High PVC Film-Forming Composite Latex Particles via Miniemulsification, Part 1: Preparation

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ABSTRACT: Miniemulsification technology was used to encapsulate TiO_2 particles inside a styrene/*n*-butyl acrylate copolymer with high loading levels (11 to 70% PVC (pigment volume concentration)). In this approach, a St/BA copolymer dissolved in toluene in the presence of a costabilizer (hexadecane) was mixed with a dispersion of TiO_2 particles in toluene and sonified, and then emulsified in an aqueous surfactant solution by sonification. The effect of sonification time on both the dispersibility of the TiO_2 particles in the presence of the copolymer and hexadecane and on the encapsulated particle size was investigated. Particle size analysis by dynamic light scattering showed that these composite latexes are quite stable. It was also found that as the TiO_2 loading increased from 11 to 43% PVC, the particle size of the TiO_2 dispersion decreased while the polymer-encapsulated TiO_2 particle size increased. The effect of surfactant concentration (sodium lauryl sulfate, SLS) on the encapsulated particle size was investigated using four different SLS concentrations in the 11% PVC system. The 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. The role of HD in the recipe was studied for an artificial latex containing no TiO_2 and one prepared at 11% PVC, in terms of particle size before and after solvent stripping, and its effect on the T_g. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4504–4516, 2006

Key words: miniemulsification; titanium dioxide; microencapsulation; dispersions; shear

INTRODUCTION

Latexes can be classified in one of three categories based on their origin and method of preparation (1) natural latices, which are the metabolism products of various plants and trees; (2) synthetic latexes, which are prepared by emulsion polymerization of their corresponding monomers; and (3) artificial latexes (also referred to as pseudolatexes), such as epoxy resins, polyester, and polyurethane, which are prepared by dispersion of the bulk polymer (or a solution of polymer) in an aqueous medium using conventional surfactants and emulsification methods.[1–3] Latexes are widely used in the coatings, adhesives, plastics, and rubber industries. In general, artificial latexes are not as easy to prepare as synthetic latexes and are used in cases where (1) the polymer cannot be prepared as synthetic latex by a free-radical emulsion polymerization process; or (2) it is not available as a natural latex and if special properties are to be gained by using it. In recent years, artificial latexes have been gaining more industrial interest as a means to produce latexes of various synthetic rubbery polymers that are prepared by processes other than emulsion polymerization. Artificial latexes can be prepared by several different methods[4] as follows:

1. A solution-emulsification technique[5–8] in which the polymer is dissolved first in, or is swollen by, a volatile solvent to form a solution before being emulsified in water with the aid of one or more surfactants using a conventional emulsification method. The final step is removing the solvent by steam-distillation.[4]
2. A phase-inversion technique[9–12] in which a water-in-polymer emulsion is inverted to a polymer-in-water emulsion as more aqueous phase is added and finally the solvent is removed by steam-distillation (if a solvent is used).
3. A mutual solvent technique in which the polymer is dissolved in a water-miscible solvent and then mixed with water to give a three-component system comprising a dispersion of the polymer in an aqueous phase with the polymer in solvent distributed between the two phases (this technique is applicable only to more polar types of polymers). The final step is removing the solvent by steam-distillation.[4]

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4. A self-dispersion technique[13–15] in which the polymer is functionalized first with ionizable groups, either acidic or basic, before it is dispersed in an aqueous phase containing either an alkali or an acid.

Artificial latexes can also be prepared by the miniemulsification process,[2,16–21] which involves shearing a polymer/solvent solution in water in the presence of a surfactant and costabilizer, such as sodium lauryl sulfate and hexadecane (a long-chain alkane) or cetyl alcohol (long-chain fatty alcohol) respectively. The resulting product is a stable oil-in-water emulsion with an average droplet diameter in the range of 100–500 nm.[1,2] The solvent is subsequently stripped by the usual methods leaving a stable latex. The miniemulsification process has been used in the preparation of a wide range of polymer latexes, which include polystyrene, poly(vinyl acetate), epoxy resins, epoxy resin curing agents, ethylcellulose, cellulose acetate phthalate, polyesters, alkyd resins, synthetic natural rubbers, poly(vinyl butyral), Kraton (triblock styrene-butadiene-styrene copolymer), and silicones.[1,2,22–24] The miniemulsification process could also be used as an alternative approach to prepare a seed latex for a subsequent second-stage conventional emulsion polymerization process to obtain core–shell latexes, typically used in application areas such as adhesives, sealants, self-crosslinking thermoset coatings, paper coatings, and as impact modifiers for polymer matrices. In the miniemulsification approach, the solvent or mixture of solvents is used to reduce the original viscosity of the polymer to a level suitable for emulsification.[1,2,25] In addition, this process has proven advantageous in producing composite latexes, such as hybrid latexes,[26,27] and in pigment encapsulation.[28–30]

This study describes the preparation of artificial latexes, whereby miniemulsification was used to encapsulate TiO_2 particles in styrene-butyl acrylate copolymer particles. The benefits of this approach are that it is relatively easy to carry out and it is capable of producing encapsulated copolymer particles with high TiO_2 loading and stability. This process still meets the requirement of a VOC-free material through removal of the water-immiscible organic solvent. This approach is being evaluated owing to the limitations of the miniemulsion polymerization approach, which was used previously to evaluate the encapsulation of 3 wt % TiO_2 particles.[31–36] These limitations included low TiO_2 loading (3 wt % based on the monomer), which was determined to be 0.76% PVC for PS and 0.75% PVC (<1% PVC) for the copolymer, and the relatively high amount of unencapsulated polymer (free polymer).[35] In this study, titanium dioxide is being used as a model inorganic pigment to elucidate the basic requirements for the high loading encapsulation via the miniemulsification process and its final impact on the optical properties of the films cast from latexes of encapsulated particles as will be discussed in a subsequent article in this series.

EXPERIMENTAL

Materials

Styrene (>99%, Sigma-Aldrich, St. Louis, MO) and *n*-butyl acrylate (>99%, Sigma-Aldrich) monomers were purified of inhibitors by passing them through columns filled with an appropriate inhibitor removal packing material (Sigma-Aldrich). Sodium lauryl sulfate (SLS; Fisher, Pittsburgh, PA), sodium diamyl sulfosuccinate (Aerosol AY; Stepan, Northfield, IL), nonylphenoxy poly(oxyethylene) ethanol (Igepal CO 880; Stepan), isooctyl 3-mercaptopropionate (IOMP, Sigma-Aldrich), sodium bicarbonate ($NaHCO_3$; Sigma-Aldrich), toluene (VWR, Bridgeport, NJ), and hexadecane (HD; Sigma-Aldrich) 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[37–40] 32,000 (100% active; Avecia Inc., Wilmington, DE), which is basically a comb polymer with several anchors and several tails connected together in one molecule, was used as received. Solsperse 32,000 is chemically a polyamine/polyester.[41] Chloroform (Sigma-Aldrich), which is used in the determination of the amount of Solsperse 32,000 retained on the TiO_2 surface, was used as received. Deionized water was used for all experiments.

