High PVC Film-Forming Composite Latex Particles via Miniemulsification, Part 2: Efficiency of Encapsulation

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ABSTRACT: The application of a density gradient column (DGC) method using sodium polytungstate (SPT) solutions as the medium was investigated for determining the encapsulation efficiency of 11–30% pigment volume concentration (PVC)) latex particles prepared by the miniemulsification process. The encapsulation efficiencies for 11, 20, and 30% PVCs were found to be 100% of the TiO_2 encapsulated inside 86.3, 98, and 98.9% of the styrene/n-butyl acrylate copolymer, respectively. The copolymer not participating in the encapsulation (free copolymer) was found in the 1.04 g/mL density layer of the DGC. Particle size analysis by DLS (dynamic light scattering) showed that the encapsulated particle size increased with increasing density. Thus, the number of TiO_2 particles (primary particles) inside each encapsulated particle increased to accommodate both the increased size and density. The results obtained by DLS for each DGC layer of the 30% PVC system were confirmed qualitatively by TEM in terms of the increasing encapsulated particle size and broadening of the size distribution as the density increased in the DGC. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4517–4525, 2006

Key words: miniemulsification; titanium dioxide; microencapsulation; dispersions; shear; density gradient column

INTRODUCTION

The miniemulsification process was applied successfully to produce film-forming submicron-sized particles of poly(styrene-*co*-*n*-butyl acrylate) (p(S/BA)) copolymer encapsulating solid pigment particles (TiO_2).[1] This process has proven to be relatively easy to carry out and is capable of producing encapsulated copolymer particles with high TiO_2 loading (11–70% PVC) and stability. In addition, it still meets the requirement of a VOC-free environment through the removal of water-immiscible organic solvent. This encapsulation approach by miniemulsification is being evaluated owing to the limitations of the previous approach, where TiO_2 particles were encapsulated via miniemulsion polymerization.[2–8] These limitations included low TiO_2 loading (3 wt % based on the monomer), which was determined to be 0.76% PVC for the PS and 0.75% PVC for the S/BA copolymer systems. In addition, the encapsulation efficiency, determined via density gradient column (DGC) separations employing sucrose solutions, showed that complete encapsulation, meaning all of the polymer/copolymer encapsulating all of the TiO_2, was not achieved. The maximum encapsulation efficiencies (79.1% TiO_2 inside 61.74% polystyrene and 63.64% TiO_2 inside 38.48% St/BA copolymer) were achieved using hydro-philic TiO_2 particles stabilized with 1 wt % Solsperse 32,000.[7] Moreover, the contrast ratio (CR) measurements showed that all the films cast from the encapsulated latices produced low CRs, not even close to that needed to achieve hiding power (98% CR).[8] The optical properties of encapsulated latex films with high loading (11–70% PVC) prepared successfully by the miniemulsification technique are discussed elsewhere.[9]

Sodium polytungstate as a medium in isopycnic density gradient centrifugation

Sucrose, which was used previously[2,7] in the DGC preparation, is considered the universal gradient material and has been selected as the ideal density gradient solute owing to several advantages, namely, low cost, inertness, stability, high solubility, transparency, and nontoxic nature.[10,11] Therefore, it was used in the preparation of the DGC medium for use in evaluating the encapsulation efficiency of TiO_2 inside both polystyrene and St/BA copolymer particles prepared by miniemulsion polymerization. The results have shown clearly its limitation especially at high pigment loading: the maximum density that can be prepared in the DGC is only 1.339 g/mL (bottom layer) while the density of the TiO_2 inorganic particles is ~4.1 g/mL. In addition, we reported that the weight percent of polystyrene associated with the TiO_2 particles in the bottom layer of the column was about 11 wt % of the amount of latex polymer loaded into the DGC, while

for styrene-butyl acrylate copolymer (50 : 50 wt %), the amount constituted 12 wt % of the copolymer loaded.[7] The limitations of sucrose led to a search for an alternative material with the capability of preparing a DGC medium with higher densities.

Sodium polytungstate (SPT), $Na_6(H_2W_{12}O_{40})H_2O$ (sodium metatungstate), was introduced in 1983 as a new material for density gradient separations. It is nontoxic, easy to use, and recoverable, so that it may be reused several times. It has a density of 3.1 g/mL, which can be reduced to any desired lower density simply by adding DI water. It is available as a salt (in powder form) or in solution with a 2.8 g/mL density. SPT can be used to replace toxic and possibly carcinogenic organic liquids that are traditionally used, such as bromoform, tetrabromoethane (TBE), and diiodomethane for gravity separation studies. The applications of SPT are found in macromolecular chemistry, biochemistry, geology, geophysics, and mineralogy. Also, it is used in paleontology to separate fossil bones and minerals. It is freely soluble in water, with the resulting solutions exhibiting neutrality although it is also stable over a wide pH range (2–14).[12–19]

The aim of this study is twofold. The first goal is to study the applicability of determining the encapsulation efficiencies of 11, 20, and 30% PVCs using a DGC comprising various aqueous SPT solutions as the medium and its effects, if any, on the encapsulated particle size. Second is the estimation of the number of TiO_2 particles per encapsulated particle in each DGC layer for the three PVCs based on the results from the first part.

