* *First Place Winner in 1996 Roon Awards Competition* *

Mechanistic Considerations of Particle Size Effects on Film Properties of Hard/Soft Latex Blends

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Blends of hard ($T_g \sim 60°C$) and soft ($T_g \sim 0°C$) latexes were studied as a function of particle size ratio (R_{soft}/R_{hard}) and blend ratio (mass soft phase/mass hard phase). Addition of hard phase latex to the soft film forming latex significantly improved block resistance, even at blend ratios as low as 70/30. Film properties were not sacrificed, except at high concentrations of the hard phase (50/50). For a given blend ratio, the particle size ratio had a dramatic effect on the block resistance. For a 70/30 blend ratio, the block resistance of a blend with R_{soft}/R_{hard} = 4.0 was equivalent to that of a control latex having the same overall composition, but with a minimum film temperature 20°C higher than the blend.

The phenomenon can be explained in terms of the bulk and surface contributions to adhesion. The hard phase increases the elastic modulus (G′) of the film. The magnitude of G′ was found to increase with increasing R_{soft}/R_{hard}, an effect that is consistent with percolation theory. The effect of particle size ratio on the surface contribution to adhesion can be explained by particle packing. Visual models indicate that a high apparent surface concentration of hard particles would be expected for a large value of R_{soft}/R_{hard}, given ideal packing conditions. This effect was confirmed by scanning electron microscopy.

INTRODUCTION

The trend toward reducing the volatile organic content (VOC) of architectural coatings is motivating the development of a new generation of low or zero VOC water-based coatings. These latexes form coherent films below room temperature with minimal (or no) coalescent present to function as a plasticizer. While this is easy to achieve using a latex with a low glass transition temperature ($T_g < 10°C$), significant film properties are sacrificed, in particular block resistance. Blocking is the tendency of film surfaces to adhere to one another. In practice, blocking is seen when painted surfaces are brought into contact (e.g., shutting a recently painted window).

The challenge is to develop room temperature film forming latexes which exhibit improved block resistance. One approach is to blend latexes having two distinct glass transition temperatures. The blend is comprised of a low T_g latex (soft phase) which forms a coherent film at room temperature and a latex with a T_g well above room temperature (hard phase). As we will demonstrate, the blended latex exhibits desirable characteristics of both of the blend components.

The use of blended latexes in coatings has been the focus of recent attention. Friel[1] described the blending of a binder latex ($T_g \sim 5°C$) with a hard latex ($T_g \sim 60°C$), where the two constituent latexes were synthesized from the same co-monomers. The weight ratios of the two latexes were such that the soft latex was always present in a greater proportion. Significant improvement in the block resistance of the blends as compared to the soft binder latex alone was reported. It was claimed that the soft latex particle size should be substantially larger than that of the hard latex. Heuts et al., investigated a similar system.[2] They reported results for minimum film temperature (MFT), storage modulus, and hardness as a function of blend ratio. In all of the blend systems discussed, the constituent latexes had equal particle sizes.

Other latex blend technologies are described in the patent literature. Snyder[3] describes blending of a multistage film forming latex and a hard non-film forming

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Table 1—Typical Emulsion Polymerization Recipe (Control Latex)

	Wt%
Reactor Charge:	
Deionized water	41.4
Polystyrene seed latex (30%)	0.6
Monomer Feed:	
Butyl acrylate	26.1
Styrene	24.1
Methacrylic acid	1.0
Aqueous Feed:	
Deionized water	5.2
Dowfax 2EP (45%)	1.1
$(NH_4)_2S_2O_8$	0.3
NH_4OH (28%)	0.2

latex. Schmidt et al.,[4] produced bimodal blends of poly(styrene-co-butyl acrylate) particles; the only differences between the constituent latexes being the particle sizes. It was claimed that the bimodal latex produces a film with superior luster, presumably due to improved packing efficiency of the bimodal latex particles. Buckmann and Bakker[5] described the rheology, film formation behavior, and drying behavior of bimodal latex blends having equivalent glass transition temperatures.

Investigations of the drying rates of blends have been recently published. Winnik and Feng[6] described the drying behavior of blends of hard and soft latexes. They found that blends of hard and soft latexes dried more slowly than the corresponding soft latex alone. This phenomenon was observed up to a limiting ratio of hard/soft particles. These same authors also investigated the transparency of latex films as a function of soft phase T_g and particle diameter.[7]

Boyce et al.,[8] described work in which small quantities of a small particle size latex containing wet adhesion monomer were blended with large-size, low-cost binders such as poly(vinyl acetate-co-butyl acrylate). The advantage of this approach was the achievement of good wet adhesion at low cost due to the very small amount of a cyclic ureido monomer required.

The characteristics of blends made from equal particle size latexes have been thoroughly investigated in reference (2). It was the intention of this research to explore the advantages of blends composed of latexes having different particle size hard and soft components. Single component latex systems were included as comparative controls. Mechanistic considerations of film formation and the resulting film performance were also explored.

EXPERIMENTAL

Emulsion Polymerization

Poly(styrene-co-butyl acrylate) latexes were prepared by seeded, semi-continuous emulsion polymerization in an agitated one-gallon reactor. Reaction temperature was 90°C. The monomer mixture was fed to the reactor over a period of four hours, and the aqueous stream was fed over a period of 4.5 hr. A typical recipe is given in *Table* 1. The surfactant employed was Dowfax® 2A1 (sodium salt of dodecylated sulfonated diphenyl ether). Following polymerization, the latexes were neutralized with 28% NH_4OH to a final pH of 8.6-9.0. The latexes were characterized as described in the following.

Minimum Film Temperature

The method used for measuring MFT followed ASTM Method D 2354-68.[9] Minimum film temperatures for five different latexes were measured concurrently. Four subsequent tests were performed for the same latexes, yielding five replicate measurements which were then averaged. The position of the latexes on the MFT bar was randomized to minimize the effect of air flowrate. This procedure was used to minimize the error associated with the poor reproducibility and subjectivity of the single point determination.

Dynamic Mechanical Spectroscopy

A Rheometrics RDS-II dynamic mechanical spectrometer was used in forced oscillation mode. Film samples were approximately 2 mm thick. A parallel plate geometry (8 mm) was employed. Temperature sweeps were conducted between -20 and 120°C at a frequency of 1 rad·s^{-1}. Prior to each temperature sweep, a strain sweep was performed at the lowest temperature in the range, in order to confirm linear viscoelasticity and to select an initial strain for the temperature sweep. The initial strain selected ranged from 0.02 to 0.03%. The strain was increased throughout the run in order to maintain sufficient signal as the modulus decayed with temperature.