Analytical methods

For all miniemulsion and dispersion experiments, a sonifier (Branson, Model 450; Ultrasonics Corp., Danbury, CT) was used with 3/4 in diameter horn. The sonifier functions in two modes: pulsed and continuous. In pulsed mode, the ultrasonic vibrations are transmitted to a solution at a rate of one pulse per second. This pulse duration can be adjusted from 0.1 to 0.9 per second.[42] In all our experiments, the pulsed mode was used. A rotor-stator homogenizer (Model PRO 300D, PRO Scientific, Oxford, CT) was used as a relatively low energy input device (compared to the sonifier). During homogenization with the rotor-stator homogenizer, the continuous phase, along with the dispersed phase, is pulled up into the center of the rotor and then forced radially outward through the stator slots resulting in a decreasing droplet size. A membrane filtration device was used with nylon filters (GE Osmonics; Kent, WA) having 450 and 650 nm pore sizes. Dynamic light scattering (Nicomp, Model

TABLE I
Conventional Emulsion Polymerization Recipe for Preparing Styrene/*n*-Butyl Acrylate Copolymer Latex at 70°C

Ingredient	Amount (g)
Deionized water	116.57
Sodium diamyl sulfosuccinate (Aerosol AY)[a]	3.643
Nonylphenoxy polyoxyethylene ethanol (Igepal CO 880)	0.291
n-Butyl acrylate	16.03
Styrene	13.11
Potassium persulfate (KPS)	0.175
Sodium bicarbonate ($NaHCO_3$)	0.175
Isooctyl 3-mercaptopropionate (IOMP)[b]	0.145

St/BA: 45/55 wt %; solids content: ~19%.
[a] 5 wt % based on aqueous solution.
[b] 0.5 wt % based on comonomers.

370; Particle Sizing Systems, Santa Barbara, CA) was used to measure the resulting polymer particle size as well as the dispersed TiO_2 particle size. In all Nicomp measurements, only the Gaussian distribution was considered unless otherwise noted. Capillary hydrodynamic fractionation (Model CHDF 1100, Matec Applied Sciences, Northborough, MA) was also used to measure the latex particle size and particle size distribution. Prior to measurement, samples were first sonified in a sonifier bath (Commonwealth Scientific, Alexandria, VA) to break up any particle aggregates and then filtered through a 5 μm filter. The molecular weight and molecular weight distribution of the poly(styrene-*co*-*n*-butyl acrylate) prepared by conventional emulsion polymerization was determined by gel-permeation chromatography (GPC; Waters, Milford, MA) using a differential refractometer (Waters 410) with THF as solvent. A UV/Vis spectrophotometer (SPECTRONIC® GENESYS™; Thermo Electron, Waltham, MA) was used to determine the amount of Solsperse 32,000 retained on the TiO_2 particles as a function of sonification time. An ultracentrifuge (LB-70M; Beckman Coulter, Fullerton CA) equipped with a 6-tube swinging-bucket rotor (SW-41) was used for the adsorption studies. The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (DSC 2920 TA Instruments, New Castle, DE).

Procedure

Preparation of styrene/*n*-butyl acrylate copolymer via conventional emulsion polymerization

Poly(styrene-*co*-*n*-butyl acrylate) latex was prepared by conventional emulsion polymerization using a previously developed recipe (Table I), modified by addition of a chain-transfer agent to limit the molecular weight.[43] The experimental procedure was as follows. The Aerosol AY, Igepal CO 880 (nonionic surfactant), and sodium bicarbonate ($NaHCO_3$) were dissolved in deionized water, while the chain-transfer agent (IOMP) was dissolved in the comonomers (styrene/*n*-butyl acrylate). The aqueous and oil solutions were then mixed, and the aqueous potassium persulfate initiator (KPS) solution was injected into the reaction flask. The polymerization was carried out under an inert nitrogen atmosphere in a three-necked round bottom stirred reactor (100 rpm) at 70°C for 8 h. The latex was designed to have a T_g close to zero (−4°C, estimated using the Fox equation)[44] in order for it to be used as a film-forming material. It was left overnight in the freezer to coagulate, and then filtered. Fresh DI water was added quantitatively and the conductivity measured. This process was repeated several times until the conductivity leveled off, which is an indication that the copolymer has been cleaned of the surfactant and other electrolytes. The polymer was characterized by GPC and found to have a broad molecular weight distribution (M_n = 49,920 g/mol; M_w = 188, 510 g/mol; PDI = 3.776). This surfactant-free copolymer was used as the polymer in the miniemulsification studies as described later.

Stabilization of the TiO_2 pigment

A detailed dispersion study of the TiO_2 particles is described elsewhere where Solsperse 32,000 was selected as the best stabilizer among those tested.[35] Sonification was used to breakup the TiO_2 aggregates, allowing the adsorption of Solsperse 32,000 stabilizer on the freshly exposed surfaces. The amount of the stabilizer retained and the particle size obtained as a function of sonification time will be reported. This study was important to determine the optimum amount of stabilizer needed to stabilize the TiO_2 pigment. It was performed by first establishing a calibration curve using a UV spectrophotometer at λ_{max} of 243 nm.

The recipe used to study the adsorption of Solsperse 32,000 on the TiO_2 particles consisted of 35 g (40.4 mL) toluene, 2.33 g (33 wt % based on the amount of TiO_2 used) Solsperse 32,000, and 7 g (20 wt % based on oil phase) hydrophilic TiO_2 (~30 nm primary particle size). This recipe was designed to simulate the same oil phase volume used to disperse TiO_2 stabilized with Solsperse 32,000. This is important because the efficiency of the sonifier is strongly affected by the volume of the system being sonified. The procedure was as follows. The stabilizer was first dissolved in the toluene followed by the addition of freshly dried TiO_2 particles. The dispersion was stirred for 20 min and then sonified for 20 min at a duty cycle of 70% and an output power of 10. Samples were withdrawn at specific time intervals for adsorption and particle size studies by DLS. Owing to the overlapping absorbance

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.

TABLE III
Calculated Density for the Encapsulated Particles as a Function of Pigment/Binder Ratio

PVC (%)	Weight ratio of TiO_2 : polymer	Calculated density (g/cm^3)
No TiO_2	NA	1.0340
11	1 : 2	2.0560
20	1 : 1	2.5671
30	1.7 : 1	2.9656
43	3 : 1	3.3330
50	4 : 1	3.4868
60	5.96 : 1	3.6594
70	9.29 : 1	3.8022

of toluene with the absorbance band of Solsperse 32,000, chloroform was used instead for the UV determination of the unadsorbed Solsperse dispersant. The samples were ultracentrifuged at 25,000 rpm for 1 h at room temperature to separate the TiO_2 particles with adsorbed Solsperse 32,000 from the unadsorbed Solsperse 32,000 in the oil phase. After centrifugation, a clear supernatant was obtained, indicating that there were no TiO_2 particles left in the supernatant. The large difference in densities between toluene (0.867 g/mL) and TiO_2 (4.1 g/mL) particles facilitated the separation. The supernatant was then collected without disturbing the sediment. It was dried and the Solsperse was redissolved in a known amount of chloroform. The final step was to measure the absorbance of the chloroform containing Solsperse 32,000 by UV spectroscopy at a wavelength of 243 nm and determine the amount of Solsperse 32,000 adsorbed on the TiO_2 surface based on the calibration.

