High PVC Film-Forming Composite Latex Particles via Miniemulsification, Part 3: Optical Properties

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ABSTRACT: The optical properties of films cast from latexes comprising TiO_2 particles encapsulated in poly(styrene-*co*-*n*-butyl acrylate) prepared by miniemulsification and having high loading (11–70% pigment volume concentration (PVC)) were investigated. Contrast ratio (CR) measurements for all batches showed that a 3 mil film (obtained at 43% PVC) was the minimum thickness at which 98% CR could be achieved. Also, the greatest hiding power (HP) (535 ft^2/gal) was obtained at 43% PVC. In addition, gloss measurements showed that as the TiO_2 loading increased, the gloss decreased, indicating that the increasing amount of TiO_2 contributed to a reduction in the surface smoothness. The effects of surfactant concentration (sodium lauryl sulfate) on the encapsulated particle size and the optical properties of the encapsulated films for the 11% PVC system are described. The effect of varying the sonifier operating conditions on the TiO_2 particle size, encapsulated particle size, and the optical properties of the encapsulated films for the 43% PVC system was also investigated. A comparative study of the optical properties of films cast from encapsulated latex particles with films cast from physical blends of polymer particles and pigment at the same TiO_2 loading and film thickness was made. The optical properties (i.e., CR and gloss) showed a clear advantage of the miniemulsification process over the blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4526–4537, 2006

Key words: miniemulsification; titanium dioxide; microencapsulation; films; gloss

INTRODUCTION

TiO_2 has become the only white pigment of commercial significance because of its optical performance, safety, and cost. It has one of the highest refractive indexes of all materials. It is a very effective scatterer of visible light and therefore, provides great hiding power.[1–7] Mie theory predicts theoretically that there is an optimum pigment particle size for light scattering, below which light scattering decreases as the particle size is further reduced.[8] This theory can be called the single-particle theory because scattering is obtained from single spherical particles. In addition, the theory can be applied precisely only to very dilute dispersions of particles, which is equivalent to 7×10^{-8} pigment volume concentration (PVC).[1,9] This complex theory has not yet been translated from spheres into particles of elongated, angular shapes, from a single, isolated particle to assemblies of many, and from monosize particles to particle size distributions. In practice, some aggregation of primary particles always occurs, and consequently, practical pigment performance is always below that which is theoretically possible. In addition, the formulator is really concerned with "multiple scattering" that occurs with a population of particles. Overall, pigment performance varies with PVC and film thickness.[3,6,10]

Several methods have been applied to calculate the optimum particle size of white pigments that scatter light with a wavelength of 550 nm. It has been found that for rutile TiO_2 in linseed oil, the particle diameters should fall between 0.18 and 0.23 μm (180–230 nm). It was also demonstrated that the optimum diameter decreases with decreasing wavelength of light.[11]

Properties affecting opacity

Opacity may be qualitatively defined as the property of a paint film that enables it to prevent the passage of light and thereby hide the substrate on which it has been applied. Note that opacity is a film property, whereas HP is a property of the whole paint. Hiding is a more general term used frequently to refer to either opacity or HP.[12]

There are a number of pigment variables that may be manipulated to affect the opacity of a system. The major ones are pigment-binder formulation (loading, PVC), refractive index, particle size, and degree of pigment dispersion. The PVC is considered to be the most important variable in that major changes in the opacity of films can be produced by varying it while smaller changes can be made by the pigment particle

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TABLE I
Relationship Between Pigment Volume Concentration (PVC) and Surface-to-Surface Spacing (*S*)

PVC	S^a
5	1.43
10	0.95
20	0.55
30	0.35
40	0.23
50	0.14
60	0.072

[a] *S* is expressed in terms of particle diameters (*d*).

size, mixtures of pigments and extenders, and the type of binder.[13] It was mentioned earlier that Mie theory can be applied only to dilute dispersions of particles. In practical paint systems, however, it has been found that the spaces between pigment particles are seldom greater than the diameters of the particles according to the following relationship:

$$S = \sqrt[3]{\frac{0.74}{\mathrm{PVC}}} - 1.0 \tag{1}$$

$$C = S + 1 \tag{2}$$

where *S* is the surface-to-surface distance between the pigment particles and *C*, the center-to-center distance (units of particle diameter).[1,14] This equation is used to calculate the space that theoretically exists between uniformly dispersed spherical pigment particles of the same size at any desired PVC.[15] Some examples of the surface-to-surface distance in relation to PVC are given in Table I, where *S* is expressed in sphere diameters (*d*). Thus it has been found that, for any size of monodisperse spheres, the average separation is equal to one particle diameter at a PVC of 9.25%. Therefore, the average interparticle distance for this concentration is about 200 nm, and for smaller particles at the same volume concentration the distance is proportionately smaller.[16,17]

The ability of the paint to completely obscure the substrate is known as its HP. It is expressed physically as the area of substrate that is hidden per unit volume of paint; the paint may be white or having color. Since the HP of the paint is due primarily to the pigment in the paint, assessment of HP is one of the fundamental measurements in pigment technology.

One of the common and simple measures of HP is the area of contrasting black and white surfaces that can be obscured to a contrast ratio (CR) of 0.98 (98%) by a unit volume of paint or a unit weight of pigment [eq. (3)]. HP can be determined from the thickness at which a CR of 98% is obtained according to eq. (4).

$$\mathrm{CR} = \frac{\text{Reflectance of film over black}}{\text{Reflectance of film over white}} \times 100 \tag{3}$$

$$\mathrm{HP}(\mathrm{ft}^2/\mathrm{gal}) = \frac{1604.17}{\text{Film thickness at CR (98\%)}} \tag{4}$$

Gloss

Gloss is an important surface appearance property of a material. The degree of gloss often varies with the angle of illumination and/or viewing. Qualitatively, the appearance of surfaces can be classified as high gloss (full gloss), semigloss, eggshell-gloss, low gloss, or matte (flat). For gloss measurements, the illuminating and viewing conditions are chosen to obtain the best discrimination. For instance, angles for illumination and viewing of 10–30° should be used for good discrimination between high gloss surfaces, whereas for semi- and low-gloss surfaces, angles of 60–85° generally provide the best discrimination. The gloss of a material is highly dependent on the roughness of the reflecting surface. Since the presence of particles in a coating can greatly affect its surface smoothness or roughness, the glossiness of such a coating can be quite dependent on pigmentation as will be seen later.[18,19]

Another factor that could affect film gloss is the pigment loading or PVC; as the PVC is increased, there is a point where the particle crowding produces a roughness of the film surface and a resulting loss of gloss.

In this study, the optical properties (CR and gloss) of films cast from latexes comprising polymer-encapsulated TiO_2 particles are evaluated at different film thicknesses and loadings. For comparison, properties of films cast from latex and pigment blends at the same TiO_2 loadings and film thicknesses are also evaluated. The effects of surfactant concentration on the encapsulated particle sizes and optical properties of the films are investigated for the 11% PVC system. Also, the TiO_2 particle size, encapsulated particle size, and thus, the optical properties of the films for the 43% PVC batch are studied as a function of the sonifier operating conditions. This approach of encapsulation by miniemulsification is being evaluated owing to the limitations of the original approach, which applied miniemulsion polymerization to encapsulate TiO_2 particles.[20–24] These limitations included low TiO_2 loading (3 wt % based on the monomer; 0.75% PVC) and a relatively high amount of unencapsulated polymer (free polymer particles). Moreover, the CR measurements showed that all the encapsulated films produced very low CRs, not even close to that needed to achieve HP.