Table 2—Latex Characteristics

Latex	Styrene	Butyl Acrylate	Methacrylic Acid	D (nm)	Tg (°C)	MFT (°C)
C	47	51	2	176	24	25 ± 1
SS	37	61	2	115	10	0.9[a]
SM	37	61	2	306	6	3 ± 1
SL	37	61	2	475	9	1 ± 1
HS	70	28	2	118	62	ND[b]
HL	70	28	2	441	54	ND

(a) Some measured values < 0°C.
(b) MFT values were not determined for the high T_g polymer.

Tensile Testing

Ultimate tensile strength and elongation were measured using an Instron, Model 4501, with a crosshead speed of 0.5 cm·s^{-1}. Testing was done on films 1.3 cm wide, 6.0 cm long and approximately 6 mils thick. Films were cast on PTFE to facilitate removal and then dried and conditioned for approximately 24 hr at constant temperature and humidity (21°C, 50% RH). Six replicate measurements were made. The values reported are the mean ultimate tensile strength and the mean percent elongation at break.

Differential Scanning Calorimetry

Glass transition temperatures were determined by differential scanning calorimetry using a DuPont Thermal Analysis system. Samples were conditioned with a temperature cycle up to 120°C, maintained at 120°C for two minutes, cooled to -40°C, then scanned at 10°C·min^{-1}. The inflection point of the curve was assigned as T_g.

Particle Size Determination

Latex particle sizes and particle size distributions were determined using hydrodynamic chromatography, as described in reference (10). All the latexes were monodispersed. The value reported is the volume median diameter.

Scanning Electron Microscopy

Electron micrographs were obtained on an ISI DS130F field emission gun scanning electron microscope at an accelerating voltage of 3 kV. This technique allows good imaging using a low accelerating voltage, reducing the problem of beam damage in low T_g polymers. Micrographs were obtained of both the “as-cast” latex film surface and liquid nitrogen cryo-fracture surfaces of the film interior.

Block Testing

The procedure employed to evaluate block resistance is comparable to other procedures used by the paint industry. A 6 mil thick film of latex was drawn down on a Leneta chart and dried for 24 hr at room temperature. This yielded a dry film thickness of approximately 3 mils. The dried films were cut into squares ~ 4 x 4 cm^2 and the squares were placed together with film/film contact established. Weights were placed on the specimens yielding a pressure of 0.16 kg·cm^{-2}. Blocking was evaluated after the weights had been in place for one hour, 24 hr, and one week according to the following scale:

10 .... no adhesion, no tack
9 .... very slight tack (aural observation)
8 .... slight tack (aural observation)
7 .... slight picking (visual observation)
6 .... moderate picking
5 .... significant picking
4 .... 0-25% film removal
3 .... 25-50% film removal
2 .... 50-75% film removal
1 .... 100% film removal (i.e., complete failure)

Four evaluations of each sample were made. It should be noted that this procedure differed in some respects from a typical paint test. In such a test, the paints are dried for different lengths of time and then the weight is placed on the specimen for 30 min. This tests the effect of drying time on the evaporation of fugitive coalescents, and is obviously not applicable to the solvent-free systems studied here.

RESULTS AND DISCUSSION

As noted in the Introduction, blending of a hard and a soft latex is reported to yield a film forming latex having good coalescing properties and superior block resistance.[1,2] There are a number of parameters that can be adjusted in a blend system. The parameters considered here include blend ratio (mass soft phase/mass hard phase) and the particle sizes of the constituent latexes.

The characteristics of the constituent latexes are given in *Table* 2. The latexes are identified by a two letter designation, for instance, “SL.” The first letter (S) identifies the latex as soft; that is, it forms a film at room temperature. The contrary being the hard latexes (H), which do not coalesce. The second letter identifies the

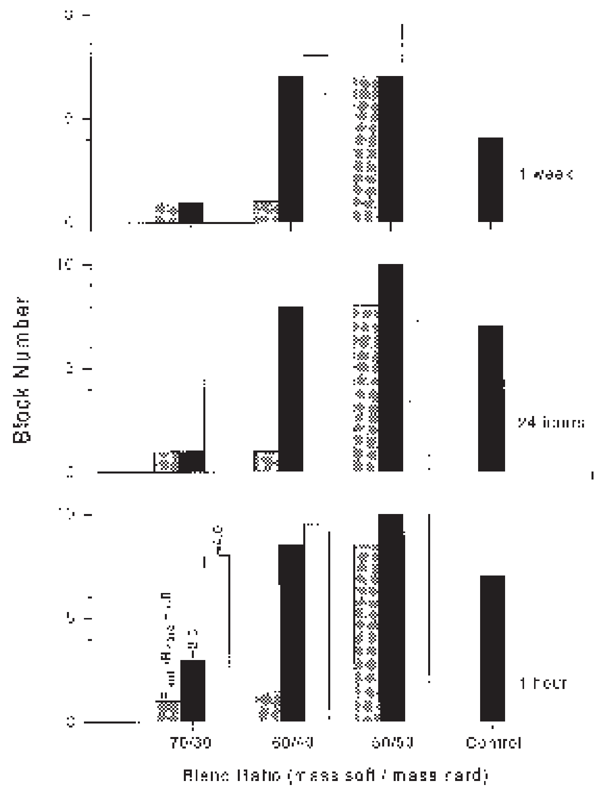


Figure 1—Blocking as a function of blend ratio and particle size ratio for blends with HS hard phase latex.

