Encapsulation of Inorganic Particles via Miniemulsion Polymerization

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SUMMARY: The encapsulation of TiO_2 particles via miniemulsion polymerization is strongly dependent on the size and stability of the inorganic particles in the monomer medium in which they are initially dispersed. It was found from XPS and FT-IR studies that both the hydrophilic and hydrophobic TiO_2 particles, which were studied, have hydroxyl groups present on their surfaces, which can strongly interact with the amine end-groups of the polymeric stabilizer, OLOA370 (polybutene-succinimide diethyl triamine). It was found from the dispersion and adsorption studies that the amount of OLOA370 retained on the TiO_2 particles is strongly dependent on the area exposed by the sonification that is applied to break up the aggregates in the dispersion process. The TiO_2 dispersions in styrene monomer were themselves dispersed as miniemulsion droplets and subsequently polymerized. It was concluded from the density gradient column (DGC) analysis of the latexes obtained from the encapsulation polymerizations, that the stability of the inorganic particles in the monomer, as well as their particle size, significantly influence the encapsulation efficiencies. The use of the hydrophilic titanium dioxide particles in combination with the stabilizer, OLOA370, resulted in a good dispersibility, dispersion stability, and small TiO_2 particle size. This lead to better encapsulation efficiencies compared to the hydrophobic particles. The poorer results obtained with the hydrophobic TiO_2 particles were attributed to their larger particle size, which resulted from the reduced adsorption of the OLOA370. Fewer hydroxyls and the presence of the trimethoxy octyl silane (TMOS) groups, which themselves are unable to provide sufficient steric stability, are proposed to explain these findings.

Introduction

Encapsulation of inorganic pigment particles in a polymer shell will help to prevent their agglomeration during latex film formation and provide better mechanical properties such as film strength, appearance, and durability. In order to obtain these improved physical and mechanical properties, a good dispersion of the inorganic particles in the initial dispersion (oil or aqueous) medium, and thus in the final matrix, should be obtained.

Several methods have been investigated to achieve the encapsulation of inorganic particles within a polymer shell. The surface properties of the inorganic particles and the nature of the dispersion medium largely determine how they are to be dispersed in the dispersion medium subsequent to the encapsulation polymerization. Several methods have been employed for the dispersion of the inorganic particles in different media (organic or aqueous) [1-7]. Surface

modification and the use of steric stabilizers are the most successful among these methods. While surface treatment requires a meticulous pretreatment of the particles[1,2], steric stabilization relies on the adsorption of a layer of polymer chains on the pigment surface. These chains typically possess a tail that stays in solution thus providing a steric interfacial barrier to close approach of the particles[8,9]. The dispersion of the inorganic particles directly into the hydrophobic monomer phase, followed by emulsification of the oil in water to form submicron miniemulsion droplets and their subsequent polymerization is proposed to provide several advantages over other methods of pigment encapsulation.

In conventional emulsion polymerization[10], the principal locus of particle nucleation is either in the aqueous phase or in the monomer swollen micelles. The dominant site for particle nucleation will depend on the degree of water solubility of the monomers and the amount of surfactant. However, miniemulsions are relatively stable submicron dispersions of oil-in-water[11]. The monomer droplets can range from 50 to 500 nm in diameter and are typically obtained by shearing a system containing oil, water, surfactant, and a costabilizer. Because of their small size, the droplets can compete effectively for radical capture. As a result, the monomer droplets in a miniemulsion become the dominant site for particle nucleation[12]. The stability of these droplets arises from the use of an ionic surfactant coupled with a low molecular weight, highly water-insoluble costabilizer. The presence of costabilizer (e.g., cetyl alcohol or hexadecane) in the droplets substantially retards the diffusion of monomer out of the miniemulsion droplets, allowing them to become the main locus of polymerization, thereby bringing about the encapsulation.[10]

Table 1: Recipe used for the miniemulsion encapsulation polymerization.

Component	Amount (g)	Concentration
Styrene (or cyclohexane[†])	178-180	17.3-19.2 wt%[a]
Polystyrene [c]	0.18	1.0 wt% [b]
Titanium dioxide	5.4	3.0 wt%[b]
Deionized water	742.5	79.3 wt%[a]
Sodium lauryl sulfate (SLS)	2.163	10 mM[d]
Hexadecane	5.254	40 mM[d]
Potassium persulfate (KPS)	0.201	1.33 mM[d]
Sodium bicarbonate	0.838	1.33 mM[d]
OLOA370	0.9-3.6	0.5—2.0 wt%[b]

† used in studying the dispersibility of the TiO_2 particles
(a) Based on total recipe
(b) Based on monomer
(c) M_w=102,000 g/mole (Dow Chemical Co.)
(e) Based on aqueous phase

In this paper, the ability to carry out particle nucleation in miniemulsion droplets containing the inorganic particles plus the ability to nucleate all of the droplets created will be shown to lead to an efficient encapsulation of the inorganic particles. A good dispersion and dispersion stability of inorganic particles, such as titanium dioxide (ca. 30 nm particle diameter), in the hydrophobic monomer medium requires the adsorption of a dispersing agent at the solid/oil interface. The functional group at one end of the stabilizer adsorbs on the surface of the inorganic particles while the tail remains in the oil medium and provides steric stabilization, preventing particle aggregation. On the other hand, the stabilization of the miniemulsion droplets (ca. 100-200 nm diameter) containing the inorganic particles is provided by a water-insoluble costabilizer within the droplets (in the case of hexadecane) and an anionic surfactant adsorbed on the surface of these droplets. The anionic surfactant adsorbed at the oil/water interface creates an electrostatic repulsion between the droplets, resulting in their stabilization. Thus, the oil phase, comprised of TiO_2 particles dispersed in styrene monomer, was dispersed in water as miniemulsion droplets and subsequently polymerized using a persulfate initiator. The final latexes were characterized using a density gradient column (DGC) method for the determination of the encapsulation efficiencies.

