Notes

Atomic Force Microscopy Studies of the Film Surface Characteristics of Poly(vinyl acetate) Latexes Prepared with Poly(vinyl alcohol)

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Synthetic poly(vinyl acetate) (PVAc) latexes prepared by emulsion polymerization using poly(vinyl alcohol) (PVA) as a stabilizer are important industrial products widely used in the paper, paints, coatings, and adhesives industries. The essential feature of such applications is the formation of a continuous latex film. It is now well recognized that film formation from latex involves three stages: (a) evaporation of water resulting in packing of latex particles, (b) their deformation, and (c) coalescence by interdiffusion of polymer chains between adjacent particles.[1] The final stage of the interdiffusion of polymer chains across the particle−particle interface leads eventually to the formation of a coherent film. The nature of this interface thus has a profound influence on the mechanical strength of the film formed.

During drying, as the particles coalesce during the annealing process, the surfactant migrates out of the bulk phase and concentrates at the substrate−film and film−air interfaces. It has been shown that surfactant molecules preferably go to the film−air interface,[2] where they align with their hydrophobic tails pointing toward the air. Calculations from ESCA spectra show that a lacquer film containing 1% surfactant may have an average surface surfactant concentration of roughly 50%.[3] Such a high concentration of a nonchemically incorporated, water-soluble component at the film surface will adversely affect the adhesion properties and the water resistance of the film. The use of surfactants that are either grafted and/or chemically bound to the surface of the particles avoids this problem. This was recently shown in a study using reactive or polymerizable surfactants.[4] Attenuated total reflectance−Fourier transform infrared (ATR-FTIR) spectroscopy was used to study surfactant migration, water absorption, and colloidal properties of latexes prepared with reactive surfactants in heterophase polymerizations. After polymerization, the surfactant was chemically bound to the polymer and desorption from the latex−particle surface could not occur. Migration of the surfactant in the film was hindered.

Since its invention, AFM[5] has become a powerful tool for studying surface structures from the micron scale down to the atomic scale.[6] AFM has been used to study the steps of film formation from latex colloidal dispersions (close-packing, deformation, and coalescence of particles),[7−11] subsequent flattening of particles at the film surface,[12−16] and the exudation of surfactants.[17,18]

For soft samples, such as latexes having glass transition temperatures (T_g) at or below ambient temperatures (≤ 25 °C), the tip-force in the normal AFM contact mode may induce an irreversible destruction of the surface so that imaging itself might become impossible.[19] To overcome such difficulties, noncontact or intermittent contact AFM was introduced.[10,12,20−23] In this method the cantilever oscillates vertically near its resonance frequency, so that the tip makes contact intermittently with the sample surface only briefly in each cycle of oscillation. As the tip is brought close to the sample surface, the vibrational characteristics of the cantilever (i.e., the amplitude, resonance frequency, and phase angle of vibration) change due to the tip−sample interaction. Usually, the feedback mechanism of AFM is controlled by the set-point amplitude ratio, $r_{sp} = A_{sp}/A_0$, where A_0 is the amplitude of the free oscillation and A_{sp} is the set-point amplitude such that during scanning the observed amplitude of oscillation is maintained at A_{sp} by adjusting the vertical position of the sample. Because of its advantages, AFM has been used to measure many organic and biological samples.[24]

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A relatively recent development of AFM allows one to detect shifts in the cantilever's vibration when it interacts with the sample surface.[25] The detection of this shift provides enhanced image contrast, especially for heterogeneous surfaces. Since this mode of AFM is widely used to examine polymer surfaces, it is essential to investigate how image contrast depends on experimental parameters.