Preparation of encapsulated artificial latexes via miniemulsification

The cleaned poly(styrene-*co*-*n*-butyl acrylate) polymer 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 II. The PVC of each batch, its pigment/binder ratio, and its corresponding density are shown in Table III. The experimental procedure for the preparation of encapsulated artificial latexes via miniemulsification is shown in Figure 1. The water phase containing SLS (anionic surfactant) was mixed with the oil phase containing HD, dissolved polymer, and TiO_2, dispersed and stabilized with Solsperse 32,000 in toluene, by magnetic stirrer for ~15 min at room temperature. Then the crude emulsion was sonified for different times to determine the effect of sonification time on the resulting particle size. The sonification, which was performed at an output power of 10 and a duty cycle of 70%, was carried out with the mixture immersed in an ice bath to prevent a substantial increase in the temperature. All of the encapsulated artificial latexes were prepared using the sonifier alone unless otherwise noted. Later, in some experiments, the homogenized latexes were passed through 450 nm and/or 650 nm pore size nylon membranes using a membrane filtration unit. The filtration process, carried out with a nitrogen pressure of about 50 psig was used to narrow the size distribution of the encapsulated latexes. Subsequently, the toluene solvent was removed by rotary evaporation at 50°C under vacuum. A broad range of encapsulated latexes were prepared with different PVCs.

PVC is defined as the ratio of the total pigment volume to the total volume of pigment and binder. It is usually expressed as a percentage as defined by the expression:

$$\text{Pigment volume concentration(PVC)} = \frac{V_p}{V_p + V_b} \times 100 \quad (1)$$

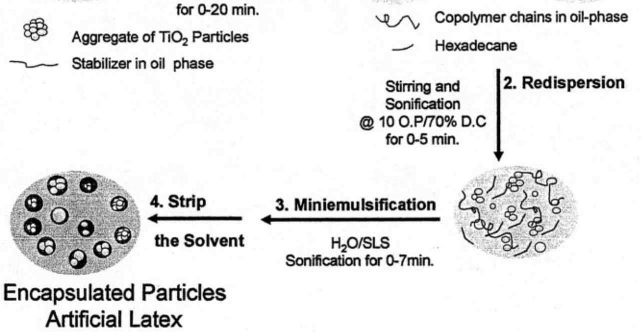


Figure 1 Scheme for preparation of TiO_2-encapsulated artificial latexes by the direct miniemulsification technique.

where V_b is the volume of binder (copolymer) and V_p is the volume of pigment (TiO_2).[45–51] In current paint technology, there is a trend to approach formulating problems in terms of volume rather than weight relationships because replacement of components purely on a weight basis often does not achieve the effects intended.[52] The volume of pigment does not include any pores or spaces between the particles, and it is calculated from the mass and density of the pigment (4.1 g/cm^3 for TiO_2). The density of the binder is calculated using the densities of PS and PBA, 1.044 g/cm^3 and 1.026 g/cm^3, respectively.[53] Thus, the density of the binder is 1.034 g/cm^3. It has been known for a long time that the relative amount of pigment and binder in paint has a large influence on its properties. This recipe was used successfully to prepare encapsulated latex with high TiO_2 loading, as shown in Table III, in which the density of the encapsulated particles was calculated via eq. (2).

$$\rho_{\text{encap.}}(\text{g/cm}^3) = \rho_{\text{TiO}_2} \times \left(\frac{M_{\text{TiO}_2}}{M_{\text{polym.+TiO}_2}}\right) + \rho_{\text{polymer}} \times \left(\frac{M_{\text{polym.}}}{M_{\text{polym.+TiO}_2}}\right) \quad (2)$$

where $\rho_{\text{encap.}}$ is the density of encapsulated particles (g/cm^3). M_{TiO_2} and M_{polym} are the masses of the TiO_2 and copolymer in the recipe for each PVC system, respectively. $M_{\text{polym.+TiO}_2}$ is the mass of both TiO_2 and copolymer, ρ_{TiO_2} is the density of the TiO_2 (4.1 g/cm^3), and ρ_{polymer} is the density of the copolymer (1.034 g/cm^3).

RESULTS AND DISCUSSION

Dispersion studies

Effect of copolymer/HD addition on the TiO_2 dispersibility

TiO_2 is the most important single pigment employed by the paint industry because of its ability to impart whiteness, brightness, and opacity in paint systems. To achieve these end results, the pigment must first be dispersed by breaking down any large aggregates that exist in the dry state (clusters of primary particles). The pigment must also be stabilized in this dispersed state, so that it will neither flocculate excessively (affects opacity and gloss), nor settle as a result of poor shelf stability. A detailed dispersion study of TiO_2 particles in nonaqueous media using five different functional stabilizers has been discussed elsewhere.[35] Solsperse 32,000 was selected as the best stabilizer, which gave stable particles having long shelf-life stability at the polymerization temperature and relatively small TiO_2 particle aggregates. Here, the dispersion of TiO_2 particles in toluene is investigated along with the effect of the addition of poly(styrene-*co*-*n*-butyl acrylate) and HD on their dispersibility. The effect of sonification time on the 20 wt % TiO_2 particles in toluene using Solsperse 32,000 is shown in Figure 2. The sonification was performed at an output power of 10 and a duty cycle of 70%. This dispersion is used as the stock dispersion in the preparation of different TiO_2 encapsulated latexes with different PVCs. Figure 2 shows the TiO_2 volume-weighted Gaussian analysis of the particle size distribution measured by DLS (Nicomp) and expressed in frequency of the distribution as a function of sonification time. As the sonification time increased, the TiO_2 particle size decreased and as was noted elsewhere,[35] ~20 min is the optimum sonification time beyond which there is no further decrease in the TiO_2 particle size.

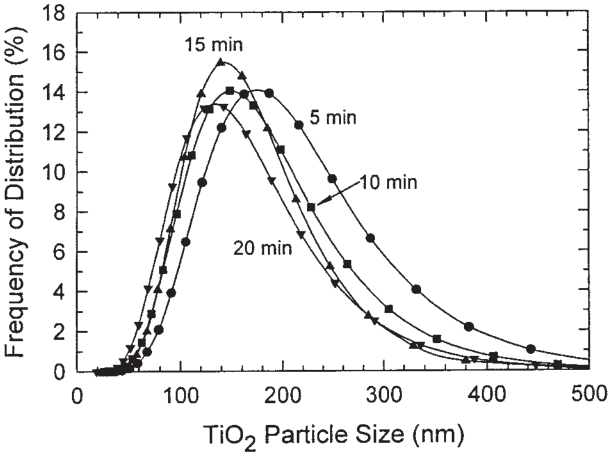


Figure 2 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of sonification time on the TiO_2 particles (20 wt %) stabilized with Solsperse 32,000 in toluene.