TABLE II
Miniemulsification Recipe for the Preparation of TiO_2-Encapsulated Artificial Latexes

Ingredient	Amount (g)
Water phase	
Deionized water	140
SLS	1.6128 (40 m*M*)[a]
Oil phase	
Toluene	35
Copolymer (St/BA)	2.333–0.34[b,c]
TiO_2	1.167–3.16[c]
Solsperse 32,000	0.389–1.0428[d]
Hexadecane	1.268 (3.62 wt %)[e]

Solids content: 3.68%.
[a] Based on aqueous phase.
[b] St/BA in copolymer: 45/55 wt %.
[c] To prepare encapsulated latexes ranging from 11–70% PVC.
[d] Based on TiO_2 loading: 33 wt %.
[e] Based on toluene.

EXPERIMENTAL

Materials

Poly(styrene-*co*-*n*-butyl acrylate) latex was synthesized by conventional emulsion polymerization, cleaned of surfactant (SLS) and electrolytes, and then used as the encapsulating polymer in the preparation of TiO_2-encapsulated artificial latices by the direct miniemulsification technique.[25] Sodium lauryl sulfate (SLS; Fisher, Pittsburgh, PA), toluene (VWR, Bridgeport, NJ), and hexadecane (HD; Sigma-Aldrich, St. Louis, MO) were used as received. The solid to be encapsulated in this work was TiO_2 (hydrophilic, 30 nm, Degussa, Parsippany, NJ) under the brand name P-25. The TiO_2 sample was dried in a vacuum oven overnight at 110–130°C to remove all the moisture adsorbed on the surface and left to cool in a desiccator for further use. Solsperse[26–29] 32,000 dispersant (100% active; Avecia, Wilmington, DE), a polyamine/polyester,[30] was used as received. Deionized water was used for all experiments.

Analytical methods

For all miniemulsification and dispersion experiments, a sonifier (Branson, Model 450; Ultrasonics, Danbury, CT) was used with a 3/4″ diameter horn. The sonifier functions in two modes: pulsed and continuous. In the pulsed mode, the ultrasonic vibrations are transmitted to a solution at a rate of 1 pulse per second. The pulse duration can be adjusted from 0.1–0.9 s.[31] In all our experiments, the pulsed mode was used. Dynamic light scattering (Nicomp Model 370; Particle Sizing Systems, Santa Barbara, CA) was used to measure both the TiO_2 and encapsulated polymer particle sizes. In all DLS measurements, only the Gaussian distribution was considered unless otherwise noted. A Rotavapor (Model RE 111, Büchi, New Castle, DE) was used at 50°C under vacuum to strip the toluene solvent and also to concentrate the latexes for casting films. A color reflection densitometer (X-Rite 418, Grandville, MI) was used to measure the reflectance of the film over black and white paper. The CR, expressed as a percentage, is obtained from the reflectance of the film over black paper divided by the reflectance of the film over white paper. A Glossometer (Gardco Glossometer, Paul N. Gardner Company, Pompano Beach, FL) was used to measure the gloss at 75°. The thickness of the film cast from the inorganic/polymer composite latex particles was measured using a micrometer (E. J. Cady and Co., Chicago, IL).

Procedure

Preparation of encapsulated artificial latices via miniemulsification

The details of preparation of the poly(styrene-*co*-*n*-butyl acrylate) used in the encapsulation are described in the first article of this series.[25] The recipe for the preparation of TiO_2-encapsulated artificial latexes by the direct miniemulsification technique is shown in Table II. The detailed description of the preparation procedure can also be found in the previous paper.[25] Latexes with varying TiO_2 loadings (11–70% PVC) were prepared. These latexes were used to cast films at different thicknesses, which were then characterized in terms of their optical properties, as will be discussed later.

Preparation of artificial latexes via miniemulsification

Artificial latices were prepared similarly by the direct miniemulsification of the copolymer based on the recipe shown in Table III. The water phase containing SLS was mixed with the oil phase, containing HD and copolymer

TABLE III
Miniemulsification Recipe for the Preparation of Artificial Copolymer Latexes

Ingredient	Amount (g)
Water phase	
Deionized Water	140
SLS	1.6128 (40 m*M*)[a]
Oil phase	
Toluene	35
Copolymer (St/BA)	2.333–0.875[b]
Hexadecane	1.268 (3.62 wt %)[c]

Solids content: 2.57–1.53%.
[a] Based on aqueous phase.
[b] St/BA: 45/55 wt %.
[c] Based on toluene.

TABLE IV
Miniemulsification Recipe for the Preparation of Toluene/TiO_2 Miniemulsion

Ingredient	Amount (g)
Water phase	
Deionized water	140
SLS	1.6128 (40 m*M*)[a]
Oil phase	
Toluene	35
TiO_2	1.167–2.625
Solsperse 32,000	0.389–0.875[b]
Hexadecane	1.268 (3.62 wt %)[c]

Solids content: 2.02–3.41%.

[a] Based on aqueous phase.

[b] Based on TiO_2 loading: 33 wt %.

[c] Based on toluene.

dissolved in toluene, using a magnetic stirrer for 10–15 min at room temperature. Then the crude emulsion was sonified for 3 min. The sonification was performed at an output power of 10 and a duty cycle of 70% and was carried out with the mixture immersed in an ice bath to prevent a substantial increase in the temperature from the high shear. The direct miniemulsification technique was also used to prepare a TiO_2-containing miniemulsion using the recipe shown in Table IV. These two dispersions were mixed together at room temperature for about 30 min using a magnetic stirrer. Then a rotary evaporator was used at 50°C under a slight vacuum to remove the toluene solvent and concentrate the latex for casting films. The materials prepared from these two recipes when mixed together (physical blends of pigment/binder) are equivalent to the 11, 20, and 43% PVC encapsulated miniemulsion latexes.

Preparation of encapsulated latex films

Films with five different thicknesses were prepared from each system (11–70% PVC). The pigmented film thickness is measured in mils (1 mil equals 25 μm). Each latex (30% solids) was poured into a $10.1 \times 8.2 \times 0.1$ cm^3 glass mold and dried at room temperature and 50% humidity for more than 24 h.

Effect of varying the sonifier operating conditions

The sonifier is easy to use and is more effective in reducing the particle size compared to both the Manton-Gaulin and rotor–stator homogenizers. A high energy input is necessary to break the TiO_2 aggregates into small, stable particles. However, TiO_2 dispersions and emulsions with broad size distributions may be produced because the energy input is not uniform, depending on the distance from the sonifier tip and the number of passes under the tip.

The most important property required of a pigment, such as TiO_2, to achieve HP is the particle size. To obtain maximum HP (scattering) from TiO_2 particles dispersed in a film, the TiO_2 particle size that results in the greatest HP needs to be determined. This can be done by first studying the effect of varying the sonifier operating conditions (varying output power at a fixed duty cycle (70%)) on the particle size of the TiO_2 dispersed in the oil phase containing Solsperse 32,000, copolymer, and HD.

The basic recipe used for this study is given in Table II for the 43% PVC batch. This recipe was selected because it was found that pigmented films with 43% PVC gave the minimum film thickness (3 mil) at which 98% CR was achieved. So this study is expected to reveal whether changing the sonifier operating conditions will yield better optical properties in terms of high CR at low film thickness (<3 mils) or not and also what will be the effect on the gloss of the pigmented films.

RESULTS AND DISCUSSION

Optical properties of encapsulated latex films

The CR was determined by measuring the reflectance of an incident light from a film placed on a black and white substrate. In these measurements, the reflectance of the white area of the test substrate was 77.62 and 4.68% for the black area. In paint technology, the CR of the pigmented film has to be measured relative to a known substrate. Standard black and white opacity test substrates are defined in paint technology as having maximum reflectances of 1 and 80%, respectively. In practice, the white area of a commercially available black and white substrate normally deviates somewhat from ideal reflectance of 80%, but eq. (5) is used to correct to that standard:

$$C_{0.80} = f(R_0, R_w, W) = \frac{WR_0(1 - 0.80R_0)}{R_0(W - 0.80) + 0.80R_w(1 - WR_0)} \times 100 \quad (5)$$

where W is the reflectance of the white area of the test substrate, R_w is the reflectance of the paint film over a white area of reflectance W, R_0 is the reflectance of the paint film over the black area, and $C_{0.8} = R_0/R_{0.80}$, the CR when $W = 0.8$.[12]

Figure 1 shows the effect of PVC on the CR as a function of film thickness. It was corrected using eq. (5). In this figure, a zero reading on the y-axis represents complete transparency and a reading of 100 represents total opacity. As the film thickness increased, the CR increased in all systems (11–70% PVC) up to a 98% CR except for the films containing no TiO_2 (i.e., only copolymer). Generally in all the systems, the CR reached the maximum (98%) and then leveled off. The increase in the CR is mainly due to a combination of increasing TiO_2 loading (Table V), the TiO_2 particle

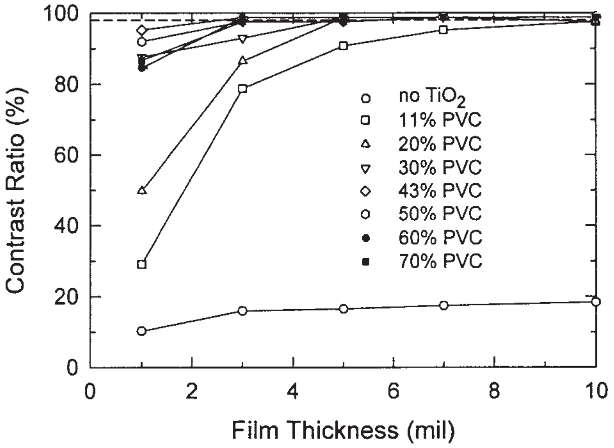

Figure 1 Effect of pigment volume concentration (PVC) on the CR ($C_{0.80}$) as a function of the film thickness. The dashed line represents 98% CR.

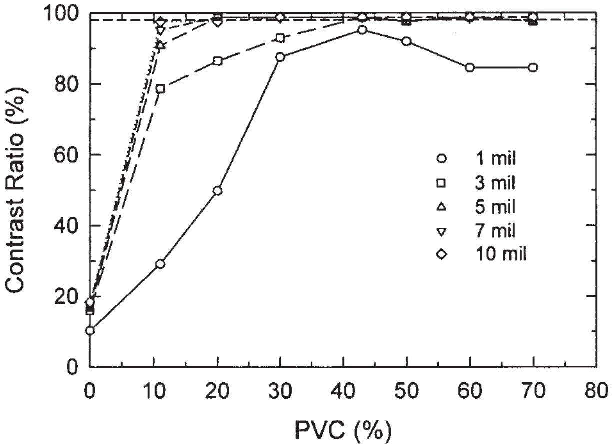

Figure 2 Influence of PVC (%) on the contrast ratio at different film thicknesses.

size, and the interparticle distance in the film. In fact, TiO_2 pigments have the ability to scatter light more efficiently than any other white pigment owing to its high refractive index. It can be seen from Figure 1 and Table V that the 3 mil film for the 43% PVC system was the thinnest film that gave 98% CR (HP) at this TiO_2 loading. However, increasing the pigment concentration (TiO_2 loading) to 70% PVC resulted in the need for a thicker film to reach 98% CR (7 mils). In this case, CR reached 97.5% for the 5 mil film and increased to 98.8% for the 7 mil film. This can be explained by the fact that not only the TiO_2 content (loading) plays a major role in determining the CR (scattering), but also the TiO_2 particle size in the film and its interparticle distance as will be discussed later. In addition, even though the loadings at 20 and 30% PVC and at 43, 50, and 60% PVC are different, they resulted in the same film thicknesses for 98% CR, namely 5 and 3 mils, respectively. One reason for this could simply be that too few samples with various film thicknesses were prepared to be able to distinguish between the various PVCs. Or as mentioned before not only the TiO_2 loading plays a major role in determining CR but rather a combination of all factors including the TiO_2 loading, particle size, and interparticle distance in the film. The theoretical densities of all batches are given in Table V. As the TiO_2 loading increased, the density increased from 1.0340 g/mL for no TiO_2 to 3.8022 g/mL for 70% PVC.

Figure 2 represents another way of examining the results shown in Figure 1, where the CR values are plotted against PVC (%) for different film thicknesses. However, here the CR increases with an increase in the PVC (TiO_2 content) up to 98% CR and then levels off. This graph is important from the design point of view as it helps to select the appropriate PVC system and the film thickness that will best suit the end-use application. For instance, if one would like to select a minimum film thickness that gives 98% CR, it is clear from the graph that the lowest film thickness is 3 mils for 43% PVC and this implies that a 1 mil film cannot be used at all because 98% CR is not achieved at any PVC. In addition, it is also possible to select a low PVC system such as 11% PVC and also select the film thickness that gives 98% PVC, which in this case is 10 mil.

Film thickness values that give 98% CR for each PVC system were determined from Figures 1 and 2

TABLE V
Film Thickness at 98% Contrast Ratio (CR) Resulting from the Contrast Ratio Measurements as a Function of TiO_2 Loading (different PVCs)

PVC (%)	Weight ratio of TiO_2:polymer	Calculated density (g/mL)	Film thickness at 98%CR (mil)
No TiO_2	NA	1.0340	NA
11	1 : 2	2.0560	10
20	1 : 1	2.5671	5
30	1.7 : 1	2.9656	5
43	3 : 1	3.3330	3
50	4 : 1	3.4868	3
60	5.96 : 1	3.6594	3
70	9.29 : 1	3.8022	7

TABLE VI
Calculated TiO_2 Particle Spacing (Standoff Distance) and the Copolymer Layer Thickness on the TiO_2 Particles in the Film as a Function of Pigment Volume Concentration (PVC)

PVC (%)	TiO_2 particle (D_v) (nm)[a]	D[b] (nm)	TiO_2 center-to-center (nm)[c]	Copolymer thickness (nm)[d]	Film thickness at 98% CR (mil)	HP (ft^2/gal)
No TiO_2	NA	NA	NA	NA	NA	NA
11	169	150	319.4	75.0	10	160.4
20	155	84.7	240.3	42.4	5	320.8
30	142	49.9	191.7	25.0	5	320.8
43	131	26.0	157.2	13.0	3	534.7
50	130	18.2	148.2	9.1	3	534.7
60	148	10.7	158.4	5.4	3	534.7
70	140	2.6	142.8	1.3	7	229.2

[a] TiO_2 particle size in the presence of HD and copolymer in toluene after 3 min sonification.

