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Surface Enrichment by Conventional and Polymerizable Sulfated Nonylphenol Ethoxylate Emulsifiers in Water-Based Pressure-Sensitive Adhesive

Jilin Zhang, Yuxi Zhao, Matthew R. Dubay, and Steven J. Severtson*

Department of Bioproducts and Biosystems Engineering, University of Minnesota, 2004 Folwell Avenue, St. Paul, Minnesota 55108, United States

Larry E. Gwin

Franklin International, 2020 Bruck Street, Columbus, Ohio 43207, United States

Carl J. Houtman

Forest Products Laboratory, USDA, One Gifford Pinchot Drive, Madison, Wisconsin 53726, United States

ABSTRACT: Comparisons of properties are made for pressure-sensitive adhesives (PSAs) generated via emulsion polymerization using both conventional and reactive emulsifiers. The emulsifiers are ammonium salts of sulfated nonylphenol ethoxylates with similar chemical structures and hydrophilic−lipophilic balances. The polymerizable surfactant possesses a reactive double bond at its phenyl ring allowing for participation in free-radical polymerization reactions. Incorporation of the polymerizable surfactant into the adhesive polymer was confirmed via reverse-phase liquid chromatography. Surfactant distributions in PSA films were characterized using confocal Raman microscopy and contact angle measurements. Increasing conventional surfactant concentrations in emulsion polymerization reactions resulted in proportional increases in concentrations at the surfaces of latex-cast films. No surface enrichment of adhesive films was observed when reactive emulsifiers were employed. Variations in measured depth profiles and contact angles are consistent with observed performance properties, for example, tack, peel strength, and shear times. Increasing concentrations of conventional surfactants decreased adhesive performance, while adhesives generated with polymerizable surfactants showed little or no such decreases in film performance properties. It is concluded that the polymerizable surfactant is bound in the adhesive in such a way that its migration to film surfaces during drying and formation is inhibited, preventing degradation of adhesive performance.

INTRODUCTION

Synthetic polymer latexes produced via emulsion polymerization are used in the manufacturing of a wide variety of commercial products. One such product is pressure-sensitive adhesive (PSA). Water-based PSAs dominate the self-adhesive label market with the most prevalent types being those produced predominantly with acrylic monomers. Upward of 98 wt % of the solids in a water-based PSA latex formulation is the polymer, which composes the colloidal particles of the latex dispersion. The remaining solids fraction consists primarily of surfactants. Surfactants are a necessary component in the synthesis and storage of latex adhesive polymers (emulsifiers) as well as the manufacturing of adhesive films (wetting agents). They can also compose a fraction of tackifying dispersions, which are often used to formulate adhesive latexes. Once films are formed, the surfactants have served their purpose but are retained and can have a detrimental impact on the performance of adhesive films, which is why the surfactants used in emulsion polymerization are sometimes described as a necessary evil.

Although the overall content of surfactants in latex-cast films is an important factor in determining their influence, it is likely their distribution that primarily governs the impact on properties. Previous studies have reported that surfactants have a tendency to concentrate at the interfaces of adhesive films cast from latexes.[1−14] This enrichment has been studied using a variety of techniques including Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy,[2−5] atomic force microscopy (AFM),[1,6,8−14] and more recently confocal Raman microscopy (CRM).[15−18] These studies indicate that surfactant is released during film formation (i.e., drying and coalescence), and its distribution within a film depends on several factors such as its compatibility with the latex polymer and activity in aqueous systems. For those species that have a strong tendency to migrate to film surfaces, concentrations can accumulate to levels several times that found in the bulk region. The authors have reported that conventional anionic surfactants often concentrate at the interfaces of water-based PSA films to substantially higher levels than their nonionic analogues and that the extent of the