The dispersion of TiO_2 particles in the oil phase containing copolymer and HD started with dilution of the stock dispersion (20 wt %) to 10 wt % by adding toluene only. This led to an increase in the TiO_2 particle size (Fig. 3) probably caused by desorption of Solsperse 32,000 from the TiO_2 particles surface resulting in some instability and the formation of larger TiO_2 particles. As can be seen from the graph, the addition of copolymer followed by HD also led to an increase in the TiO_2 particle size, which is probably also caused by some flocculation. Flocculation can occur after copolymer addition either because the polymer chains are long enough to adsorb onto more than one particle (bridging flocculation) and/or the desorption of Solsperse 32,000 has increased the chances for adsorption of polymer extending from one particle to another. It has been found that the addition of a free (nonadsorbing) polymer induces flocculation, which cannot be explained by charge neutralization or bridging flocculation. This type of flocculation caused

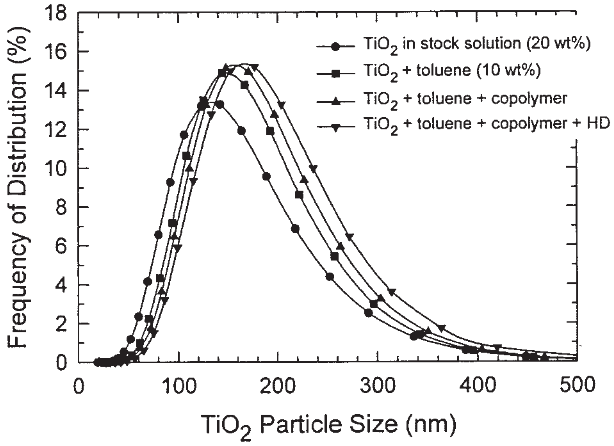


Figure 3 Volume-weighted Gaussian analysis of the particle size distribution showing the effect on the dispersibility of TiO$_2$ particles of adding copolymer and HD during magnetic stirring.

by free polymer is called "depletion flocculation."[54] Figure 3 shows clearly that the TiO$_2$ particles need to be redispersed after adding HD and copolymer. Steel-ball milling was investigated as a method to enhance the dispersion, but, as shown in Figure 4, it was not effective even after 48 h of milling. The graph shows clearly that the sonifier is more effective in redispersion of the TiO$_2$ particles than steel-ball milling at only one sonification time, which is 5 min. The effect of different sonification times on the TiO$_2$ particle size in the presence of copolymer and HD was investigated next and the results for 11% PVC and 43% PVC, shown in Figures 5(a) and 5(b), indicate that the decrease in the TiO$_2$ particle size is not significant. It can be concluded that for the redispersion of the TiO$_2$, the use of sonification is important, but the sonification time is not. Thus, in the redispersion procedure, 3 min will be used unless otherwise noted. A comparison of the TiO$_2$ particle size (stabilized with Solsperse 32,000 in the presence of HD and copolymer) for the 11% PVC and 43% PVC systems is shown in Figure 6, which indicates that the higher loading of TiO$_2$ (43% PVC) resulted in a reduced TiO$_2$ particle size.

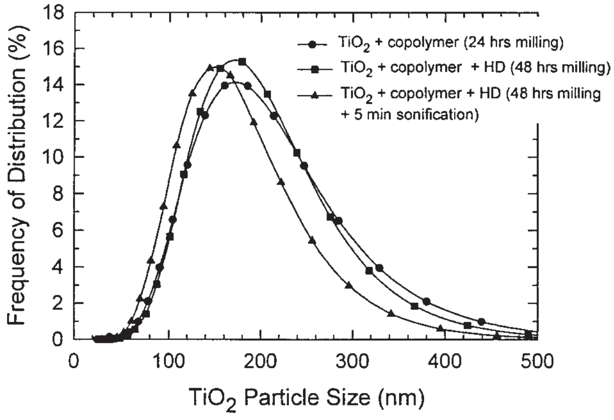
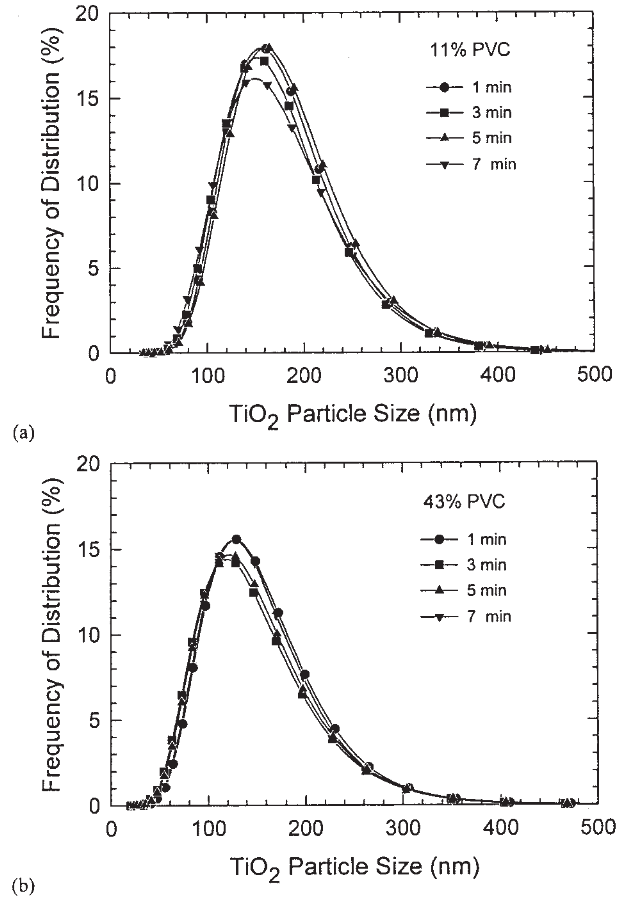


Figure 4 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of steel-ball milling on the TiO$_2$ particle size in the presence of copolymer/HD.



(a)

(b)

Figure 5 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of sonification time on the dispersibility of TiO$_2$ particles in the presence of HD and copolymer: (a) 11% PVC and (b) 43% PVC.

Shelf-life stability of the dispersed TiO$_2$ particles in the presence of HD and copolymer

Shelf-life stability refers to the stability of the dispersed TiO$_2$ particles undergoing Brownian motion over a specific period of time. It also gives an idea about the effectiveness of the stabilizer (i.e., Solsperse 32,000) in maintaining the dispersed TiO$_2$ particles against agglomeration. Thus, the repulsive forces between the TiO$_2$ particles in a nonaqueous medium (toluene) that are responsible for maintaining dispersion stability are mainly steric since charge stabilization will not be effective in media of low dielectric constant (the vast majority of organic solvents and plasticizers).[55] The shelf-life stability of the TiO$_2$ particles stabilized with Solsperse 32,000 in the presence

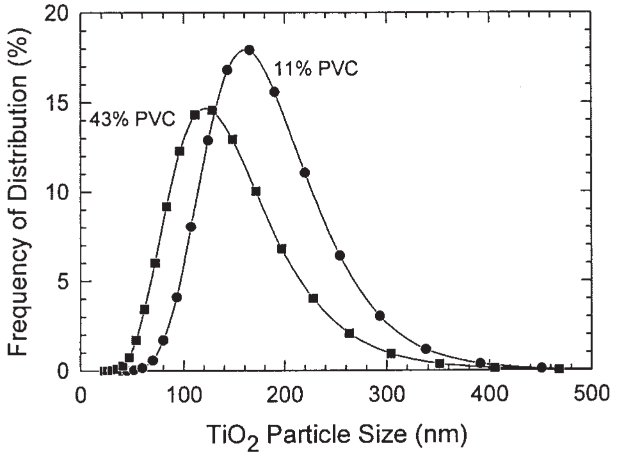


Figure 6 Comparison of the volume-weighted Gaussian analysis of the particle size distribution of the TiO_2 (stabilized with Solsperse 32,000 in the presence of HD and copolymer in toluene) for 11% PVC and 43% PVC after 3 min sonification.

of HD and copolymer for both 11% PVC [Fig. 7(a)] and 43% PVC [Fig. 7(b)] was determined by following the changes in the TiO_2 particle size versus time at room temperature. As can be seen from Figure 7, the TiO_2 particle size and size distribution did not change significantly with time, which indicates that the TiO_2 particles are stable over many days.