This article reports on the investigation of the effect of the degree of blockiness (intramolecular sequence distribution of residual acetyl content) and molecular weight of four different poly(vinyl alcohol)s (PVAs) used in the emulsion polymerization of vinyl acetate (VAc) on the latex film morphology development during film formation as visualized by intermittent contact AFM. Here, determination of spatial variations of height (topographic mode) and interaction (phase shift) allows simultaneous imaging of surface topography and fine morphological features. The AFM images of the PVAc latex films containing PVA reveal different film morphologies and packing structures, as revealed by the surface roughness (root-mean-square, R_{rms}, and average, R_a), which is dependent on the degree of blockiness and molecular weight of the PVA used. As such, the degree of surfactant migration to the surface (extent of bonding/grafting) differed for the four different PVAs and a correlation between the grafting and surface roughness was investigated. The latexes were previously synthesized and the particle size and degree of grafting determined.[26] The particle size distributions were found to range from 20 to 100 nm and were bimodal. The amounts of grafted PVA and PVAc were determined as a function of fractional conversion in emulsion polymerizations of VAc carried out employing the two PVAs differing the most in blockiness (Poval 217 vs 217EE). The PVAc grafted by polymerization onto the PVA stabilizers increased similarly with conversion, particularly approaching the end of each reaction. Similar amounts of PVAc were grafted in the final latexes (37−39%). The amounts of PVA onto which the grafting occurred, however, differed significantly, whereby the more random PVA (Poval 217) had about three times the extent of grafting as the more blocky PVA (∼30% vs ∼10%), as described elsewhere.[26,27] The lower molecular weight PVA (Poval 205) was also studied in the same manner and found to be grafted to an even greater extent (∼39%).

Experimental Section

Materials. Three different PVA samples with different degrees of blockiness [Poval 217 (low), 217E (medium), and 217EE (high)] and similar degrees of polymerization (DP ∼ 1750) were used in this study. A low molecular weight Poval 205 with a degree of polymerization of ∼480 and a similar degree of blockiness to that of Poval 217 (low) was also used in this study. These partially hydrolyzed PVAs (87−89% hydrolyzed, as characterized by the supplier) were all obtained as samples from Kuraray Co. Ltd., Japan. The average degrees of hydrolysis of the Poval samples and their blockiness indexes were determined by ^{13}C NMR spectroscopy as reported previously.[28] Latex preparation was described elsewhere.[26]

Atomic Force Microscopy. Latex films were prepared by applying 3 drops of the latex on a glass microscope slide, which had been carefully cleaned with chromic acid. The latex films were cast at room temperature (25 °C) and allowed to dry for 3 days in a desiccator before imaging with AFM. The PVA/PVAc weight ratio was 0.424. AFM experiments were performed at ambient conditions (ca. 25 °C, relative humidity of 30−40%) using a CP Autoprobe AFM from TM Microscopes (formerly Park Scientific Instruments). The height and phase images were obtained simultaneously while operating the instrument in the intermittent contact mode. A silicon cantilever with a force constant of 17 N/m was used. Images were taken at the fundamental resonance frequency of the Si cantilever of 340 kHz. Images were recorded with typical scan speeds of 0.5−0.7 line/s, and a first-order flattening was applied. It is important to note that the set-point amplitude ratio was kept the same for all the experiments. To obtain images that are typical for each sample, the samples were screened at 4 μm × 4 μm scan size, and representative areas were selected. Then, smaller areas were scanned, down to 0.5 μm × 0.5 μm. The digital resolution of all images is 256 × 256 points.

Results and Discussion

Film Formation. During drying of a latex film, any chemically bound or grafted surfactant would remain at the surface of the polymer particles, whereas the physically adsorbed surfactant may either remain adsorbed at the particle surface or phase separate from the polymer. If the surfactant undergoes phase separation, the water flux may carry it to the film surface. Alternatively, it may accumulate in the interstices between the particles. From there it can migrate to the film−air or film−substrate interface through a long-term exudation process.

The mobility of surfactants during film formation has been the subject of many studies. In this study, AFM was used to observe the surface morphology of the films directly and to monitor possible migration of unanchored (ungrafted or physically adsorbed) PVA.