Experimental

The recipe used for the preparation of latexes by miniemulsion polymerization is listed in Table 1. The two titanium dioxide powders, P25-450 (hydrophilic, 29 nm, Degussa) and T805 (hydrophobic, 21-29 nm, Degussa) were dried in a vacuum oven at 125 °C for 24 h and kept in a dessicator until their use. For the adsorption and dispersion studies, three different concentrations (0.5, 1.0, and 2.0 wt%) of the OLOA370 stabilizer based on the oil phase (cyclohexane) were prepared. The titanium dioxide particles (3.0 wt% based on the oil phase) were slowly added to the mixture, which was stirred for ~20 minutes and then sonified for 0-30 minutes at an output power of 10 (Branson Inc.). Samples collected before and during the sonification process were used for the determination of particle size and the amount of the stabilizer retained on the titanium dioxide particles. The particle size analyses were carried out by employing dynamic light scattering (DLS) (Submicron Particle Sizer Model 370, NICOMP). A UV spectrophotometer (SPECTRONIC® GENESYS™) was used to determine the stabilizer concentration in the medium after separation of the TiO_2 particles by centrifugation and, by mass balance, the amount retained on the surface of the particles. The

molecular weight of the OLOA370 stabilizer (M_n = 1255 g/mole), whose chemical structure is shown in Figure 1, was determined by vapor pressure osmometry (VPO) at 40 °C using benzil (Aldrich, MW = 210.23 g/mole) for the calibration of the instrument.

The preparation of the miniemulsions was carried out after the conditions to obtain the smallest particle size, and good dispersion stability of the inorganic particles in the oil phase were established. The monomer dispersion containing TiO_2 particles was gradually added to the sodium lauryl sulfate (SLS) (Fisher Scientific) and sodium bicarbonate (Fisher Scientific) aqueous solution while stirring, followed by sonification and Microfluidization to create the miniemulsion droplets containing the inorganic particles. The average droplet sizes of the miniemulsions were estimated by a surfactant (SLS) titration method using surface tension measurements. The monomer in the miniemulsion droplets is subsequently polymerized in a stirred reactor (90 rpm) at 70 °C for 2 to 4 hours by addition of a water soluble initiator (KPS) generating free radicals, which enter the droplets to bring about the encapsulation. The resulting latexes were characterized by density gradient column (DGC) measurements to estimate the encapsulation efficiencies. In these experiments, seven different concentrations of sucrose solutions are prepared from 1.000 g/cm^3 to 1.3390 g/cm^3. These solutions are placed in a scaled column (centrifuge tube) with the highest density at the bottom and the lowest density on the top. Then, the latex dispersion is carefully placed on the top of the column in order not to disturb the interfaces between the levels. The tube is then placed in a Beckman-type high-speed ultracentrifuge and the whole system is centrifuged at 37,000 rpm for two hours. The process must be carried out at low temperature (4.0 °C) in order to prevent the different sucrose densities from mixing during centrifugation. The encapsulated particles separated in different density zones based on their densities were further used in the quantitative determination of encapsulation efficiencies.

R = C$_2$H$_4$

Fig.1. Chemical Structure of OLOA370 (polybutene-succinimide diethyltriamine).

