Water Absorption by Acrylic-Based Latex Blend Films and Its Effect on Their Properties

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ABSTRACT: The absorption of moisture, from liquid as well as gaseous states of water, is known to strongly influence the properties of many polymeric materials. In this article, we examine the unusually high affinity for water of acrylic-based latex blend films, which lose their transparency and turn white upon water absorption. Composed of rubbery and glassy phases at room temperature, these blends absorb significant amounts of water, which results in only a minor plasticization of the glassy component. When redried at elevated temperatures, the blend films return to their original transparent state but remain white and opaque when freeze-dried at −70°C. Scanning electron micrographs of the freeze-fractured surfaces of wet samples exhibit micronsized holes that suggest clusters of water inside the bulk of the films. A qualitative model associates these water clusters to residual surfactant inside the samples that is left behind after the drying of original latices. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1407–1419, 1999

Key words: latex blend coatings; moisture absorption; relative humidity; water clusters; surfactant; mechanical properties

INTRODUCTION

The first evidence of the interaction of water with a latex-based film was reported by Wheeler et al.[1] in 1954, who noticed that a poly(vinyl acetate) (PVAc) film became white and opaque when placed in water and began disintegrating within a few seconds. He attributed this to the presence of poly(vinyl alcohol) (PVOH), which, in the absence of water, forms a stabilizing network between the PVAc particles but loses its integrity when exposed to water. The PVAc particles do not coalesce to form a homogeneous film; rather they are held together by PVOH, which provides the final film with reasonably good mechanical properties. Wilkes

and Marchessault[2] and Côté et al.[3] reported similar observations regarding the turbidity of PVAc–PVOH system and confirmed the presence of a continuous PVOH phase (when present in high concentrations) with dispersions of PVAc particles by small-angle light scattering and microscopy data.

Bindschaedler et al.[4] noted that films of cellulose acetate (CA) containing 2–5% sodium dodecyl sulfate (SDS) by weight of CA, turned translucent or white when soaked in water and showed dark regions of well-defined shapes under an optical microscope. These films were prepared with large quantities of plasticizers and, presumably, were homogeneous in bulk due to extensive coalescence of particles. Unlike the PVAc–PVOH system studied by Wheeler et al., their system evidently involved expulsion of SDS from the particle interface and its agglomeration in separate domains.

These observations have prompted several researchers to probe the role of surfactants and emulsifiers in determining the ultimate proper-

ties of films obtained from drying of latices, as they are inevitably present in the final product. Ionic surfactants, such as SDS, for example, significantly affect the water absorption characteristics of an otherwise hydrophobic latex owing to their amphiphilic nature. The distribution of such surfactants inside the final film, naturally, has become the focus of attention among scientists in academia as well as in the paints and coatings industry.

The objective of this work is to quantify the water absorption characteristics of acrylic-based latex blend films and its effect on their mechanical properties. The original latices are stabilized by ammonium lauryl sulfate (ALS), which is similar to SDS in its nature and stabilizing action. Although our focus is not on studying the distribution of ALS inside these blend films, we propose a qualitative model to explain the large water uptake in terms of its distribution inside the bulk of the films. We provide, as a background, a comprehensive review of the literature on the distribution of surfactant in latex films to lay the ground for the proposed model.

BACKGROUND

A brief review of the mechanism of the drying process during film formation from latices is necessary to understand the data on the distribution of surfactant in these films. According to the commonly accepted model, the drying process involves three stages: (1) evaporation of water that brings the surfactant-stabilized latex particles in close proximity to each other; (2) coalescence of particles to form a homogeneous structure; and (3) polymer interdiffusion across the particle interfaces to yield good mechanical properties (stiffness, strength, toughness, etc.). The particles undergo large inelastic deformation during the coalescence; consequently, homogeneous films are obtained only above a certain minimum film formation temperature (MFFT) when such a deformation is possible. Details of these steps are beyond the scope of the current study and are available in several excellent reviews.[5–7]

It is evident that the stabilizing surfactant layer on the particles has to collapse in order to facilitate their close contact and subsequent deformation. This applies only to the case of low-molecular-weight ionic surfactants, such as SDS and ALS, since there are other types of emulsifiers that remain grafted to the polymer particles and prevent their coalescence or form a continu-

ous phase to hold the particles. Voyutskii[8] suggested, first in 1958, that this desorbed surfactant layer either dissolves in the polymer resulting in its plasticization or is retained inside the homogeneous film as an independent network. Based on a review published by Bindshaedler et al.[4] and Kientz and Holl,[9] the following is a summary of various possible modes of surfactant distribution upon drying of latices:

1. Solubilization of the surfactant in polymer;
2. exudation of the surfactant to the film–air interface by the flux of evaporating water;
3. exudation of the surfactant to the film–substrate interface;
4. formation of a network due to stratification of the surfactant in the interfacial regions between the particles;
5. formation of agglomerated surfactant domains inside the bulk of the homogeneous polymer film;
6. localization of the surfactant on the surface of the particles that remain discrete and uncoalesced.

Focusing our attention on ionic surfactants, such as SDS, we find ample evidence of their desorption from the particles during their coalescence. Using the technique of Fourier transform infrared–attenuated total reflection (FTIR–ATR), Zhao et al.[10] have demonstrated the presence of surfactant molecules at the film–air as well as the film–glass interfaces for poly(methyl methacrylate-co-butyl acrylate) latex films. This copolymer had a T_g of around 2°C, and the films were prepared at 22°C, a temperature certainly higher than the MFFT. Depending upon the wavelength, the refractive indices of the sample and the crystal (germanium versus KRS-5) and the incident angle of reflection, a depth of roughly 1–5 μm can be probed by this technique. Zhao et al. monitored the ν_4 bending vibration of the —SO$_4^-$ group at 588 cm^{-1} and followed its normalized absorbance with respect to the α-methyl band at 755 cm^{-1} as a function of film aging at both the film–air and film–substrate interface. Their results clearly show the presence of surfactant on the film surface right at the end of water evaporation (stage 2 of the film drying process) in the film. There is a preferential enrichment of the film–air interface compared to the film–glass interface shown by higher relative absorbance values for this side. Some of the SDS is lost on the glass substrate during the peeling of the film, as they verified

later by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS).[11]

A very extensive examination of the surface enrichment by the surfactant in latex films has been carried out by Dr. Marek Urban's group at North Dakota State University using FTIR–ATR and step-scan photoacoustic (SSPAS) FTIR spectroscopy.[12,13] One of the major advantages of SSPAS is that the sampling depth from which the acoustic signal is generated can be controlled by the modulation frequency of the incident radiation as it is inversely related to the thermal diffusion wavelength. A penetration depth of as high as 100 μm can be probed by selecting appropriate frequencies of modulation.

In a five-part series beginning in 1991, Urban and his coworkers have studied the influence of copolymer–surfactant interactions,[14,15] the nature of the substrate,[16] the structure of the surfactant,[17] and the copolymer composition[18] on surfactant exudation and particle coalescence. Their work has focused on latex copolymers of ethyl acrylate (EA) and methyl acrylic acid (MAA) ($T_g = -3$ to -5°C) stabilized by a variety of surfactants that included sodium dioctylsulfosuccinate (SDOSS), sodium dodecylbenzene sulfonate (SDBS), SDS, sodium sulfonate adduct of nonylphenol ethylene (SNP2S), and nonylphenol ethylene oxide (NP) and dried over a variety of substrates, such as polyethylene, poly(tetrafluoroethylene) (PTFE), and mercury. Their results again demonstrated the role of polymer–surfactant compatibility (varied by neutralization of the acid groups), nature of the surfactant (ionic versus nonionic), and the differences in the interfacial energies at the film–air and film–substrate interfaces.

Amalvy and Soria[19] have presented similar evidence based on their examination of the poly(methyl methacrylate-*co*-ethyl acrylate-*co*-methyl acrylic acid) terpolymer film ($T_g = 3.5$°C) prepared from a latex stabilized with SDS. They report an equivalent enrichment of both the interfaces with a nearly parabolic distribution of the surfactant in the film. The incorporation of small quantities of the acid monomer ($\sim 2\%$), they argue, changes the polarity of the system and modifies the polymer–surfactant compatibility by providing an additional degree of hydrophilicity at the surface of the particle. In addition, the T_g of the bulk polymer also plays an important role in the exudation of the surfactant towards the interfaces.

Juhué et al.[20] examined the surfaces of poly-(butyl methacrylate) (PBMA) films from latices containing 2 wt % SDS by atomic force microscopy (AFM) and found hilly agglomerates of the surfactant on the surface. Upon washing with water, these aggregates disappeared and 10–100-nm-wide pores appeared in their place. Feng et al.[21] observed crystals of SDS on the surfaces of their soft latex films (copolymers of butyl methacrylate and butyl acrylate; T_g of these films ranged from -33 to 10°C depending upon the copolymer composition) containing 8.8% SDS. These structures were not seen in films prepared from surfactant-free latices.

A major limitation of these techniques is that few details are available regarding the distribution of the surfactant, if any, in the bulk of the polymer film. Chesne et al.[22] examined ultrathin sections taken from the bulk of their PVAc ($T_g = 38.6$°C) and poly(methyl methacrylate-*co*-butyl acrylate) ($T_g = 19.5$°C) films prepared above the MFFT from latices stabilized by SDS, using energy filtering transmission electron microscopy (EFTEM). Using an energy filter with a TEM, it is possible to obtain an element–specific contrast in the imaging electrons arising due to inelastic interactions with the constituents of the sample. Upon adequate compensation for the mass thickness contrast, such an image provides unambiguous phase information based on elemental composition. Application of structure-sensitive contrast (SSC) imaging to the electron micrographs of these samples show rather randomly scattered bright spots corresponding to the presence of sulfur. Such domains were also seen at the film surfaces that supported the conclusions regarding surfactant exudation by ATR–FTIR and AFM studies. Interestingly, they did not find any sulfur domains at the film surface or in the bulk sections for films prepared below the MFFT. Apparently, the surfactant remains adsorbed on the particles as they are not able to coalesce below the MFFT.

EXPERIMENTAL

Materials and Sample Preparation

Methylmethacrylate-based copolymer latices were synthesized by Dr. G. D. Andrews of the DuPont company. The first latex was poly(methyl methacrylate-*co*-ethyl acrylate), P(MMA-*co*-EA), with a T_g of 45°C, and the second was poly(methyl methacrylate-*co*-butyl acrylate), P(MMA-*co*-BA), with a T_g of -5°C. The comonomer molar ratios in the two latices were 3 : 2 and 2 : 3, respectively, and these were stabilized by 0.35 and 0.17% (on

molar basis) ammonium lauryl sulfate (ALS). Particle sizes of these latices, as measured by dynamic light scattering, were of the order of 100 nm. Unless mentioned otherwise, these two co-polymers will be referred to as "hard" and "soft" in the subsequent description.

Blend films of the two copolymers were cast from the aqueous dispersions on a glass plate, dried at 70°C for 3–4 h and annealed at 130°C for 20 min. Films were easily removed from the glass plates with the aid of water. Time of exposure to water was minimized so as to limit the amount of absorbed water, and the excess water was wiped off from the surface with Kimwipes®. The films were later left to dry at room conditions. The composition of the blends was varied from 0% hard to 100% hard to obtain a complete set. A comprehensive characterization of the mechanical and thermal properties of these blends has been presented elsewhere.[23,24]

Measurement of Water Absorption

The blend films were first dried in a vacuum oven for 2 days at around 80°C to remove residual moisture. Next, these were immersed in distilled water in a glass vial, and the change in weight was monitored regularly for a period of 8 months while the samples remained soaked in water at room temperature (20–25°C). The surface of the wet sample was first wiped dry with Kimwipes®, and then its weight was measured with a Sartorious balance sensitive to 0.01 mg. A set of five different samples were studied for each of the blend composition that ranged from pure soft to pure hard phase in increments of 10–20% hard phase.

A second study of moisture absorption from the gas phase was carried out in homemade proximity equilibration cells (PECs)[25] using saturated salt solutions to regulate relative humidity (RH) in the vapor phase above the films. Samples were kept inside these PECs for a month, and their weight change was periodically monitored by a Sartorius balance sensitive to 0.01 mg. The temperatures of the PECs fluctuated with the local laboratory temperature, approximately in the range of 23–26°C, well within the applicable span of RH values for the salt solutions.

Scanning Electron Microscopy

Freeze fracture surfaces of wet samples were examined using a JEOL 35CF scanning electron microscope (SEM) at a magnification of 5400×. Higher magnifications caused extensive beam damage of the material at 20-kV beam voltages. Samples were coated with gold in a Polaron sputter coater after evacuating the chamber with vacuum for 20 min. Samples were subsequently transferred to the sample chamber in the microscope. The sample chamber was maintained under low vacuum of the order of 10^{-7} torr. Typical duration of the sample examination was approximately 1 h.

Dynamic Mechanical Testing of Wet Films

Changes in mechanical properties were measured by a DMTA MarkIV from Rheometric scientific in tension mode at 1 Hz with a heating rate of 2°C per min. All the calculations of stress and moduli were based on the initial swollen dimensions of the wet films. Samples were typically 15 mm long, 2–3 mm wide, and 0.1–0.3 mm thick. Small tabs, cut out of a thin aluminum shim, were glued to the ends of the samples by epoxy to prevent their deformation inside the grips. The samples were equilibrated inside the instrument at −120°C for half an hour. An initial static force of 1–2 N was applied, which was programmed to decrease as the samples softened upon heating by maintaining the ratio of static to dynamic force constant at 1.1. The amplitude of strain oscillation was maintained at 0.05%.

Measurement of Swelling Strains by TMA

Swelling strains upon exposure to a moist gas were measured as a function of relative humidity of the carrier gas (nitrogen) in a TMA2940, from TA Instruments, at 25°C. A small static load of 50-mN was maintained on the sample throughout the experiment. First, any residual moisture was removed by purging the thermomechanical analysis (TMA) sample chamber with dry nitrogen (80 mL min) for a period of 1–2 h. Thereafter, the purge gas was bubbled through saturated salt solutions to generate a specific relative humidity before introducing it in the sample chamber. Changes in length of the sample upon absorption of moisture from the purge gas was monitored at constant temperature and stress over long periods of time. In the second stage, the purge gas was switched back to pass through a drier to monitor the desorption of the absorbed moisture.

Figure 1 Weight of water absorbed per 100 g dry weight of blends of varying composition.

RESULTS AND DISCUSSION

Water Absorption

These blend films, especially with higher proportions of the soft phase, absorb large amounts of liquid water, as shown in Figure 1. The pure soft phase absorbs nearly 100% of its own weight after 8 months compared to a 6% gain by the hard phase. The weight gain by the other blend films, having an intermediate composition, lies within these extremes. As shown in Figure 2, all of the samples lose their initial transparency and turn white and opaque upon absorption of water. Even to the naked eye, a slight gradient in the intensity of the whiteness is apparent as a function of the amount of water absorbed; the pure soft phase is the most intensely white, whereas the pure hard phase is slightly translucent. Another feature of the liquid water absorption by these materials is that the pure soft phase and the blend with 20% hard phase do not show a steady state in water absorption even after 8 months. When soaked in water at 65°C (20°C above the T_g), the pure hard phase absorbs nearly 100% of its dry weight in just 2 weeks and becomes as opaque and white as the pure soft phase kept in water at room temperature. A large amount of swelling is caused by water absorption; the cross-sectional area of the pure soft phase increases by 50% compared to around 10% swelling in that of the pure hard phase. The soft blends (with less than 50% hard phase) showed an inward curling of the edges likely due to an uneven absorption between the film–air and the film–substrate sides of the sample.

These wet films were later freeze-dried in a vacuum sublimating unit for a week. First, the samples were frozen at −70°C for 5 h in a freezer and then placed inside a glass vessel that was connected to the sublimating unit. Measurements

Figure 2 Physical appearance of dry and wet blend film samples. The numbers (%) indicate the hard phase content in the blend.

Figure 3 Moisture absorption from the gas phase in PECs by 100% soft phase over a period of 1 month.

of their weights, after freeze-drying, indicate that they return to their original dry weight and lose all of the absorbed water. Although the pure soft phase and the blend with 20% hard phase lose most of their whiteness upon drying and turn rather translucent, the remaining blends retain their whiteness in the dry state.

Figures 3 and 4 display a similar trend in the moisture absorption by the pure soft and hard phases, respectively, from the gas phase in PECs, although the percentage of weight gain is much lower than that in liquid water. Within the time frame of this experiment (around 1 month), both the pure soft and pure hard samples absorb similar amounts of moisture, around 5–6 g per 100 g dry weight at 100% RH; however, the weight gain has not reached a steady state. From the data shown in Figure 1, it is clear that the hard phase is very close to its steady state value, whereas the soft phase continues to absorb increasing quantities of moisture. At lower RH values, these samples reach a fairly steady state in their moisture absorption in 1–2 days. At RH values greater than 70%, the samples turn white and increasingly more opaque. Therefore, the minimum amount of water required to cause whiteness, based on this data, is around 0.6–0.8 g per 100 g dry polymer.

SEM of Freeze-Fractured Surfaces

A striking difference between the surface morphologies of dry and wet films is clearly shown by Figures 5 and 6. A featureless surface of the pure soft phase in the dry state, for example in Figure 5, is filled by large holes in the wet state. These holes correspond to the space left by water that

evaporates under the vacuum of the sample chamber in the microscope. These holes are several microns in size, and a considerable deformation of the rubbery matrix is clearly evident in Figure 5. Even the pure hard phase is filled by such holes, although much smaller than in the pure soft phase, upon water absorption, as displayed in Figure 6.

The surface morphology of blends containing increasing proportions of the hard phase are shown in Figures 7–10. Despite the artifacts left by the cracks during freeze fracture, all of the blends show similar holes arising from water evaporation. The size of these holes is smaller than those seen for the pure phases; however, a quantitative analysis is not possible since the surfaces were not microtomed to remove the artifacts introduced during the fracture. The presence of both phases is also apparent in these figures, which show dispersed particles of the minor phase in a continuous matrix. These particles are in the submicron range and are certainly much smaller than the empty holes. The opacity of the wet film is therefore due to these large water-filled domains present inside the bulk of the film.

EFFECT OF WATER ABSORPTION ON MECHANICAL PROPERTIES

There is a significant change in dynamic mechanical properties of the wet samples (those exposed to liquid water), as shown in Figure 11. At very low temperatures, of the order of $-100°C$, the soft blends containing a large amount of water exhibit a higher storage modulus E' compared to the hard blends. It is possible that the absorbed mois-

Figure 4 Moisture absorption from the gas phase in PECs by 100% hard phase over a period of 1 month.

As the wet blends are heated, they show a decrease in E' through melting of water and the glass transitions of each phase. The profiles of E' with temperature beyond $-10°C$ are very similar to those obtained for the dry samples,[24] although the absolute values are comparatively lower. This is partly due to the use of wet cross-sectional area in the modulus calculations and partly due to a slight plasticization caused by water. Once the frozen water melts, its reinforcing effect on the soft blends is lost, and their stiffness returns to that in the dry state.

(a) Dry Film

(b) Wet Film

Figure 5 SEM micrographs of the freeze-fractured surfaces of dry and wet films of pure soft phase.

ture freezes into ice and results in a higher modulus for the composite blend and ice system. Langleben et al.[26] have reported the elastic parameters of cold arctic sea ice by acoustic methods, and their results predict a tensile modulus of 10 GPa in the limit of zero brine content. Using this value for the modulus of ice, a simple rule of mixtures yields a value around 6.0 GPa for the 0% hard sample (pure soft phase), which, in the wet form, can be treated as a 50/50 mixture of ice and polymer. This value is in excellent agreement with that observed at $-50°C$, as shown in Table I.

(a) Dry Film

(b) Wet Film

Figure 6 SEM micrographs of the freeze-fractured surfaces of dry and wet films of pure hard phase.

Figure 7   Freeze-fractured surface SEM of the blend with 30% hard content.

Figure 9   Freeze-fractured surface SEM of the blend with 50% hard content.

The transitions associated with melting of ice and glass transitions of each phase are better seen in Figures 12 and 13. The curves are shifted along the y-axis by an arbitrary value to enhance the clarity of these transitions. Compared with the dry blends, the wet blends exhibit much broader transitions for the soft phase due to the overlapping melting of ice. There is a slight plasticization of the hard phase due to the absorbed water as indicated by lower peak values of E'' and tan δ. This is further supported by lower values of E' in comparison to those of the dry blends, as shown in Table I.

Eckersley and Rudin[27] studied the plasticization effect of water on surfactant-free films of poly(butyl acrylate-*co*-methyl methacrylate) (nearly 50/50 mixture with slight incorporation of methylacrylic acid) using dynamic mechanical testing. The addition of different modifiers in their polymerization recipe yielded copolymers with T_g values around 15 and 30°C, respectively, based on their complex shear modulus data. Upon immersion in water for 2 months, the final complex shear modulus for these films was slightly lower than the corresponding dry values; an effect ascribed to water-induced plasticization of the copolymer. Judging by their data on complex shear moduli, a depression of around 5°C in the T_g is ascertained. It should be emphasized that their copolymers were surfactant-free; and though they present no data on the amounts of water absorbed, it is likely that these samples did not contain significant quantities of free water in discrete domains. In addition, a lack of data at tem-

Figure 8   Freeze-fractured surface SEM of the blend with 40% hard content.

Figure 10   Freeze-fractured surface SEM of the blend with 80% hard content.

Figure 11 Storage modulus of wet samples at 1 Hz, 2°C per min.

peratures lower than the melting point of water makes it hard to speculate on the nature of absorbed water in this system. The plasticization effect, at best, can be considered as a minor effect compared with the much more dramatic mechanical reinforcement by frozen water in our soft blends.

Figure 14 shows the swelling strain for the 100% pure hard phase caused by moisture absorption from the moist purge gas in the TMA. That there is no true steady state at high relative humidities is clearly shown by all the curves. The 0% RH curve shows that the sample undergoes a small creep even at a small force of 50 mN (stress

~ 0.06 MPa). Upon desorption of moisture to the dry purge gas, there is a residual strain, which is not entirely explained by creep. Based on the freeze-drying experiment, the sample retains the voids left behind by the desorbed moisture upon drying, resulting in a net residual strain. The diffusion of moisture, therefore, is clearly non-Fickian as the absorption and desorption curves do not superimpose on each other.

A Qualitative Model of Water Absorption

All of the above observations indicate that water exists as an independent entity within the bulk of

Table I Comparison of Storage Moduli from DMTA for Wet and Dry Blends

Hard Phase (%)	Wet Blends			Dry Blends	
	−130°C (GPa)	−50°C (GPa)	25°C (GPa)	−50°C (GPa)	25°C (GPa)
0	6.58	5.01	0.0083	2.02	0.0056
20	6.41	4.69	0.014		
30	4.83	3.48	0.044	2.16	0.071
40	2.26	1.64	0.149	2.23	0.209
50	3.31	2.38	0.385	2.72	0.487
60	3.06	2.24	0.487	2.83	0.827
80	4.64	3.34	0.836	3.13	1.75
100	3.09	2.36	1.032	3.73	2.563

Figure 12 Loss modulus of wet samples at 1 Hz, 2°C per min.

Figure 14 Swelling strains for the 100% hard phase caused by moisture absorption from moist purge gas in TMA at 25°C.

the polymer film. Although the carbonyl groups of the carboxyl ester functionality in the acrylic copolymers provide a potential for specific interaction with water by hydrogen bonding, this would result in large plasticization, an effect seen only to a small extent in these experiments. In addition, the size of such water domains is much greater than the wavelength of light, presumably of the order of 1 μm or more, as the wet films appear white and opaque. These domains, in our view, serve as reservoirs connected to the liquid water outside the film through channels that provide a pathway for water diffusion. A continuous addition of water to this reservoir results in considerable swelling of the surrounding polymer, which, if compliant enough, could expand easily under the hydrostatic pressure exerted by the water reservoir. If the polymer is above its T_g, as is the case for the pure soft phase, the absorption

Figure 13 Tan δ of wet samples at 1 Hz, 2°C per min.

of water should continue for a long time, limited only by the modulus of the material. A lack of steady state for the pure soft phase, even after 8 months, is likely explained by this idea. A further support for this suggestions is provided by the fact that the pure hard phase absorbs only a limited amount of water at room temperature, but its water absorption is comparable to that of the pure soft phase, and much more rapid, at temperatures above T_g. Clearly, the only limitation to the water absorption is the resistance to the diffusion of water into these reservoirs inside the bulk of the film.

Blend morphology also plays an important role in the ultimate water absorption by these films. A closer examination of the data in Figure 1 indicates that there is a very sharp decrease in the amount of absorbed water when there is 30–40% hard phase in the blend. This composition range corresponds to a transformation of a continuous soft matrix with dispersions of hard phase to a continuous hard matrix with soft dispersions.[23] The analysis of effective blend moduli as a function of composition based on a percolation concept also implies the existence of a co-continuous blend morphology in this range. Blends with a hard phase content in excess of 40% by volume evidently comprise a hard matrix which results in a much lower water content than those with a continuous soft phase.

The main objective of a model to explain this behavior, therefore, is to provide an understanding of the driving force for the creation of the proposed water reservoirs inside the material. In the light of the extensive literature review on the distribution of surfactant presented in section, we

hypothesize that even though the incompatibility and the surface energy argument imply a complete segregation of the surfactant from the bulk polymer, and its total exudation to the film–air and film–substrate interfaces, significant quantities remain trapped inside the bulk. Sulfur imaging data from EFTEM presented by Chesne et al.[22] clearly support this hypothesis. Further, Chevalier et al.[28] have provided a classic thermodynamic argument to suggest the creation of fragmented surfactant stabilized hydrophilic domains upon evaporation of water by the inversion of the curvature of the surfactant monolayer from the polymer towards the remaining water phase. Driven by the difference in surface tension with respect to the organic phase, these domains are finally expelled to form independent droplet-like structures that still contain significant amounts of water. Upon further drying, the water from these hydrophilic droplets diffuses out of the surrounding polymer phase, and the previously ionized surfactant precipitates out as a neutral salt to form phase-separated domains in the bulk of the polymer film. Such structures are stable as the concentration of the exuded surfactant at the interfaces of the dried latex film does not change significantly with further aging.[9,10]

We extend the ideas of Chevalier et al. to suggest that these islands of the surfactant salt retain a certain memory of their hydrated past with respect to the alignment of their hydrophilic head groups. Such relatively ordered structures are potential reservoirs for the subsequent water absorption in our experiments. A pathway for water diffusion to these reservoirs is likely provided by traces of surfactant left in the channels that form along the escape route of water as it evaporates through the latex during its initial drying stage. Indeed, such channels (or cracks) were seen by Bindschaedler et al.[4] in cellulose acetate (CA) films upon exposure to water and subsequent drying. They also observed large micron-sized pores, after washing with water, at the film surface that was on the air side during drying of the latex. These pores result from washing away the surfactant that exuded to the film–air interface during the original drying. We emphasize here that these channels, or aggregates of the surfactant, do not imply a presence of voids or cracks in the material since drying above the MFFT enables the polymer particles to coalesce throughout all the available space. A clear and homogeneous film is thus obtained.

We summarize these ideas in Figure 15. Stage I in Figure 15 corresponds to the starting latex containing surfactant-stabilized polymer particles. Minor quantities of unreacted monomer, initiator, and radicals may be present in the surrounding aqueous phase as well as the polymer particles. During the drying process, these unreacted small molecules escape from the latex along with the evaporating water, and the polymer particles are brought in close proximity to each other, as shown in Stage II. Upon further loss of water (Stage III), the particles are brought in much closer contact, and the surfactant molecules begin to desorb from their surface. A thin water layer carries these desorbed surfactant molecules, and the counterion pairs, towards the film–air interface. Finally, the surfactant molecules desorb completely from the polymer particles following their coalescence and form salt precipitates inside the bulk of the film. Stage IV shows the proposed structure of the final dry film that contains these independent salt clusters and channels. The absorption of water occurs by the proposed mechanism through these channels.

A question arises, then, regarding the absorption of water by films prepared from surfactant-free latices. Feng and Winnik[29] for example, have reported significant water uptake values, of the order of 15 wt %, by poly(butylmethacrylate) (PBMA) and copolymers of poly(methacrylic acid-*co*-butylmethacrylate) prepared after removal of the surfactant from the starting latices. Neutralization of the acid groups in the copolymer by NH_3 or NaOH increased the extent of water absorption. Results of Okubo et al.[30] on surfactant-free copolymers of ethyl acrylate and methyl methacrylate also show considerable water absorption and degree of whitening, which increases further upon postaddition of sodium sulfate, a destabilizing agent, and decreases on adding an emulsifier, sodium dodecyl benzene sulfate (DBS).

There is evidence of considerable porosity due to particle flocculation and incomplete coalescence in these systems. The films are clear despite the presence of interstitial voids, indicating a tight packing of particles. According to Okubo et al., the film–air and film–glass interfaces are rich in these porous structures owing to the formation of a skin in the early stages of the drying process. The mechanism of water absorption is one due to a capillary action of these pores and voids. This is further supported by much lower permeabilities of the water vapor in these films.[29,31,32] The presence of ionic neutralizing agents, in the case of Feng and Winnik,[29] leads to an increase in the water absorption by providing sites that could be hydrated by water.

(a) Stage I

(b) Stage II

(c) Stage III

(d) Stage IV

Figure 15   Qualitative model for water absorption (see text for details).

In summary, therefore, it is proposed that the surfactant-laden blend films absorb significant amounts of water from the liquid, as well as the gas, phase through diffusion pathways. The exuded surfactant does not play any role in water absorption as it is washed away from the surface when the latex film is soaked in water. The absorbed water accumulates in ordered assemblies of surfactant molecules inside the bulk of the film by forming a hydrated complex. Water absorption by this mechanism continues for a long time, limited only by the rigidity of the polymer film. Upon freeze-drying of the wet films, large voids are left behind in the place of these reservoirs, which cause the film to retain its original whiteness. When these void-filled films are heated, the polymer molecules are able to relax back into the open space, and the films return to their dry transparent state; surface tension within the voids is a driving force for this recovery.

CONCLUSIONS

Acrylic-based latex blend films absorb large quantities of water, which results in significant changes in their appearance and mechanical properties. The extent of water uptake is determined by blend composition and phase morphology; blends with large proportions of the soft phase as a continuous matrix absorb much larger amounts of water compared with those with greater concentrations of the hard phase. All of the blend films turn white and opaque upon water absorption but regain their transparency upon redrying. SEM micrographs of the freeze-fractured surfaces of wet films show large holes left behind by the evaporating water. Dynamic mechanical spectra of wet films indicate a slight plasticization effect; however, most of the water remains separated from the bulk polymer as an independent entity.

A qualitative model accounts for water absorption by diffusion-driven pathways to clusters of

surfactant in the material that act as water reservoirs. Hydration of these surfactant salts by water provide ample driving force for prolonged water absorption, which is limited only by the bulk strength of the polymer. Enlargement of these hydrated domains due to increasing amounts of water causes them to scatter light, thereby rendering the otherwise transparent film white and opaque. Water absorption is completely reversible, as the wet film, when redried above its T_g, regains its original weight and transparency. Freeze-drying of wet samples, however, yield dry films that stay opaque owing to the presence of large voids left behind by the absorbed water upon sublimation.

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