Morphology of PVAc Latex Films Made with PVA. Topographical images of 0.5 μm × 0.5 μm scans were used to obtain information of the PVAc latex films stabilized with PVA. These are shown in Figure 1. The same *x*−*y* scales are used in all the images while the *z*-dimension varies slightly and is plotted at approximately 15 times larger magnification than the *x*- and *y*-dimensions. It is observed that as the degree of blockiness and molecular weight decreased, the surface smoothness of the films increased. Indeed, the root-mean-square surface roughness (R_{rms}) and average surface roughness (R_a) generally increased with degree of blockiness and molecular weight of the PVA, as shown in Table 1, except for the PVA with the highest degree of blockiness. The R_{rms} values for the films containing Poval 217E and Poval 217EE were found to be approximately 2 times larger than that given for Poval 205. For Poval 205 (low MW and low degree of blockiness), the overall film surface was fairly smooth. The R_{rms} and R_a (surface roughness) values of these films were rather low, 15 nm, compared to 39 and 32 nm for Poval 217E and 217EE, respectively. The surface roughness is seen in Figure 2 to decrease with increasing degree of grafting for three latexes prepared with different PVAs. This might be explained by reduced phase separation of the PVA from the PVAc at the film surface whereby the grafted PVA acts as a compatibilizer between the two materials, thus leading to a smoother film.

The AFM phase image sequence displayed at two scan sizes in Figure 3 shows the effect of the degree of blockiness and molecular weight of the PVAs on the surface morphology development in PVAc latex films. For heterogeneous samples, AFM phase imaging[25] provides compositional maps because of its sensitivity to variations in local material properties. In AFM phase imaging, the difference between the phase angle of vibration of the free oscillating

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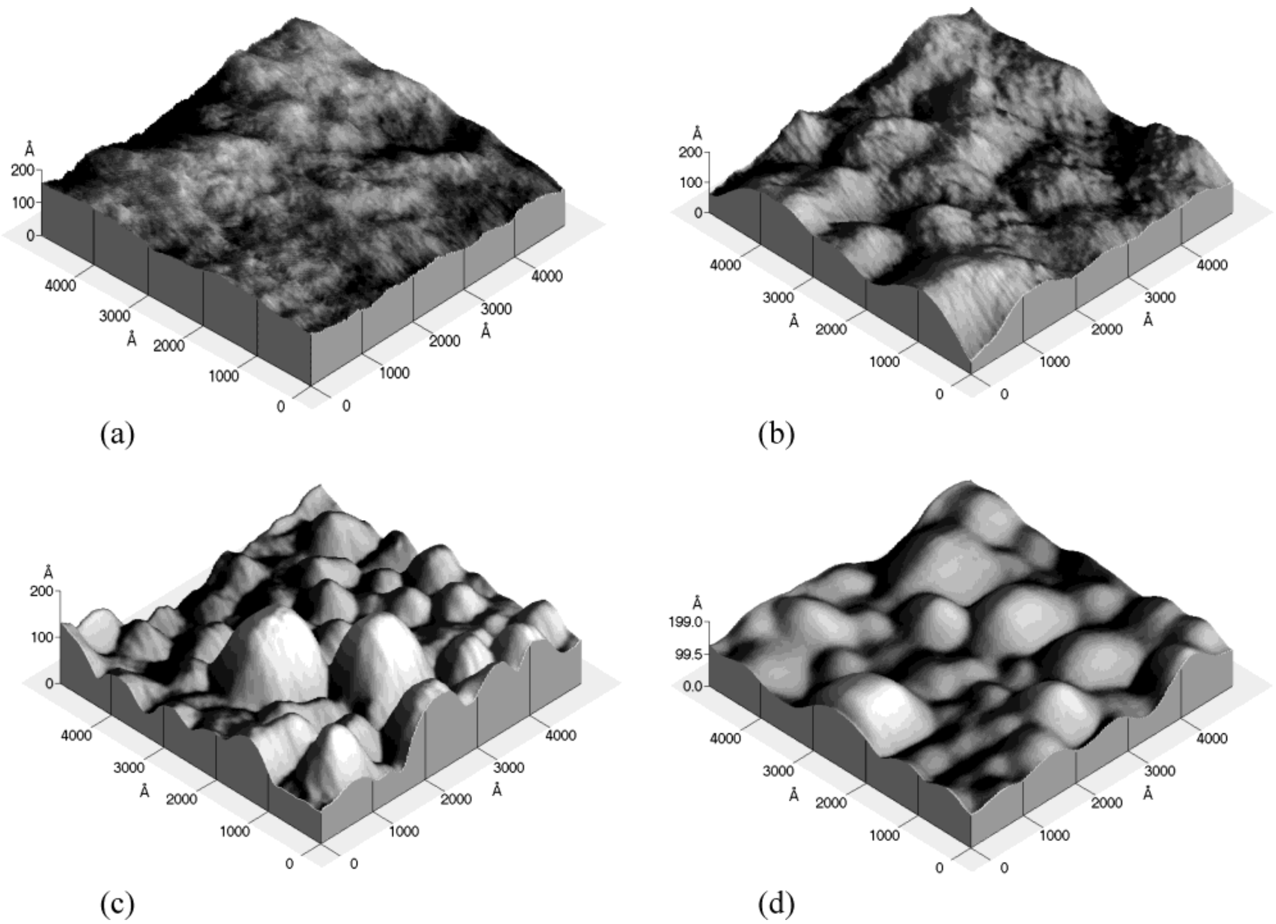