Dispersion of TiO$_2$ Particles Using OLOA370 as Stabilizer

The study of the particle size variation and the amount of OLOA370 retained on the particles as a function of sonification time provides important insights into the dispersion of the TiO$_2$ particles in the oil phase. The effect of OLOA370 concentration on the particle size and the amount of the OLOA370 retained on the hydrophilic titanium dioxide particles (P25-450) without applying any sonification is shown in Figure 2. It can be seen that the amount of stabilizer retained on the surface of the titanium dioxide particles and the particle size of the TiO$_2$ particles obtained, have only a slight dependence on the concentration of the stabilizer present. At the lowest concentration (0.1 wt% OLOA370), almost 95 wt% of the initial stabilizer (2.65×10^{-5} moles/g TiO$_2$) was retained on the TiO$_2$ particles. However, when the concentration was doubled (0.2 wt% or 5.31×10^{-5} moles/g TiO$_2$), only 55.0 wt% of the stabilizer (2.91×10^{-5} moles/g TiO$_2$) was retained by the aggregates. With further increases in the amount of the stabilizer, only a small fraction of the OLOA370 was retained by the particles (perhaps on and in the interstitial cavities between the aggregated titanium dioxide particles). This proves that the retention of the stabilizer on the titanium dioxide particles is a surface area related process. The stabilizer preferentially adsorbs on the bare surface of the titanium dioxide particles until this surface is fully occupied. The remainder remains in solution. As shown here, the same amount of OLOA370 was adsorbed on the available surface of the particles, regardless of the OLOA370 concentration in the medium. As a result, there was little change in the size of the titanium dioxide particles (D$_v$ ~610-620 nm) over the 0.1-1.0 wt% concentration range. When the concentration of the stabilizer was increased from 1.0 wt% to 2.0 wt%, a slight increase in the amount of the stabilizer retained by the particles was observed; moreover, this change was reflected in the average particle size, which decreased slightly (D$_v$ ~574 nm). This decrease was probably due to some limited break-up of the aggregates caused by the penetration of the stabilizer in between the loosely-packed titanium dioxide aggregates, which increases the osmotic pressure.
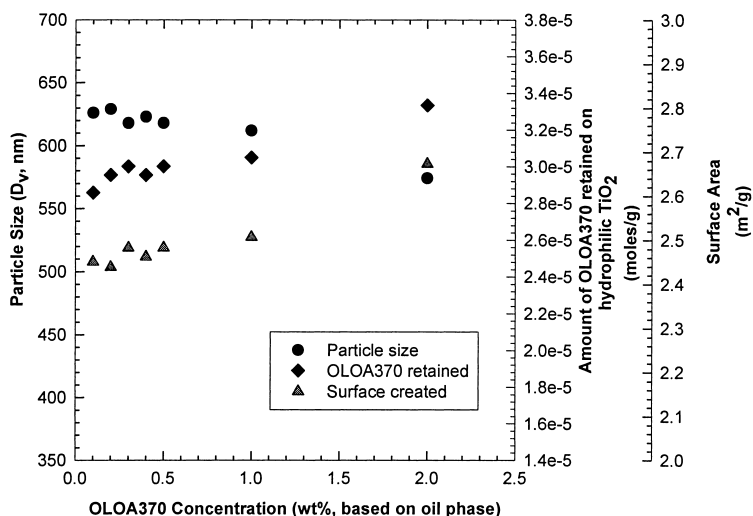
Fig. 2. The effects of OLOA370 concentration on the amount of OLOA370 stabilizer retained on the hydrophilic titanium dioxide particles and surface area created after 20 min stirring (no sonification); [TiO$_2$] = 3 wt% on cyclohexane, [OLOA370]= 0.1wt% (2.91x10^{-5} moles/g TiO$_2$)-2.0 wt% (5.54x10^{-4} moles/g TiO$_2$) (based on cyclohexane).

The effects of sonification time and the amount of OLOA370 stabilizer added on the particle size and amount of OLOA370 retained on the TiO$_2$ particles are shown in Figure 3. As the sonification time increased, a smaller particle size was obtained and more stabilizer was adsorbed on the surface of the TiO$_2$ particles as a result of the increased available surface area. At the two lower stabilizer concentrations (i.e., 0.5 wt% and 1.0 wt%), nearly all of the stabilizer was adsorbed on the surface of the particles (99.0 wt% and 98.5 wt%, respectively) after 20 minutes of sonification. In these cases almost 80 wt% of the OLOA370 rapidly adsorbed on the surface of the particles during the first 5 to 10 minutes of sonification. As the sonification time was increased, the aggregates continued to break up, and more OLOA370 was retained by the titanium dioxide particles. Finally, almost 100 % of the OLOA370 was retained on the titanium dioxide particles after 15 to 20 minutes of sonification. This shows that the adsorption of the OLOA370 on the surface of the TiO$_2$ particles has dependency on the number of the hydroxyl sites available.
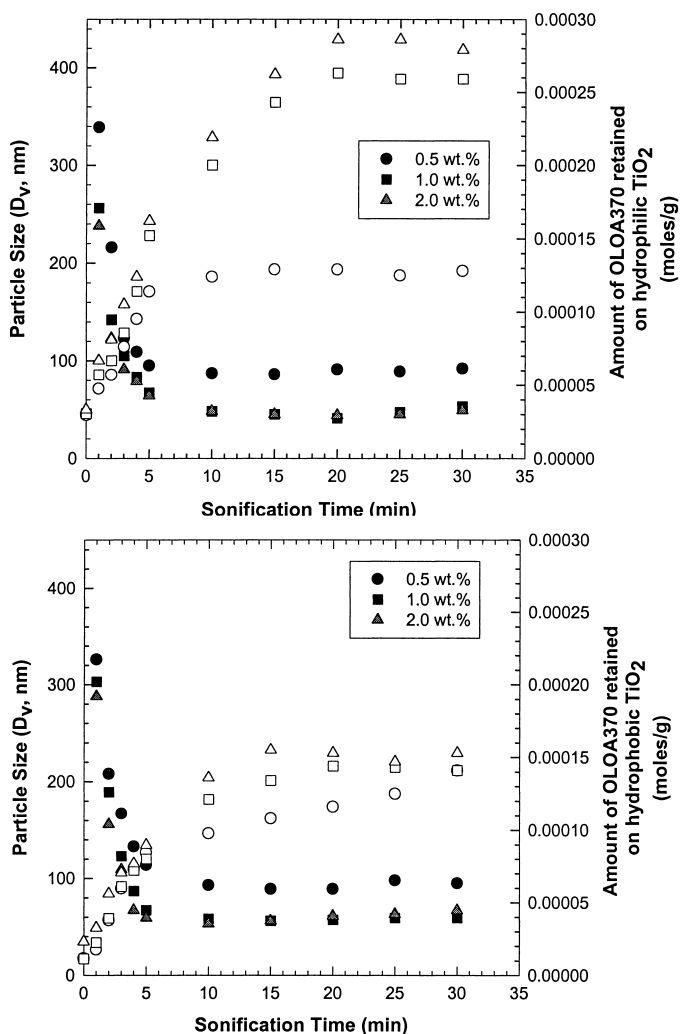
Fig. 3. Particle size (filled symbols) and amount of OLOA370 retained on the hydrophilic (top) and hydrophobic (bottom) TiO$_2$ particles (open symbols) versus time before and during the sonification at an output power of 10 and a duty cycle of 70 %; [TiO$_2$] = 3 wt% on cyclohexane, [OLOA370]= 1.33x10^{-4} moles/g TiO$_2$ (0.5 wt%), 2.65x10^{-4} moles/g TiO$_2$ (1.0 wt%) and 5.31x10^{-4} moles/g TiO$_2$ (2.0 wt%), based on cyclohexane.