Table 3—Homogeneous Latex and Latex Blend Performance

Latex/ Blend	Size Ratio Rsoft/Rhard	MFT (°C)	One Hour Block	Tensile Strength (psi)	% Elongation
C	—	25±1	7	1200	290
SS	—	0.9[a]	1	730	780
SM	—	3 ± 1	1	720	770
SL	—	1 ± 1	1	670	770
			Small Hard Phase		
SSS70/HS30	1.0	2 ± 1	1	1040	560
SM70/HS30	2.6	4 ± 1	3	960	380
SL70/HS30	4.0	3 ± 1	8	1070	510
SS60/HS40	1.0	2 ± 2	1-2	ND[b]	ND
SM60/HS40	2.6	8 ± 2	8-9	ND	ND
SL60/HS40	4.0	6 ± 2	9-10	1050	390
SS50/HS50	1.0	6 ± 1	8-9	ND	ND
SM50/HS50	2.6	17 ± 3	10	ND	ND
SL50/HS50	4.0	12 ± 7	10	1230	10
			Large Hard Phase		
SS70/HL30	0.26	2 ± 1	1	740	600
SM70/HL30	0.69	2 ± 1	1	780	630
SL70/HL30	1.08	2 ± 1	1	790	620
SS60/HL40	0.26	2 ± 1	1	670	430
SM60/HL40	0.69	3 ± 1	3	720	370
SL60/HL40	1.08	3 ± 2	1	800	400
SS50/HL50	0.26	4 ± 2	2	790	30
SM50/HL50	0.69	6 ± 1	8-9	770	40
SL50/HL50	1.08	7 ± 1	10	820	270

(a) Some measured values <0°C.
(b) Not determined.

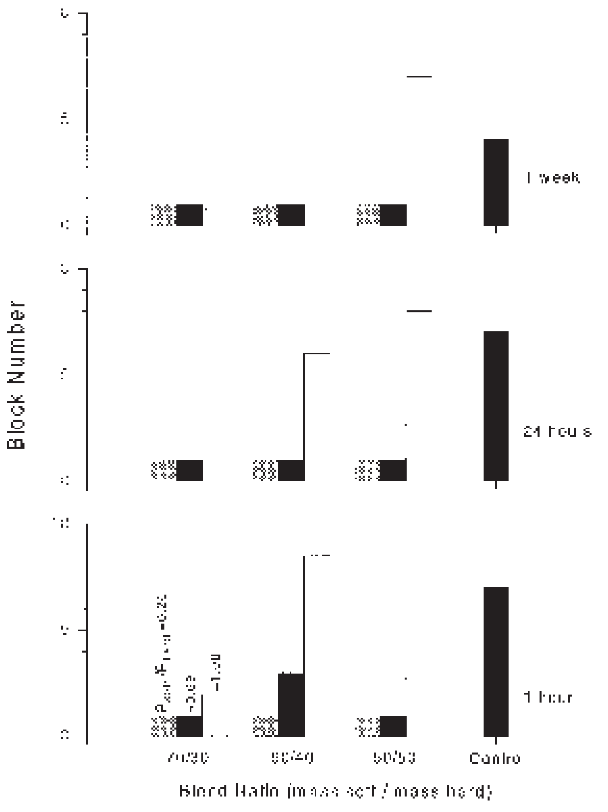


Figure 2—Blocking as a function of blend ratio and particle size ratio for blends with HL hard phase latex.

latex particle size. For instance, SL refers to the soft, large latex. In the case of the soft latexes, three particle sizes were made [small (S), medium (M) and large (L)]. In the case of the hard latexes, only the small and large particle sizes were produced.

The co-monomer ratios used for each of the latexes is given in *Table* 2, along with the latex characteristics. The MFT is reported as the average and standard deviation. The MFT's of the three soft latexes were approximately equal as were the glass transition temperatures of the two hard latexes. A control latex was also designed for this study. It had the same overall comonomer ratio as a 70/30 (mass ratio) blend of the constituent soft and hard latexes.

Blend Ratio and High Particle Size Ratio

Performance characteristics of all the systems studied here are summarized in *Table* 3. The blends are identified by the relative mass ratios of the constituent latexes. For example, blend latex SS70/HS30 is a 70/30 blend of SS (soft, small) and HS (hard, small).

A series of blends was prepared of HS (118 nm) as the discrete phase hard particle with film forming latexes having increasing particle sizes. The results for the nine blends are given in the second section of *Table* 3.

In order for the blend technology to be effective, it is necessary that the blended latex be a low temperature film former. The results of *Table* 3 demonstrate that for high levels of the soft phase, the presence of the secondary hard phase was not detrimental to film coalescence.

For relatively high blend ratios of soft to hard (70/30 and 60/40), the MFT was increased only slightly above the MFT of the neat soft latex (SS, MFT ~ 0°C). The 70/30 blends can be compared with the control latex C, which is a uniform copolymer having the same overall composition as the 70/30 blends. The MFT of C was slightly higher than room temperature (25°C) and would require coalescing solvent in a coating formulation.

As the hard-phase fraction was increased, the MFT also increased. At a blend ratio of 50/50, the influence of the discrete hard phase was evident. The MFT was substantially increased (from 0°C for the base soft latex to > 6°C). The standard deviation of the MFT measurement also increased with increasing blend ratio. This is not surprising, since at high hard-phase fractions, the continuity of the soft phase in the film is not assured. This point will be discussed in further detail in a later section. In effect, the hard phase functions as an inert, non-binding filler. This places practical limitations on the level of the hard phase that can be used.

Films were dried for 24 hr and the block numbers were measured after various lengths of time with the weights in place. Block numbers for one hour are given in *Table* 3. Block numbers for one hour, 24 hr and one week are depicted in *Figure* 1. A block number of 10 corresponds to a completely non-blocking film. A value of one indicates complete failure (off-scale negative). *Figure* 1 shows the blocking behavior as a function of both blend ratio and particle size ratio, R_{soft}/R_{hard}. The effect of the blend ratio on the block resistance was clear. For a given particle size ratio, as the fraction of the hard phase was increased, the block number also increased. This is in agreement with the results of reference (2). Given that the hard phase can be viewed as inert filler, this result was expected.

The effect of particle size ratio was more interesting. *Figure* 1 indicates that the particle size ratio had a significant effect on the block resistance (for a given blend ratio). As the ratio R_{soft}/R_{hard} was increased, the block number also increased. This observation was consistent for all of the blend ratios studied. The results for the 70/30 blends were perhaps the most revealing. The blend (SS70/HS30) having equivalent particle sizes, $R_{soft}/R_{hard} = 1$, failed within one hour. The blend (SL70/HS30) with the highest particle size ratio, $R_{soft}/R_{hard} = 4$, continued to show reasonable performance after one week.

The SL70/HS30 blend can also be compared to the neat soft latexes. The blend and the neat latexes had equivalent MFT's (within experimental error). The neat soft latexes all failed the blocking test within one hour. The addition of only 30% of the HS latex was sufficient to raise the blocking number from one to eight (after one hour). A block number of eight was defined to be slight tack.

