factors that also affects distribution and orientation of surfactant molecules near the interfaces is the latex copolymer composition. In essence, compatibility between the copolymer chemistry and surfactants will determine to what
extent surface tension at the substrate will influence surfactant mobility. For that reason we modified the Sty/n-BA particle composition. When the concentration of styrene in the latex copolymer is diminished, the SDOSS surfactant concentration near the F-A and F-S interfaces is smaller. For the 30% Sty/70% n-BA and 10% Sty/90% n-BA latex copolymers cast on the PTFE surface, no surfactant is detected at the F-A or F-S interfaces, for either parallel (TE) or perpendicular (TM) polarizations. However, when the same latex copolymers were cast on the liquid Hg substrate, the surfactant concentration and its distribution throughout the latex films changes, especially near the F-S interface. For the 30% Sty/70% n-BA latex films cast on liquid Hg substrate, the F-A interface spectra show no surfactant bands present at this interface for either parallel (TE) or perpendicular (TM) polarizations, but at the F-S interface 1046 cm\(^{-1}\) surfactant bands are detected for both polarizations. Furthermore, concentration of the SDOSS surfactant groups parallel to the surface decreases slightly when going deeper into the film for the parallel (TE) polarization. However, for the perpendicular (TM) polarization spectra recorded at the F-S interface, an increase of the 1046 cm\(^{-1}\) band while penetrating deeper into the film is detected. These observations indicate that for this monomer composition, the F-S interface of the latex films contains most surfactant groups that are parallel to the surface near this interface, and the SO\(_3\)Na\(^+\) groups become perpendicular to the surface while going deeper into the F-S.

For 10% Sty/90% n-BA latex films cast on liquid Hg substrate the SDOSS intensities remain constant throughout the examined depths near the F-A interface with the parallel (TE) polarization. However, they slightly decrease while penetrating deeper from the F-A interface with a perpendicular (TM) polarization. These observations indicate that the amount of SDOSS surfactant groups parallel to the surface throughout the examined portion of the latex film remains constant, and the amount of the surfactant groups perpendicular to the surface decreases, while going deeper into the latex film.

No surfactant bands were detected over the examined depth near the F-S interface for 10% Sty/90% n-BA composition with the perpendicular (TM) polarization. However, the 1046 cm\(^{-1}\) surfactant band is detected for the parallel (TE) polarization, indicating that most of the surfactant present at this interface is parallel to the surface.

When 30% Sty/70% n-BA and 10% Sty/90% n-BA latex films cast on liquid Hg were examined, the 1056 cm\(^{-1}\) band was not detected at either F-A or F-S interfaces, indicating that, for this composition, the mobility of surfactant is limited. However, as we recall the data shown in Figures 10a and 12a, the 1056 cm\(^{-1}\) band, due to association of the SO\(_3\)Na\(^+\) surfactant groups with the acid groups, was detected only for the 50% Sty/50% n-BA copolymer mixture. Therefore, latex composition clearly affects the mobility of SDOSS. For a higher concentration of styrene, the acid groups were driven towards the F-A interface, but when the styrene concentration is lowered to 30% Sty and 10% Sty, the surfactant groups are found to be only associated with water.

In summary, the presented data allow us to depict a scenario concerning the orientation of SDOSS and the effect of the substrate surface tension for a core/shell
latex films. A schematic representation of the effect of surface tension on the surfactant mobility through the latex copolymer film is depicted in Figure 14a. As shown in Figure 14a, the low surface tension of the PTFE substrate drives the hydrophilic SO₃Na⁺ surfactant groups towards the F-A interface of the latex film. However, when the surface tension of the substrate is increased (by using liquid Hg), the surfactant migrates toward the F-S interface of the latex film (Figure 14b). There is also the effect of latex composition which influences the surfactant mobility through the latex film. A schematic representation of the effect of monomer composition on the surfactant mobility through the latex copolymer film is depicted in Figure 15. As the styrene concentration in a latex composition increases, the surfactant tends to migrate towards the F-A interface.