As was the case for the hydrophilic TiO$_2$ particles, the particle size of the hydrophobic particles (T805) decreased with increasing sonification time, and correspondingly more stabilizer was retained on their surfaces as shown in Figure 3 (bottom). Dispersions with a

TiO$_2$ particle size (D$_v$) of about 60 nm were obtained with the two higher levels of OLOA370, while larger particles were obtained at the lower concentration (0.5 wt%). However, these results differ from those obtained with the hydrophilic particles. While the amount of the OLOA370 retained on the hydrophilic TiO$_2$ particles was 99.0 wt% of the initial amount when 1.0 wt% of OLOA370 was used, the amount of OLOA370 retained on the hydrophobic TiO$_2$ particles was only 54 wt% of the initial amount. Similar behavior was found using 2.0 wt% OLOA370, where 67.0 wt% of the initial amount covered the hydrophilic particles while only 28.7 wt% covered the hydrophobic particles. This lower level of adsorption of the OLOA370 on the hydrophobic TiO$_2$ particles might be related to the number adsorption sites available on the surface of the TiO$_2$ particles. Even though the surface was modified with trimethoxy octyl silane (TMOS), the surface of these particles still contains hydroxyl groups[13]. While a smaller particle size (D$_v$ $\approx$ 39 - 41 nm) was obtained for the hydrophilic TiO$_2$ particles with both 1 wt% and 2 wt% of the stabilizer, only 57-60 nm (D$_v$) hydrophobic TiO$_2$ particles could be produced, even though both have the same reported primary particle size. In both cases, the increase in the stabilizer concentration to 2.0 wt% did not result in any further reduction in the size of the TiO$_2$ particles. Moreover, a significant difference was observed in the amount of the OLOA370 retained on the two types of TiO$_2$ particles. This means that the adsorption of OLOA370 on the surface of the TiO$_2$ particles is strongly dependent on the number of adsorption sites on the surface of the particles and the OLOA370 has a strong affinity for the hydroxyls.

The preceding results can be examined in an alternate manner by plotting the amount of OLOA370 retained on the surface of the hydrophilic particles as a function of the surface area created as shown in Figure 4. The surface area was calculated assuming that the TiO$_2$ particles were solid spheres having a diameter as determined by the dynamic light scattering measurements. No consideration was given to the nature of the aggregates (i.e., their shape and porosity). For the hydrophilic particles (Figure 4 (top)), there is a roughly linear relationship between the total surface area created and the amount of the OLOA370 retained up to surface areas of 32 m^2/g. As more surface area was created, more OLOA370 was retained on the particles. These results show that OLOA370 adsorbs readily on the TiO$_2$ particles as long as free surface is available for adsorption. Beyond this point, there is a steeper increase in the amount of the OLOA370 retained on the surface of the particles with only a modest increase in the surface area. This might be due to the entrapment (or an excess) of OLOA370 molecules as the particles became packed during the centrifugation.
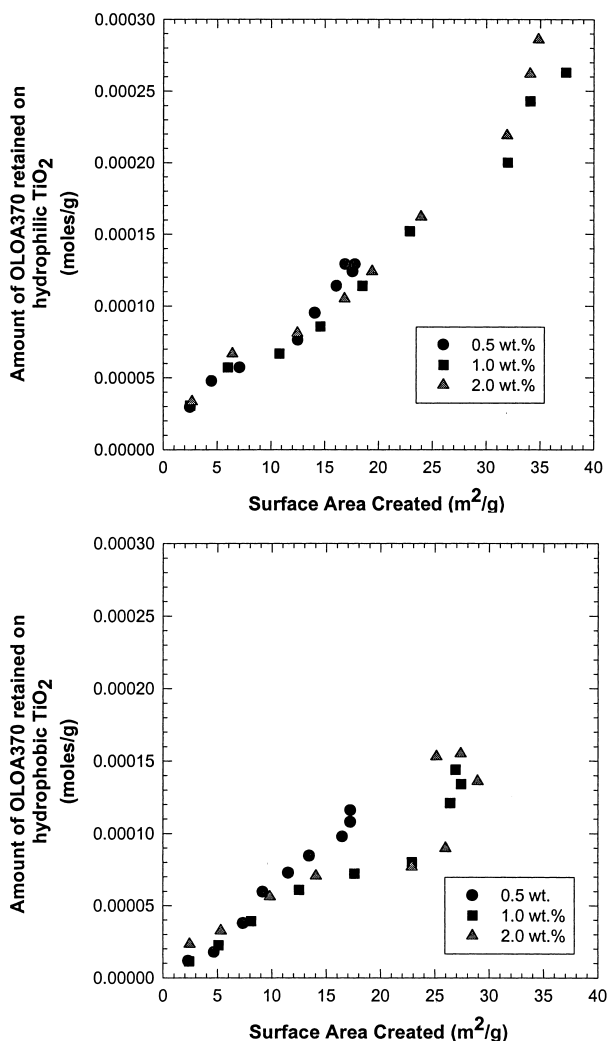
Fig. 4. Total surface area versus the amount of OLOA370 retained per gram of the hydrophilic (top) and hydrophobic (bottom) TiO$_2$ particles; [TiO$_2$]= 3 wt% on cyclohexane, , [OLOA370]= 1.33x10^{-4} moles/g TiO$_2$ (0.5 wt%), 2.65x10^{-4} moles/g TiO$_2$ (1.0 wt%) and 5.31x10^{-4} moles/g TiO$_2$ (2.0 wt%), based on cyclohexane.