EXPERIMENTAL

Materials

Poly(styrene-*co-n*-butyl acrylate), synthesized by conventional emulsion polymerization and cleaned of surfactant (SLS) and electrolytes, was used as the encapsulating polymer in the preparation of TiO_2-encapsulated artificial latexes by the direct miniemulsification technique.[1] Sodium lauryl sulfate (SLS; Fisher, Pittsburgh, PA), toluene (VWR, Bridgeport, NJ), and hexadecane (HD; Sigma-Aldrich, St. Louis, MO) were used as received. The colloidal 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[20–23] 32,000 (100% active; Avecia Inc., Wilmington, DE), a polyamine/polyester[24] was used as received. Sodium polytungstate (MSDS; Sometu-USA, Sherman Oaks, CA) was used as received to prepare the density gradient columns (DGC) for the determination of the encapsulation ef-

TABLE I
Miniemulsification Recipe for the Preparation of TiO₂-Encapsulated Artificial Latexes

Ingredient	Amount (g)
Water phase	
Deionized water	140
SLS	1.6128 (40 mM)[a]
Oil phase	
Toluene	35
Copolymer (St/BA)[b]	2.333–0.34[c]
TiO₂	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 to 70% PVC.
[d] Based on TiO₂ loading: 33 wt %.
[e] Based on toluene.

ficiency by ultracentrifugation. Igepal CO-977 (nonylphenol ethoxylate, Stepan, Northfield, IL) was used as received. Deionized water was used for all experiments.

Analytical methods

Dynamic light scattering (Nicomp, Model 370; Particle Sizing Systems, Inc., Santa Barbara, CA) was used to measure the polymer particle size and the dispersed TiO_2 particle size. In all DLS measurements, only the Gaussian distribution was considered unless otherwise noted. A LB-70M Beckman ultracentrifuge equipped with a 6-tube swinging-bucket rotor (SW-41; Beckman Coulter, Inc., Fullerton CA) was used for the separation of encapsulated particles in the different DGC layers. The encapsulated particles in each DGC layer were subjected to serum replacement[25] to remove the SPT prior to any TEM observation. A transmission electron microscope (TEM; Phillips, Model 400; New York, NY) was used to obtain micrographs of the encapsulated particles in different DGC layers.

Procedure

Preparation of encapsulated artificial latexes via miniemulsification

Poly(styrene-*co-n*-butyl acrylate) was used as the encapsulating polymer in the preparation of TiO_2-encapsulated artificial latexes by the direct miniemulsification technique based on the recipe shown in Table I. The details of both preparing and cleaning the poly(styrene-*co-n*-butyl acrylate) were described previously, as were those for preparing the different latexes with high TiO_2 loadings (11–70% PVC).[1] These latexes were used to cast films of varying thickness and then

measure the optical properties, as described in another paper in this series.[9]

Preparation of density gradient column

In separations applying a DGC, centrifugation is usually used to perform the separation in a centrifuge tube. This process can be called density gradient centrifugation.[10] It is basically used to separate particles on the basis of the particle densities by employing a medium (e.g., SPT solutions) that increases in density in a gradient down the centrifuge tube. In DGC, particles separate according to their density where the denser particles sediment farther than less dense ones and, after a sufficient time and speed of centrifugation, the particles move to positions in the gradient where the density in the zone just below them is higher than their own densities while the density of the zone in which they reside is less that or equal to this.

The DGC was prepared as follows. Layers of media with different densities were manually layered one on top of the other where the densest layer was added first followed by less dense layers. Note that the solution must drain down the side of the tube because dropping one layer on top of the other will produce mixing. After placing all of the layers in the DGC tubes, a small latex sample was layered on top of the column. The centrifuge tubes were placed inside swinging buckets and then centrifuged at 19,000 rpm (the acceleration was determined to be 27,065 × g, where g is the gravitational constant) for 3 h at 4°C. When removing the tubes from the centrifuge rotor, they are handled carefully so that the gradients are not disturbed. The removal of the individual layers from a gradient column after centrifugation requires considerable care.

To minimize the error in the final results, layers were collected from six tubes for each density. The SPT was removed from each layer by diluting it in a centrifuge tube containing DI water followed by centrifugation at 37,000 rpm (the acceleration was determined to be 102,638 × g, where g is the gravitational constant) for 1 h and then the clear serum (i.e., no TiO$_2$) was removed carefully. This step was repeated at least three times after the decantation step to ensure that all the SPT was removed. Finally, the encapsulated copolymer was dried overnight in a crucible at 75°C to evaporate all of the water; the crucible was weighed periodically until a constant weight was achieved. The final step was the removal of the copolymer and other organic materials by incineration in the crucible using a Bunsen burner until a constant weight was obtained. From the amount of material remaining in the crucible (i.e., TiO$_2$) and the weight before the incineration, the amount of copolymer and TiO$_2$ and their ratio (i.e., PVC) in each corresponding
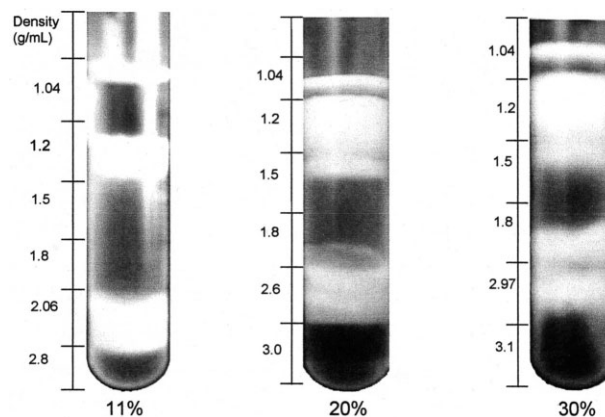