The blocking behavior of the 70/30 blends can also be compared to the control latex C, which had the same overall composition. Blend SL70/HS30 and latex C showed equivalent block resistance. However, the MFT of the control latex was 20°C higher than that of blend SL70/HS30 and would have to be formulated with coalescent. It is reasonable to conclude that the latex blend shows highly desirable properties, provided R_{soft}/R_{hard} is large. A mechanistic explanation of this phenomenon will be offered in a later section.

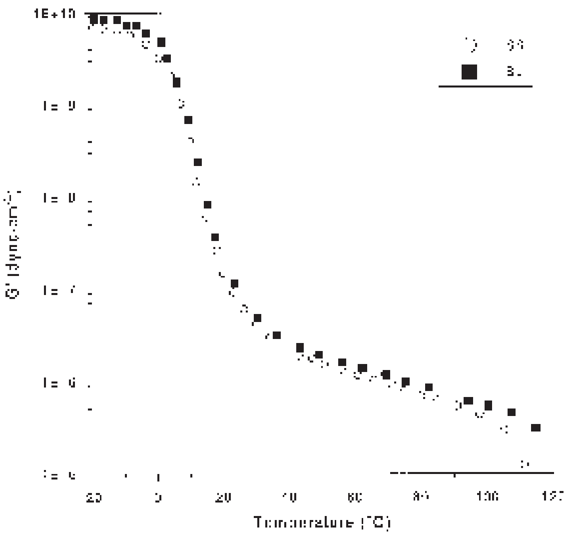


Figure 3—Dynamic mechanical behavior of the soft blend components.

Mechanical properties of the films were also studied (*Table* 3). The tensile strength of the soft latex films increased with the addition of hard phase. However, as the proportion of the hard phase was increased, the elongation at break decreased, from 770% for SL to 510% for SL70/HS30, to 10% for SL50/HS50. In other words, the films became more friable, indicating that the soft phase was not continuous. Film integrity was compromised at very high levels of the hard phase. The maximum tensile strength values of the 70/30 blends were slightly lower than that of the control. However, the elongation at break values were considerably higher.

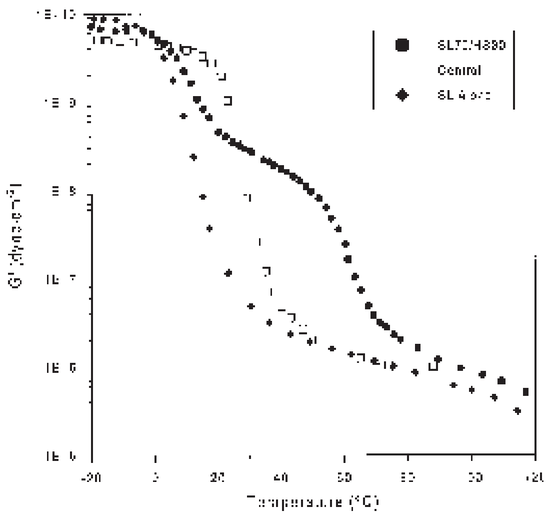


Figure 4—Dynamic mechanical behavior of SL70/HS30 blend, SL alone and control latex.

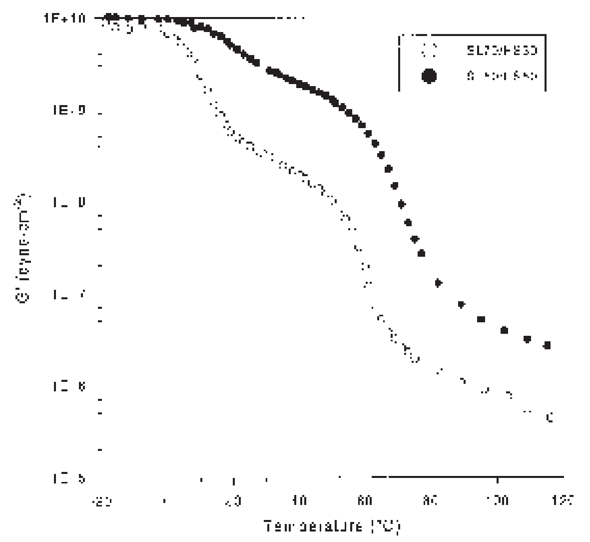


Figure 5—Dynamic mechanical behavior of blends of SS and HS at blend ratios of 70/30 and 50/50.

Low Particle Size Ratio

The effect of particle size ratio was probed further by evaluating blends of the same three soft latexes with a large hard latex, HL. The results are shown in the last section of *Table* 3. The MFT results for the 70/30 and 60/40 blend ratios were similar to those of the blend series with HS. The 50/50 blends behaved somewhat differently, in that the MFT did not increase to the same extent as with HS. This is reasonable, since the number average concentration of the large particles will be much smaller than for the previous series. It would be expected that the soft polymer would form a continuous film with the HL particles embedded in the soft matrix.

The tensile behavior of the blends with a high fraction of soft component was comparable to the neat soft latex. A soft film containing isolated HL particles would be expected to fail in the soft region. The effect of the hard filler is only apparent at high filler loading (50%).

The block numbers for the series are shown in *Figure* 2. The addition of the hard phase did not contribute to block resistance, except at impractical levels (i.e., 50/50) where the film integrity is sacrificed. Overall, the blends performed poorly in comparison with the control. Comparison of the blends of *Figures* 1 and 2 clearly demonstrates the effect of particle size ratio. The blends with a small value of R_{soft}/R_{hard} showed inferior block resistance when compared with blends with a high particle size ratio (for a given blend mass ratio).

Mechanistic Considerations

Blocking (or adhesion) of two chemically identical polymer films in contact can be considered to have both bulk and surface components. The intrinsic adhesive fracture energy is the sum of the contributions of the various failure modes, according to the following general expression[11]:

$$G_o = aG_{o,interfacial} + bG_{o,polymer} + cG_{o,substrate} \qquad (1)$$

In this general expression, $G_{o,interfacial}$ is related to the thermodynamic wetting at the interface. In the case of two polymer films in contact, the interfacial component will be related to the degree of interdiffusion of the polymer chain across the interface. Interdiffusion has been shown to be a function of time and polymer material properties, including molecular weight and T_g.[12-14] In particular, it is related to the difference between the T_g and the annealing temperature. It has been shown,[15-17] that the tensile strength of latex films is related to the degree of interdiffusion during annealing.