![Figure 14a](image1.png)  ![Figure 14b](image2.png)

Figure 14 a  Figure 14 b

Low surface tension substrate  
○ surfactant  
High surface tension substrate  
○ surfactant

![Figure 15](image3.png)

Figure 15

High styrene concentration  
○ surfactant

Step-Scan Photoacoustic Depth Profiling

By changing modulation frequency of an FT-IR interferometer equipped with a photoacoustic cell, it is possible to obtain information from various surface depths. Step-scan PAS FT-IR spectra recorded from the F-S interface of a 50%/50% Sty/BA latex film, using 400, 300, 200, and 100 Hz phase modulation frequencies are shown in Figure 16, Traces A–D, respectively. Trace A recorded at 400 Hz shows
two weak bands at 1056 and 1046 cm\(^{-1}\) which are due to SO\(_3\textsuperscript{-}\)Na\(^+\)…HOOC and SO\(_3\textsuperscript{-}\)Na\(^+\)…H\(_2\)O associations, respectively. However, when the modulation frequency is decreased to 100 Hz, the 1056 and 1046 cm\(^{-1}\) bands decrease to become eventually non-detectable (Trace D). At the same time, a new band at 1050 cm\(^{-1}\), which is due to the symmetric S-O vibrations of free SO\(_3\textsuperscript{-}\)Na\(^+\) hydrophilic end groups, is detected at lower modulation frequencies. This band dominates the spectra recorded with 100 Hz (Figure 16, Trace D). Since the depth of penetration of IR light is inversely proportional to the phase modulation frequency,\(^{20}\) for 400 Hz phase modulation frequency, the depth of penetration is shallowest. In an effort to establish penetration depths at these modulation frequencies, equation 1 can be used. Using the values of α = 1.57\times10^{-3} cm\(^2\)/s for PMMA,\(^{21}\) the penetration depths at all examined frequencies were determined and are summarized in Table I. Based on the data shown in Figure 16, Traces A–D, a higher content of non-bonded SO\(_3\textsuperscript{-}\)Na\(^+\) hydrophilic end groups exist at the greater depths near the F-S interface. This is because water evaporates out of the latex film, resulting in less water molecules trapped at greater depths. Therefore, there are less chances for the SO\(_3\textsuperscript{-}\)Na\(^+\) hydrophilic end groups to associate with H\(_2\)O.

![Figure 16. Step-scan PAS FT-IR spectra recorded at different modulation frequency near the F-S interface: A - 400Hz; B - 300Hz; C - 200Hz; and D - 100Hz.](image-url)
and COOH groups. However, the presence of the 1056 and 1046 cm\(^{-1}\) bands is detected at the shallower depths, indicating that there are traces of water molecules near the F-S interface.

<table>
<thead>
<tr>
<th>Penetration Depth ((\mu m))</th>
<th>Modulation frequency ((\omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 Hz</td>
</tr>
<tr>
<td>Penetration</td>
<td>11 (\mu m)</td>
</tr>
</tbody>
</table>

The 1056 and 1046 cm\(^{-1}\) bands detected at the shallower penetration depths, and the 1050 cm\(^{-1}\) band detected deeper into the F-S interface, indicate that the surfactant molecules migrate towards the interface to minimize the interfacial surface tension. Furthermore, their presence detected at different penetration depths in the step-scan IR spectra indicate that there are significant differences in the film formation near the F-S interface. In the case of the F-S interface, it is far more difficult for water molecules to evaporate from the F-S interface because they may coalesced top layers which inhibit this process.

In order to determine the distribution of SDOSS molecules at various penetration depths, the step-scan spectra were also recorded with 0° and 90° phase, which referred to as in-phase (I) and in-quadrature (Q) spectra. Before we analyzed these data, it is necessary to determine relative penetration depths for 0° and 90° spectra because the relative penetration depths for 0° and 90° spectra depend on the phase modulation angle. In an effort to define the shallow and deep depths and their positions with respect to 0° and 90° spectra, a reference carbon black spectrum was collected. Since carbon black absorbs almost all of the IR radiation and it is thermally thick, stronger peak-to-peak signals recorded from the step-scan PA spectra are attributed to the surface of carbon black, and weak signals come from deeper penetration depths. For that reason, a series of the carbon black spectra were recorded at various phase angles and utilized as references to determine the relative depth penetration for 0° and 90° spectra. The results are shown in Figure 17 with curves \(A_0\) and \(A_{90}\) illustrating the peak-to-peak intensity (Volts) vs. phase modulation angles for 0° and 90° spectra at 1000 Hz modulation frequency, respectively. In this Figure, both \(A_0\) and \(A_{90}\) are cosine waves, and are shifted by 90°. These data also show that, when the phase angle is 0°, \(A_{90}\) has the higher peak-to-peak intensity, thus the signal comes from the surface and it is in-phase (I) with the incident radiation, and \(A_0\) comes from deeper penetration depths, thus represents in-quadrature (Q) spectra.

On the other hand, when the phase modulation angle is 90°, the 90° spectrum comes
Figure 17. A plot of peak-to-peak intensity vs. phase modulation angle at 1000 Hz modulation frequency: (A0) - 0° phase and (A90) - 90° phase.

From the bulk spectrum (Q), and the 0° spectrum comes the surface (I). The same trends were detected at modulation frequency of 400 Hz.

With this in mind, let us go back to the main theme and analyze distribution of SDOSS molecules across the latex film. Figure 18 (A-D) illustrates a series of spectra recorded from the F-S interface from 0° to 90°, in 10° increments, at 400, 300, 200 and 100 Hz, respectively. In this experimental setup, the phase modulation angle is 0°, thus the 0° phase (Q) spectrum represents the signal from deeper penetration depths, and a 90° (I) is a photoacoustic signal from shallower depths. As shown in Figure 18 (A), the bands at 1056 and 1046 cm⁻¹ gradually increase, as the phase angles increases from 0° to 90°. The phase angle at 0° provides deeper depth of penetration than the phase angle at 90°. Since the 1046 cm⁻¹ band intensity is not detected, distribution of SDOSS molecules is not homogeneous within a 11 μm layer from the F-S interface.

In a series of the step-scan spectra shown in Figure 18 (B), a 300 Hz phase modulation frequency from 0° to 90° was used. Although the bands at 1056, 1050 and 1046 cm⁻¹ are detected, the band intensities at 1056 and 1046 cm⁻¹ decrease to minimum, and the 1050 cm⁻¹ band increases, as the phase angles change from 90° to 0°. This observation again indicates that the SDOSS molecules are not uniformly distributed near a 13 μm layer from the F-S interface. Since water evaporation is one of the major driving forces during coalescence, film formation at this depth from the F-S interface will be significantly affected. The amount of water molecules decreases as the penetration depths increase after coalescence. Therefore, the 1050 cm⁻¹ band becomes detectable at 13 μm layer and the band at 1046 cm⁻¹ due to the SO₃⁻ Na⁺...H₂O association decreases, to become non-detectable.
Figure 18. 10 steps of step-scan PAS FT-IR spectra recorded at various modulation frequency with 0° and 90° phase angles near the F-S interface: A - 400Hz; B - 300Hz; C - 200Hz; and D - 100Hz.
When the modulation frequency is set at 200 Hz, the bands at 1056 and 1046 cm\(^{-1}\) are not detected, and only 1050 cm\(^{-1}\) band is present. This is shown in a series of spectra in Figure 18 (C). The band at 1050 cm\(^{-1}\) is strongest for the (Q) spectra, and decreases as the phase angle decreases (I). Similar trends for the band at 1050 cm\(^{-1}\) are detected for 100 Hz modulation frequency with the 0\(^\circ\) and 90\(^\circ\) phase angles at the F-S interface. These spectra are shown in Figure 18 (D). Again, this observation indicates that a fewer of SDOSS molecules are present at the greater depths from the F-S interface.