Adsorption studies

As shown in Figure 8 and also as noted in a prior publication,[31] the TiO_2 particle size decreased with increasing sonification time, and correspondingly more surface area was created. The surface area was calculated assuming that the TiO_2 particles were solid spheres having a diameter (D_v) as determined by DLS (Nicomp). No consideration was given to the nature of the aggregates (i.e., their shape and porosity). In addition, it has been noted that increasing the sonification time (more than 20 min) does not decrease the TiO_2 particle size any further. On the other hand, Figure 9 shows that in the initial stages of the adsorption (at zero sonification time), where the initial amount of Solsperse 32,000 per gram of pigment was constant for all three loadings as shown in Table IV, the adsorbed amount was low and increased rapidly as the sonification time increased. As the TiO_2 particles surface became saturated, adsorption decreased and eventually the adsorbed amount did not change any further; a plateau was reached after 7 min sonification. At the end of the sonification, the amount of Solsperse 32,000 adsorbed was 2.72×10^{-4} mol/g, which constitutes 88% of the initial amount of Solsperse 32,000 in the oil phase prior to sonification as shown in Table IV. On the other hand, the preceding results were for the TiO_2 stock dispersion (20 wt %) and the question now was what would be the effect if any of the presence of polymer on the adsorbed Sol-

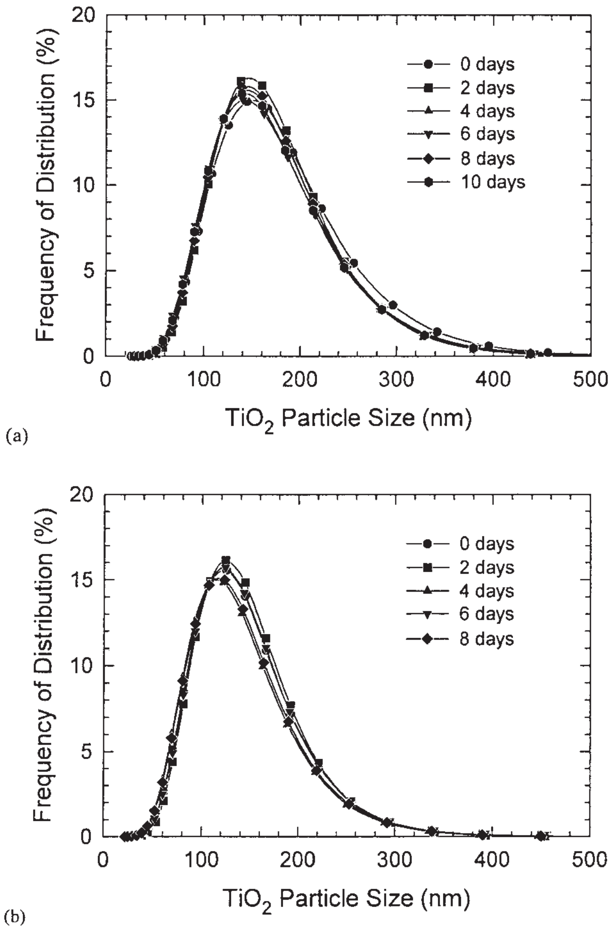


Figure 7 Volume-weighted Gaussian analysis of the particle size distribution determining the shelf-life stability of the TiO_2 particles in the presence of HD and copolymer: (a) 11% PVC and (b) 43% PVC.

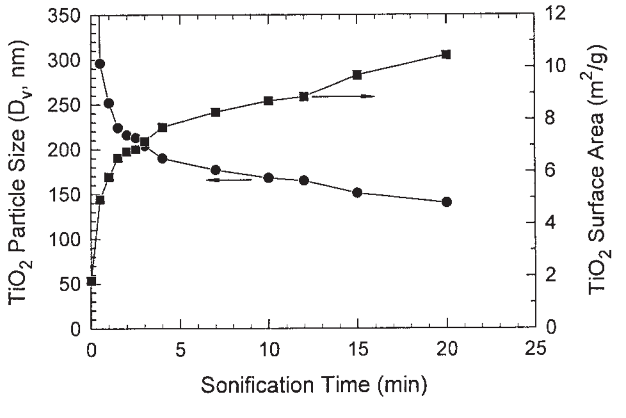


Figure 8 TiO_2 particle size and surface area created as a function of sonification time for 20 wt % TiO_2 stock dispersion stabilized with Solsperse 32,000 in toluene.

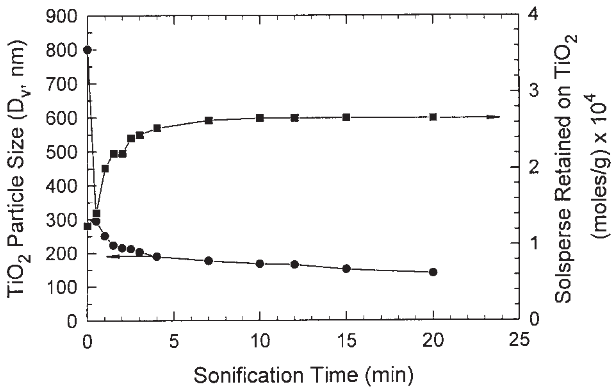


Figure 9 Amount of Solsperse 32,000 retained per gram of TiO_2 particles, and TiO_2 particle size as a function of sonification time for 20 wt % stock dispersion of TiO_2 in toluene.

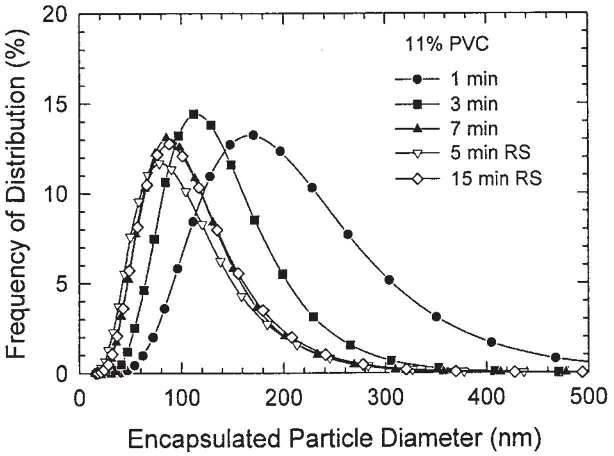


Figure 10 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of sonification time and rotor-stator (RS) homogenization on the latex particle size for 11% PVC.

sperse 32,000 for the different PVCs. As shown in Table IV, as the loading increased from 11% PVC to 43% PVC, the initial amount of Solsperse 32,000 was the same and after 3 min sonification, the amounts adsorbed were 2.82×10^{-4} and 2.95×10^{-4} mol/g, which constitute 91.1 and 95.6% of the initial amount of Solsperse 32,000 in the oil phase prior to sonification, respectively. A comparison of the TiO_2 particle size for the 11% PVC and 43% PVC systems (Table IV) indicates that the higher loading of TiO_2 (43% PVC) helped in reducing the TiO_2 particle size.