The term $G_{o,polymer}$ is related to the cohesive failure of the polymer itself. Finally, the term $G_{o,substrate}$ is related to failure of the bond between the substrate and the polymer film. This failure mechanism can be discounted unless the films delaminate from the substrate, a situation not encountered here. Equation (1) emphasizes that block resistance is likely related both to the surface and bulk properties of the polymer film.

Bulk Film Characteristics

Dynamic mechanical analysis was employed to probe the film structure. *Figure* 3 shows the storage modulus (G') as a function of temperature for both the smallest (SS) and largest (SL) soft latexes. The overlap of these two curves demonstrates that the effect of particle size on blocking is not caused by differences in the neat latexes.

The dynamic mechanical spectra of neat latex SL, control latex C, and blend SL70/HS30 are shown in *Figure* 4. The curves for SL and C are typical of thermo-

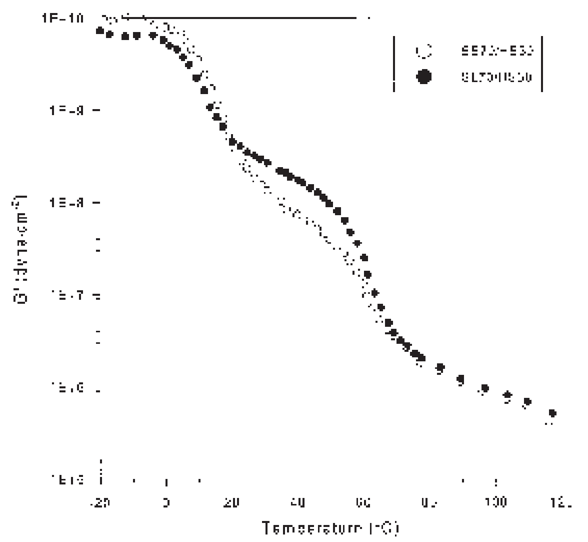


Figure 6—Dynamic mechanical behavior of 70/30 blends as a function of blend particle size ratio.

plastic polymers. The film prepared from the latex blend (SL70/HS30) shows two transitions, which is characteristic of films with two distinct domains. At temperatures between the T_gs of the soft and hard phases, the modulus of the SL70/HS30 is far above that of the soft component alone. This is expected, since the system can be considered as a soft polymer matrix filled with hard spheres. The effect of blend ratio is seen in *Figure* 5. The hard phase has a more pronounced effect as its concentration is increased. This effect is not surprising, and corroborates the work of Cavaillé et al., for poly(styrene)/poly(butyl acrylate) emulsion blends.[18]

The effect of particle size ratio on the dynamic mechanical behavior is shown in *Figure* 6 for blends SS70/HS30 and SL70/HS30. The moduli of both blends are well above that of the neat soft latexes. More interestingly, the two blends do not have the same modulus—temperature curves, despite having identical volume fractions of each phase. The modulus of blend SL70/HS30 with $R_{soft}/R_{hard} = 4$ is significantly higher than that of blend SS70/HS30 with $R_{soft}/R_{hard} = 1$, for temperatures between the two transitions. This is in agreement with the work of Dayong and Jiang,[19] where the elastic modulus of polyepichlorohydrin was found to be a function of the size of the glass beads used as filler as well as the volume fraction of filler. For a given volume fraction of filler, the elastic modulus was found to increase with a decrease in the filler size. In the case of our blend systems, increasing R_{soft}/R_{hard} gives a higher value of the storage modulus at temperatures above ambient, as well as improved block resistance.

Figure 6 shows that the storage modulus of the blends is a function of the soft phase latex particle size. This result is analagous to that of Dickie[20] for a heterogeneous acrylate system. In Dickie's work, the composite was demonstrated to preferentially display the property of the material which forms the continuous phase. For example, Dickie studied a 50/50 blend of a glassy polymer and a rubbery polymer. When the glassy material formed the continuous phase, the modulus was higher than when the rubber formed the continuous phase. The blend produced from latex SL displays more of the hard phase character than the blend produced from SS. This suggests that there is more connectivity of the hard phase in the blend containing SL. The concept of the high T_g particles forming a connected network in the latex film was explored further and was interpreted using percolation theory.

Percolation Theory

One aspect of percolation theory is concerned with the dispersion of one phase in another, a fertile area of research for latex-based coatings. The concept of the critical pigment volume concentration (CPVC) has been examined in terms of percolation theory.[21,22] For latex blend systems, the dispersed phase is the hard latex component. The individual hard particles will remain discrete throughout the film formation process. Provided the concentration of the hard phase does not exceed a critical value, it will be dispersed in a matrix of coalesced soft polymer. In the case of polymer blends, the parameter of interest is often the connectivity of the dispersed phase. In this context, connectivity can be defined to be continuous contact or connection between the hard particles. This is a function of both phase volume and the particle size ratio (R_{soft}/R_{hard}) between the soft matrix phase and the discrete secondary phase. The continuous phase is not necessarily the phase present in the greater

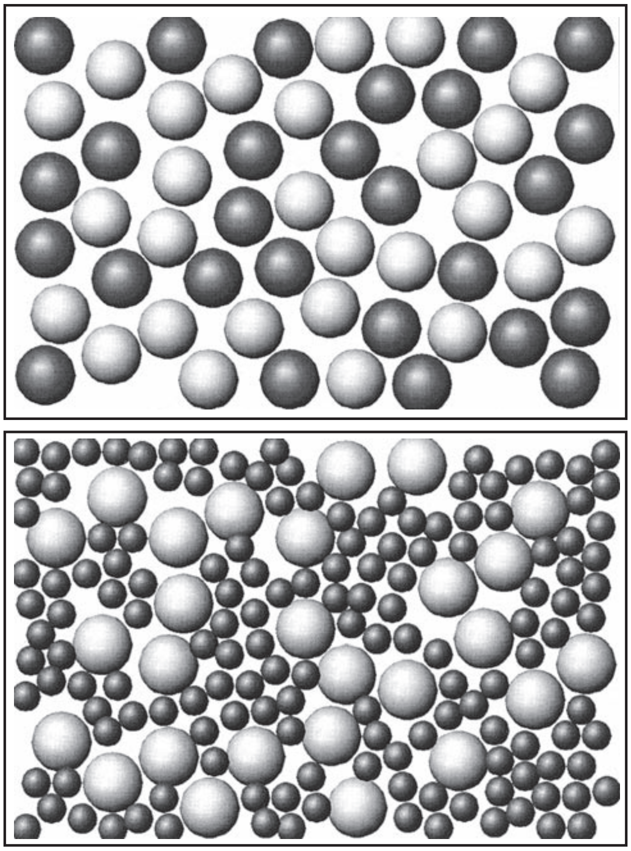


Figure 7—Illustration of the percolation threshold volume, V_p with $V_{soft}/V_{hard} = 70/30$.