Figure 1 Photograph of density gradient columns after centrifugation of the 11% (left), 20% (middle), and 30% (right) PVC latexes at 19,000 rpm for 3 h at 4°C.

density layer could be calculated. The weight percent of TiO$_2$ in each layer was calculated as follows:

$$\text{TiO}_2(\text{wt \%}) = \left(\frac{M_{\text{TiO}_2}}{M_{\text{TiO}_2 \text{ in loaded sample}}}\right) \times 100 \qquad (1)$$

where M_{TiO_2} is the mass (g) of the TiO$_2$ remaining after burning and $M_{\text{TiO}_2 \text{ in loaded sample}}$ is the total initial mass (g) of TiO$_2$ in the sample loaded into the DGC tube. The density of the particles in each layer can be estimated by knowing the weight fractions of copolymer and TiO$_2$ using eq. (2).

$$\text{Density (g/mL)} = \rho_{\text{TiO}_2}$$
$$\times \left(\frac{M_{\text{TiO}_2}}{M_{\text{polymer}+\text{TiO}_2}}\right) + \rho_{\text{polymer}} \times \left(\frac{M_{\text{polymer}}}{M_{\text{polymer}+\text{TiO}_2}}\right) \qquad (2)$$

where ρ_{TiO_2} and ρ_{polymer} are the densities of TiO$_2$ (4.1 g/mL) and copolymer (1.034 g/mL), respectively. M_{TiO_2} and M_{polymer} are the masses of TiO$_2$ and polymer, respectively, in each layer while $M_{\text{polymer}+\text{TiO}_2}$ is the total mass of both TiO$_2$ and polymer in each layer.[5]

RESULTS AND DISCUSSION

Encapsulation efficiency determination via DGC

In the DGC experiments, different concentrations of SPT solution were prepared having densities ranging from 1.04 to 3.1 g/mL. The same volume of each solution was used for the preparation of the DGC (centrifuge tube). The encapsulation efficiencies were determined for 11, 20, and 30% PVC encapsulated latexes. These particles have theoretical densities of 2.06, 2.6, and 2.97 g/mL, respectively, assuming an even distribution of the TiO$_2$ in all particles. Noting the separations achieved in the DGC columns for the three systems in Figure 1, it is clear that these distri-

TABLE II
Gravimetric Determination of the Encapsulation Efficiency of Hydrophilic TiO$_2$ Particles in S/BA Copolymer at 11% PVC

ρ (g/mL)	Copolymer in each layer (wt %)[a]	TiO$_2$ in each layer (wt %)[b]	Calculated density of particles (g/mL)	PVC of particles (%)
1.04	13.71	0	–	–
1.2	56.09	35.54	1.47	4.123
2.065	30.20	63.51	2.14	12.49

Solids content = 3.65 wt %; latex loaded = 0.8547 g (0.0312 g solids).
[a]Based on the total amount of copolymer in the sample (0.0246 g).
[b]Percentage of TiO$_2$ in each layer based on the total amount of TiO$_2$ in the loaded sample (0.0066 g).

butions were not even throughout all the particles. The encapsulation efficiencies determined for each PVC system at the different densities are reported in Tables II–IV and are graphically represented in Figure 2.

It can be seen from Figure 1 and Table II that the 11% PVC latex sample was separated into three distinctive bands at 1.04, 1.2, and 2.06 g/mL. Interestingly, particles were not found in two of the intermediate density layers (1.5 and 1.8 g/mL). No clear explanation for this improbability can be offered. No TiO$_2$ (density of 4.1 g/mL) was found at the bottom of the DGC tube indicating that 100% encapsulation of the TiO$_2$ was achieved. The 1.04 g/mL density layer contained 13.7% of the copolymer not participating in encapsulation (i.e., free copolymer), this indicating a 86.3% efficiency of encapsulation by the copolymer. The 1.2 g/mL density layer contained 56.09% of the encapsulating copolymer and 35.54% of the encapsulated TiO$_2$. Finally, the 2.06 g/mL density layer contained 30.20% encapsulating copolymer and 63.51%

TABLE III
Gravimetric Determination of the Encapsulation Efficiency of TiO$_2$ Hydrophilic Particles Encapsulated with Copolymer for 20% PVC

ρ (g/mL)	Copolymer in each layer (wt %)[a]	TiO$_2$ in each layer (wt %)[b]	Calculated density of particles (g/mL)	PVC of particles (%)
1.04	1.55	0	–	–
1.2	45.01	13.00	1.38	3.13
1.5	34.16	24.91	1.78	7.54
2.6	19.28	62.07	2.83	26.47

Solids content = 3.52 wt %; latex loaded = 1.0815 g (0.0380 g solids).
[a]Based on the total amount of copolymer in the sample (0.0264 g).
[b]Percentage of TiO$_2$ in each layer based on the total amount of TiO$_2$ in the loaded sample (0.0117 g).