Miniemulsification studies

Effect of sonification time on the encapsulated latex particle size

The encapsulated latex particle size was measured by DLS (Nicomp). Although the toluene was not stripped from the latex, it was expected that the excessive dilution during sample preparation effectively removed it, leaving behind unswollen latex particles. The effect of solvent stripping on the latex particle size and size distribution will be discussed later. The experimental results for the effect of sonification time (output power of 10 and 70% duty cycle) on the encapsulated latex particle size for the 11% PVC latex are shown in Figure 10. It follows the same trend observed for the dispersion of the TiO_2 particles stabilized with Solsperse 32,000 in toluene (prior to adding the HD and copolymer). As the sonification time increased from 1 min to 7 min, there was a decrease in the latex particle size from 184 to 95 nm (Fig. 10). The sonifier may produce an emulsion with a broad size distribution because the energy experienced by the droplets depends on the distance from the sonifier tip, the time of exposure, and the number of passes below the tip. To narrow the encapsulated latex particle size distribution, it was believed that employing another homogenization technique such as a rotor-stator (RS) homogenizer, a lower energy input device, could help. In Figure 10, the emulsion was subjected to 5 and 15 min of homogenization using the rotor-stator (RS) homogenizer after 7 min sonification. Neither the particle size nor size

TABLE IV
Effect of TiO_2 Loading on the Adsorption of Solsperse 32,000 at Different PVCs

Experiment	Initial [Solspere 32,000] (mole/g)[a]	Solsperse 32,000 retained on TiO_2 mole/g (wt %)[b,c]	Particle Size of TiO_2 (D_v, nm)
20 wt % TiO_2 Dispersion[d]	3.09×10^{-4}	2.72×10^{-4} (88.16%)	140[e]
11% PVC[f]		2.82×10^{-4} (91.26%)	169[g]
43% PVC[f]		2.95×10^{-4} (95.47%)	131[g]

[a] Amount of Solsperse 32,000 used was calculated based on the pigment loading (33 wt% of pigment loading).
[b] Based on initial amount of Solsperse 32,000 in the recipe.
[c] Determined by UV spectrophotometer at 243 nm wavelength in chloroform.
[d] 20 min sonification in toluene containing only Solsperse 32,000 at 10 OP and 70% DC.
[e] TiO_2 particle size in the oil phase containing Solsperse 32,000 only determined by DLS.
[f] In oil phase (toluene) containing Solsperse 32,000, copolymer and HD after 3 min sonification at 10 OP and 70% DC.
[g] TiO_2 particle size in the oil phase containing copolymer and HD determined by DLS in toluene.

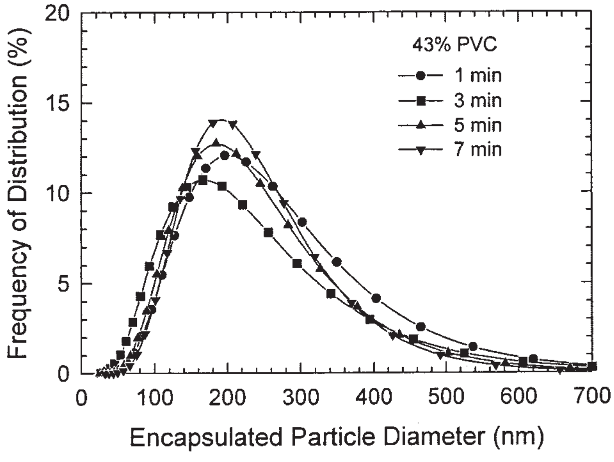


Figure 11 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of sonification time on the latex particle size for 43% PVC.

distribution improved, however, using the rotor-stator homogenizer.

For the 43% PVC system, the effect of sonification time on the encapsulated latex particle size differed from the 11% PVC system, as shown in Figure 11. As the sonification time increased, the latex particle size decreased up to 3 min and with a further increase in the sonification time, led to an increase in the latex particle size. This could be due to flocculation as a result of the high loading of TiO_2 particles. In this system, the weight ratio of binder (copolymer) to TiO_2 was 1:3 compared to 2:1 in the 11% PVC system.

Figure 12 summarizes the particle sizes obtained in the various stages of the process starting from the TiO_2 stock dispersion after 20 min of sonification to the encapsulated latex particles for both the 11% PVC and 43% PVC systems. For 11% PVC [Fig. 12(a)], the TiO_2 particles increased in size from 127 nm (D_v) in the 20 wt % stock dispersion to 169 nm by adding HD and copolymer with 5 min sonification. This means that in the dispersion, the TiO_2 particle size in the presence of HD and copolymer has reached a minimum particle size and cannot be decreased further under the given conditions. Any decrease in size will result in reaggregation, forming particles close to that size (~169 nm) at this loading, as shown in Figure 5(a). However, for the 43% PVC system [Fig. 12(b)], the TiO_2 particle size before (stock dispersion) and after adding HD and copolymer remained almost unchanged. This could be the result of the higher loading of TiO_2 (Fig. 6). However, in the emulsion, the encapsulated latex particle size for 11% PVC decreased to 95 nm with 7 min sonification. One explanation for this is that the TiO_2 particles inside the droplets may be broken into sizes even smaller than the TiO_2 in the original dispersion and these are separated into different droplets and thus do not have a chance to reaggregate to their equilibrium size because of the presence of water as an intervening barrier. Another possibility is that some of the emulsion droplets have no or few TiO_2 particles within them. In contrast, at 43% PVC, with the increase in TiO_2 loading, the encapsulated latex particles increased in size and the copolymer layer on the TiO_2 particles decreased in thickness as shown in Figure 12. In this case, the emulsion droplets did not break into smaller sizes but instead aggregated to produce larger particles, as shown in Figure 13.

Effect of membrane filtration on the encapsulated latex particle size distribution

It was reported by Mohammadi et al.[25] that a model polystyrene latex could be produced with a narrow size distribution of submicron particles by applying a membrane filtration process after miniemulsification of polystyrene (dissolved in cyclohexane) in water with a sonifier. This method was now applied here. In this process, after homogenizing the crude emulsion

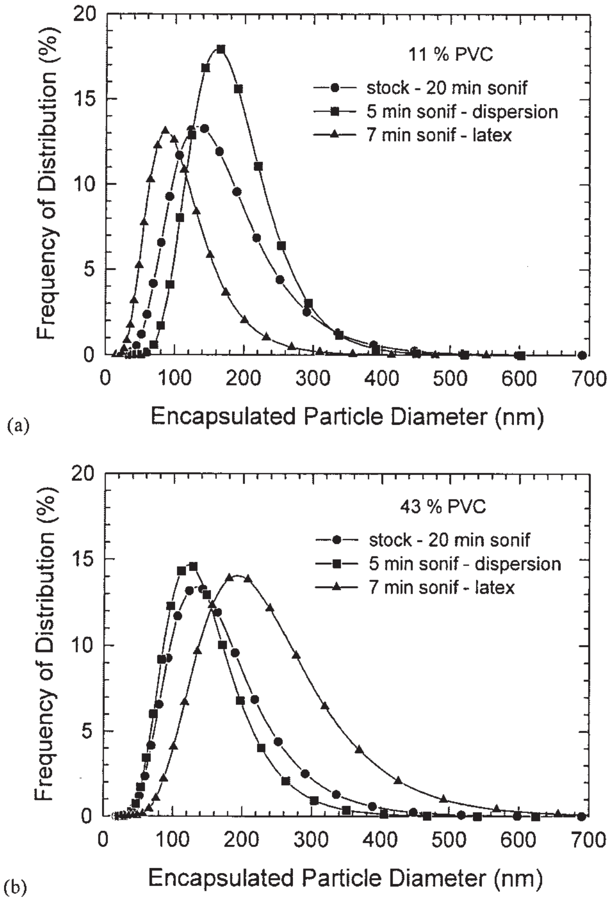


Figure 12 Volume-weighted Gaussian analysis of the particle size distribution comparing the particle size of TiO_2 particles in the 20 wt % stock dispersion dispersed in the presence of HD and copolymer, and latex particle size: (a) 11% PVC and (b) 43% PVC systems.