Figure 1. Three-dimensional topographic (height) images of PVAc latex films prepared using PVA/VAc weight ratio = 0.424: (a) Poval 205 (low MW, low degree of blockiness); (b) Poval 217 (medium MW, low degree of blockiness); (c) Poval 217E (medium MW, medium degree of blockiness); and (d) Poval 217EE (medium MW, high degree of blockiness) PVA. The scan size is 0.5 μm × 0.5 μm.

Table 1. Surface Roughness of PVAc Latex Films as a Function of PVA

Poval PVA	mol wt[a]/degree of blockiness	rms roughness 0.5 μm × 0.5 μm, R_{rms} (Å)	avg surface roughness 0.5 μm × 0.5 μm, R_{a} (Å)
205	DP ~ 480/low	14.9 ± 2.0	11.7 ± 2.0
217	DP ~ 1750/low	24.3 ± 2.0	19.4 ± 2.0
217E	DP ~ 1750/med	39.3 ± 4.0	30.7 ± 4.0
217EE	DP ~ 1750/high	32.3 ± 4.0	24.3 ± 4.0

[a] DP ~ 480 = low molecular weight; DP ~ 1750 = medium molecular weight.

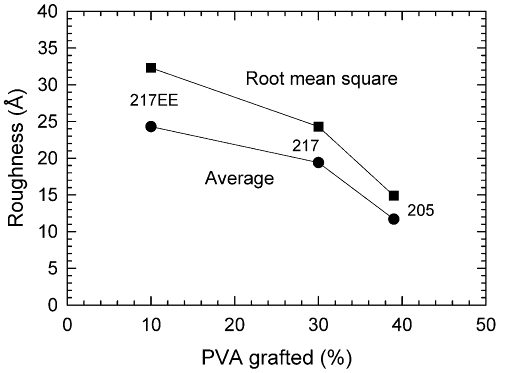

Figure 2. Surface roughness of latex films as a function of the amount of PVA grafted during emulsion polymerization of vinyl acetate using Poval 205, 217, and 217EE as stabilizers.

tip and the phase of the tip as it interacts with the sample surface describes the characteristics of the tip−sample force interactions. Monitoring these phase changes allows one to obtain the above-mentioned compositional maps. It should be noted, however, that the assignment of the cause of the phase contrast to specific property differences of the sample components can be difficult.[29] Nevertheless, the ability of AFM phase imaging to differentiate the local mechanical and adhesive differences and the high sensitivity of the phase contrast to sample composition has been demonstrated.[30]

A very contrasted picture is obtained in the phase mode. Here, one can clearly identify near spherical particles (black, low phase shift) that are embedded in a continuous matrix (white) (see Figure 3). The phase images shown in Figure 3 (right) of the 0.5 μm × 0.5 μm scan complement the set and essentially repeat the contrast of the topographical (height) images shown in Figure 1.