TABLE IV
Gravimetric Determination of the Encapsulation Efficiency of TiO$_2$ Hydrophilic Particles Encapsulated with Copolymer for 30% PVC

ρ (g/mL)	Copolymer in each layer (wt %)[a]	TiO$_2$ in each layer (wt %)[b]	Calculated density of particles (g/mL)	PVC of particles (%)
1.04	1.11	0	–	–
1.2	46.24	8.08	1.33	2.60
1.5	17.34	8.82	1.76	7.20
1.8	16.90	22.78	2.42	17.15
2.97	18.41	59.52	3.06	33.04

Solids content = 3.47 wt %; latex loaded = 1.0407 g (0.0361 g solids).
[a]Based on the total amount of copolymer in the sample (0.0225 g).
[b]Percentage of TiO$_2$ in each layer based on the total amount of TiO$_2$ in the loaded sample (0.0136 g).

encapsulated TiO$_2$ particles. According to this distribution of both copolymer and TiO$_2$ in these two DGC layers, each layer will have a different PVC value as shown in Table II. The calculated PVCs for each DGC layer were determined to be 4.12% for the 1.2 g/mL layer and 12.49% for the 2.06 g/mL layer. The density of particles in each DGC layer was also calculated using eq. (2), and found to be 1.47 and 2.14 g/mL for the 1.2 and 2.06 g/mL layers, respectively. The calculated densities are slightly greater than the density of the layer, but still lower than the ones in the next layer down, as expected.

Similar observations can be made for the other two systems. At 20% PVC, four distinct bands appeared with one vacant at 1.8 g/mL (the appearance of this zone in the picture is an artifact of the photography), while five bands at all densities, except the highest, were produced at 30% PVC (Fig. 1). No particles were found in the bottom of either tube, again indicating 100% of the TiO$_2$ was encapsulated. The encapsulation efficiencies are reported in Tables III and IV, respectively. Note that the percentage of free copolymer decreased to 1.55 and 1.11% for the 20 and 30% PVC systems, respectively, indicating increased efficiencies of 98.45 and 98.89% with increasing PVC. The calculated PVCs and densities of the particles in each DGC layer are also reported in the tables.

Unfortunately, it is not possible to characterize the higher loading batches ($\geq$43% PVC) due the fact that the calculated density for the next batch (43% PVC) is 3.33 g/mL while the highest density for the SPT medium is 3.1 g/mL.

The distributions of both St/BA copolymer and TiO$_2$ in each layer of the DGCs are illustrated in Figure 2 where it is clear that the ratio of copolymer to TiO$_2$ increases with increasing density of the particles as expected. The question remains as to why the polymer
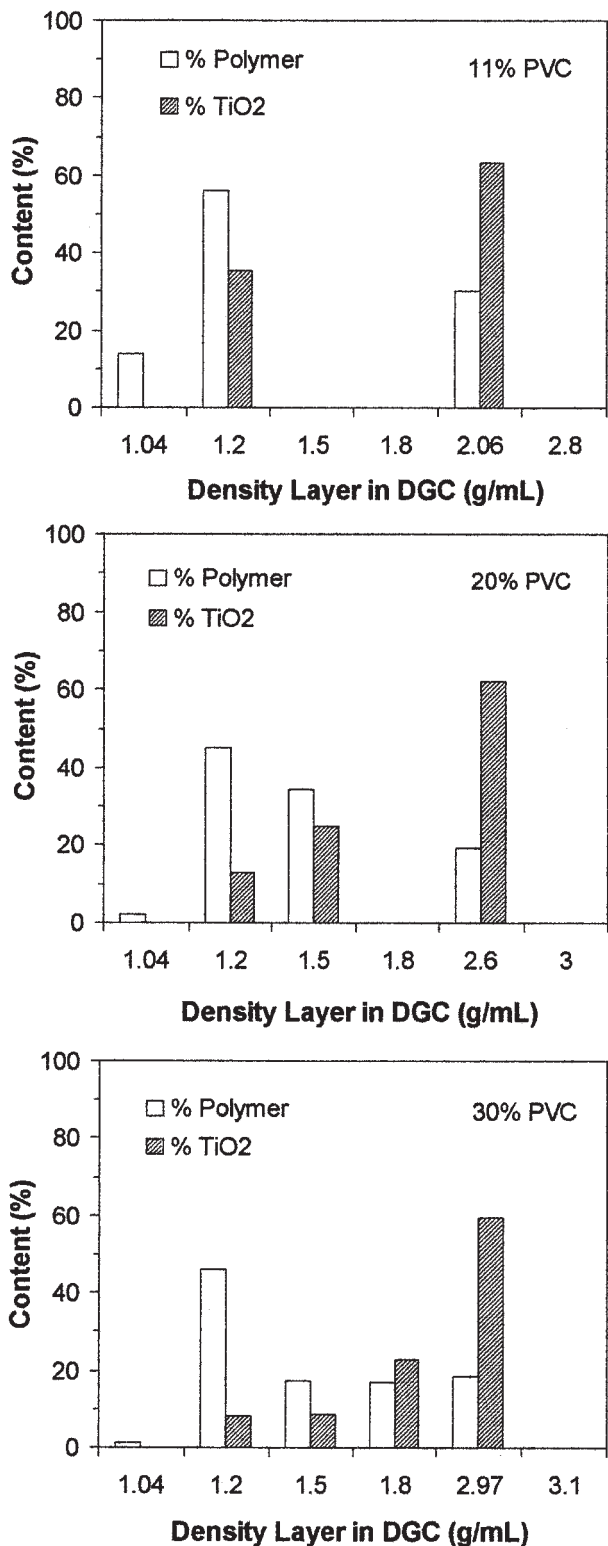
Figure 2 Distribution of St/BA copolymer and TiO$_2$ in each layer of DGC for 11% (top panel), 20% (middle panel), and 30% (bottom panel) PVC.