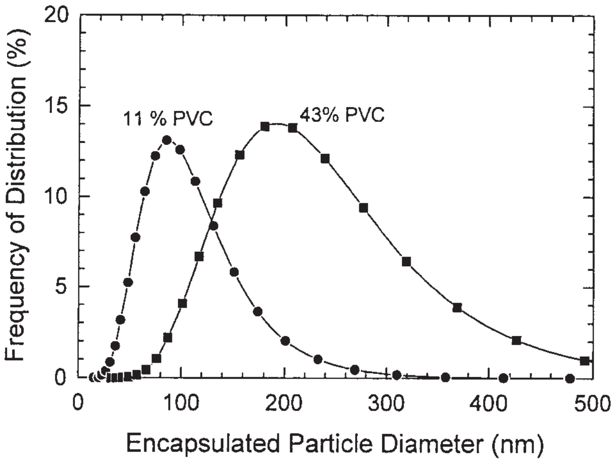


Figure 13 Volume-weighted Gaussian analysis of the particle size distribution showing the comparison of latex particle size for 11% PVC and 43% PVC systems after 7 min sonification.

for different sonification times (power output of 10 and 70% duty cycle), the dispersion was forced through the pores of a membrane having a uniform pore size under 50 psig nitrogen gas pressure. The membrane filtration technique was applied only to the 11% PVC system. It was noted that at short sonification times (i.e., 1 min), membrane filtration could not be applied successfully with a 450 nm pore size membrane. This was because a large number of large encapsulated droplets are formed, which formed a paste-like cake on the membrane after applying pressure, resulting in a blockage of the membrane. However, a larger pore size, 650 nm, could be used, as shown in Figure 14(a). This graph shows that the encapsulated particle size distribution narrowed after the first pass through the membrane filter; however, any further passes had no influence on the distribution. At longer sonification times (3 min), the membrane filtration was not useful for either pore size filter, and there was no measurable effect of the number of passes, as shown in Figure 14(b).

Shelf-life stability of encapsulated latex particles

The shelf-life stability of the emulsions (toluene present) were monitored by following the changes in particle size in both the 11% PVC and 43% PVC systems with time at room temperature. As can be seen from Figure 15, the particle size and size distribution did not change significantly with time, indicating that they are stable over 8–10 days.

Effect of solvent stripping on the encapsulated latex particles

Figure 16 shows the effect of solvent removal (stripping) on the encapsulated latex particle size and size distribution for both the 11 and 43% PVC systems. The average particle size before solvent removal (unstripped) was smaller than that obtained after stripping and the distribution broadened, which is an indication that there was some aggregation of latex particles. The reason could be the elevated stripping temperature, 50°C, which could lead to some SLS desorption from the surface of the latex particles.

Role of hexadecane in the recipe

Even though, the main function of HD in a miniemulsion recipe is to impart stability to the droplets by retarding the diffusion of solvent (toluene) from the small toluene droplets to the large ones (Ostwald ripening), it might also have an affect on the T_g of the poly(styrene-*co*-*n*-butyl acrylate) copolymer if it is not removed during the stripping process. The recipe shown in Table II was used to prepare 11% PVC artificial latexes with and without HD present. The encapsulated particle size of the 11% PVC sample,

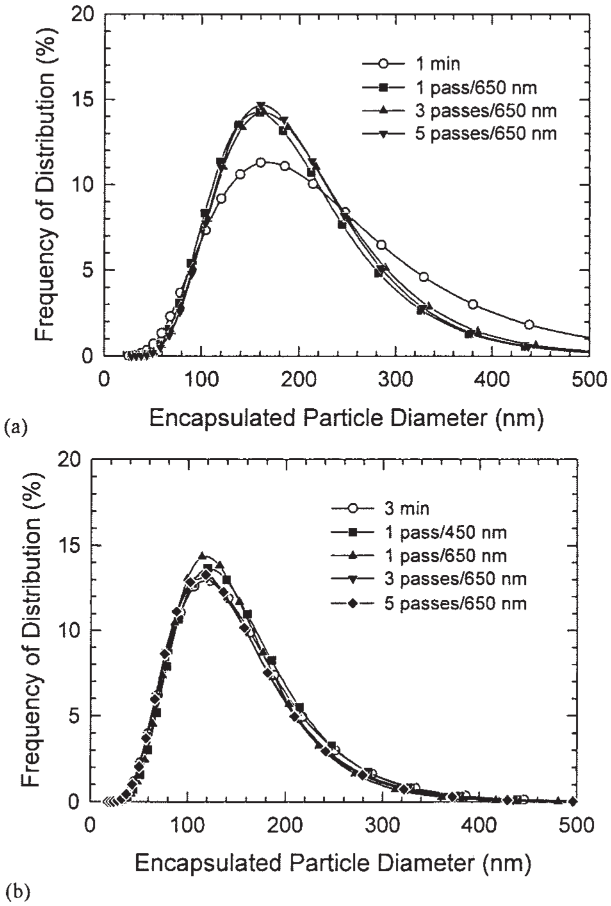


Figure 14 Volume-weighted Gaussian analysis of the particle size distribution showing the effect of number of passes through different pore size filters on the encapsulated particle size and size distribution for the 11% PVC system after (a) 1 min sonification and (b) 3 min sonification.

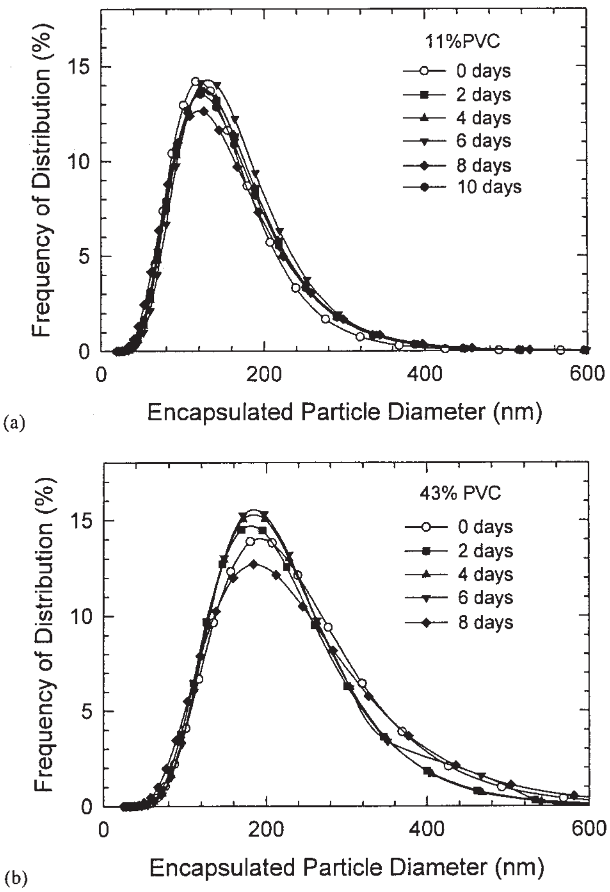


Figure 15 Effect of aging time (shelf-life) on the volume-weighted Gaussian analysis of the particle size distribution of the TiO_2 encapsulated in emulsion droplets: (a) the 11% PVC and (b) 43% PVC systems.