Figure 4 (bottom) shows the variation of the amount of OLOA370 retained by the hydrophobic TiO$_2$ particles as a function of the surface area estimated from the average particle size. By comparing these results with those obtained for the hydrophilic particles, it

can be seen that the amount of the OLOA370 remaining on the hydrophobic TiO_2 particles was lower under the same conditions. In addition, the adsorption behavior also differs. Initially, there is a roughly linear relationship between the surface area created and the amount retained as found in the preceding data. Then, almost no additional stabilizer was found to be adsorbed on the particles despite an increase in the surface area, indicating the disintegration of the loose TiO_2 aggregates whose surface and cavities are saturated with OLOA370. This is followed by an opposite phenomenon, where the amount retained on the particles increased with only a small change in the estimated surface area. Again, the latter is considered to be a reflection of an "excess" adsorption of OLOA370. This was supported by the fact that this "excess" of OLOA370 could be readily removed (desorbed) by washing the particles with fresh cyclohexane

The long-time dispersion stability of the TiO_2 particles was also investigated and results are reported in Figure 5. For the hydrophilic particles, the stability was quite good at 25 ^{o}C as long as sufficient stabilizer was adsorbed on the surface of the particles while the size of the TiO_2 particles prepared using only 0.5 wt% of OLOA370 kept increasing with increasing time (Figure 5(top)). At 70 ^{o}C, the particle size only increased slightly for 1.0 and 2.0 wt% OLOA370, which is the temperature at which the polymerizations are to be carried out. It seems that some limited aggregation occurred in all cases at the elevated temperature. These measurements indicate that the adsorption of the OLOA370 on the hydrophilic TiO_2 particles has only a slight dependence on the temperature. Therefore, this stabilizer can effectively be used at the higher temperatures required for polymerization.

The stability results for the hydrophobic TiO_2 particles at 25 ^{o}C and 70 ^{o}C are shown in Figure 5 (bottom). At 25 ^{o}C, the particle size increased significantly when 0.5 wt% of OLOA370 was used and reached a plateau (~160 nm) after 48 hours. This increase might be due to the combination of an insufficient amount of stabilizer on the surface of the particles and a weak interaction between the hydrophobic sites on the TiO_2 particles and the hydrophobic tail of the OLOA370 stabilizer. This would cause the hydrophilic end-groups of the OLOA370 to extend toward the hydrophobic medium while the hydrophobic tails physically interact with each other. Even though a smaller particle size was obtained as the amount of the stabilizer was increased from 0.5 wt% to 2.0 wt%, the particle size of the hydrophobic TiO_2 particles also increased (from 89 nm to 106 nm) over 60 hours. The aging temperature had a more significant effect on the stability. After 10 hours at 70 ^{o}C, the particle

size of the hydrophobic TiO_2 particles grew to 250 nm using 0.5 wt% of OLOA370. This change in the stability of the hydrophobic TiO_2 particles is evident at all OLOA370 concentrations. The amount of OLOA370 in cyclohexane monitored at 70 ^{o}C showed that there was an increase in the amount of the stabilizer in the supernatant[13]. This indicated that the OLOA370 desorbed from the surface of the hydrophobic TiO_2 particles, causing limited aggregation.
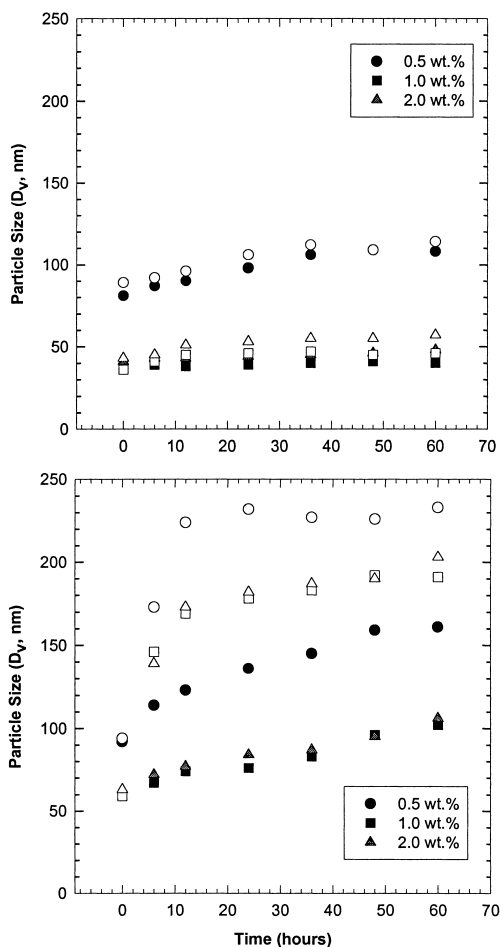