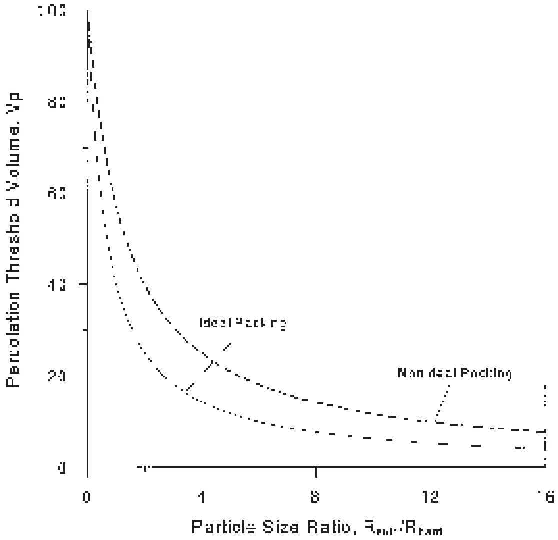


Figure 8—Percolation threshold volume as a function of particle size ratio.

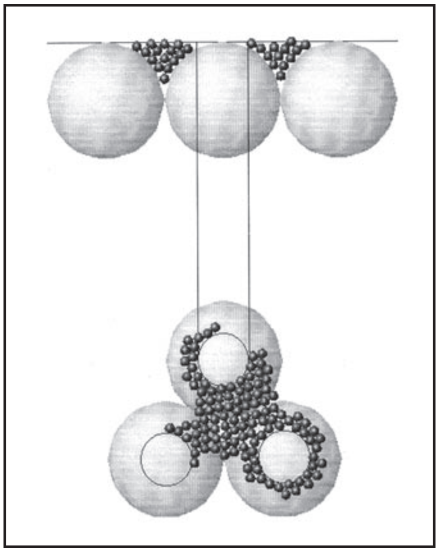


Figure 9—Illustration of particle packing for a 76/24 blend ratio of soft/hard with R_{soft}/R_{hard} >>1.

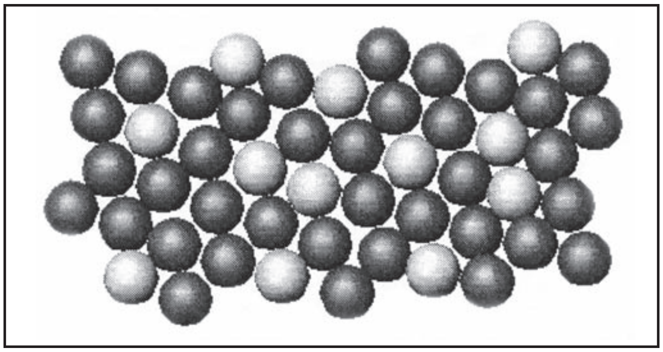


Figure 10—Illustration of particle packing for a 76/24 blend ratio of soft/hard with R_{soft}/R_{hard} = 1.

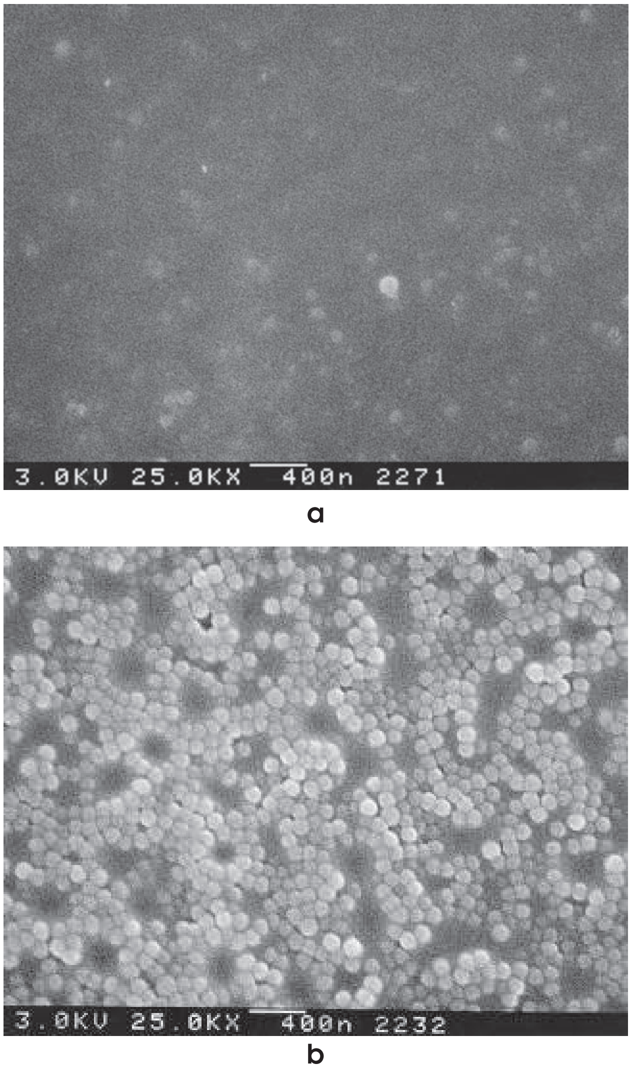


Figure 11—Scanning electron micrographs of the surfaces of 70/30 blends.

concentration, but depends on the volume fraction of each phase and the particle size ratio.

The effect of particle size ratio on the continuity of a network is illustrated in *Figure* 7, where the light-colored spheres represent the soft phase and the dark-colored spheres represent the hard phase. *Figure* 7 is a two dimensional representation of a three dimensional phenomenon. Therefore, the effect is somewhat exaggerated. This illustration depicts two systems where the volume fraction of the soft phase is approximately 0.7. The upper illustration shows that when the two phases have equal particle sizes (R_{soft}/R_{hard} = 1), and the particles are randomly packed, continuity of the secondary phase does not occur. If, on the other hand, there is a marked difference in particle sizes between the particles (R_{soft}/R_{hard} >> 1), the secondary phase forms a continuous network. The lower illustration of *Figure* 7 shows that for R_{soft}/R_{hard} = 2, the hard phase forms a percolated network (continuous hard/hard particle contact). This is an important concept for the design of nonblocking blended latexes, as the presence of networks of hard particles may be responsible for reduced blocking.