[b] D: TiO_2 surface-to-surface distance in the film (in nanometers) resulting from multiplying S in eq. (1) by the TiO_2 particle diameter (nm) in the dispersion.

[c] Estimated TiO_2 center-to-center distance in the film.

[d] Copolymer layer thickness on the TiO_2 particles in the film equals half of the particle spacing (S).

and the results are tabulated in Table VI. Pigment particle spacing at various PVCs can be determined as shown in Table VI using eq. (1) after applying simplifying assumptions. The particle spacing is the surface-to-surface distance (S, standoff distance) between any two TiO_2 particles in the film. Moreover, the center-to-center distance (C) between any two TiO_2 particles can also be determined using eq. (2). In the case of 74% PVC, where the TiO_2 particles are assumed to be spherical, C is equal to the particle diameter (d). If we increase the center-to-center distance by moving the particles further apart, as would happen with the addition of binder, the space between pigment particles would increase.

The effects of PVC on film thickness at 98% CR, HP (ft^2/gal) [estimated using eq. (4)], and on the particle spacing (S and C) are shown in Figure 3. The upper graph shows that as the PVC level increases, HP increases up to the highest level, 535 ft^2/gal at 43% PVC, and then levels off at 50 and 60% PVC followed by a strong decrease at 70% PVC. This could be explained as pointed out earlier by the interparticle spacing and particle size effects. For the highest CR (scattering) achieved at a low film thickness (3 mil), any increase in loading could either give the same scattering as in the 50 and 60% PVC cases or decrease the scattering as for 70% PVC (less scattering) owing to the effect of crowding. This crowding is a result of the TiO_2 particles being brought so close together that two or more TiO_2 particles behave optically like a single large particle with low scattering. The scattering that led to the highest HP (43, 50, and 60% PVCs) at low film thickness (3 mil) means that most, if not all, of the light entering the film is reflected back and reemerges without having reached the substrate. As pointed out earlier, these three loading levels (43, 50, and 60% PVC) gave the same film thickness and thus the same HP, although it is believed that among these, there might be a maximum HP. A more detailed study is needed to determine this. As can be seen from Table VI, 43% PVC has a HP value of 535 ft^2/gal compared to 160 ft^2/gal for 11% PVC and 229 ft^2/gal for 70% PVC. This means that 1 gallon of latex prepared at 43% PVC has the ability to completely hide 3.3 and 2.3 times the area of the substrate compared to 11 and 70% PVC, respectively, while maintaining 98% CR.

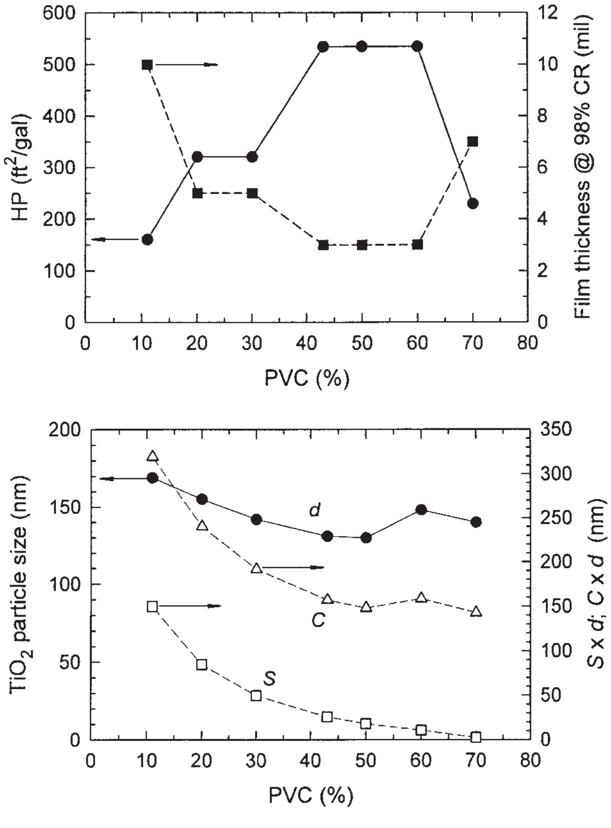

Figure 3 Effect of pigment volume concentration (PVC) on (top panel) HP (ft^2/gal) and film thickness required for 98% CR and (bottom panel) S and C relative to the average TiO_2 particle size ($d = D_v$).

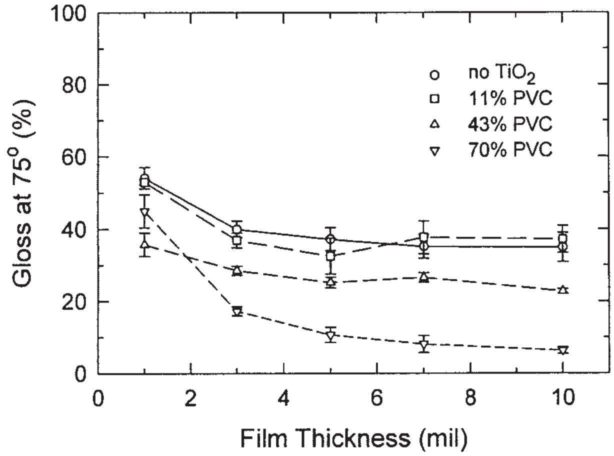

Figure 4 Effect of pigment volume concentration (PVC) on the gloss as a function of film thickness.

It is well-known that powders do not have significant gloss; only continuous surfaces can be glossy. Particulates in paint films, such as pigments, extenders, and some additives, reduce gloss by their contribution to surface roughness. Therefore, the greater the amount of particulates that are present in the film, the lower is the expected gloss.[10] Figure 4 shows the effect of PVC on the gloss (measured at 75°) as a function of film thickness. The thickness of the nominal 1 mil films in all systems was not notably uniform, most likely being the result of uneven drying during the film formation process because of the low solids content. This would explain the variation in the gloss results at this film thickness, as shown in Figure 4. The gloss of clear films (i.e., no TiO_2 present) at various film thicknesses is slightly higher than the ones that contain TiO_2 except for the 11% PVC films at 7 and 10 mils where the gloss is slightly higher, although within experimental error. As the film thickness increased, the gloss generally decreased in all films up to a certain film thickness and then leveled off. In addition, the gloss results show that as the TiO_2 loading increased, the gloss decreased indicating that the increasing amount of TiO_2 adversely affects the surface smoothness.