Fig. 5. Dispersion shelf-life stability of the hydrophilic (top) and hydrophobic (bottom) TiO_2 particles prepared in the presence of different concentrations of OLOA370 stabilizer after 20 minutes of sonification at an output power of 10 and 70 % duty cycle; [TiO_2]= 3 wt% on cyclohexane, [OLOA370]= 1.33×10^{-4} moles/g TiO_2 (0.5 wt%), 2.65×10^{-4} moles/g TiO_2 (1.0 wt%) and 5.31×10^{-4} moles/g TiO_2 (2.0 wt%), based on cyclohexane; 25 ^{o}C (filled symbols) and 70 ^{o}C (open symbols).

Characterization of the Miniemulsion Droplets Containing TiO$_2$ Particles

Miniemulsions were characterized in terms of the free surfactant present in the aqueous phase and the average droplet size. The former was determined by measuring the surface tension, while the latter employed the well-known soap titration method originally applied to determine latex particle sizes[14]. These measurements are important in assessing the extent of droplet nucleation that might be expected in the subsequent polymerization. Low free surfactant concentrations (< CMC) and small droplets (large in number) favor nucleation in droplets as opposed to homogeneous or micellar nucleation. These would, therefore, favor the successful encapsulation of the TiO$_2$ already contained within the droplets.

In the soap titration method, SLS was added to the miniemulsion until the CMC (7.6 mM) was surpassed (constant surface tension) as monitored by drop volume surface tension measurements. The initial measurement with no additional SLS yields the free surfactant (through a calibration curve) and by mass balance the amount adsorbed on the surface of the droplets. At the CMC, the surface and aqueous phase are saturated with surfactant. Knowing this and the effective molecular surface area of the SLS at the interface between the monomer and aqueous phases, allows the determination of the average diameter (volume-surface; $D_s = 6 \ V_t/A_t$, where V_t and A_t represent the total volume and surface area of the droplets, respectively) of the droplets. The area per SLS molecule (a_s) at the oil (styrene plus 1 wt% polystyrene and 2.9 wt% hexadecane)/ aqueous phase interface was previously determined by interfacial tension measurements to be 85.6 Å^2/molecule (25 °C).[15]

The soap titration results for two miniemulsions prepared with and without TiO$_2$ particles in the styrene (10mM SLS) are illustrated in Figure 6. The initial surface tension values differ. The miniemulsion prepared with TiO$_2$ particles present has a lower surface tension indicating more free surfactant (~1 mM) as compared to that prepared without TiO$_2$ (0.36 mM). Using this information the initial surface coverages of the droplets were estimated to be 70% and 61%, respectively. The total amounts of SLS required to reach the respective CMC's varied similarly as reported in Table 2. The estimated average droplet sizes based on these data are 189 nm with TiO$_2$ present and 154 nm without. As mentioned above, these represent the volume-surface average diameters, which lie in between the volume and weight average diameters (i.e., weighted to larger diameters). Table 2 also presents results for miniemulsions prepared with double the SLS concentration (20 mM). As expected, the droplet size decreases

although not in proportion to the amount of extra surface area that could be stabilized; the surface coverages increased. In this case, the difference between with and without TiO_2 is larger or seen from another point of view, the reduction in size with TiO_2 present is much less than without. This would seem to indicate that the presence of the TiO_2 in the monomer limits the miniemulsion technique in terms of making smaller droplets. Nonetheless, the droplet sizes were considered to be in the range that were favorable for successfully carrying out the polymerizations with substantial nucleation occurring in the monomer droplets, i.e., favoring encapsulation.
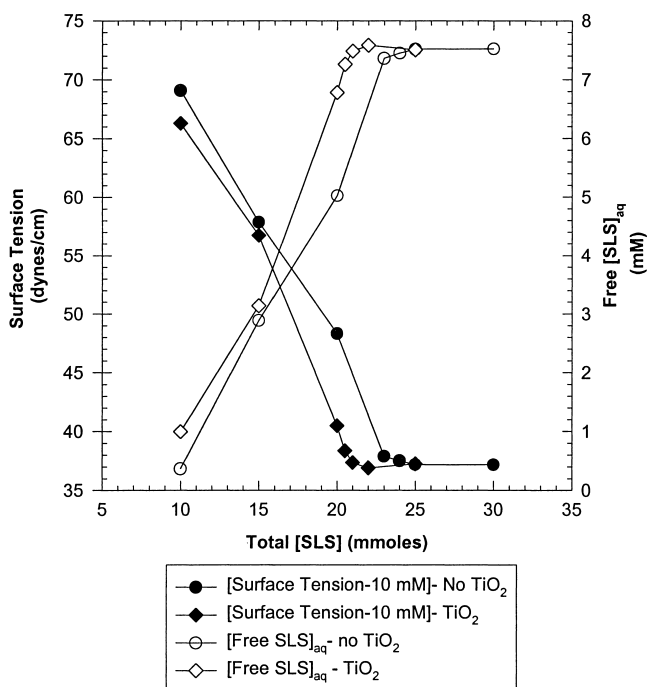

Fig. 6. Surface tension (filled symbols) and free SLS (open symbols) with increasing added SLS in the miniemulsion prepared with 10 mM SLS with and without TiO_2 particles present (3.0 wt% based on monomer); 30 seconds of sonification and 10 passes through the Microfluidizer were employed for the preparation of the miniemulsions.