and inorganic particles distribute unevenly in this process. A look at the particle sizes was next pursued in hopes of clarifying these findings.

Determination of the particle size and PSD in DGC layers

Since SPT is a polyelectrolyte, it can be expected to affect the stability of the encapsulated particles, which are stabilized by an electrostatic stabilizer (i.e., SLS). To determine the extent of this effect on the colloidal stability and at which density (concentration) levels, the particle size was determined by dynamic light scattering at the different densities as shown in Figure 3. Indeed, the results show that as the density increased (increasing concentration of SPT), the particle size increased. This instability of the encapsulated particles could be resolved by using some type of a nonionic surfactant as poststabilizer. Igepal CO-977, a nonylphenol ethoxylate, was selected for this purpose. Immediately after the preparation of the 20% PVC latex, 1 wt % Igepal CO-977 was added. The particle size was then determined by dynamic light scattering in SPT solutions of varying density as shown in Figure 4. The results show that the particle size is stable under these conditions, indicating that Igepal CO-977 imparted additional stability against electrolyte. This result demonstrates the utility of adding this poststabilizer after miniemulsification and also during the preparation of the DGC.

The particle size characterization results for each DGC layer in the 11, 20, and 30% PVC systems are shown in Figure 5 as obtained by DLS. Determination of the particle size in each density zone allowed comparisons between the encapsulated particle sizes and distributions and that of the dispersed TiO$_2$ particles in the oil phase (containing St/BA copolymer, HD, and Solsperse 32,000 stabilizer). In all three systems, the St/BA copolymer particles not containing any TiO$_2$ had the smallest particle sizes of around 100 nm (Fig. 5). The presence of the TiO$_2$ particles inside the St/BA copolymer particles resulted in the particle size
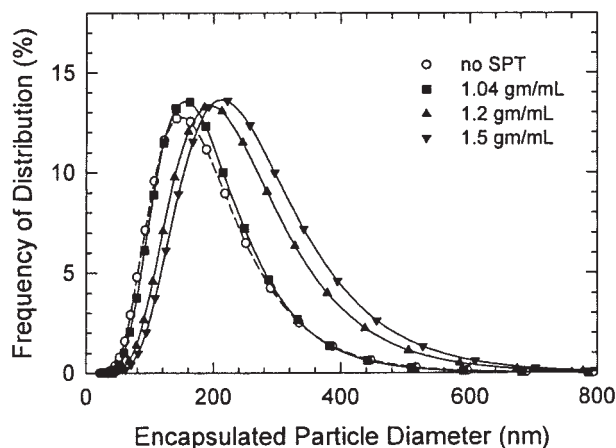

Figure 3 Effect of sodium polytungstate (SPT) concentration on the encapsulated particle size (nm) for the 11% PVC latex particles.
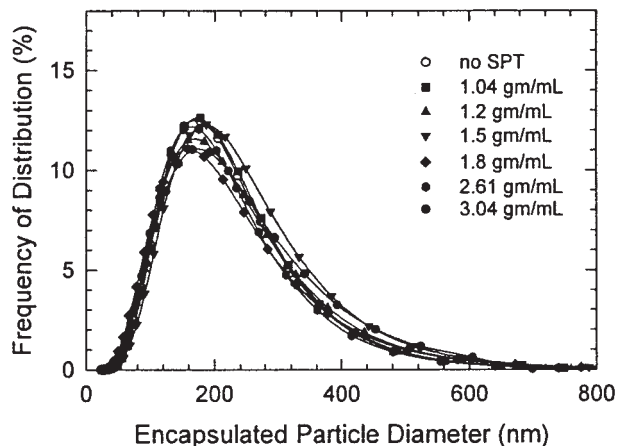
Figure 4 Effect of adding poststabilizer (Igepal CO-977) on the stability of 20% PVC encapsulated particles against sodium polytungstate (SPT) at different densities (concentrations).