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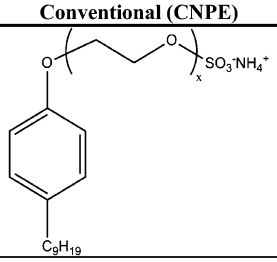
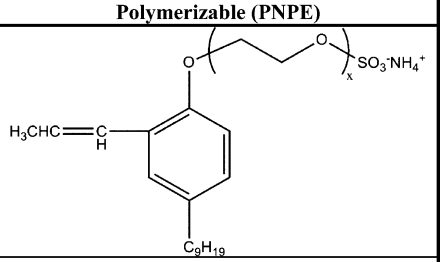
Table 1. Surfactant Properties

Property	Conventional (CNPE)	Polymerizable (PNPE)
Structure		
Average M_w (g/mol)	581 (x=6)	797 (x=10)
Critical Micelle Concentration (CMC) (wt%)	7.7×10^{-5}	9×10^{-4}
Hydrophilic-Lipophilic Balance (HLB)*	15.3	15.2
Log K_{ow}†	1.83	2.05

*Values calculated using Davies' method.[24] †Values estimated using KowWin application of EPI suite software v1.67.

surface enrichment by anionic surfactants is strongly dependent on the nature of their hydrophobes.[16,17]

More recently, it was demonstrated that the tendency of sodium alkyl sulfate homologues to enrich the interface is related to the size of their hydrophobes.[18] It was proposed that as moisture exits the forming latex film during the drying process, it carries surfactant species with it. More hydrophilic homologues, those with smaller hydrophobes, tended to enrich film interfaces to a greater extent. Specifically, it was shown that sodium dodecyl sulfate (SDS) collected within the outermost layer of latex particles in adhesive films, primarily at the tops of films, where the moisture flow is uninhibited during drying. The enrichment of SDS was significantly greater than that of sodium tetradecyl sulfate (STS), which was greater than that for sodium octadecyl sulfate (SODS), while both also showed greater enrichment at the top surfaces of films. The relative extent of the enrichment was shown to roughly correlate with the inverse of the log K_{ow} value for the surfactant, which is used as a gauge of the species tendency, or that of their hydrophobes, to distribute out of aqueous solutions.

Eliminating the negative impacts of surfactants has long been an important and perplexing issue for the paints and coatings industry. In this Research Note, the authors more clearly demonstrate the role of surfactant distributions in diminishing the performance of these materials by comparing the properties of latex-cast films generated with a conventional surfactant against those generated with a polymerizable species. The surfactants are chemical analogues with similar hydrophilic-lipophilic balance (HLB) values. Confocal Raman microscopy and contact angle meaurements are used to characterize surfactant distributions in formed films. These results show that the incorporation of polymerizable surfactants within the adhesive polymer impedes and nearly prevents their migration to film surfaces. This change in surfactant distribution not only helps maintain properties such as tack and peel adhesion, it also increases film cohesive strength as gauged by standard industry shear tests.

EXPERIMENTAL SECTION

Materials. *N*-butyl acrylate (≥99%), sodium persulfate, 1-dodecanethiol, HPLC grade acetonitrile, tetrahydrofuran-d8, HPLC grade water, phosphoric acid, and pleated dialysis tubing were purchased from Sigma Aldrich (St. Louis, MO). Vinyl acetate (≥99%) was obtained from Acros Organics (Fair Lawn, NJ). Methacrylic acid (≥99%) was obtained from Alfa Aesar (Ward Hill, MA). The conventional nonylphenolethoxylate surfactant (Aerosol NPES-458) identified in the paper as CNPE was obtained from Cytec Industries (West Paterson, NJ), while the polymerizable nonylphenolethoxylate surfactant (Hitenol BC-1025), identified as PNPE, was obtained from Dai-ichi Kogyo Seiyaku Co., LTD (Kyoto, Japan). Sodium hydroxide pellets used to adjust the phosphate buffer to pH 7 were obtained from Mallinckrodt Chemicals, Inc. (St. Louis, MO).

Emulsion Polymerization. Seeded semicontinuous emulsion polymerizations were used to generate water-based PSA latexes. Seeds consisted of samples generated with CNPE and dialyzed to remove surfactant. Monomers included *n*-butyl acrylate, vinyl acetate, and methacrylic acid. Sodium persulfate was used to initiate free-radical polymerizations. Samples were generated with either CNPE or PNPE as emulsifiers at concentrations of 2, 4, 6, and 8 wt % (of solids). The degree of incoproration of the polymerizable surfactant was determined by measuring the amount of free surfactant remaining in latex samples using reverse-phase liquid chromatography (RPLC).

Characterization of Latexes and Adhesive Polymers. Glass transition temperatures (T_g) were determined using a TA Instruments (New Castle, DE) DMA 2980 dynamic mechanical analyzer. Tested samples were composite strips formed by dipping a glass support cloth (30 mm × 10 mm × 0.3 mm) into the liquid adhesive emulsion. The samples were dried in a desiccator overnight. Thermal locations of peaks in the loss moduli (E'') for scans carried out at 1 Hz were reported as the T_g values. Average latex particle sizes were characterized by dynamic light scattering (DLS) using a CILAS 1064 particle size analyzer (Orleans, France).

Characterization of Adhesive Films. Films were prepared by casting solutions of the latex dispersions onto a 2 mil thickness polyethylene terephthalate (PET) film with an average size of about 10 in. × 12 in. The films were dried at 90 °C for 5 min, followed by storage in a 50% humidity conditioned room overnight prior to testing. Latex solutions were diluted in order to produce cast films with coating weights of 28 ± 2.8 g/m^2 (approximately 1 mil). Performance

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Table 2. PSA Latex and Polymer Properties

property	2% CNPE	2% PNPE	4% CNPE	4% PNPE	6% CNPE	6% PNPE	8% CNPE	8% PNPE
gel content (%)	1	0	1	0	0	0	0	0
pH	4−5	4−5	4−5	4−5	4−5	4−5	4−5	4−5
solids content (wt %)	56.6	58.8	58.0	59.1	57.2	57.9	58.0	57.3
particle size (nm)	270	320	280	350	350	390	290	290
PDI[a]	6.08	4.96	6.08	3.98	5.57	3.97	5.15	3.73
T_g (°C)[b]	−42.6	−42.1	−42.8	−38.4	−41.0	−42.1	−40.7	−42.3
incorporated degree into adhesive's backbone[c]	NA	86.7%	NA	85.8%	NA	85.6%	NA	85.6%

[a]Based on poly(styrene) standards in THF. [b]From dynamic mechanical analysis. [c]From HPLC analysis. NA = not applicable.

properties of adhesive films cast from formed latexes were measured using ASTM standard methods.[19−23]

CRM characterization of PSA films was carried out using an Alpha 300R confocal Raman microscope equipped with a UHTS200 spectrometer and a DV401 charge-coupled device (CCD) detector from WITec (Ulm, Germany). An Ar ion laser with a wavelength of 514.5 nm and maximum power of 50 mW was used for excitation. Lateral resolution of the CRM instrument according to the theory of light diffraction is about 250 nm, and the vertical resolution is about 500 nm. Measurements were conducted at several random locations on the film to minimize the variation. Raman spectra of film samples were measured (in triplicate) with an integration time of 20 s and laser power of 30 mW. Concentrations were calculated using an approach described in previous papers.[2,3]

Contact angles (CAs) were determined using a Krüss (Hamburg, Germany) DSA10-MK2 CA measurement system. Deionized water was used as a probe liquid with droplet volumes of 3−5 μL. Average CA values were determined at room temperature from 3 measurements for which water droplets were placed at different locations on film surfaces.

RESULTS AND DISCUSSION

Properties of Emulsifiers and Adhesive Latexes and Polymers. Table 1 lists various properties for both CNPE and PNPE. The two surfactants have similar chemical structures. The major difference is the reactive vinyl group attached to the phenyl ring of PNPE, and its larger hydrophile, that is, longer ethylene oxide or EO chain, which compensates for this difference to provide for a similar hydrophilic−lipophilic balance (HLB). This value was found to provide optimal stability to the emulsions (pre-emulsions) used in polymerization processes. However, there are differences in properties such as the critical micelle concentration (CMC), and the logarithm of their *n*-octanol−water distribution coefficients (log K_{ow}), with PNPE being slightly more hydrophobic relative to the CNPE structure.

On the basis of previous measures of migration tendencies, it is expected that these differences are minor, even negligible. In fact, it was expected that the binding of the PNPE to the adhesive polymer backbone should reduce or eliminate surface enrichment, and thus provide a substantially different surfactant distribution when compared with films cast from latexes generated with CNPE. To gauge the degree to which the PNPE surfactant was incorporated into the adhesive polymer, HPLC was used. An average value of incorporation of 86 ± 1 wt. % was obtained (Table 2). In addition to this parameter, other properties for latexes and adhesive polymers produced from the two surfactants at concentrations of 2, 4, 6, and 8 wt % (of solids) are summarized in Table 2. The table lists gel contents, latex pH values, solids contents, latex particle size information, and glass transition temperatures (T_g) for the adhesive polymers.

Surfactant Distributions in PSA Films. Raman spectral peaks at 1612, 1662, and 1735 cm^{-1} were identified as an aromatic C−C ring stretching mode for both the CNPE and PNPE surfactants, vinyl bond C═C stretching mode of the PNPE surfactant, and C═O carbonyl stretching mode associated with the acrylic polymer, respectively (Figure 1a).[2,3] As would be expected given their structures, Raman spectra for CNPE and PNPE are similar. The only detectable

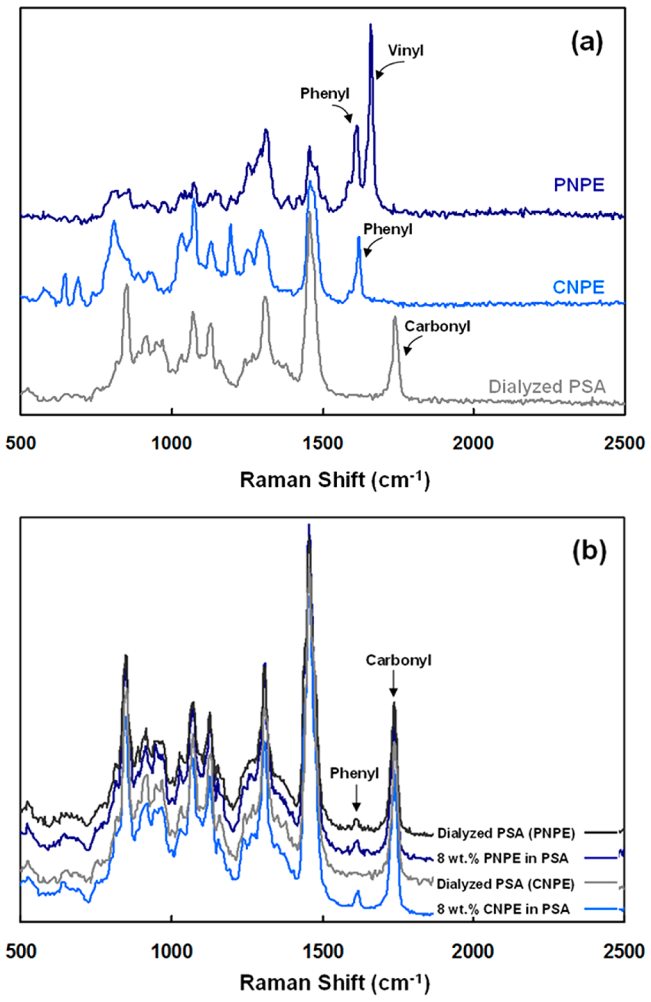

Figure 1. (a) Spectra collected using confocal Raman microscopy (CRM) of the PNPE surfactant, CNPE surfactant, and films cast from dialyzed latex. (b) CRM spectra from films cast from latexes generated using 8 wt % of the PNPE surfactant, 8 wt % of the CNPE surfactant, and films cast from both latexes after dialysis.

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difference is that the PNPE surfactant has an additional reactive vinyl group, which produces a distinct peak at 1662 cm^{-1}. It can be seen that the peak associated with the surfactants at 1612 cm^{-1} is not detectable in films cast from dialyzed latex generated using the CNPE surfactant consistent with removal of the surfactant. It was determined that peaks near 1612 cm^{-1}, associated with the surfactants, and at 1735 cm^{-1}, associated with the polymer, were sufficiently isolated and intense for use in quantifying surfactant levels at various depths in polymer films. The ratios of the surfactant peak areas to the polymer peak areas were used to quantify the surfactant concentrations.

Figure 1b shows the CRM spectra for PSA films cast from latexes containing 8 wt % emulsifier and dialyzed latexes. Both samples generated with CNPE and PNPE are shown. It can be seen that the peak at 1662 cm^{-1} associated with a vinyl stretching mode on PNPE surfactant is absent subsequent to emulsion polymerization, which indicates the incorporation of the PNPE surfactant during reactions. In addition, the peak at 1612 cm^{-1} associated with an aromatic ring stretching mode of the surfactant is absent subsequent to dialysis of the PSA latex generated with 8 wt % CNPE indicating that the surfactant is not strongly associated with the polymer and it can be removed via dialysis. On the other hand, the same peak at 1612 cm^{-1} still exists subsequent to dialysis for the PSA generated with 8 wt % PNPE. This result is consistent with the grafting of the PNPE surfactant into the backbone of the adhesive polymer.

Quantitative depth profiles indicating surfactant concentrations at various depths in 1 mil PSA films are shown in Figure 2. Results are presented for films cast from latexes generated with 8 wt % CNPE (Figure 2a) and PNPE (Figure 2b). From Figure 2a, it can be seen that CNPE surfactant enriches film surfaces. Surfactant concentration at the film−air interface (e.g., 0%) is ∼14 wt %, which is slightly higher than that at the film−substrate interface (e.g., 100%). For the same measurement on films cast from the latex generated with 8 wt % PNPE, no surface enrichment is observed. It appears that the surfactant is evenly distributed throughout the entire adhesive film. The results are as would be expected if the surfactant is covalently bound to the backbone of the adhesive polymer preventing its migration during drying processes.

As was discussed in previous publications, contact angle measurements using water as the probe liquid are as sensitive as spectroscopic techniques at gauging the extent of surfactant enrichment at polymer film surfaces.[18] The orientation of surfactants that migrate to the surface are such that they lower the contact angle with water with greater enrichment. Figure 3 shows the contact angle results for water on films cast from dialyzed latex and on films cast from latexes generated with 2, 4, 6, and 8 wt % of the CNPE and PNPE emulsifiers. The contact angle for water was the highest on the dialyzed film, 126°, indicating this surface is strongly hydrophobic. It is evident that the film cast from the latex containing CNPE is more hydrophilic, with the contact angle for water decreasing sharply with increasing surfactant levels. Films originating from latex samples containing 2, 4, 6, and 8 wt % CNPE surfactant had static contact angles with water of 96, 42, 24, and 18°, respectively. This change from surfaces that are strongly hydrophobic to strongly hydrophilic is attributed to the enrichment of CNPE surfactant at film surfaces. Films cast from latexes produced with the PNPE emulsifier do not experience such a dramatic change. Films from latexes containing 2, 4, 6, and 8 wt % PNPE surfactant are all

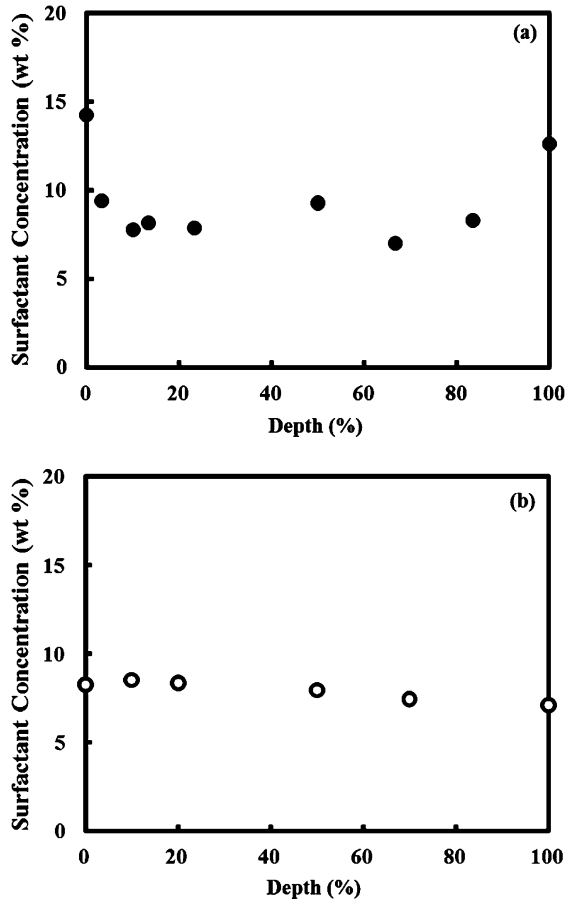

Figure 2. Calculated surfactant concentrations at different film depths based on CRM spectra for the latexes generated using (a) 8 wt % CNPE surfactant and (b) 8 wt % PNPE surfactant.

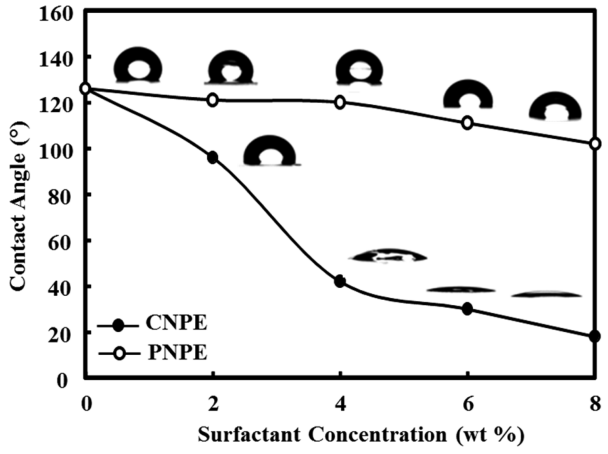

Figure 3. Contact angles for water measured on films cast from a dialyzed sample and from films cast from latexes generated with various concentrations of CNPE and PNPE surfactant.

relatively hydrophobic with measured angles for water of 121, 120, 112, and 104°, respectively.

Influence of Surfactant Distributions on Performance Properties. When reporting the performance of self-adhesive materials, results are typically provided for tack, peel and shear. Tack is a measure of the ability of an adhesive to rapidly wet a surface and form an adhesive bond. In practice, tack is commonly gauged via loop tack,[21] in which a looped filmic

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substrate, such as PET, coated on the outside with the PSA (1 mil) is lowered onto a flat metal plate to form a particular contact area (typically 1 square inch) for a short dwell period and removed. The maximum force per width of the test strip is reported. The most commonly used peel test measures the force recorded while removing an inch wide, film-backed PSA (1 mil) from a metal plate. Tests can be carried out at various angles, but 180° is the most common,[22] and results are reported as the maximum force recorded per width of the test strip. Shear testing involves the application of a constant shear stress to a laminate. This is commonly done by attaching a weight to the backing material of a label that is bonded to a vertically oriented metal plate producing a fixed overlap region (commonly 0.5 in. × 0.5 in.).[23] Results are reported as the time required for the eventual failure of the laminate reported in minutes. The greater the time required for failure, the higher the (cohesive) strength of an adhesive.

Figure 4 compares loop tack (Figure 4a), 180° peel (Figure 4b) and shear (Figure 4c) results for PSA films cast from latexes generated with various levels of CNPE and PNPE surfactant. It can be seen that the adhesive films cast from latexes generated with the CNPE surfactant showed substantially lower values for all three tests. As the CNPE surfactant amount increases from 2 to 8 wt %, tack values decrease from 1.7 to 0.9 lb_f/in., 180° peel decreases from 2.0 to 0.8 lb_f/in., and shear times decrease from 45 to less than 10 min. These results clearly show the negative impact of the conventional surfactant on PSA performance properties. The results also show the ability of the PNPE surfactant to retain performance properties. With the same increases from 2 to 8 wt %, tack, peel, and shear values were contant at 1.5 lb_f/in., 2.3 lb_f/in., and 200−300 min, respectively.

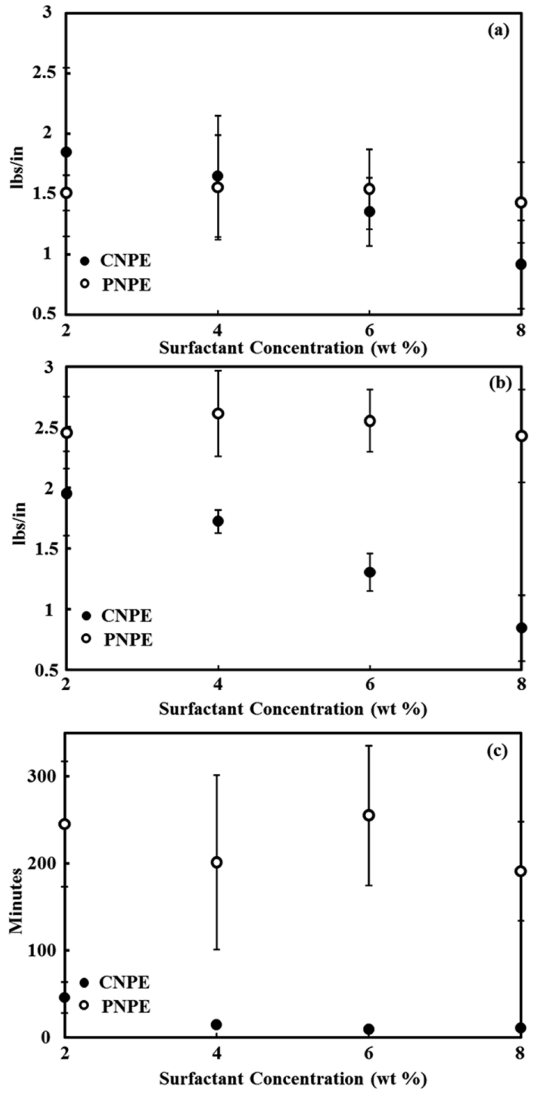

Figure 4. Adhesive performance properties, including (a) loop tack, (b) 180° peel strength, and (c) shear time, for films cast from latexes generated with various concentrations of CNPE and PNPE surfactant.

CONCLUSIONS

A study on the influence of adding a reactive double bond on the distribution of an anionic nonylphenol ethoxylate (NPE) surfactant in latex films was reviewed. Films of a commercial PSA were generated using both conventional (CNPE) and reactive or polymerizable (PNPE) forms of surfactant. Incorporation of the polymerizable form of the surfactant was determined to be >85 wt % at all of the surfactant levels used. Significant differences in surface and performance properties were observed between films cast from latexes generated with the different surfactants. In fact, films from the PNPE latexes demonstrated substantially greater levels of tack, peel, and shear performance. It is concluded that the binding of surfactant to the adhesive polymer backbone inhibits its movement to film surfaces during film formation, which helps maintain the performance of the adhesive film.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sever018@umn.edu.

Notes

The authors declare no competing financial interest.

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