Having identified spectral features near the F-S interface, let us analyze SDOSS at the F-A interface. The step-scan photoacoustic FT-IR spectra recorded with 400, 300, 200, and 100 Hz of phase modulation frequency at the F-A interface are shown in Figure 19, Traces A–D, respectively. Similarly to the discussion above, the depths of penetration for 400, 300, 200, and 100 Hz of phase modulation frequency are 11, 13, 16, and 22 µm, respectively. The 1056 and 1046 cm\(^{-1}\) are the strongest for 400 Hz (Trace A). However, both decrease as the phase modulation frequency decreases, and become almost non-detectable above 200 Hz phase modulation (Traces C and D). Instead, the 1050 cm\(^{-1}\) band due to non-bonding SO\(_3\)^−Na\(^+\) hydrophilic end groups on SDOSS is detectable at 200 Hz. These data suggest that, when going deeper into the F-A interface, there is less H-bonding between SO\(_3\)^−Na\(^+\) and water, and no associations between SO\(_3\)^−Na\(^+\) hydrophilic end group and water and COOH groups are present. Therefore, both 1056 and 1046 cm\(^{-1}\) bands are non-detectable. Similarly, the 1056 and 1046 cm\(^{-1}\) bands are detected at the shallower depths and the 1050 cm\(^{-1}\) band is detected at the deeper penetration depths from the F-A interface. Due to equilibrium between inner water molecules, which tend to evaporate out of film, and water molecules from atmosphere, which tend to diffuse into the film, the film formation near the F-A interface still continues.

Figure 20 (A-D) illustrates a series of step-scan FT-IR spectra recorded at 400, 300, 200, and 100 Hz phase modulation frequencies, with 0\(^\circ\) and 90\(^\circ\) phases. As shown in Figure 20 (A), while the band at 1046 cm\(^{-1}\) remains constant, the 1056 cm\(^{-1}\) decreases as the phase angle changes from 0\(^\circ\) (I) to 90\(^\circ\) (Q). This observation indicates that the water molecules are present near a 11 µm depth, and form SO\(_3\)^−Na\(^+\)···H\(_2\)O associations. On the other hand, the strongest band intensity at 1056 cm\(^{-1}\) is detected with Q spectrum, and as the phase angle increases, this band decreases, indicating that more acid groups are present near 11 µm into the F-S interface. This behavior is attributed to the fact that water molecules are trapped near this interface, while the acid groups are closer to the deeper portions of 11 µm depth. Similarly, the same trends are found in the spectra recorded at the 300 Hz (Figure 20, B). However, the band intensity of the 1046 cm\(^{-1}\) decreases as the phase angle decreases. Hence, at greater depths, less water molecules are present, then inhibiting SO\(_3\)^−Na\(^+\)···H\(_2\)O associations. Again, a weak band intensity of the 1056 cm\(^{-1}\) is detected for Q spectrum. Since water evaporated towards the film surface interface, more water molecules are able to stay in shallower penetration depths. Based on these spectra recorded from 13 µm into the F-S interface, detected concentrations of water molecules increase parallel with the water evaporation direction, and decrease with the penetration depths.
Figure 19. Step-scan PAS FT-IR spectra recorded at different modulation frequency near the F-A interface: (A) 400Hz; (B) 300Hz; (C) 200Hz; and (D) 100Hz.

Similar trends are observed near the F-A interface for modulation frequencies at 200 and 100 Hz. This is shown in Figures 20, C and D, respectively. In this case, the 1050 cm⁻¹ band is detected at a 16 μm layer near the surface, and decreases at greater depths, indicating that there are no SDOSS molecules beyond 22 μm boundary. By combining spectroscopic data from the F-S and F-A interfaces, it can be seen that SDOSS molecules exude towards the F-A and F-S interfaces, but they are not homogeneously distributed across the film. Since 50% of Sty is incorporated in this composition, hydrophobicity is relatively high, resulting in that the copolymer expels water molecule from latex particles interstices during coalescence. Therefore, one can detect free SDOSS surfactant near a 13 μm layer from F-S interface. Because only the 1050 cm⁻¹ band is detected below 13 μm, coalescence is complete below this thickness from the F-S interface. At the F-A interface, water molecules from the
surroundings are able to diffuse into the surface during coalescence, thus SO$_3^-$
Na$^+$·H$_2$O associations are detected at the 11, 13 and 16 μm depths from the F-A
interface.

Figure 20. 10 steps of step-scan PAS FT-IR spectra recorded at various modulation
frequency with 0° and 90° phase angles near the F-A interface: (A) 400Hz; (B)
300Hz; (C) 200Hz; and (D) 100Hz.
Although we are interested in quantitative assessments of SDOSS distributions near interfaces, at this point such analysis is not available. Therefore, a semi-quantitative analysis will be employed. One of the beneficial features of the step-scan PAS is that the spectra are not wavenumber dependent. Therefore, the relative band areas can be used as a measure of the relative concentrations of SDOSS. However, before the analysis of the relative band areas as a function of penetration can be accomplished, it is necessary to convert the phase angles to penetration depths. Although R-G theory predicts that the $2\pi\mu_b$ layer is the deepest detectable penetration depth beneath the surface, for any practical purposes, due to a low signal-to-noise ratio beyond $3\mu_b$, $3\mu_b$ is the deepest penetration depth that can be detected. In order to obtain relative quantities of SDOSS, the relative areas of the 1046, 1056, and 1050 cm$^{-1}$ bands, normalized to the strongest band at 1068 cm$^{-1}$, due to the C-C vibrational modes, were utilized. The plots of the band areas as a function of the phase rotation angles are shown in Figures 21 and 22 for F-S and F-A interfaces, respectively. In Figure 21, A, relative quantities of SDOSS molecules forming $SO_3^−\cdot Na^+\cdots COOH$ associations (1056 cm$^{-1}$) remain constant throughout the entire film thickness, whereas the amount of the $SO_3^−\cdot Na^+\cdots H_2O$ entities (1046 cm$^{-1}$) decreases, as the phase angle decreases from 90° to 0°. Thus, there are fewer $SO_3^−\cdot Na^+\cdots H_2O$ associations at greater penetration depths. In the case of 300Hz shown in Figure 21, B, the relative amounts of $SO_3^−\cdot Na^+\cdots H_2O$ and $SO_3^−\cdot Na^+\cdots COOH$ species continuously decrease to become non-detectable. However, relative concentrations of the non-bonding SDOSS molecules (1050 cm$^{-1}$) gradually increase, while going further away from the F-S interface. Concentration of the non-bonding SDOSS molecules further increases at approximately 16 μm penetration depths into the film. This is shown in Figure 21, C. Furthermore, concentration of the non-bonding SDOSS (1050 cm$^{-1}$) decreases as the penetration depth increases. This is shown in Figure 21, D. Similar trends are observed for the relative concentrations of $SO_3^−\cdot Na^+\cdots H_2O$, $SO_3^−\cdot Na^+\cdots COOH$, and non-bonding SDOSS molecules near the F-A interface. This is shown in Figure 22 (A-D). However, a comparison of the data shown in Figure 21 and 22 indicate that the concentration of SDOSS near the F-A interface is almost as twice as large as compared to the F-S interface.

