Polymer Bulletin 55, 477–484 (2005)
DOI 10.1007/s00289-005-0457-3

Polymer Bulletin

Encapsulation of TiO_2 by emulsion polymerization with methyl metacrylate (MMA)

Adriano Marim de Oliveira; Maria Lúcia Caetano Pinto da Silva; Gizelda Maria Alves; Pedro Carlos de Oliveira; Amilton Martins dos Santos (✉)

Department of Chemical Engineering, Faculty of Chemical Engineering of Lorena - FAENQUIL, P.O. Box 116, Lorena – SP – Brazil

E-mail: amsantos@dequi.faenquil.br

Received: 10 June 2005 / Revised version: 8 October 2005 / Accepted: 9 October 2005
Published online: 4 November –

SUMMARY

This paper presents a methodology of encapsulation of TiO_2 (Titanium dioxide) by emulsion polymerization on the proposal to modify the physical-chemical properties of the pigment surface. In the proposed methodology the TiO_2 was previously modified by isopropoxy-titanium-tri-isostearate, before being encapsulated by emulsion polymerization using Methyl Methacrylate as monomer.
The effects of the polymerization process, type of initiator and monomer concentration in the efficiency of encapsulation were studied. The encapsulated pigment was characterized by Thermogravimetric Analysis (TGA), Light Scattering (LS) and Transmission Electron Microscopy (TEM).

Keywords: Titanium dioxide; methyl methacrylate; encapsulation; emulsion polymerization

INTRODUCTION

On the last years, water-borne paints are conquering a quite important position in the vast market of paints. Despite the ecological advantages of such paints, in some cases, films obtained from water-borne paints can show lower resistance than those obtained from oil based paints. In a water-borne paint where TiO_2 is used as pigment, the pigment surface is poor in polymer due to its hydrophilic character. The incompatibility between the polymer and the pigment can result in its agglomeration during the film formation. The occurrence of agglomeration of the pigment can lead to the formation of points of fragility, decreasing the mechanical resistance of the films.
This problem may be overcome by encapsulating the pigment with a polymer that may have or not the same chemical nature of the binder but able to eliminate the difference among the properties of the pigment surface and the binder. During the film formation the encapsulated pigment will be homogeneously distributed in the polymer media, avoiding, by this way, the agglomeration and creation of fragility points [1 – 6].
This work presents a methodology of encapsulation of TiO_2 by emulsion polymerization, using a pigment previously modified by a titanate (isopropoxy-titanium-tri-isostearate) and Methyl Methacrylate (MMA) as monomer.

EXPERIMENTAL

Materials

The TiO_2 used in this work was the rutile type, R902, from DuPont, and supplied by Chemical Ipiranga S.A.. The chemical modification of the pigment was carried out in n-heptane of analytical grade (QUIMEX), using as coupling agent the Isopropoxy-titanium-tri-isostearate, TYZOR ISTT, from DuPont. The monomer Methyl methacrylate (MMA), was distilled under vacuum at 30ºC before utilization. Azo-bis-isobutironitrile of chemical grade (AIBN), from DuPont, and ammonium persulfate ($(NH_4)_2S_2O_8$) were used as initiators. The surfactant used was sodium dodecyl sulfate (SDS). Methyl methacrylate, ammonium persulfate and SDS were supplied by Rhodia do Brasil Ltda. The ammonium persulfate and the SDS, both of technical grade, were used as received.

Purification and chemical modification of the TiO_2

Traces of sulfate were removed by washing the pigment three times with de-ionized water. The pigment was subsequently dried at 130ºC to remove water. The modification reactions were realized according to the methodology described by Janssen [3]. In a bottle of polystyrene were added 150g of pigments, 186 ml of heptane, 225g of glass beads and 2,25g of titanate. The bottle was placed on a roller-bench for 2 hours. After this time, the glass beads were separated from the modified pigment by means of filtration. Then, the dispersion was centrifuged in a Damon IEC CU-5000 equipment at 3500 rpm for 5 minutes to separate the pigment from the solvent. The pigment was re-dispersed in fresh heptane and centrifuged again. Finally the modified pigment was dried at room temperature for 12 h. The efficiency of modification of pigment was determined by TGA [3] using SHIMADZU TGA 50 equipment.
The efficiency of modification was given by:

$$R_M = \frac{PM - I}{TI} x100 \qquad (1)$$

where:
R_M = efficiency of pigment modification (%)
PM = loss mass (wt%)
I = amount of impurities in the unmodified pigment (% w)
TI = initial concentration of titanate (wt%)