Table 2: Effect of the SLS concentration used for the preparation of the miniemulsions on the distribution of surfactant and the droplet size created

Miniemulsion	[SLS] (mM)	[TiO$_2$] (wt%)	[SLS]$_{aq}$ (mM)	[SLS]$_{CMC}$ (mM)	D$_{vs}$[a] (nm)	Initial Surface Area	
						Occupied (Å^2/molecule)	Coverage (%)
[St + PS +HD]	10	-	0.36	15.9	154	141	61.34
[St + PS +HD]	10	3.0	0.99	13.0	189	123	69.59
[St + PS +HD]	20	-	3.52	22.6	109	117	73.16
[St + PS +HD]	20	3.0	6.59	14.4	171	92	93.04

[a] Calculated using 85.6 Å^2/molecule as the surface area occupied per molecule of SLS on the droplets.

Miniemulsion Encapsulation Polymerizations

The efficiencies of the miniemulsion encapsulation polymerizations were determined by using a density gradient column separation method, which not only separates the encapsulated particles from unencapsulated TiO$_2$ particles and free polystyrene particles but also can distinguish between different "degrees" of encapsulation. A good distinctive separation of encapsulated particles in the column was obtained by this method, allowing us to quantitative determination of the efficiencies of the encapsulation. The overall encapsulation efficiencies defined as the percentage of titanium dioxide particles encapsulated and the amount of polystyrene participating in the encapsulation are shown in Figure 7. It can be seen that the miniemulsion encapsulation polymerizations of the hydrophilic TiO$_2$ particles using 0.5 wt% of OLOA370 stabilizer (based on oil phase) resulted in poor encapsulation efficiencies; only 36 wt% of the initial amount of TiO$_2$ particles and 29.2 wt% of the initial amount of styrene were involved in the encapsulation. However, 81 - 83 wt% of the initial TiO$_2$ particles and 72 - 73 wt% of the polystyrene were involved in the encapsulation process when the amount of stabilizer was increased from 0.5 wt% to 1.0 or 2.0 wt%. This increase in the encapsulation efficiency was clearly due to a better dispersion stability and smaller size of the TiO$_2$ particles obtained with the higher concentrations of the OLOA370 stabilizer. As seen in Figure 7 (top), the encapsulation efficiencies of the hydrophilic particles exhibited a strong dependence on the particle size of the dispersed TiO$_2$. There was no significant change in the amount of the inorganic particles encapsulated by the polystyrene with the further increase of the stabilizer

concentration from 1.0 to 2.0 wt%. These results suggest that there is a strong dependence of the encapsulation efficiencies on the dispersion stability and particle size of the TiO_2 particles used in the miniemulsion polymerizations. In order to be able to obtain small TiO_2 particles and to keep them within the miniemulsion droplets, their surfaces must be saturated by the OLOA370.
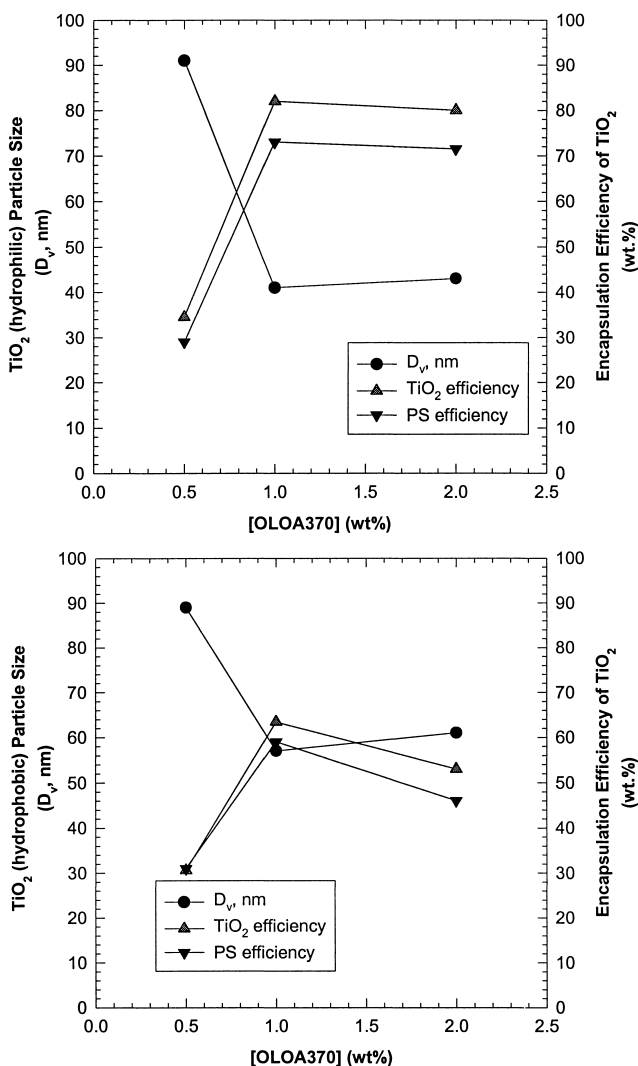

Fig. 7. Encapsulation efficiencies as a function of the size of the hydrophilic (top) and hydrophobic (bottom) TiO_2 particles and the OLOA370 concentration; $[TiO_2]= 3$ wt%, $[OLOA370]= 1.33 \times 10^{-4}$ moles/g TiO_2 (0.5 wt%), 2.65×10^{-4} moles/g TiO_2 (1.0 wt%) and 5.31×10^{-4} moles/g TiO_2 (2.0 wt%).