For any given particle size ratio, a percolation threshold volume fraction (Vp) exists. This is the minimum volume fraction of dispersed phase material required to form a monolayer network of connected hard particles throughout the film. At concentrations below Vp, continuous contact between the hard particles is not established. This is represented in the upper illustration of *Figure* 7. At concentrations in excess of Vp, the additional particles form multiple layers and fill the interstices between the soft matrix particles. This case is depicted in the lower illustration of *Figure* 7.

Kusy and others have studied the phenomenon in metallurgy, where fine metallic powders are dispersed with polymer spheres.[23,24] Continuity of the dispersed phase is required for electrical conductivity. These authors developed expressions for the percolation threshold volume as a function of the packing arrangement of the dispersed phase, and the fraction of primary phase surface covered by the dispersed phase. In the ideal case, this is simply the volume of the discrete phase required to form a monolayer of contacting particles throughout the matrix. In reality, not all the hard phase particles are efficient: there is a tendency to pack in the soft particle interstices and to penetrate the soft particle surfaces. Kusy has derived an expression for Vp as a function of R_{soft}/R_{hard} for the non-ideal case. Further details and derivations are available in references (23) and (24). *Figure* 8 is a graphical representation of these expressions for both the ideal and non-ideal packing situations, where the hard particles are assumed to pack in a hexagonal arrangement. *Figure* 8 shows the effect of the particle size ratio on the amount of hard phase required for network formation. Kusy's work focused on the percolation behavior of polymer/metal aggregates and, therefore, may not apply quantitatively to latex systems. However, these relationships can be used conceptually to understand the performance of latex blends.

The blocking results presented in *Table* 3 are in accordance with the percolation theory model of the blend systems. As the R_{soft}/R_{hard} was increased, the block resistance of the blend improved. Considering *Figure* 8, it is apparent that increasing the particle size of the hard phase relative to the soft phase (or decreasing the particle size ratio) increases the volume of hard particle required for percolation. For example, in the non-ideal case, when $R_{soft}/R_{hard} = 0.5$ (i.e., the hard particles are twice as large as the soft ones), the percolation threshold volume is ~70%. That is, the latex must contain 70% hard particles in order to form a network. Obviously, this is prohibitively high for coating applications since film coalescence would be prevented. On the other hand, if $R_{soft}/R_{hard} = 4$ (e.g., blends of SL and HS), only 26% of the hard phase is required to form a percolated network. The minimum film and tensile results indicate that there is sufficient coalescence of the soft phase material to form tough, coherent films at low concentrations of the hard phase.

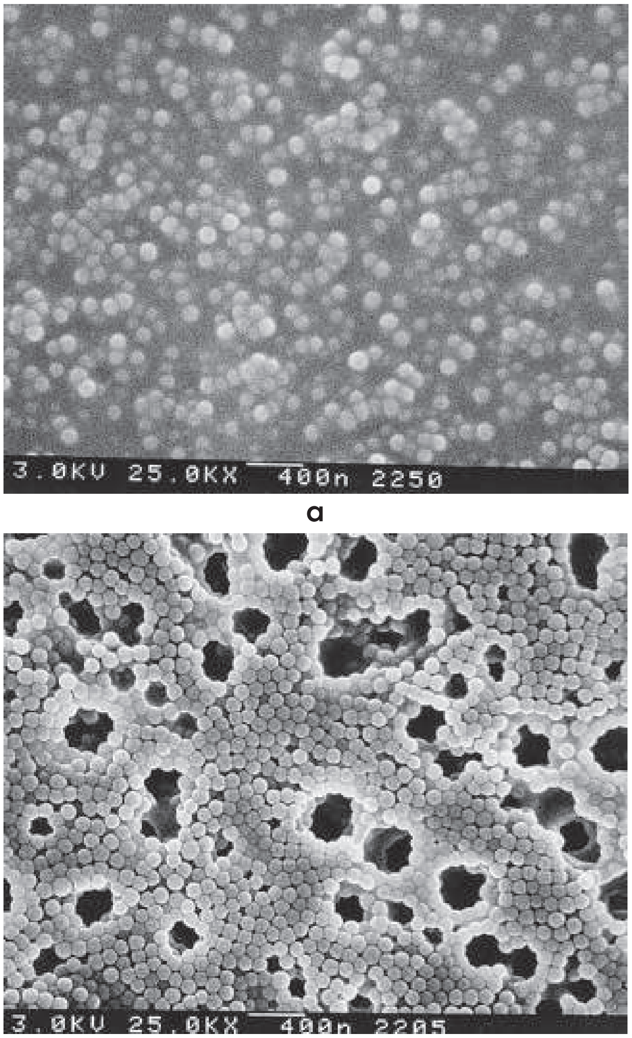
The results of Feng and Winnik[7] are also consistent with a percolation model of latex blends. These authors examined the effect of blend ratio on the transparency of blends of hard and soft latexes. They found that there was a critical volume fraction of soft polymer required to give a transparent film. The critical volume increased as R_{soft}/R_{hard} increased. It can be hypothesized that this should occur, since a continuous network of soft film is necessary for transparency.

The blocking behavior of latex blends has been established to be consistent with a percolation model of film reinforcement by the hard latex phase. However, this mechanistic view assumes that blocking is solely a bulk phenomenon. It is likely to have a surface contribution. Consequently, the effect of particle size on packing at the film surface was also examined.

Particle Packing

An illustration of the surface cross-section of a film with $R_{soft}/R_{hard} >>1$ is shown in the upper illustration of *Figure* 9. The large soft particles are arranged in the closest packing geometry. This configuration represents the most conservative case in the following discussion. The smaller hard particles are packed in such a manner that they fill the void space at the surface. Given closest packing conditions, the void space corresponds to 26% of the volume. This depiction of the surface is then rotated 90° to give the view shown in the lower illustration of *Figure* 9. The excluded circle shown is the only soft phase surface exposed. This can be contrasted with the situation illustrated in *Figure* 10 where the hard and soft particles are of equal size. Here, the amount of the soft phase exposed at the surface is equal to the concentration of the soft phase in the bulk. For instance, the illustration shown is a 74/26 volume ratio with 74% of the soft phase exposed on the surface. These two contrasting examples illustrate the effect of particle size on the relative amounts of the hard latex at the film surface. As the particle size difference is increased, a greater proportion of the hard phase is present at the film surface.

The electron micrographs of actual latex blends match the illustrations of *Figures* 9 and 10 remarkably well and demonstrate that blocking behavior can be explained in terms of surface particle packing. *Figures* 11 and 12 show electron micrographs of the film surfaces of the 70/30 and 50/50 blends, respectively. The hard polymer is visible as discrete particles. The soft polymer has fully coalesced into a smooth film. Micrographs 11a (SS70/



a

b

Figure 12—Scanning electron micrographs of the surfaces of 50/50 blends.

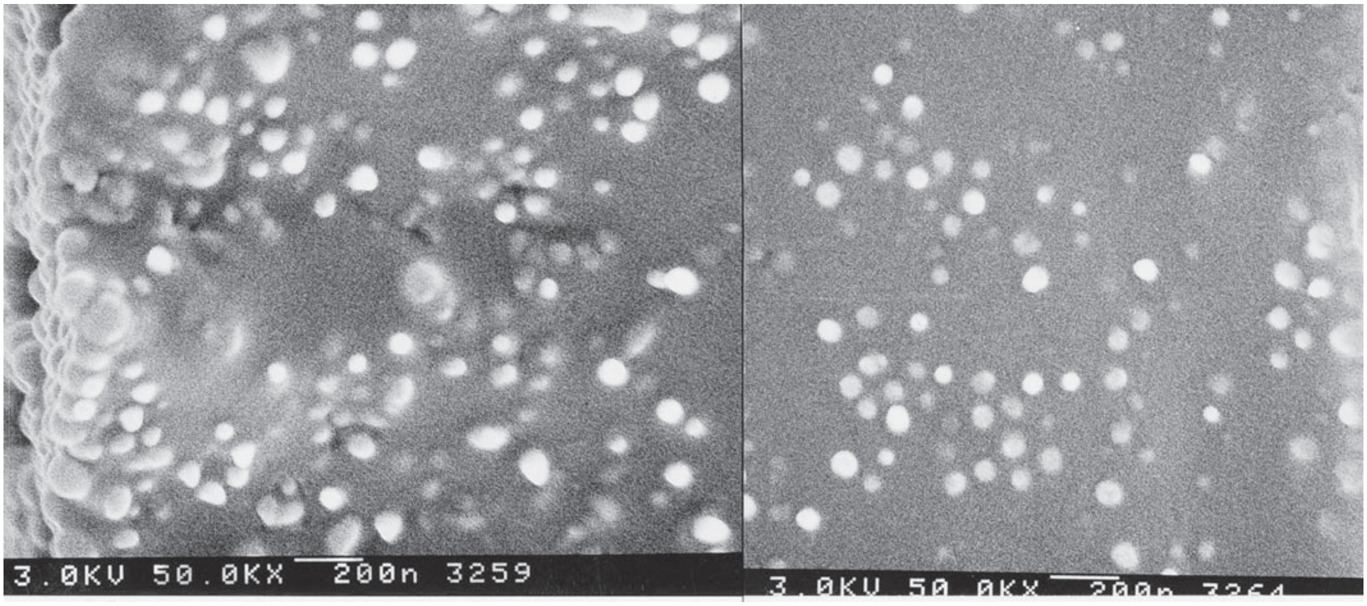


Figure 13—Scanning electron micrographs of a cross-section of SL60/HS40 blend.

HS30) and 12a (SS50/HS50) are for blends of equal size particles ($R_{soft}/R_{hard} = 1$). The hard particles are present at the film surface in the same proportion as in the interior of the film, in direct proportion to their concentration. This would be expected from random packing of compatible latexes having equal particle sizes.

Micrographs 11b (SL70/HS30) and 12b (SL50/HS50) are for blends where the hard particle is small ($R_{soft}/R_{hard} = 4$). These micrographs show that there is a greater concentration of the small-hard particles at the surface than in the comparable film with $R_{soft}/R_{hard} = 1$. Inspection of *Figure* 11b reveals the large soft latex particles surrounded by the small hard particles. This structure is due solely to the particle packing. It appears that there is sufficient penetration of the hard particles into the soft particles to achieve good film formation. The structure of the film in *Figure* 12b is similar to that of *Figure* 11b, in that the soft particles are surrounded by the small hard particles. However, the higher concentration of the hard phase produced some changes in film morphology. The surface shows defects in the form of air voids. It appears that there is insufficient soft binder for good film formation, an observation that supports the tensile testing result.

Figure 13 shows two electron micrographs of a film cross-section of the 60/40 blend (SL60/HS40) where the particle size ratio is again 4. The specimen was prepared by drying the film on a polytetrafluoroethylene (PTFE) substrate. The film was then freeze fractured by submersion in liquid nitrogen. *Figure* 13 shows the cross-section of the film from the top (air interface) to the bottom (PTFE interface). This figure demonstrates that the concentration of the small-hard particles is higher at the film surface than in the bulk (on average). This observation is consistent with the view of particle packing illustrated in *Figure* 9.

The electron micrographs clearly support the concept that a particle size differential (soft/hard) is desirable for enhanced performance in blend systems. The surface is rich in the hard phase component. There is reduced opportunity for diffusion of the polymer chains at the surface, since the effective glass transition is increased. Therefore, adhesion (or blocking) is effectively reduced in the blend, relative to the neat soft film.

CONCLUSIONS

Blends of hard and soft latexes were studied with respect to film block resistance, film formation characteristics, and mechanical properties. It was found that addition of the hard phase improved block resistance without sacrificing film formation or tensile properties, up to hard phase concentrations of 50%. Particle ratio (R_{soft}/R_{hard}) was found to have a dramatic effect on block resistance. For a given blend ratio, the best performance was seen for the highest value of R_{soft}/R_{hard}.

Adhesion between two surfaces has both bulk and surface components. The results presented in this article support a model where the small hard particles produce a percolated network in a blend film. The hard phase acts to reinforce the bulk film, thereby increasing the bulk modulus. In addition, the effective concentration of the hard particles at the film surface is high when the particle size ratio is also high, as shown by scanning electron microscopy. These experimental observations are consistent with a mechanism where a hard particle network structure in the bulk of the film and hard particle packing at the surface of the film act to enhance the block resistance of the film.

The results presented indicate that blending of hard and soft latexes can improve block resistance in neat latex films without compromising other properties. Further experimentation would be required to establish if similar behavior would be observed in formulated paints.

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