Encapsulation

Figure 1 shows a scheme of the methodology utilized in the encapsulation of the TiO_2. The encapsulation was carried out in a glass reactor of 500 ml, using two different processes: batch and semicontinuous. In the case of the semi-continuous process with a hydrophilic initiator ($(NH_4)_2S_2O_8$), the reactor was initially loaded with water, TiO_2 and surfactant. The system was kept under agitation for 30 minutes at 250 rpm. After this time, 10% of monomer was added and the system was kept under agitation for 45 minutes, before being started with the addition of 10% of the initiator. The remainder monomer and initiator were added by using a programmable syringe pump at

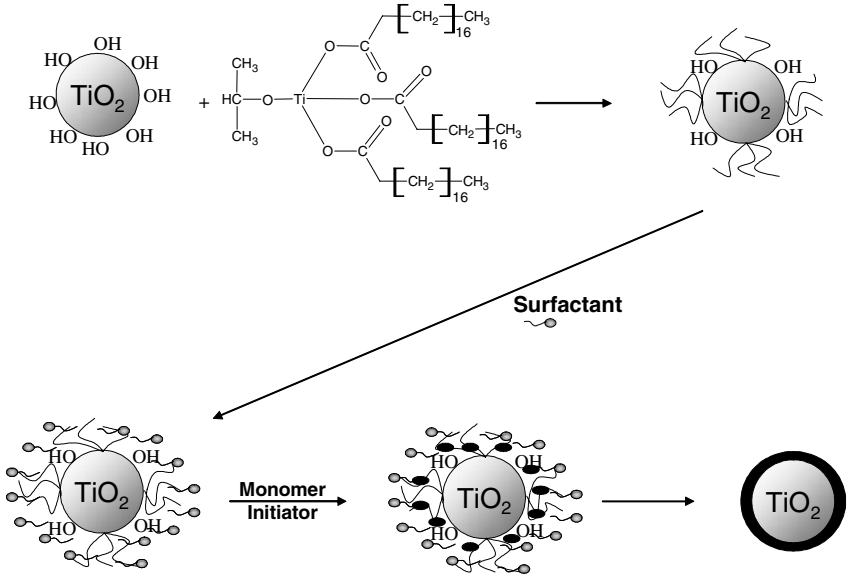

Figure 1: Scheme of the methodology utilized in the encapsulation of TiO_2.

0.04 mL/min. When the hydrophobic initiator (AIBN) was used, the reactor was initially loaded with water, TiO_2 and surfactant. The reaction medium was agitated during 30 minutes at 250 rpm and after this time all the amount of initiator was added in the reactor. After 45 minutes under continuous agitation, the polymerization was started with the addition of 10% of monomer. The remainder monomer was added using the programmable syringe pump at 0.04 ml/min. After the encapsulation step the material was centrifuged at 3500 rpm and then washed two times with a 3M SDS solution and finally washed with de-ionized water to remove all SDS. The encapsulated pigment was dried at room temperature.
Table 1 shows the recipes and experimental conditions used in the encapsulation reactions.

Table 1: Recipes and experimental conditions for encapsulation of TiO_2.

Reagents (g)	Reactions 1^b and 2^{sc}	Reactions 3^b and 4^{sc}	Reactions 5^b and 6^{sc}
MMA	10	3	3
Modified TiO_2	10	10	10
SDS	0.29	0.29	0.29
$(NH_4)_2S_2O_8$	0.05	0.05	-
AIBN	-	-	0.05
water	190	190	190

b = batch process; sc = semi-continuous process; Temperature = 60 °C; Reaction time = 4 h.

The efficiency of encapsulation was calculated by TGA. The final products were observed by both LS (Zetasizer 1000, Malvern) and TEM (200C, JEOL) to investigate the presence of free polymer particles and the morphology of the encapsulated pigment.