As in the case of the hydrophilic TiO_2 particles, an improvement in the encapsulation efficiencies was also obtained with the hydrophobic particles as the OLOA370 concentration was increased from 0.5 wt% to 1.0 wt%. Using 0.5 wt% OLOA370 stabilizer, the encapsulation efficiencies were poor being similar to those obtained using the hydrophilic TiO_2 particles; only 30.6 wt% of the TiO_2 particles and 31.2 wt% of the polystyrene participated in the encapsulation. By increasing the amount of OLOA370 to 1.0 wt%, almost 60 wt% of the initial amount of TiO_2 particles and 59.7 wt% of the polystyrene participated in the encapsulation, which are significantly lower than found for the hydrophilic TiO_2 particles. This increase in the encapsulation efficiency is clearly due to the better dispersion stability and smaller size of the TiO_2 particles obtained with the higher concentration of the stabilizer. The encapsulation polymerizations using the hydrophobic TiO_2 particles also had a strong dependence on the dispersed TiO_2 particle size (Figure 7 bottom). As the size of the TiO_2 particles decreased with increasing concentration of OLOA370, an increase in the amount of encapsulated TiO_2 particles was obtained. However, as a result of the larger particle sizes obtained with the hydrophobic particles, a lower encapsulation efficiency was obtained compared to the hydrophilic particles. Furthermore, as the OLOA370 was further increased to 2.0 wt%, there was a decline (~10 % decrease) in the amount of TiO_2 particles encapsulated by the polystyrene. Certainly, the adsorption of the OLOA370 stabilizer on the surface of these particles improved their dispersion and stability in the monomer when a sufficient amount of OLOA370 (e.g., 1.0 wt %) was used but their dispersion stability was not as good as that of the hydrophilic TiO_2 particles. This could lead to some of the TiO_2 particles being excluded from the droplets, which would subsequently aggregate in the continuous phase during the emulsification or polymerization. This would result in both the formation of free TiO_2 and polymer particles with no TiO_2 particles within them following the miniemulsion polymerization.

The characterization of the final encapsulated particles by dynamic light scattering (NICOMP) showed that (Table 3) while the polystyrene particles not containing TiO_2 particles had sizes around 105 - 115 nm, the size of the encapsulated particles increased as the density (ratio of TiO_2 to polystyrene) increased. The presence of the TiO_2 particles inside the polymer particles resulted in an increase in the final particle size. This was basically due to an increase in the number of TiO_2 particles in each polystyrene particle. The same trend for both hydrophilic and the hydrophobic particles was observed. This means that the encapsulated particles collected from the higher density zones had a larger particle size due to the

incorporation of a larger number of TiO$_2$ particles within each polystyrene particle. Transmission electron microscopy revealed that the shape of the encapsulated particles became slightly irregular as the TiO$_2$ content within the polymer particles increased.

Table 3. Characterization of encapsulated particles collected from different density zones of the DGC

Density (g cm^{-3})	Hydrophilic TiO$_2$		Hydrophobic TiO$_2$	
	Particle Size (D$_v$, nm)	N$_{TiO_2}$/PS[*]	Particle Size (D$_v$, nm)	N$_{TiO_2}$/PS[*]
1.0507	105	-	114	-
1.0810	150	1.9	117	1.5
1.1267	154	2.4	145	2.3
1.1785	186	3.4	179	3.3
1.2295	205	5.5	209	5.6

[*]estimated average number of TiO$_2$ particles per polystyrene particle

Summary

The encapsulation of TiO$_2$ particles within polystyrene particles was investigated by the miniemulsion polymerization approach. Both hydrophilic and hydrophobic TiO$_2$ particles were evaluated. Encapsulation efficiencies of the TiO$_2$ particles as high as 80% were achieved using hydrophilic TiO$_2$ particles. These were first dispersed and stabilized in the monomer using a polymeric stabilizer containing amine groups (OLOA370), which interacts with hydroxyls shown to be present on the surface of the TiO$_2$ particles. This dispersion was subsequently sheared to form a miniemulsion and polymerized at 70 $^{\circ}$C using persulfate initiator. The resulting latexes were characterized using a density gradient column separation technique to estimate the degree of encapsulation. To achieve the greatest encapsulation efficiencies (83 wt% TiO$_2$ (hydrophilic) and 73 wt% polystyrene), it was determined that the TiO$_2$ particles should be produced as small and as stable as possible in the styrene monomer. This was achieved with 1.0 wt% OLOA370 (based on monomer) after 20 minutes of sonification. However, the size of the hydrophobic TiO$_2$ particles could not be made as small as the hydrophilic TiO$_2$ particles, resulting in poorer encapsulation (60 wt% TiO$_2$, 63 wt% polystyrene). This was attributed to a more limited adsorption of the OLOA370 on the particles because of the presence of TMOS (hydrophobizing agent) and thus fewer number of hydroxyl sites being available. The density gradient column separations showed that the

particle size increased in the higher density zones accompanied by an increase in the number of TiO₂ particles per polystyrene particle.

Acknowledgment

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