The importance of the critical pigment volume concentration (CPVC) lies in the fact that it represents a transition point between nonporous and porous films. A highly disperse system shows a high CPVC while a poorly dispersed system shows a low CPVC. This is related to the fundamental packing characteristics of the pigment, which are determined by many properties, such as size distribution, shape, and surface characteristics.[32] The high value of the CPVC (~60% PVC as inferred from Fig. 3) in our system is an indication that it is a highly disperse system, achieved by using the sonifier and a good stabilizer (Solsperse 32,000).

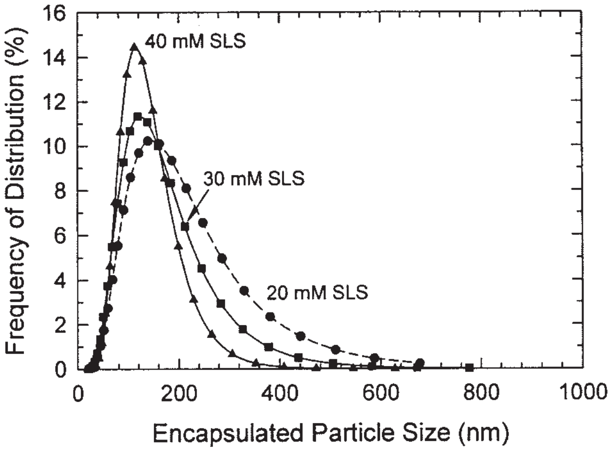

Figure 5 Effect of SLS concentration on the encapsulated particle size.

Effect of SLS concentration

Emulsifiers are used to reduce the interfacial tension between the two immiscible liquids and thus reduce the amount of mechanical work required to break the discontinuous phase into dispersed droplets. Their presence at the interface also decreases the rate of coalescence of the dispersed phase. Experiments were carried out using the model miniemulsification recipe (Table II) with varying levels of the surfactant (10, 20, 30, and 40 m*M* SLS) for the 11% PVC system. It was noted that there was some phase separation after emulsification when the SLS concentration was 10 m*M*. This may indicate that the minimum surfactant concentration that gives stable encapsulated TiO_2 particles lies somewhere between 10 and 20 m*M* SLS. The effect of surfactant concentration on the encapsulated particle size is shown in Figure 5. As expected, the average size decreased with increasing SLS. The effect on the CR is shown in Figure 6. These results show

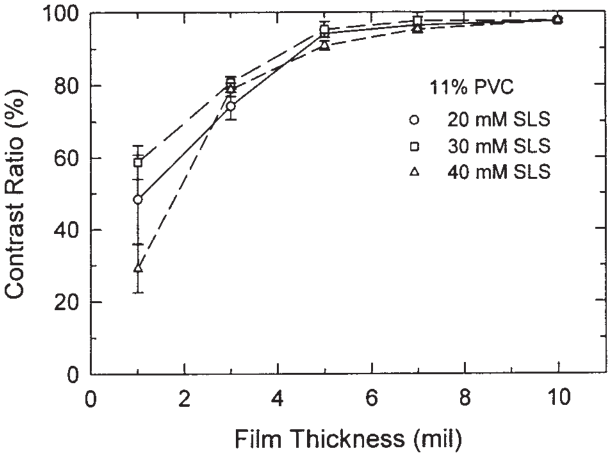

Figure 6 Effect of SLS concentration on the contrast ratio of encapsulated latex films prepared from 11% PVC latex.

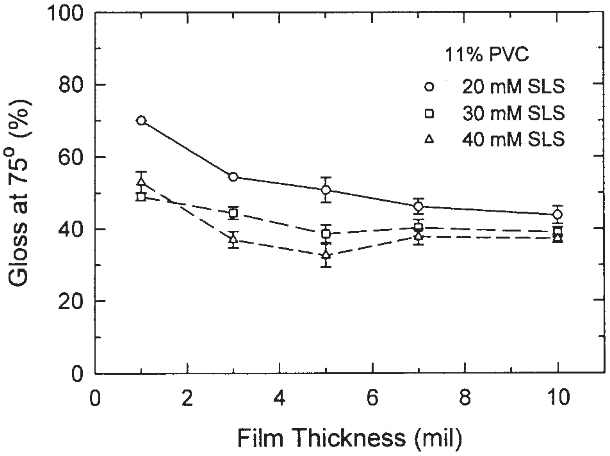

Figure 7 Effect of SLS concentration on the gloss of encapsulated latex films prepared from 11% PVC latex as function of film thickness.

that there is no significant effect on the CR and in all cases 98% CR was achieved at 10 mil film thickness. There were differences in the CRs at low film thicknesses, although these are attributed to experimental errors owing to the low film thickness. As the film thickness increases, the differences become smaller.

The effect of the SLS concentration on the gloss is shown in Figure 7. There is a significant effect of surfactant concentration on the gloss, in contrast to the CR results. The reason for this probably lies in the migration of the surfactant to the film surface during the film formation process resulting in a decrease in the gloss as the surfactant concentration was increased.

Optical properties of films cast from blends

As pointed out earlier, TiO_2 is added to coatings to obtain HP as a result of light scattering. Since TiO_2 is one of the more expensive components of a water-borne paint, it is important that it be used effectively. Encapsulation is considered to be the best way to achieve this owing to certain expected benefits including better pigment particle dispersion in the polymer matrix and improved effectiveness in light scattering in the paint film. However, in a film cast from a blend of polymer particles and pigment particles, a loss in scattering would be expected from any pigment–pigment contact. Thus, any agglomerates of pigments already present in the wet paint film or formed by flocculation during the drying process will result in reduced scattering of the dispersed pigment particles. The purpose of these experiments is to compare the optical properties of the films prepared from encapsulated TiO_2 particles and conventional blends using the recipes shown in Tables II–IV for 11, 20, and 43% PVC systems.

The simplest inorganic polymer composite is a physical blend of a polymer and inorganic particles. However, the problem often encountered is the aggregation of TiO_2 particles during film formation resulting in a decrease in the light scattering. This can be attributed to the poor compatibility between the inorganic particles and the matrix polymer. To check if this phenomenon is occurring in our system, a blend was prepared with the same ingredients and ratios as in the encapsulated latexes and films were cast to measure the optical properties at different film thicknesses.

A comparison between the optical properties of the films cast from encapsulated latex particles with films cast from the blends at the same TiO_2 loading and film thickness for 11, 20, and 43% PVC are shown in Figure 8. As the film thickness increased, the CR increased in both systems. However, for the 11% PVC blend (top), CR did not reach 98% as compared to the 11% PVC miniemulsion system, which reached 98% CR at 10 mil film thickness. On the other hand, Figure 8 (middle) shows that for a 5 mil film thickness, the 20% PVC miniemulsion achieved 98% CR, while the 20% PVC blend never reached 98% CR even at the 10 mil film thickness. Moreover, in both systems, the CR resulting from the encapsulated particles is higher than that obtained from blends for all film thicknesses. This indicates that by using the encapsulated TiO_2 even at a low loading, such as 11% PVC, one can obtain 98% CR. However, using the blend, this cannot be achieved even at a higher loading (20% PVC). These results clearly show the advantage of the encapsulated TiO_2 over blends in terms of the ability to hide the substrate at low TiO_2 loading (low PVC). The reason that the blends did not achieve 98% CR is probably the result of agglomeration of TiO_2 particles during film formation, which can be attributed to the poor compatibility between the inorganic particles and the matrix St/BA copolymer, resulting in less scattering (low HP).

Going one step further, we compare the HP of the encapsulated films with blends at 43% PVC. Figure 8 (bottom) shows that as the film thickness increased, the CR increased in both systems. However, for the 43% PVC miniemulsion, CR increased as the film thickness increased up to 98% CR, which was determined to be at a 3 mil film thickness compared to the 43% PVC blend system, which reached 98% CR at a 7 mil film thickness. Moreover, in the encapsulated systems, the resulting CR is higher than that obtained from the blend for film thicknesses up to 5 mils. This result confirms the advantage of encapsulated latex films over blend films in terms of their ability to hide the substrate at a lower film thickness, namely at 3 mils versus 7 mils at 43% PVC.

A comparison between the gloss (75°) of the films cast from encapsulated particles and blends for different TiO_2 loadings (PVCs) and different film thicknesses is made in Figure 9. The positive contribution of encapsulation is shown at all three TiO_2 loadings in terms of the formation of smoother surfaces (i.e.,

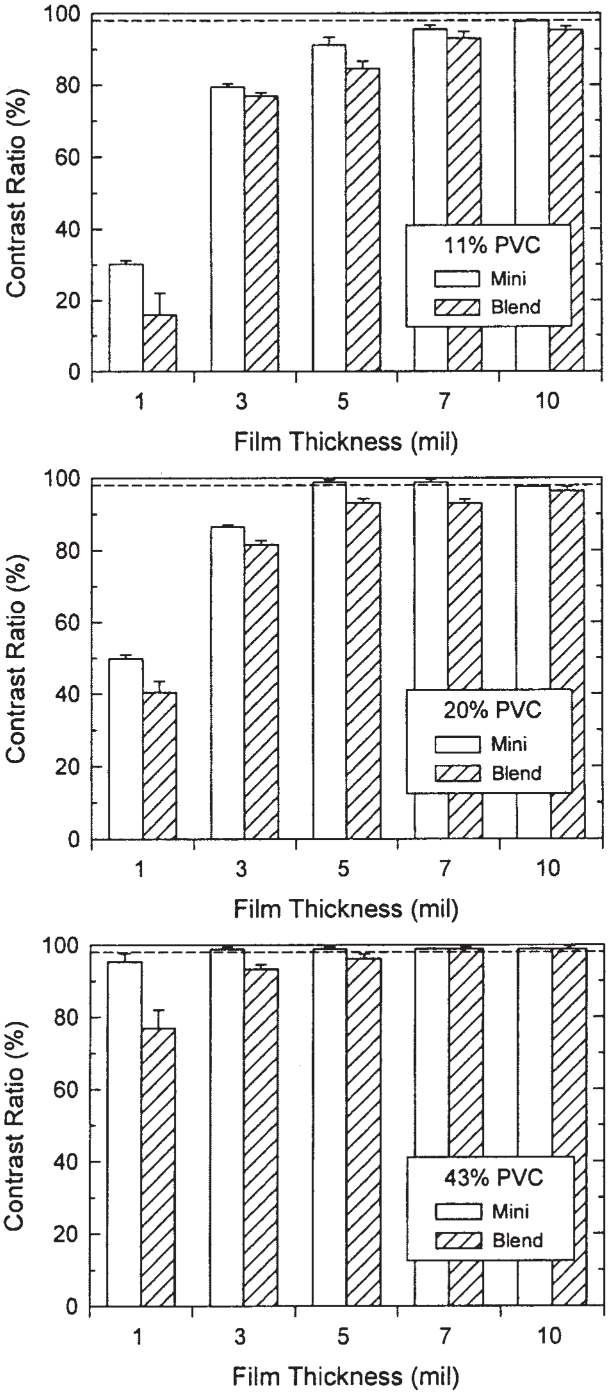

Figure 8 Comparison between the contrast ratios of encapsulated films and blends for 11% (top panel), 20% (middle panel), and 43% (bottom panel) PVC at different film thicknesses.

higher gloss) compared to the blends in which rougher surfaces contributed to the lower gloss. However, it was noted for both systems that as the TiO_2 loading (PVC) increased, the gloss decreased.

Effect of varying the sonifier operating conditions

This study begins with the dispersion of the TiO_2 aggregates in the oil phase (toluene) containing the steric stabilizer, Solsperse 32,000, using the conditions shown in Table VII ("TiO_2 Stock Dispersion"). The sonifier is used at a fixed duty cycle (70%) and varying output power setting (0–10 scale). As can be seen from Figure 10 (top panel), the TiO_2 particle size after 1 min of sonification at an output power (OP) of 3 was relatively large and broad. As the sonification time

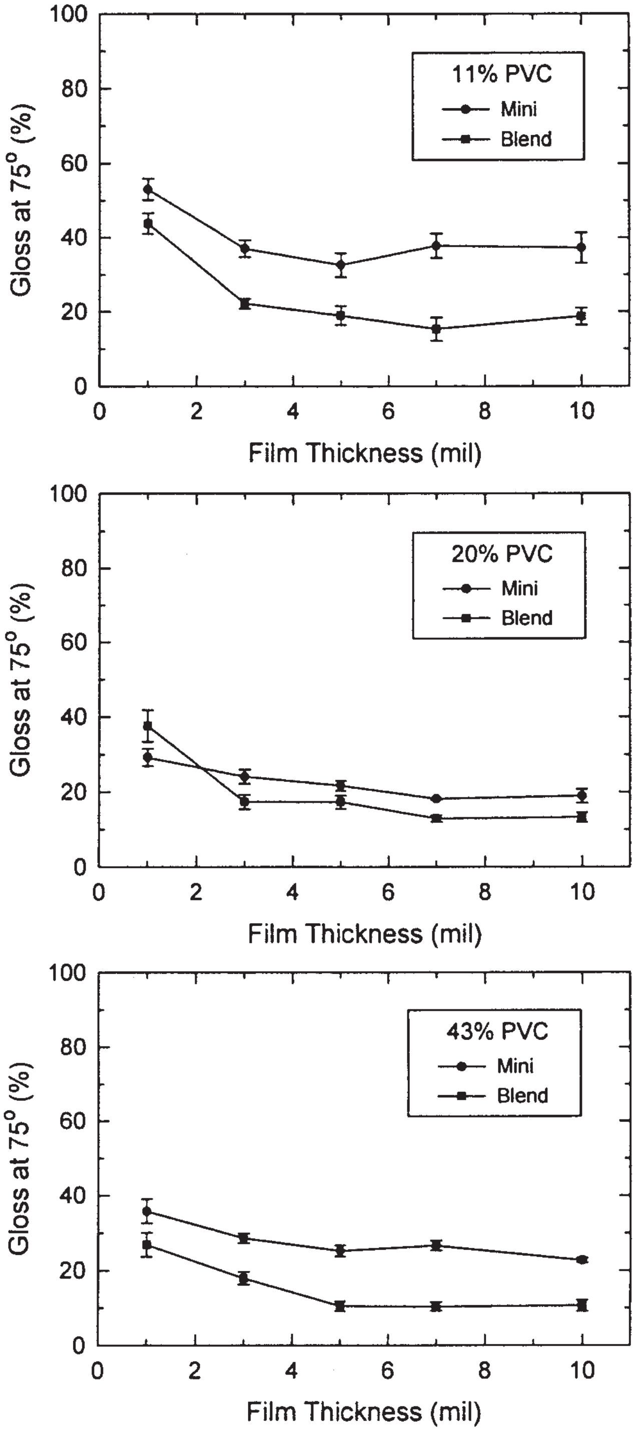

Figure 9 Comparison between the gloss of films cast from encapsulated latexes and blends for different TiO_2 loadings (PVCs) and film thicknesses.

TABLE VII
Sonifier Operating Conditions (Output Power) at Fixed Duty Cycle (70%)

	Sonifier output power setting		
Batch	TiO_2 stock dispersion[a]	TiO_2 redispersion[b]	Miniemulsification[c]
43% PVC	3	3	3
	5	5	5
	10	10	10
	3	3	10
	5	5	10

[a] 20 min sonification of TiO_2 particles in oil phase (toluene) containing Solsperse 32,000.

[b] 3 min sonification of TiO_2 particles in oil phase (toluene) containing St/BA copolymer, HD, and Solsperse 32,000.

[c] 3 min sonification.

increased from 1 to 5 min, there was a substantial decrease in the TiO_2 particle size and a narrowing of the distribution. An increase in the sonification time from 5 to 20 min did not decrease the TiO_2 particle size further. When the sonifier output power was increased from 3 to 5, the same trend was observed in terms of decreasing TiO_2 particle size as the sonification time increased from 1 to 5 min with only a slight change after 5 min sonification [Fig. 10 (bottom panel)]. These results indicate that these two output power levels are not strong enough to break all the TiO_2 aggregates and increasing the sonification time did not help to further break-up the aggregates.

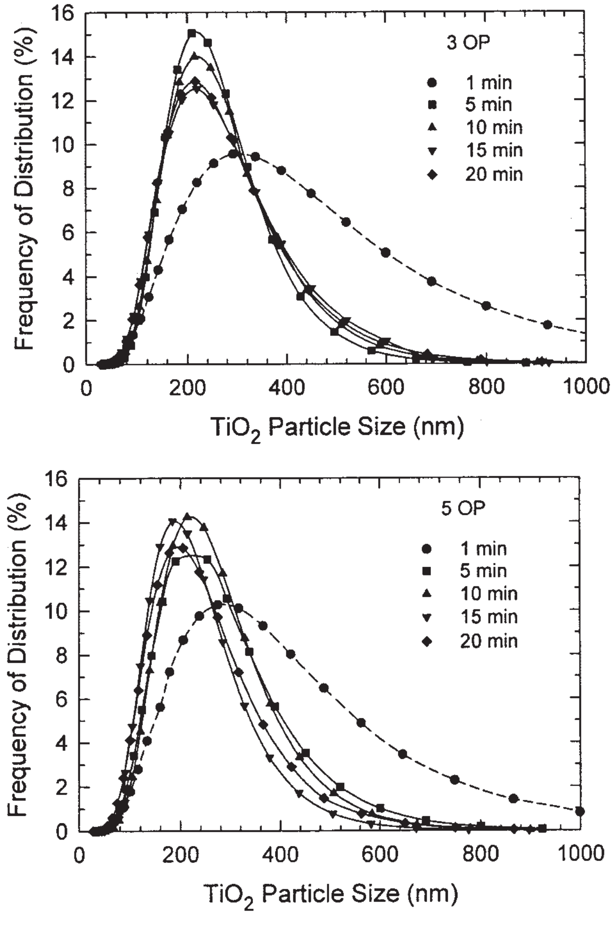

Figure 10 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of sonification time at an output power (OP) level of 3 (top panel) and 5 (bottom panel) of the sonifier and 70% duty cycle on the TiO_2 particles (20 wt %) stabilized with Solsperse 32,000 in toluene.

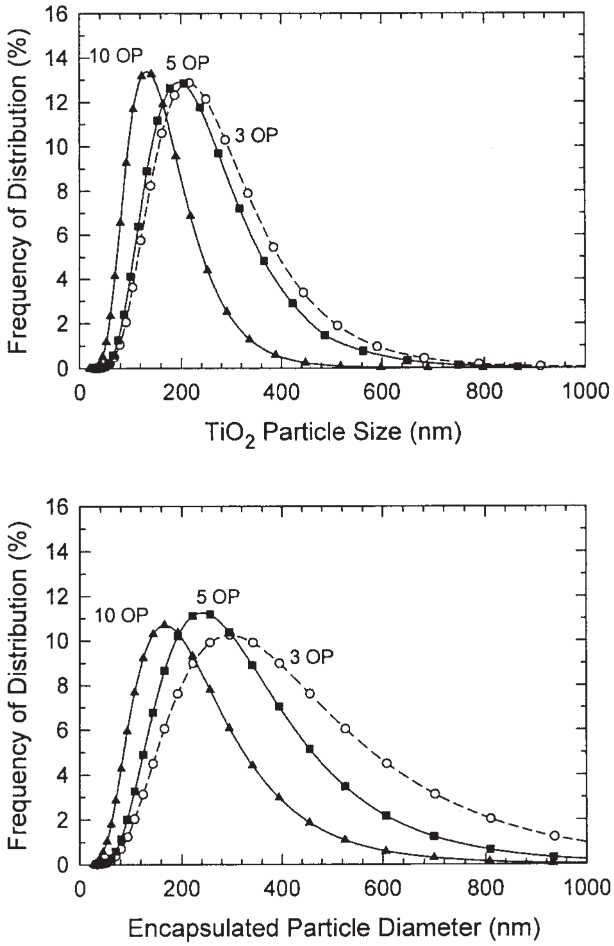

Figure 11 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of the sonifier output power (OP) level at a fixed duty cycle (70%) on the (top panel) TiO_2 particle size (20 wt %) stabilized with Solsperse 32,000 in toluene (20 min sonification) and (bottom panel) the encapsulated particle size for 43% PVC (3 min sonification).

Comparisons of the particles sizes produced at all three sonifier output power levels (3, 5, and 10) for both the TiO_2 stock dispersions and the resulting encapsulated particles are given in Figure 11 (top and bottom panels, respectively). The TiO_2 dispersions were made with 20 min sonification. The encapsulated particles were for the series of experiments that had a fixed output power in all steps (e.g., output power level of three in the stock dispersion, TiO_2 redispersion [Note: Redispersion refers to the addition of HD

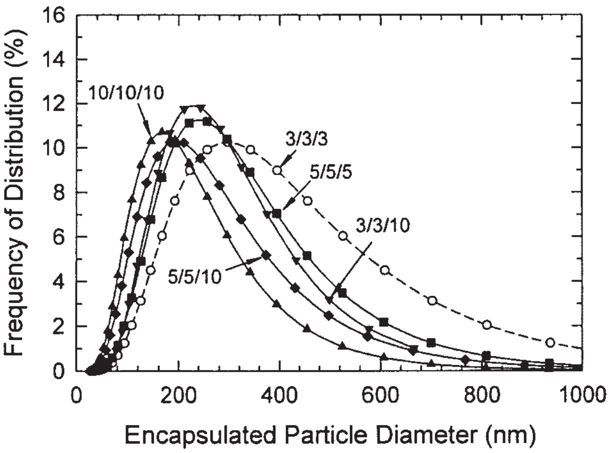

Figure 12 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of the sonifier output power (OP) level (dispersion/redispersion/miniemulsification) at a fixed duty cycle (70%) on the encapsulated particle size for 43% PVC system.

and polymer to the stock dispersion followed by 3 min sonification.], and miniemulsification as shown in Table VII). As the sonifier output power increased, the TiO_2 particle size and the encapsulated particle size both decreased and the distributions became narrower. These results revealed the importance of the sonifier output power not only in decreasing the particle size but also in narrowing the distribution.

The question was raised as to what is the controlling step in terms of the particle size that leads to the best optical properties. Is it the TiO_2 dispersion step or the miniemulsification step? To find out, two sets of experiments were carried out. In the first set, the setting for the sonifier (3, 5, and 10) was the same for all three treatments, namely preparation of the stock TiO_2 dispersion, the redispersion, and for preparation of the encapsulated particles (first three rows of Table VII). In the second set, the sonifier setting for preparing the TiO_2 stock dispersion and its redispersion were kept at the two lower levels, namely, 3 and 5, and the miniemulsification step was performed at the highest output power level of 10 as shown in the last two rows of Table VII. As can be seen in Figure 12, the encapsulated particle size resulting from OP = 3 for the TiO_2 stock dispersion and TiO_2 redispersion and OP = 10 for the emulsification step, designated 3/3/10, is slightly smaller and narrower than the 5/5/5 preparation. Moreover, the encapsulated particle size resulting from the 5/5/10 treatment lies in between the 3/3/10 particles and the 10/10/10 particles, but is narrower than the 3/3/10 ones. These results show that the history of the dispersion does affect the encapsulated particle size. In other words, the final encapsulated particle size is not solely dependent on the sonifier conditions of the emulsification alone but rather on both the dispersion and emulsification steps.

To determine the optical properties of the pigmented films, five different thicknesses were prepared for each system (1, 3, 5, 7, and 10 mil). The CRs were measured and corrected using eq. (5). In all these systems, HP (98% CR) was achieved at the 3 mil film thickness and above. These results indicate that varying the sonifier output power does not affect, either positively or negatively, the HP. This can be explained by the fact that in our system we have a broad distribution of both TiO_2 particles in the dispersion, as well as in the encapsulated latex, which could affect the outcome of this study owing to the fact that the final TiO_2 interparticle distance in the films could be nearly the same leading to high scattering in the 3 mil films. The effect of the sonifier output power level would be more pronounced if the TiO_2 particles were monodisperse, whereby the TiO_2 particle size and interparticle distance would differ and thus affect HP.

A comparison of the gloss of the films is given in Figure 13. This shows the adverse contribution to the gloss of the larger TiO_2 particles prepared at low sonifier output powers (i.e., 3/3/3 and 5/5/5). These results clearly reveal that the more pronounced effect on the gloss is the sonifier conditions during the miniemulsification where the batches prepared using OP levels of 3 and 5 for the dispersion steps and an OP of 10 for the miniemulsification step gave almost the same results as using an OP of 10 for both the dispersion and miniemulsification steps. In general, as the sonifier output power increased, the gloss increased. This is attributed to the breakage of the TiO_2 aggregates into smaller sizes resulting in a smoother film surface.

SUMMARY AND CONCLUSIONS

CRs and gloss were measured for films cast from TiO_2 encapsulated latices prepared by the miniemulsifica-

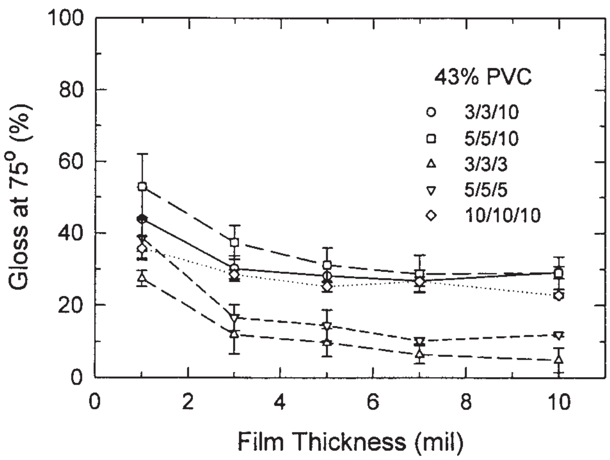

Figure 13 Gloss of TiO_2 encapsulated latex films (43% PVC) as a function of film thickness and conditions of sonification (dispersion/redispersion/miniemulsification).

tion method with varying loading (11–70% PVC). The results showed that a 3 mil film thickness was the minimum thickness that could achieve 98% CR and this required a minimum loading of 43% PVC. Thicker films required less loading. HP was determined based on the 98% CR results for all samples. HP increased to a maximum (535 ft^2/gal) at 43% PVC and decreased to a minimum (229 ft^2/gal) at 70% PVC where the TiO_2 spacing was at a minimum.

Gloss measurements were made at 75° on clear copolymer films (i.e., no TiO_2 present) and 11, 43, and 70% PVC films. As expected, the pigment-free clear films had a higher gloss than those containing TiO_2. As the TiO_2 loading increased, the gloss decreased, indicating that the increasing amount of TiO_2 reduced the surface smoothness.

A comparative study was made between the optical properties of the films cast from encapsulated latex particles and films cast from the blends at the same TiO_2 loading and film thickness for the 11, 20, and 43% PVC systems. The CR results showed the advantage of the miniemulsification process over physical latex/pigment blends in terms of hiding ability (98% CR). For the 43% PVC encapsulated latex, a low film thickness (3 mil) was required to achieve HP, while for the equivalent blend system, HP could be obtained only at a high film thickness (7 mil). Gloss measurements showed that the encapsulated latex films had higher gloss than the comparable blends.

The effect of surfactant concentration on the encapsulated particle size and the resulting optical properties of the films was investigated using four different SLS concentrations for the 11% PVC system. Particle size results showed that as the SLS concentration increased, the particle size decreased as expected. Also it was found that the minimum surfactant concentration that gives stable encapsulated TiO_2 particles is above 10 m*M* SLS. However, the CR results showed that there is little effect of surfactant concentration on the CR, and in all cases HP (98% CR) was achieved at a 10 mil film thickness. On the other hand, gloss measurements showed that as the SLS concentration increased, the film gloss decreased.

The effect of varying the sonifier operating conditions on the dispersed TiO_2 particle size and the encapsulated particle size, and the resulting optical properties of the films for the 43% PVC system was investigated. The particle size analysis showed that as the sonifier power level increased (OP 3–10), the TiO_2 particle size in the oil-phase and the encapsulated particle size decreased. The CR results showed that varying the sonifier power level had no measurable effect on both the CR and HP, where HP (98% CR) was obtained at 3 mil film thickness. However, the gloss measurements showed that as the sonifier power level increased, the film gloss increased.

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