Using the surfactant distribution data in coalesced films, it is possible to depict how coalescence process may vary at various distances from the F-A and F-S interfaces. Although one could possibly divide the film thickness into three zones: F-A, central, and F-S interfacial regions, it appears that a degree of coalescence changes across the film is continues. The schematic diagram of the distribution of SDOSS molecules is illustrated in Figure 23. One property of surfactant molecules is that these entities tend to migrate to interfaces in order to minimize the interfacial surface tension. In our previous studies, we illustrated that the surfactant migration is influenced by the surface tension of the substrate after latex coalescence. In this case, latex was cast on polytetrafluoroethylene (PTFE), with the initial interfacial surface tension $\gamma_{so}$ (H$_2$O-PTFE) equal to 50 mN/m, and the surface tension of the latex polymer being approximately 32.2 mN/m. As coalescence progresses, water evaporates, leaving the copolymer film in contact the PTFE substrate, and forming solid-solid interface. Using the concept of interfacial surface tension expressed by
\[ \gamma_{\text{int}} = \gamma_{\text{sub}} + \gamma_{\text{film}} - 2(\gamma_{\text{sub}}\gamma_{\text{film}}^{d})^{1/2} \]

The interfacial surface tension between the latex film and PTFE substrate changes to 1.9 mN/m. In this equation, \( \gamma_{\text{int}} \) is the interfacial surface tension, \( \gamma_{\text{sub}} \) and \( \gamma_{\text{film}} \) are the critical surface tensions for a substrate and a polymeric film, respectively, and \( \gamma_{\text{sub}}^{d} \) and \( \gamma_{\text{film}}^{d} \) are the dispersion components of the substrate and polymeric film, respectively. Apparently, the surfactant molecules migrate to the F-S interface due to the higher surface tension in the initial stages of coalescence, and more surfactant molecules migrate toward the F-A interface due to the lower interfacial surface tension between polymeric film and substrate after coalescence. Therefore, surfactant molecules cumulate near F-A and F-S interfacial regions.

Figure 21. Plots of relative quantities of SDOSS at various modulation frequency vs phase angles near the F-S interface: A - 400Hz; B - 300Hz; C - 200Hz; and D - 100Hz.
Figure 22. Plots of relative quantities of SDOSS at various modulation frequency vs. phase angles near the F-A interface: A - 400Hz; B - 300Hz; C - 200Hz; and D - 100Hz.

Since there are three different types of SDOSS interactions with the latex components: (1) $SO_3^-Na^+\cdots H_2O$; (2) $SO_3^-Na^+\cdots HOOC$, and (3) free SDOSS molecules, we can follow latex film formation by detecting the SDOSS behavior during coalescence. Let us go back to the step-scan IR spectra recorded with 400 Hz of modulation frequency near the F-S interface, which corresponds to the penetration depths near 11 μm. Because the band at 1046 cm$^{-1}$ is detected, water is present between the particle interstices. Furthermore, the presence of the 1056 cm$^{-1}$ band indicates that the particle inter-diffusion is not complete because the water molecules do not evaporate completely in this layer. This is schematically illustrated in Figure 23, which shows the F-S interface near 11 μm. At approximately 13 μm, it appears to
be a transition stage from the wet to dry stage of coalescence. In this transition layer, polymer particles are not completely inter-diffused, and at approximately 16 μm, there is only 1050 cm$^{-1}$ band detected (Figure 18, C), indicating that there are no SO$_3^-$-Na$^+$⋯H$_2$O associations, resulting in coalesced film. This is shown in Figure 23, 16 μm from the F-S interface.

As we recall, Figure 18, D illustrated that at 22 μm from the interface, only 1050 cm$^{-1}$ band was detected, indicating that the film formed continuous phase. Although in the case of F-A interface, the presence of water in the surrounding atmosphere allows diffusion into the F-A interface, thus affecting kinetics of coalescence process, similar trends are detected.

Conclusions

These studies show that ATR and PAS in a step scan mode of operation can be effectively utilized in the analysis of surfaces and interfaces of latexes as well as other films. Our current studies involve urethanes, thermoplastics, as well as silicone elastomers. Although at this point we are able to quantify ATR measurements, quantitative PAS analysis will require further investigations because it requires understanding of the detection processes as well as material’s properties. With the current setup, ATR is capable of effective depth profiling up to 2-3 μm, whereas PAS step-scan measurements exhibit significantly wider range, up to 100 μm, or more, when proper modulation frequency ranges are employed.
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References: