Surface Imaging and Depth Profiling of Latexes: SS-PAS and ATR FT-IR/FT-Raman Microscopy

Yaqiu Zhao and Mark W. Urban
Department of Polymers and Coatings
North Dakota State University, Fargo, ND 58105

Introduction
Previous studies indicated that the mobility of low molecular weight materials, in particular surfactant molecules, may be affected by the glass transition temperature (T_g) and subsequently, by free volume of a polymer matrix, surface tension at the film/air (F-A) and film/substrate (F-S) interfaces, compatibility, and coalescence times, to name just a few. In this paper we will expand the scope of the previous studies and utilize attenuated total reflectance (ATR), FT-Raman microscopy, and step-scan photoacoustic Fourier transform infrared (SS-PAS FT-IR) spectroscopy in an effort to elucidate a molecular origin of latex non-homogeneity.

Experimental
A 50/45/5% styrene-butyl acrylate copolymer was synthesized by a semi-continuous emulsion polymerization. Liquid latex was cast on polytetrafluoroethylene (PTFE) substrate and allowed to coalesce at 80% relative humidity (RH) for 3 days at 22°C. Approximately 200 µm thick films were prepared. SS-PAS FT-IR spectra were recorded on a Nicolet Magna 850 spectrometer equipped with a photoacoustic cell. One scan was collected 7198 sec at a 8 cm⁻¹ resolution. The spectra at 1000, 750, 400 and 200 Hz phase modulations with 0° and 90° phase angles were collected.

Microscopic ATR FT-IR spectra were recorded using Jasco™ Nic-Polar™ molecular microanalysis system. Latex samples were analyzed using ATR objective equipped with ZnSe crystal in reflection mode. Surfaces were measured using the same contact pressure between the ZnSe crystal and latex sample. Each spectrum was recorded at 4 cm⁻¹ resolution, 200 scans, and a 32 µm aperture.

Microscopic FT-Raman spectra were measured using IFS 55 FRA 106 FT-IR/Raman combination spectrometer (Bruker Instruments, Inc.). As an excitation source, a diode pumped Nd:YAG laser was used, providing a maximum power of 327 mW at the sample area. Surface mapping was performed with a computerized x/y-stage in conjunction with the OPUS™ mapping software.

Results and Discussion
The distribution of surfactants in latex films can be affected by surfactant-latex compatibility, interfacial surface tension difference, temperature and humidity, and other factors occurring during latex coalescence. Exudation phenomena of SDROSS surfactant molecules in latex films was detected in our previous studies. As a result of exudation, various external properties, including adhesion, durability, and thermal resistance may be affected. In this study, we explore a combination of vibrational surface sensitive measurements including ATR, SS-PAS, FT-IR and FT-Raman microspectroscopy to study the distribution of SDROSS surfactant in 50/50% styrene-butyl acrylate latex films.

Figure 1 illustrates ATR FT-IR spectra in the 1330-640 cm⁻¹ region of styrene-butyl acrylate latex copolymer recorded from the F-A and F-S interfaces. The bands at 1288, 1259, 1232, 1208, 1181, 1056, and 1044 cm⁻¹ are detected at the F-A interface after coalescence, and are due to SDROSS surfactant. The bands at 1259 and 1208 cm⁻¹ are attributed to asymmetric stretching mode of the S-O H-bonding associated with COOH and H₂O, and the 1056 and 1044 cm⁻¹ bands are due to symmetric stretching modes of the same species. A comparison of traces A (F-A) and B (F-S) shows that the intensity of the band at 697 cm⁻¹ due to deformation modes of polysyrene decreases. On the other hand, the bands at 1288, 1056, and 1044 cm⁻¹ are significantly weaker at the F-S interface. These results indicate that SDROSS exudes to the F-A interface, most likely because of the water flux during coalescence or lower interfacial surface tension between the polymeric film and the substrate. Therefore, the higher concentration of SDROSS is detected at F-A.

In an effort determine if SDROSS molecules are indeed present on the most outer surface, FT-IR/Raman images were collected. Figure 2 shows FT-IR images obtained from the F-A and F-S interfaces. As seen, aggregates are detected at the F-A interface, and to determine their composition, microanalysis was conducted. Figure 3 (a) shows the surface image, Figure 3 (b) illustrates a series of spectra that correspond to points A, B, C, D, and E of Figure 3 (a). It appears that intensities of the bands at 1288, 1259, 1232, 1208, 1181, 1056, and 1044 cm⁻¹ increase while going from A to E. However, the intensity of the band at 697 cm⁻¹ due to polysyrene decreases. These results show that aggregates shown in Figure 3 (a) are mainly composed of SDROSS surfactant islands.

Figure 4 (a) shows FT-Raman image of the F-A interface, and Figure 4 (b) presents a series of FT-Raman spectra recorded from points A, B, C, D, and E of Figure 4 (a). The results show that the intensity of the band at 1056 cm⁻¹ due to SDROSS decreases while going from A to D, and complement FT-IR experiments.

To determine distribution of SDROSS molecules at various depths from the surface SS-PAS spectra were recorded from the F-A interface. Figure 5, Traces A-D, show SS-PAS FT spectra recorded at 1000, 750, 400, and 300 Hz modulation frequencies. These frequencies correspond to approximate penetration depths of 7, 8, 11, and 13 µm. The bands at 1056 and 1046 cm⁻¹ (Trace A) result from the SO₃Na⁻⁻ H⁺OOC and SO₃Na⁻⁻ H₂O entities. The band intensities resulting from these interactions decrease while going from 7 (Trace A) to 8 µm (Trace B). At 11 µm depth (Trace C), only the band at 1056 cm⁻¹ due to non-bonded SO₃Na⁻ hydrophilic end groups on SDROSS is detected. The relative quantities of SDROSS associated with COOH, H₂O, and non-bonded SDROSS species, as a function of penetration depths are shown in Figure 6 and indicate that the concentration of the SO₃Na⁻⁻ H⁺OOC species decreases while going deeper into the film and become non-detectable at 9.2 µm from the F-A interface. In contrast, concentration levels of the SO₃Na⁻⁻ COOH associations increase with greater depths, but at 9.2 µm from the F-A interface, they also become non-detectable. This observation indicates that the acid groups are present near the F-A interface, but the primary component below the surface is polysyrene.

Conclusions
ATR FT-IR and FT-Raman microscopes as well SS-PAS FT-IR can be effectively utilized to study film formation of styrene-butyl acrylate latex copolymers. SDROSS aggregates are detected at the F-A interface and their concentration is significantly higher than at the F-S interface. SS-PAS FT-IR spectroscopy allows us to monitor surfactant distribution across the film thickness. These studies indicate that SDROSS...H₂O, SDROSS...COOH, non-
bonded SDOSS species exist at various penetration depths from the F-A interface.

Figure 1. ATR FT-IR spectra of poly(sty/n-BA) latex.

Figure 2. FT-IR images of 50/50 poly(sty/n-BA) latex. (a) F-A interface, (b) F-S interface.

Figure 3. (a) FT-IR image of poly(sty/n-BA) latex F-A interface, (b) ATR FT-IR spectra of poly(sty/n-BA) latex F-A interface.

Figure 4. (a) FT-Raman image of poly(Sty/n-BA) latex F-A interface, (b) FT-Raman microscopic spectra of poly(Sty/n-BA) latex F-A interface.

Figure 5. SS-PAS FT-IR spectra recorded at different modulation frequencies from latex F-A interface. A-1000 Hz, B-750 Hz, C-400 Hz, D-300 Hz.

Figure 6. The plot of relative quantities of SDOSS associated with HO2-COOH, and non-bonded SDOSS as a function of the depth penetration.

Acknowledgments The authors are thankful to the National Science Foundation Industry/University Coatings Research Center at North Dakota State University for partial support of these studies.

References: