

Novel Water Sorption Behavior of Emulsion Blends

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ABSTRACT: As waterborne emulsions continue to replace their solvent-based counterparts in various applications, the water resistance of cast films is attracting significant interest. The characterization of the water sorption kinetics and structure–property relationships related to water sorption is, therefore, an important area for investigation. In this study, the water sorption kinetics of emulsion blends were compared with those of their blend components. The investigated blends were at equal weight (dry basis) fractions for each emulsion. The initial water sorption rate for immiscible emulsion blends was found to be significantly higher than composite values of the constituents. This behavior was due to percolation networks in the blends because thermodynamic constraints prevented diffusion across the interface bordering dissimilar particles, leaving a interface enriched with water-sensitive species. The peak water sorption for the immiscible emulsion blends was lower than the composite values because of the ability of the water-sensitive species to rapidly diffuse out of the samples

due to the percolation network. This behavior existed for room-temperature-cast samples and persisted as the time and temperature exposure was increased. Atomic force microscopy results clearly showed the potential for percolation networks in the blends. Higher glass-transition emulsion polymers [e.g., poly(vinyl acetate)] exhibited similar behavior, and this indicated poor film formation like that for the immiscible emulsion blends. These results indicated that the degree of film formation was critical with respect to the water sorption characteristics of emulsion films. Immiscible emulsion blends were compared with miscible emulsion blends for which all constituents exhibited excellent film formation (unblended). The immiscible blends exhibited a significant difference in water sorption compared with the miscible blends because of the existence of percolation networks. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 933–939, 2003

Key words: blends; immiscibility; networks

INTRODUCTION

Aqueous emulsions comprise a major segment of the commercial polymeric materials used in adhesives, coatings, nonwoven binders, and sealants. These emulsions, although commercial for decades, have gained renewed interest in the past several decades as environmentally acceptable alternatives to solvent-based polymers used in similar applications. The basic deficiency of water-borne emulsions with respect to their solvent-based counterparts involves water resistance. The presence of surfactants, protective colloids, and ionic species from polymerization initiation leads to a significantly higher level of water sorption for emulsion-cast films than for solvent-based systems. The structure–property relationships for the water sorption of emulsion-cast films are, therefore, technologically important but do not appear to have been well characterized in the literature.

Emulsion blends, which are the major emphasis of this study, have been used in a myriad of commercial applications. The characterization of emulsion blends in the technical literature has not received the atten-

tion that melt-processed blends (i.e., engineering polymer blends and polyolefin blends) have enjoyed.^{1–3} Recent studies have reported on the mechanical properties of emulsion blends.^{4–8} The equivalent box model,^{9,10} employing the universal constants predicted by DeGennes,¹¹ was shown to predict both the modulus and strength of emulsion-cast blends consisting of immiscible components with similar particle sizes.⁸ Winnik and coworkers studied various aspects of emulsion blends, including atomic force microscopy (AFM),¹² the influence of glassy emulsion particles on the diffusion of lower glass-transition-temperature (T_g) emulsion blend constituents,¹³ and the morphology of an emulsion blend with T_g 's below and above the ambient temperature.¹⁴ The film formation and packing characteristics of emulsion blends with different particle sizes were studied by Tzitzinou et al.¹⁵ Soft and hard (nondeformable) emulsion particle blends were investigated, and the surface roughness and void volume concentration resulting from such blends were discussed. The segregation of a surfactant from the emulsion polymer during and at the completion of the film-formation process has been the subject of many investigations.^{16–18} Zhao and Urban¹⁹ studied the phase behavior and surfactant stratification of emulsions of styrene/*n*-butyl acrylate copolymers and blends of polystyrene and poly(*n*-butyl acrylate)

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emulsions. It was noted that the surfactant formed aggregates in the cast copolymer film, whereas the surfactant existed at the blend interface for the emulsion blend. A difference in the level of the surfactant at the film–air interface was also noted between the copolymer and the blend. Agarwal and Farris²⁰ studied the effect of water adsorption on the properties of emulsion blends of acrylics with T_g 's of the components below and above the ambient temperature (45 and -5°C). Significant water sorption was observed, and the analysis demonstrated the presence of water clusters in the emulsion blends as freeze-dried samples exhibited micrometer-sized voids. Reference 20 does not discuss the kinetics of water sorption. Cast immiscible emulsion blends leave a network structure when dried because the individual components are not thermodynamically capable of diffusion across the interface into another phase. The resultant network structure constitutes a percolation network consisting of surfactant and ionic species trapped between dissimilar particles. As will be shown, this factor is significant with respect to the amount of water sorption and the sorption kinetics.

The film formation of emulsion systems has been well-studied,^{21–23} with various theories and phenomenological explanations having been reported. The final step of emulsion film formation involves the diffusion of polymer chains across the interface with the elimination of the interface and percolation network. For immiscible emulsion blends, this step does not occur, and so the network persists in the as-cast film. The level of elimination of the network during the final stages of film formation for unblended emulsions is later demonstrated to have a major influence on the water sorption and water sorption kinetics.

EXPERIMENTAL

The chosen emulsion polymers and poly(vinyl acetate) homopolymers, prepared by suspension and solution polymerization, are detailed in Table I. The emulsion polymers were chosen to have similar particle sizes. The emulsion blends were prepared via simple mixing at a high shear rate for several minutes with a propeller blade attached to a laboratory mixer. The emulsion blends were prepared with equal weight fractions (on a dry basis) of the components. The emulsions and emulsion blends were cast onto glass plates at 23°C and 50% relative humidity, and a dry thickness of 750–1000 μm resulted. The thickness was chosen to ensure a limited effect of water desorption during the weight measurements. After 24 h of drying, the samples were removed from the glass plates and cut into 50-cm² samples. These samples were placed in a desiccator and dried to constant weights. Weight–time measurements were then deter-

TABLE 1
Polymers and Emulsions Employed in This Study

Emulsion designation	Monomer(s)	T_g ($^\circ\text{C}$)	Solids (wt %)	Particle size (μm)
PVAc-1	VAc	35	50	0.17
EVAVC-1	VAc, E, VCl	0	52	0.17
VAE-1	VAc, E	7	55	0.15
VAE-2	VAc, E, minor third monomer	2	55	0.19

Polymer designation	Description of polymer	Source
Poly(vinyl acetate) CAS No. 9003-20-7 Catalog No. 18,248-6	Solution-polymerized	Aldrich
Poly(vinyl acetate) Vinac ASB-516	Suspension-polymerized	Air Products and Chemicals, Inc.

T_g is from DSC data; VAc = vinyl acetate; E = ethylene; VCl = vinyl chloride.

mined on three samples, each immersed in distilled water. The surface water was removed with adsorbent paper towels. To prevent surfactant/ionic species diffusing out of the samples from shifting the transport boundary conditions, we replaced the distilled water approximately every 3000 $\text{s}^{1/2} \text{cm}^{-1}$. The desorption data were obtained by the water-equilibrated samples being placed in a desiccator and their weights being determined at various time intervals.

For AFM measurements, 75- μm -thick (when wet) films were prepared on Mylar [poly(ethylene terephthalate)] film substrates. After drying, the samples were transferred to a desiccator and dried for 1 week. Some of the film samples were also heated at 100°C for 1 h. Before analysis, both room-temperature-cast films and heat-treated films were washed with deionized water, and this was followed by drying. Without the washing step, exuded surfactant on the surface obscured the underlying morphology. A DimensionTM 3000 microscope with a Nanoscope IIIa controller from Digital Instruments (Santa Barbara, CA) was employed for the AFM analysis. Experiments were run in Tapping Mode, a noncontact mode of AFM, in which the cantilever was oscillated at its resonant frequency, and the feedback was provided by amplitude damping rather than simple deflection. Tapping Mode allowed for phase imaging, that is, imaging based on the phase lag between the excitation signal and actual cantilever oscillation. The phase images accentuated material differences over topographic ones. Imaging was performed with 125- μm -long silicon tapping tips, with probe apexes of under 20 nm. Dual topography phase images were collected at scan rates of 1–2 Hz. The images are presented as top-view height and phase images.

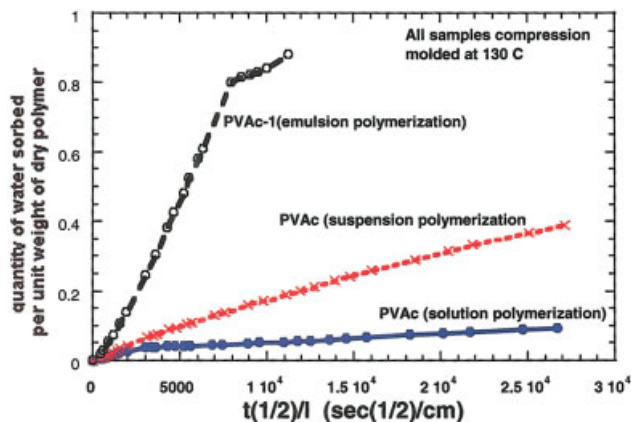


Figure 1 Water sorption results for poly(vinyl acetate) prepared by emulsion, suspension, and solution polymerization.

RESULTS AND DISCUSSION

Three variants of poly(vinyl acetate) prepared by emulsion, suspension, and solution polymerization were compression-molded at 130°C in a 40-mil cavity mold. The samples were placed in a desiccator until testing. Water immersion results were obtained and are illustrated in Figure 1. The level of water-sensitive moieties in the various samples primarily determines the level of water sorption and illustrates the significant influence of the inclusion of water-sensitive species on the sorption level. The water immersion results for emulsion-cast samples of PVAc-1, EVAVC-1, and a 50/50 blend of PVAc-1 and EVAVC-1 are shown in Figure 2. The blend water sorption results are not a composite of the constituent values but exhibit faster initial water sorption than either component, with a maximum value reached very soon in the sorption cycle. The characteristics of the blend are more similar to those of PVAc-1. As will be demonstrated, the

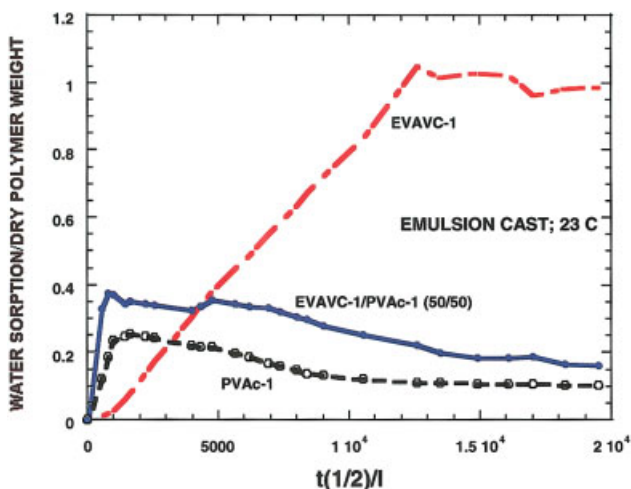


Figure 2 Water sorption results for PVAc-1, EVAVC-1, and a 50/50 (w/w) blend (emulsion-cast and dried at 23°C).

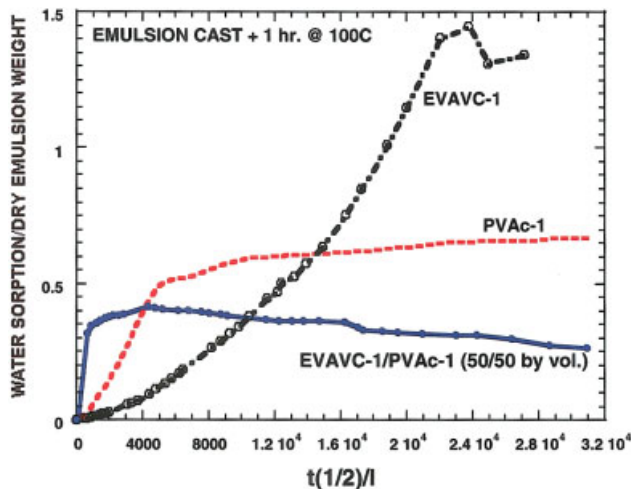


Figure 3 Water sorption results for PVAc-1, EVAVC-1, and a 50/50 (w/w) blend (emulsion-cast and dried at 23°C and for 1 h more at 100°C).

extent of film formation critically influences the water sorption results. PVAc-1 exhibits a dry T_g of approximately 35°C (according to differential scanning calorimetry) and a wet T_g lower than room temperature. Although the wet T_g is below the casting temperature and film formation can occur, yielding a coherent cast film, the level of film formation is far from complete, and so a structure exists, leaving a percolation network consisting of the water-soluble constituents of the emulsion and allowing the rapid ingress of water. The blend, which exhibits an even faster initial ingress of water than PVAc-1, also is expected to have a percolation network at the interface between the immiscible constituents of the blend. The peak water sorption for both PVAc-1 and the PVAc-1/EVAVC-1 blend occurs early in the sorption test and significantly earlier than for the EVAVC-1 sample. The existing percolation network allows rapid water ingress and also allows rapid diffusion of the water-soluble species out of the sample, shifting the equilibrium toward a sample that contains lower and lower water-sensitive species. The EVAVC-1 film with a low T_g exhibits excellent film formation, as expected and also as observed by AFM observations. As the time and temperature exposure conditions are increased, significant changes result in the water sorption behavior. Figure 3 illustrates the results for PVAc-1, EVAVC-1, and 50/50 blend emulsion-cast samples exposed to 100°C for 1 h. The results show similarities in the emulsion blend and the as-cast film (Fig. 2). PVAc-1 shows a higher peak sorption and lower initial water sorption rate with exposure to 100°C for 1 h, and this is indicative of increased film formation and a loss of percolation, which allows the rapid diffusion of water into the sample with the removal of water-sensitive species from the film. EVAVC-1 shows a lowered

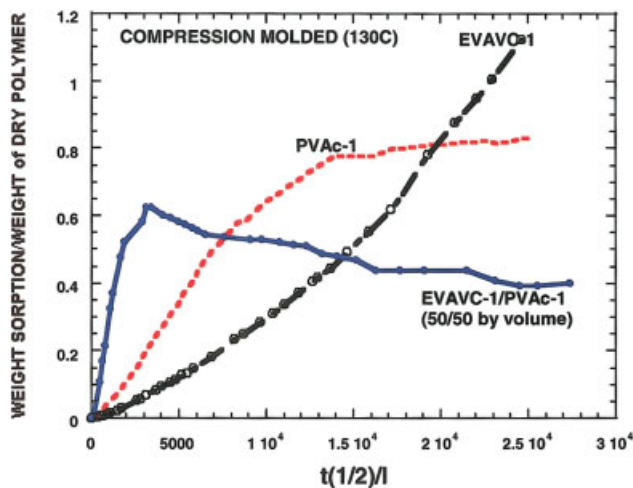


Figure 4 Water sorption results for PVAc-1, EVAVC-1, and a 50/50 (w/w) blend (compression-molded at 130°C).

overall sorption rate apparently due to further completion of the film formation. Water immersion data on compression-molded samples (of the dried and emulsion-cast films) are shown in Figure 4. The trends noted for the samples exposed for 1 h at 100°C versus the emulsion-cast films are further accentuated for the compression-molded samples, with the blend maintaining a percolation network, as judged by a comparison of the diffusion results with those of the blend constituents. The rate of water sorption for PVAc-1 maintains a higher value than EVAVC-1 for the compression-molded films. This is also the case for previously melt-mixed compression-molded samples. The higher initial rate of water sorption is believed to be inherent because the presence of vinyl chloride in EVAVC-1 reduces the diffusion rate of water over that of PVAc-1. These results have been determined with an emulsion blend consisting of equal weight (and similar volume) fractions of the components. This should be the position at which both phases are equally continuous (and likewise discontinuous), as noted in ref. 8 (when similar particle sizes are used). This is also the composition at which maximum percolation can be expected to occur.

The AFM results (Figs. 5–7) demonstrate the percolation network presumed to be responsible for the observed emulsion blend water sorption results. The surface of PVAc-1 (Fig. 5) clearly demonstrates incomplete film formation, and the original emulsion particles have maintained their shape under the conditions of emulsion casting and storage at room temperature before testing. Note that the surface is expected to show less particle coalescence than the interior as the particles at the surface rapidly dry, not allowing interdiffusion as T_g of dry poly(vinyl acetate) is above room temperature. Particles below the surface are below T_g until drying has occurred, and this allows some

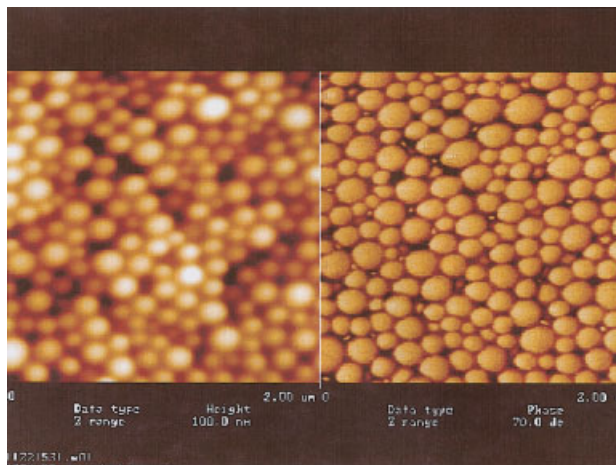


Figure 5 AFM images ($2 \mu \times 2 \mu$) of a PVAc-1 cast surface (cast and stored at 23°C).

interparticle diffusion. The emulsion blend (Fig. 6) shows particles of PVAc-1 in a matrix of EVAVC-1 that have undergone coalescence and film formation. The same testing applied to EVAVC-1 shows a featureless surface, as would be expected from the blend results. With the heating of the emulsion blend to 100°C for 1 h, the coalescence of PVAc-1 particles occurs. A PVAc-1 film exposed to 100°C for 1 h becomes featureless. The close observation of Figure 6 suggests close but less than ideal mixing of the individual particles. It must be recognized that the coalescence of one of the particles of the emulsion blend (EVAVC-1) results in the localized segregation of particles of the other noncoalescing species (PVAc-1), yielding the appearance of less than ideal mixing. Figure 7 illustrates the surface appearance of the emulsion blend (50/50 EVAVC-1/PVAc-1) after exposure to 100°C for 1 h. The PVAc-1 particles coalesce, forming islands on the surface. Although this may appear

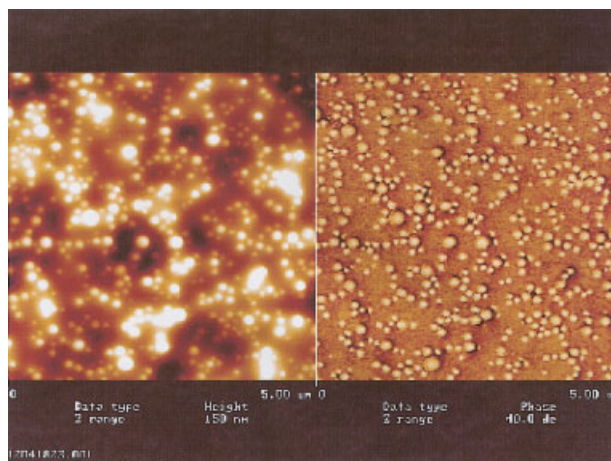


Figure 6 AFM images ($5 \mu \times 5 \mu$) of a 50/50 (w/w) dry PVAc-1/EVAVC-1 blend cast surface (cast and stored at 23°C).

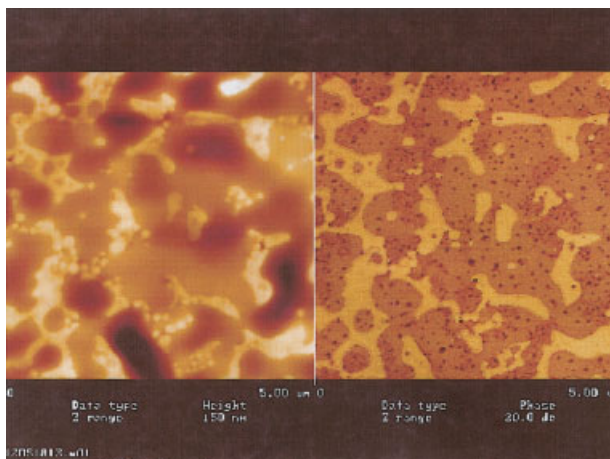


Figure 7 AFM images ($5 \mu \times 5 \mu$) of a 50/50 (w/w, dry) PVAc-1/EVAVC-1 blend cast surface (cast and stored at 23°C and for 1 h more at 100°C).

to indicate that the PVAc-1 phase is discontinuous (as the AFM surface results indicate), it should be noted that measurements of bulk properties show that both phases are equally continuous and discontinuous at the 50/50 volume ratio.⁸

After samples had been exposed to water immersion for over 3 months, desorption data were obtained. The weight measurements were obtained periodically with storage in a desiccator so that proper boundary conditions were ensured. The data are expressed as the quantity of water desorbed at time t (q_t) divided by the initial quantity of water (q_∞). With these initial and boundary conditions; q_t/q_∞ can be expressed as follows:²⁴

$$q_t/q_\infty = 1.0 - (8/\pi^2) \sum_{n=0}^{\infty} [1/(2n+1)^2] \exp[-D(2n+1)^2 \pi^2 t/l^2] \quad (1)$$

where D is the diffusion coefficient and l is the thickness.

For desorption data, a plot of q_t/q_∞ versus $(t/l^2)^{1/2}$ is linear up to approximately $q_t/q_\infty = 0.5$, as noted by Crank.²⁴ Indeed, this is the case with the data observed in this experiment. The expression for q_t/q_∞ in this linear region has been noted to be $q_t/q_\infty = 2.257(Dt/l^2)^{1/2}$, which reduces to $D = 0.0493(l^2/t)$ for $q_t/q_\infty = 0.5$. Note that eq 1 is only exact for diffusion coefficients that are Fickian (e.g., not time-dependant). In this case, the thickness varies during the desorption, and so the diffusion coefficient is not Fickian and the results are only approximate but nevertheless qualitatively comparative. The values of the diffusion coefficients calculated from the q_t/q_∞ data with the aforementioned protocol are as follows: PVAc-1, $D = 1.44 \times 10^{-8} \text{ cm}^2/\text{s}$; EVAVC-1, $D = 4.12$

$\times 10^{-9} \text{ cm}^2/\text{s}$; and PVAc-1/EVAVC-1 (50/50), $D = 1.01 \times 10^{-7} \text{ cm}^2/\text{s}$. The thickness variation during testing cannot come close to accounting for the large variations in the diffusion coefficients. The percolation network observed in the initial sorption data also allows for the rapid diffusion of the sorbed water out of the sample when the boundary conditions are changed.

After the desorption experiments were completed, the samples were subjected to water immersion for the measurement of the resorption behavior. The data shown in Figure 8 illustrate that the EVAVC-1/PVAc-1 blend still exhibits initial rapid water sorption with lower peak sorption values in comparison with the constituents. The magnitude of the water sorption is lower than the initial sorption data (Fig. 1), presumably because of the lower concentration of water-sensitive species that diffused out during the initial sorption study (ca. 5–6 wt % for the samples).

The observations for EVAVC-1/PVAc-1 were quite similar to those observed for the VAE-1/PVAc-1 blend (also immiscible), as illustrated in Figures 9 and 10 for room-temperature emulsion-cast films and for films exposed for 1 h at 100°C . For both conditions, the emulsion blend exhibits the most rapid initial water sorption, with similar peak sorption for the emulsion-cast film (no thermal conditioning) and lower peak sorption for the sample exposed for 1 h to 100°C . As for the EVAVC-1/PVAc-1 blends, the VAE-1/PVAc-1 blend data are not composite values of the constituents but exhibit a unique behavior due to the percolation network that exists because the thermodynamic constraints of the immiscible polymers do not allow diffusion across the interface. At this point, the emulsion blends consist of a low- T_g , excellent-film-forming polymer and a high- T_g , poor-film-forming polymer. The higher T_g film-forming polymer also exhibits a

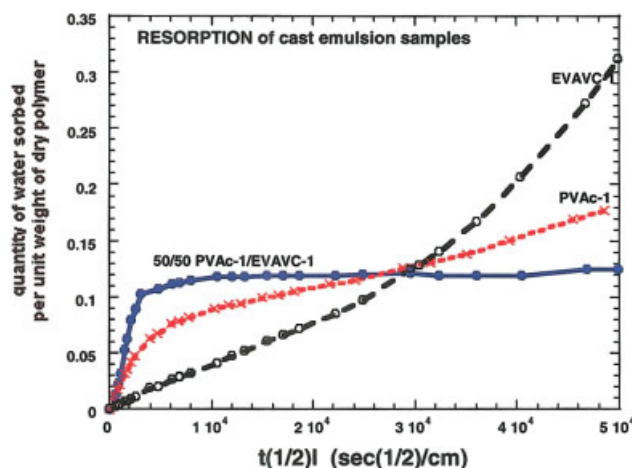


Figure 8 Water resorption results for PVAc-1, EVAVC-1, and a 50/50 (w/w) blend (emulsion-cast and dried at 23°C) (after an initial sorption and desorption cycle).

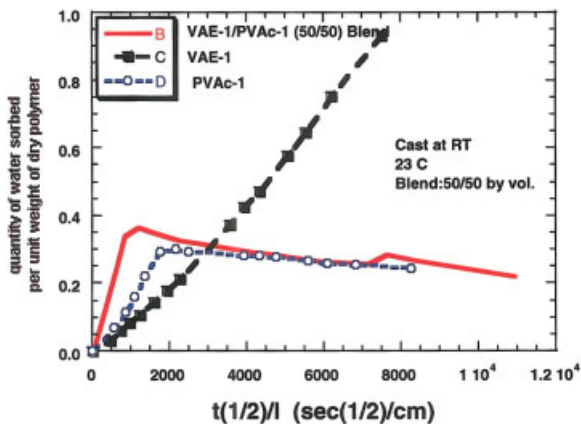


Figure 9 Water sorption results for PVAc-1, VAE-1, and a 50/50 (v/v) blend (emulsion-cast and dried at 23°C).

percolation network because of low diffusion across the interface imposed by the kinetic constraints of T_g , which are eliminated with increased temperature exposure. The combination of two excellent-film-forming immiscible polymers would be an interesting test for demonstrating that the percolation network existing in emulsion blends (of immiscible polymers) should be a general observation. In this case, blends of VAE-1 and EVAVC-1 (immiscible) and VAE-1 and VAE-2 (miscible) were cast at room temperature, and the water sorption results are illustrated in Figure 11. The results clearly show a marked difference between the immiscible blend and the miscible blend and well demonstrate that the persistence of an interface with the immiscible blend allows for rapid water sorption initially but also the rapid removal of water-sensitive species, yielding much lower peak water sorption. Note that the water sorption data for VAE-1 and VAE-2 are quite similar and that the blend is a reasonable composite of their individual results.

These observations raise several questions that have been investigated, including whether the initial film-

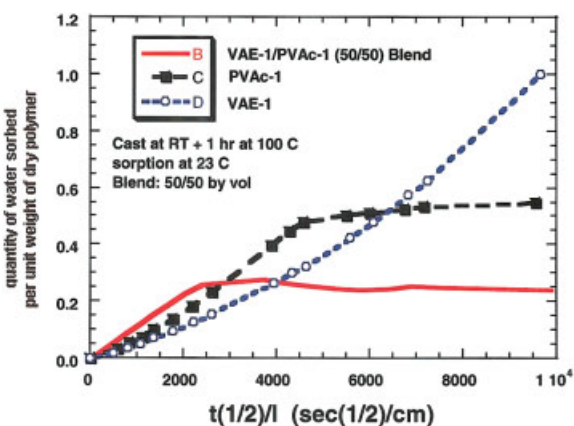


Figure 10 Water sorption results for PVAc-1, VAE-1, and a 50/50 (v/v) blend (emulsion-cast and dried at 23°C and for 1 h more at 100°C).

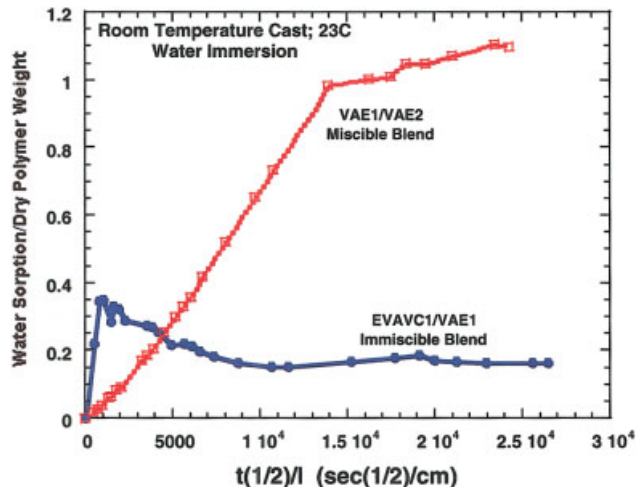


Figure 11 Water sorption results for a 50/50 (w/w) VAE-1/VAE-2 blend and a 50/50 (w/w) EVAVC-1/VAE-1 blend (emulsion-cast and dried at 23°C).

formation process (water removal) would be any different for the blend versus the individual components. Thick specimens were placed on glass plates enclosed by glass retaining rings, and weight measurements versus time in a constant temperature humidity (CTH) room (23°C and 50% relative humidity) were determined. No difference between any of the samples (PVAc-1, EVAVC-1, and a 50/50 blend) was observed. This is not surprising as the percolation network during the film-formation process exists for all samples until the later stage of polymer diffusion across the interface, at which point virtually all the water has evaporated. Another question examined in this study involved the amount of extracted species during the water sorption testing. Weight measurements after over 3 months of immersion followed by drying to a constant weight were compared with the initial dry results. The room-temperature-cast films all showed similar weight losses of approximately 6 wt %. As the time and temperature exposure were increased, the weight loss from the emulsion blend decreased more slowly than for either PVAc-1 or EVAVC-1 as the percolation network persisted, whereas improved film formation in the components made the extraction of water-soluble species more difficult.

CONCLUSIONS

The results clearly demonstrate significant differences in the water sorption behavior for immiscible emulsion blends versus their constituent values and miscible emulsion blend counterparts. The last stage typically noted in film formation involves the diffusion of polymer chains across the interface and, therefore, the elimination of the interfacial regions. This does not occur with immiscible polymers, and so an interfacial region remains that can comprise a percolation net-

work at least at intermediate concentrations. The surfactants and water-sensitive species are expected to be concentrated in the interfacial regions. With water immersion, rapid water diffusion is observed for systems for which the last stage of film formation is not complete. This includes poor-film-formation polymers (e.g., higher T_g polymers) and immiscible emulsion blends. With immiscible emulsion blends, the percolation network persists even with increased time and temperature exposure, whereas single-component, poor-film-formation polymers exhibit improved film formation and lower initial water sorption rates. The water resistance (immersion) of emulsion films is, therefore, a strong function of film-formation characteristics. Excellent film formation yields low initial rates of water sorption but high peak values. Poor-film-formation and immiscible emulsion blends yield rapid initial water sorption but lower peak sorption as the water-sensitive species can diffuse out of the film more easily and, therefore, shift the water sorption equilibrium to lower values.

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