In these examinations, the different mechanical or viscoelastic properties of the films are primarily reflected in the phase mode. The assignment of the various shades of gray to more soft and hard regions is not clear at first

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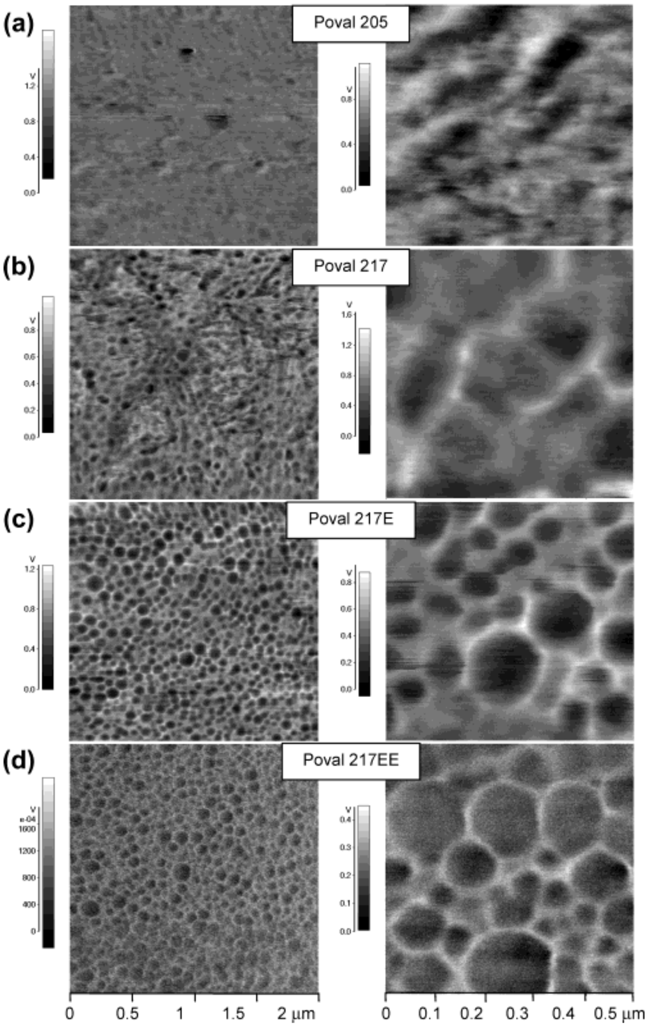

Figure 3. Phase images of PVAc latex films prepared using the same PVA/VAc weight ratio of 0.424: (a) Poval 205, (b) Poval 217, (c) Poval 217E, and (d) Poval 217EE PVA. The scan sizes are 2 μm × 2 μm (left) and 0.5 μm × 0.5 μm (right).

glance, because the contrast inverts below a critical distance of the tip from the surface.[31]

In Figure 3, the phase images show domain structures in dark contrast. For the 0.5 μm × 0.5 μm scans, the contrast difference between the domain structures and their surroundings is enhanced in the height and phase images, Figures 1 and 3 (right), respectively.

In the AFM phase images of the PVAc latex films (Figure 3), the individual particles can be distinguished for Poval 217E and 217EE. The PVAc particles appear in darker contrast in the phase image. This assignment is based on the fact that the crystalline PVA molecules are more rigid than those of PVAc. In many cases for a particular choice of measurement parameters, a brighter phase contrast is expected for stiffer materials, as described in the literature.[25] This demonstrates that free PVA forms a dense film containing isolated embedded PVAc nanoparticles, which are uniformly dispersed in the PVA matrix. In the phase image, the softer amorphous PVAc appears in dark contrast, whereas the more rigid crystalline PVA gives brighter contrast. This illustrates the high amount of PVA relative to PVAc at the surface of these films. This is primarily due to the differences in the blockiness and MW of the PVA which lead to differences in hydrophobicity that influence both the degree of grafting and adsorption of the PVA and the migration behaviors (mobility) of the PVAs. It has been shown in a prior publication[26] that, in the latexes prepared using the lower degree of blockiness PVA (Poval 217), there is a higher degree of grafting. Since grafting is an aqueous phase event in the emulsion polymerization of vinyl acetate, this suggests that the lower degree of blockiness PVA is more hydrophilic and thus more available in the aqueous phase for grafting to occur. The higher degree of blockiness PVA (Poval 217EE) would be more hydrophobic and would have a stronger tendency to become adsorbed on the PVAc, resulting in less being available in the aqueous phase for grafting to occur. Similarly, during the drying of the latex films as the water evaporates and migrates to the air−film interface, the more hydrophilic PVA, 217, will migrate with the water more so than the more hydrophobic PVA, 217EE. Hence, it is observed that there are clearly defined brighter phases in the interstices where PVA resides for the more hydrophobic 217EE (chemically or physically bound with the particle) and not as defined contrast (dark or bright images) in the phase images with the more hydrophilic 217, which has migrated with the water to the surface and forms a more dispersed layer covering the surface. For the lower MW and lower degree of blockiness PVA (Poval 205), there is a greater number of short chains for the same amount of PVA by weight used in the polymerization. These shorter chains can diffuse more readily (are more mobile). Combined with greater mobility and similar hydrophilicity compared to those of 217, 205 is expected to migrate to the surface more so than 217 (and 217E and 217EE) and spread itself over the highly grafted surface of the particles. And, this is indeed found to be the case, shown by the less contrasted phase image (Figure 3) and smoother film surface in the topographical 3D image (Figure 1) of Poval 205 PVA.

Because this unbound (not adsorbed or grafted) PVA is water-soluble while generally PVAc or grafted PVA is not, films made with these PVAs tend to be less water resistant than films containing PVA that is highly grafted onto the PVAc particles. In addition, the situation where isolated PVAc particles exist is generally not desired, because such films are porous and have poor mechanical performance compared to that of films containing PVA that is grafted onto PVAc particles.[32]

In comparing the surface topographic images in Figure 1 and the corresponding phase images in Figure 3, it is observed that the surfaces consist of *hills* and *valleys*, which vary in topography (differences in heights and depths) depending on the PVA used in preparing the latex. This morphology suggests migration of PVA to the surface in the following increasing order: Poval 217EE ∼ 217E < 217 < 205 (order of decreasing degree of blockiness and molecular weight of the PVA).

Summary and Conclusions

The surface morphology of a PVAc latex film containing PVA is strongly dependent on the degree of blockiness and molecular weight of the PVA used in the preparation of the latex. The AFM phase images clearly indicate that these latexes contain differing amounts of PVA not attached (adsorbed or grafted) to the particle surfaces. During the drying stage, this more hydrophilic, unbound surfactant migrates with the water to the film surface. The fact that a greater portion of PVA in the latexes made

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with Poval 205 and 217, compared to Poval 217E and Poval 217EE, seems to be present at the surface of the films may be due to the differences in hydrophobicity and the degree of grafting of the PVA to the particles.

On the basis of the results given above, the process of preparing PVAc latex films containing PVA molecules can be described as follows. During emulsion polymerization, adsorption and grafting of PVA onto PVAc latex particles occurs with excess free (unadsorbed) PVA remaining in the dispersion medium as a function of the molecular weight and degree of blockiness of the PVA, as described previously. As the latex dispersion dries upon being cast as a film, the excess free PVA would distribute in the spaces between the latex particles and also at the air−dispersion interface. As the water evaporates, the latex particles would pack randomly and the air−dispersion interface would be transformed into an air−PVA−PVAc interface. Finally, the deformation of the PVAc particles occurs below the surface layer of the PVA as the film dries. During the drying process, free PVA molecules migrate to the surface of the latex film and would be concomitantly concentrated in the *valleys* between the particles and dispersed as a layer covering the surface of the film. The surface morphology of the PVAc latex film containing PVA molecules, particularly the development of *hills* (PVAc particles) and *valleys* (PVA filled interstices), is found for films containing more unbound PVA.

In conclusion, intermittent AFM was used to examine and compare the surface structure and topography of films made from PVAc latexes prepared with PVAs having different degrees of blockiness and molecular weights. It was shown that PVA migration to the interstices between the PVAc particles in the drying process increased in the following order: Poval 217EE ~ 217E < 217 < 205 (order decreasing in degree of blockiness and molecular weight of the PVA). This is seen as a decrease in the extent of appearance of the *hills* and *valleys* in the AFM topographic images and decreasing contrast in the phase images.

All of these experiments not only underline the potential of the applied AFM technique for surface characterization of PVAc latex films but also prove that the differences in PVA blockiness and molecular weight may allow fine adjustment of a mechanically nanostructured latex film.

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