increasing as the density increased in the DGC as shown in all three PVC systems. In addition, this result of increasing encapsulated particle size with density is in agreement with our results for the encapsulation of 3 wt % TiO$_2$ particles inside polymer particles.[5,7] The increase was basically due to an increasing number and/or size of TiO$_2$ particles (or aggregates) in each St/BA copolymer particle. Comparing the encapsulated particle size and distribution obtained from the 1.2 g/mL layer of the DGC for the 11% PVC system with the dispersed TiO$_2$ particle size, shows that the encapsulated particle size was on average smaller than the particles in the TiO$_2$ dispersion. This indicated that the TiO$_2$ particles are being segregated during the encapsulation process where small particles are encapsulated at lower density (higher copolymer/TiO$_2$ ratio) and the larger particles are encapsulated at higher density, as shown in Figure 5 (top panel). This is apparent in all three systems (11, 20, and 30% PVC). In general, it can be seen from Figure 5 that as the TiO$_2$ loading increased, the size of the TiO$_2$ particles (aggregates) in the dispersion decreased and the size distribution became narrower leading to higher encapsulation efficiencies. A comparison between the encapsulated particle sizes found in the 1.2 g/mL density layer for the 11, 20, and 30% PVC systems (i.e., increasing number of TiO$_2$ particles in the dispersion) shows that as the TiO$_2$ loading increased, the encapsulated particle sizes increased, as shown in Figure 6.

Estimation of the number of inorganic particles per encapsulated particle

The particle size distribution of the encapsulated particles for each DGC layer was determined by DLS and used in conjunction with the densities of the layer the particles were found in and the adjacent higher density layer to estimate a range for the number of primary TiO$_2$ particles per encapsulated particle (N_{TiO_2}), eq. (3):

$$N_{TiO_2} = \left(\frac{d}{d_{30}}\right)^3 \left(\frac{p_{particle} - p_{polymer}}{p_{TiO_2} - p_{polymer}}\right) \qquad (3)$$
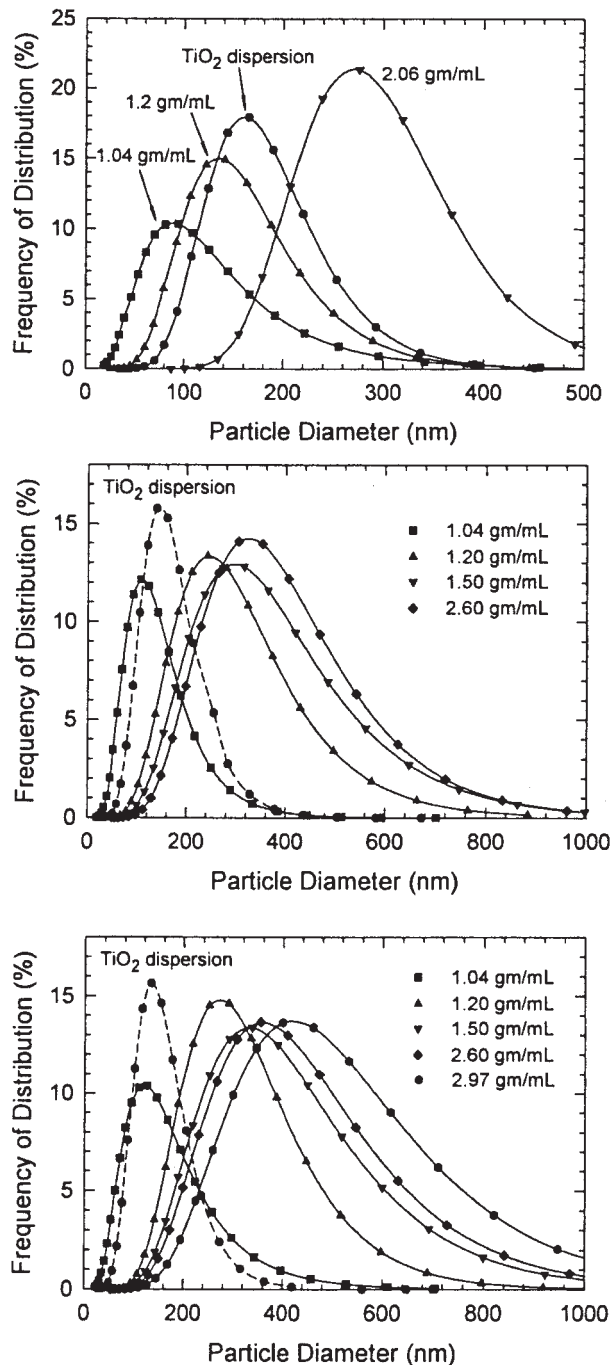