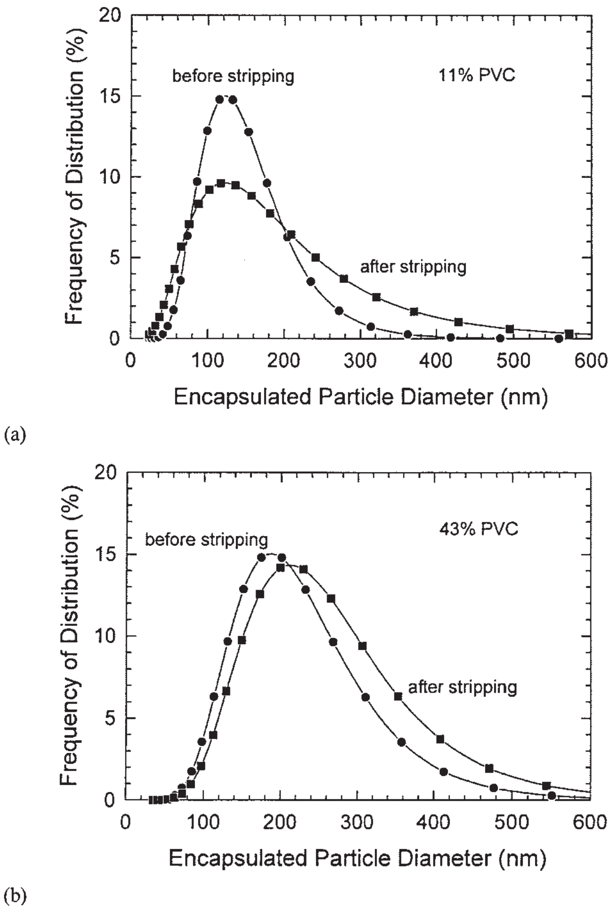


Figure 16 Effect of solvent stripping at 50°C on the encapsulated latex particle size after 3 min sonification: (a) 11% PVC and (b) 43% PVC systems.

prepared without HD before and after solvent stripping, is shown in Figure 17. The encapsulated particle size differed before and after stripping, with the size increasing after stripping. Again, this increase in encapsulated particle size is likely caused by some aggregation resulting from the high temperature of stripping (50°C). Comparing this result with the 11% PVC sample prepared with HD as shown in Figure 16(a) reveals that in the case where no HD was used, the coagulation was more significant.

Differential scanning calorimetry (DSC) was used to determine the T_g of the poly(styrene-*co*-*n*-butyl acrylate) copolymer (no HD), the artificial latex (poly(styrene-*co*-*n*-butyl acrylate) only, no TiO_2) with HD present, and the 11% PVC latex prepared by miniemulsification. A heating rate of 10°C/min under nitrogen was used for 10–20 mg samples. All samples were cleaned (SLS removed) by serum replacement. In the DSC measurements, two temperature sweeps were used to remove the thermal history effects, which are an unwanted complicating factor. Therefore, the first sweep removes the thermal history effect (if any) such as sample preparation or aging effects, while the second sweep gives the T_g.

The T_g obtained by DSC is used sometimes to check the accuracy of the T_g calculated from the Fox equation.[44] However, the experimental and calculated re-

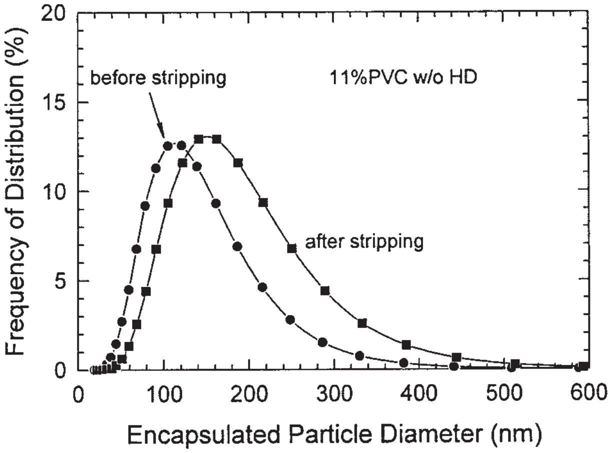


Figure 17 Volume-weighted Gaussian analysis of encapsulated particles before and after solvent stripping for 11% PVC latex prepared without HD.

TABLE V
Comparison Between the T_g Calculated from the Fox Equation and DSC Results

Sample	T_g (°C) (Calculated)[a]	T_g (°C) Measured (DSC)[b]
Copolymer[c]	−4	+7.03
Copolymer + HD[d]	NA	+3.80
11% PVC[e]	NA	+3.64

[a] Using the Fox equation.[44]
[b] Assigned to the midpoint transition.
[c] Cleaned poly(styrene-*co*-*n*-butyl acrylate) copolymer prepared by conventional emulsion polymerization; copolymer molecular weight: M_w = 188,514 g/mol and M_n =49,920 g/mol.
[d] Cleaned artificial latex prepared by miniemulsification approach.
[e] Cleaned encapsulated latex (with HD) prepared by miniemulsification approach.

sults can deviate from one another as shown in Table V. This discrepancy between calculated and experimentally obtained T_g probably stems from the combined effects of monomer sequence distribution and end group effects in the copolymer chains. Also this discrepancy between the two T_gs clearly demonstrates the importance of corroborating the calculated T_g with that measured by DSC.[56] The DSC results indicate that some of the HD is still in the polymer particles after solvent stripping and its presence resulted in a decrease in the T_g. This indicates that the HD acts as a plasticizer thus reducing the T_g.

SUMMARY AND CONCLUSIONS

The miniemulsification approach was used successfully to prepare encapsulated copolymer latexes with high loading of TiO_2 particles (11% PVC to 70% PVC). Particle size analysis (DLS) showed that as the TiO_2 loading increased (11% PVC to 43% PVC), the TiO_2 particle size in the oil phase decreased, while the latex particle size increased. Decreasing the TiO_2 particle size in the presence of HD and copolymer is dependent on the energy input and the TiO_2 loading. Aging studies showed that the TiO_2 dispersions and the encapsulated latexes are stable for many days.

Membrane filtration was applied to the 11% PVC system using two different pore size membranes (450 and 650 nm). Results showed that smaller droplets can pass undisturbed through the pores of the membrane and only droplets with diameters larger than the membrane pore size can be affected. In addition, droplets slightly larger than the pore size can squeeze through the membrane pores, while much larger droplets form a paste-like cake blocking the membrane. This could be caused by the TiO_2 being a solid material with high density. Moreover, the number of passes through the membrane did not affect the particle size distribution.

The role of HD in the recipe was studied for an artificial latex (no TiO_2 present), and 11% PVC, with and without HD present, in terms of particle size before and after solvent stripping, and its affect on the T_g. In general, the encapsulated particle sizes before and after stripping for 11% PVC, with and without HD present, are not the same. However, the encapsulated particle size increased to a large extent after stripping in the case of 11% PVC without HD present. This shows the importance of HD in the recipe. However, DSC results showed that some of the HD remained in the particles after solvent stripping and its presence decreased the T_g of the copolymer.

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