Figure 5 Comparison of the volume-weighted Gaussian analysis of the particle size distribution from the DGC layers of the 11, 20, and 30% PVC systems with the TiO$_2$ particle size in the oil phase (toluene) containing St/BA copolymer, HD, and Solsperse 32,000 after 3 min sonification at 10 OP and 70% duty cycle.
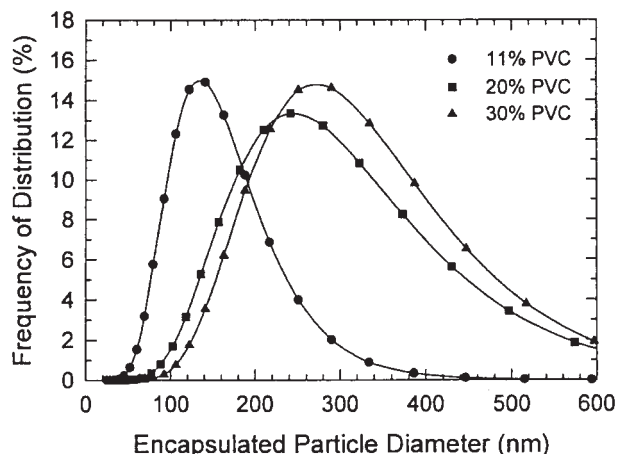
Figure 6 Comparison of the volume-weighted Gaussian analysis of the encapsulated particle size from the 1.2 g/mL DGC layer of the 11, 20, and 30% PVC systems.

where d is the diameter of the encapsulated particle, d_{30} is the average diameter of the primary TiO_2 particles (30 nm), ρ_i is the density of the ith species, namely the particle, polymer, and TiO_2. The two densities of adjacent DGC layers were used since the encapsulated particles have to have a density between the two, namely: $\rho_{\text{layer 1}} \leq \rho_{\text{particle}} < \rho_{\text{layer 2}}$ where layer 1 is where the particles were found. If a single aggregate is assumed to be encapsulated, its size (d_{agg}) is readily estimated assuming that it is a sphere having the density of TiO_2:

$$d_{\text{agg}} = d\left(\frac{\rho_{\text{particle}} - \rho_{\text{polymer}}}{\rho_{\text{TiO}_2} - \rho_{\text{polymer}}}\right)^{1/3} \quad (4)$$

Table V presents the values of N_{TiO_2} and d_{agg} esti-

mated for the various layers recovered containing particles for the 11, 20, and 30% PVC systems. As the density increased in the DGC, the encapsulated particle size and the number of TiO_2 particles inside each copolymer particle increased. The size ranges of the encapsulated particles and TiO_2 are compared in Figure 7, the latter representing sizes from the primary particles to fully aggregated single TiO_2 particles. Obviously, the actual numbers must lie in between these extremes. Moreover, as noted earlier, the number of DGC layers containing encapsulated particles increased as the TiO_2 loading increased.

TEM examination of the encapsulated particles

The particles found in the individual DGC layers of the 30% PVC sample were examined by transmission electron microscopy (TEM). If the TiO_2 had been evenly distributed throughout the particles, their density would have been 2.97 g/mL and all would have been found in this layer. Because SPT was used to prepare the DGC much of it had to be removed first from the samples as it has a high density and would prevent clear observation of the particles in the TEM. The encapsulated particles in each DGC layer were subjected to cleaning by serum replacement[25] by passing an aqueous solution of 0.1 wt % Igepal CO-977 through a stirred filtration cell (10 mL) containing the particles for a period of 72 h at a flow rate of 3 mL/h. This filtration procedure removed most of the SPT from the samples.

The particles were next treated with phosphotungstic acid (PTA) as a staining agent that reacts with surface functional groups, such as hydroxyl, carboxyl, and amines. PTA can be used for both positive and

TABLE V
Estimated Number of TiO₂ Particles per Copolymer Particle in Each DGC Layer of the 11, 20, and 30% PVC Latexes

Density (g/mL)	Encapsulated particles D_{min}–D_{max} (nm)[a]	N_{TiO_2} per encapsulated particle, range[b]	Maximum aggregate size (nm)
11% PVC			
1.05–1.2	87–199	1–14	72
1.85–2.065	204–358	82–564	248
20% PVC			
1.05–1.2	154–384	1–100	139
1.25–1.5	181–467	14–551	246
1.85–2.65	210–492	90–2310	392
30% PVC			
1.05–1.2	178–408	1–120	148
1.25–1.5	209–519	22–757	273
1.55–1.8	227–555	70–1549	347
1.85–2.97	266–650	182–6397	557

[a]Measured by DLS.
[b]Number of primary TiO_2 particles per encapsulated particle ranges from a minimum (lowest density and particle size) to a maximum (highest density and particle size).

negative staining and has been used to enhance the contrast in TEM imaging of latexes, such as poly(butyl acrylate) and poly(ethyl acrylate).[26] One drop of cleaned encapsulated latex was added to 1 mL of 2% PTA. A drop of this mixture was then placed on a carbon-Formvar coated grid. After removing the excess fluid with filter paper, the sample was placed in a TEM cold stage.

Figure 8 shows TEM micrographs of the encapsulated TiO_2 particles obtained from the various DGC layers of the 30% PVC latex. These TEM images clearly confirm what was noted earlier (in particle size analysis) that the encapsulated particle size distribution is broad in each DGC layer and also as the density increased, the encapsulated particle size increased on average as well as broadened. Unfortunately, these micrographs are not able to define the location of the TiO_2 within the particles.

SUMMARY AND CONCLUSIONS

A DGC for analyzing the encapsulation efficiencies of 11, 20, and 30% PVC poly(styrene/n-butyl acrylate)

Figure 8 TEM micrographs of encapsulated particles obtained from different DGC layers of the 30% PVC system: (a) 1.2 g/mL, (b) 1.5 g/mL, (c) 1.8 g/mL, and (d) 2.97 g/mL DGC layers.

encapsulated TiO_2 latexes was prepared successfully using SPT solutions. The encapsulation efficiencies for the three PVCs were found to be 100% TiO_2 encapsulated inside 86, 98, and 99% of the copolymer, respectively. The unencapsulated copolymer latexes (free copolymer) for all three batches were found in the 1.04 g/mL density layer of the DGC. After centrifugation, it was noted that the number of DGC layers containing encapsulated particles increased as the TiO_2 loading increased (11–30% PVC).

The particle size analysis by dynamic light scattering of each DGC layer showed that the presence of the TiO_2 particles inside the St/BA copolymer particles led to an increase in the size and broadening of the size distribution of the encapsulated latex particles as the density increased in the DGC owing to the increasing number and/or size of the TiO_2 particles (aggregates). The results obtained by DLS were confirmed by TEM in terms of increasing both the encapsulated particle size and broadening the size distribution.
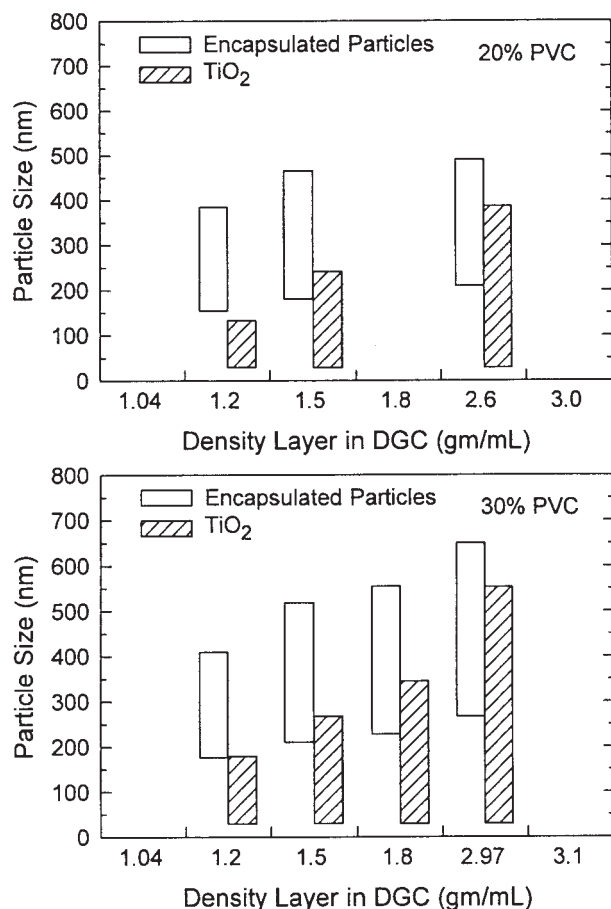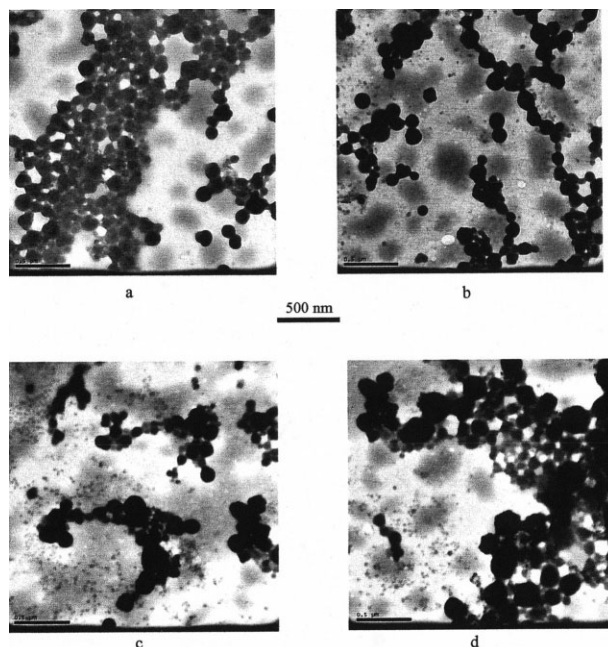
Figure 7 Ranges of encapsulated particle size and size of encapsulated TiO_2 as a function of the density in DGC for 20% (top panel) and 30% (bottom panel) PVC.

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