The efficiency of encapsulation was calculated from:

$$R = \frac{MP\ x\ MT}{Mm} x100 \qquad (2)$$

where:
R = efficiency of encapsulation (%)
MP = polymer content in pigment surface (weight polymer/ weight pigment)
MT = total mass of pigment (g)
Mm = total mass of monomer (g)

RESULTS

Effect of the polymerization process in the encapsulation efficiency
Table 2 shows that all the reactions carried out in semi-continuous processes had encapsulation efficiency higher than the batch processes. According to Janssen[1], who observed the same behavior in his work, the improvement of encapsulation efficiency could be attributed to two factors: the lower monomer concentration and the number of free micelles that is kept to a minimum amount in the semi-continuous reactions. Because of the lower monomer concentration in the aqueous phase, a low amount of oligomers is formed avoiding secondary nucleation and consequently the formation of free polymer particles in the aqueous phase [3].

Table 2: Effect of the polymerization process.

Reaction	P [mg PMMA/gTiO_2]	Efficiency (%)
1^{b}	34.70	3.47
2^{sc}	50.77	5.08
3^{b}	10.36	3.45
4^{sc}	11.28	3.76
5^{b}	19.21	6.40
6^{sc}	23.94	7.98

b = Batch process, sc = Semi-continuous process; P = Polymer content on the pigment surface.

Effect of the initiator
In this work, two different kinds of initiators were used in the pigment encapsulation: a hydrophobic initiator (AIBN) and a hydrophilic initiator (ammonium persulfate). AIBN was chosen based on the hydrophobic nature of the surface of the pigment that was previously modified by the titanate. In this case it should be expected higher adsorption of the initiator on the pigment surface, avoiding the polymerization in the aqueous phase and loss of encapsulation efficiency. TGA diagrams and data from Table 1 were used to calculate the efficiency of encapsulation (Table 3). The results showed that in the reactions where AIBN was used the efficiency values were higher than those obtained in the reactions conducted with ammonium persulfate. According to the literature, the presence of a hydrophobic initiator increases the efficiency in the TiO_2 encapsulation. This behavior is attributed to the lowest water solubility of the oligomers formed by a hydrophobic initiator [3]. It was postulated that the amount of oligomers, formed by a hydrophobic initiator and adsorbed on the pigment surface, is

higher when compared with the amount of adsorbed oligomers that were formed by a hydrophilic initiator.

Table 3: Effect of the type of initiator in the encapsulation efficiency.

Reaction	Initiator	P [mg PMMA/gTiO_2]	Efficiency [%]
3^b	$(NH_4)_2S_2O_8$	10.36	3.45
5^b	AIBN	19.21	6.40
4^{sc}	$(NH_4)_2S_2O_8$	11.28	3.76
6^{sc}	AIBN	23.94	7.98

b = Batch Process, sc = Semi-continuous Process; P = Polymer content on the pigment surface.

Effect of the monomer concentration

To verify the effect of monomer concentration on the efficiency encapsulation a comparison between reactions 2 and 4 were made and presented in Table 4. These results show that the amount of polymer on the pigment surface increased when the monomer concentration increased (e.g. 15 g/L to 50 g/L, respectively to reactions 4 and 2). The increase in the monomer concentration resulted in a higher encapsulation efficiency. According to Caris [6] and Haga *et al.* [5], the efficiency in the encapsulation of TiO_2 decreased with the increase of the monomer concentration in the reactions. The difference between our results and those found by Caris and Haga could be explained by the kind of process used in the current work (semi-continuous), which avoid the micelles nucleation, favoring the pigment encapsulation.

Table 4: Effect of the monomer concentration.

Reaction	[Monomer] [g/L]	P [mg PMMA/gTiO_2]	Efficiency [%]
2^{sc}	50	50.77	5.08
4^{sc}	15	11.28	3.76

sc = Semi-continuous Process; P = Polymer content in the pigment surface.

Average particle diameter (DP)

The light scattering technique was used in this work with the purpose of evaluate, in a qualitatively way, the efficiency of the encapsulation reactions. The presence of only one family of particles with a DP close to the diameter of the TiO_2, could indicate that all the polymer formed during the encapsulation reaction should be at the surface of the pigment.

Table 5 shows the DP and polydispersity of all the TiO_2 encapsulated in the present work. These results allowed to observe only one family of particles with DP around 400 nm, which indicate a lack of free polymer particles in the aqueous medium. It is important to remind that the particles of polymer, synthesized under these experimental conditions (table 1), should have DP close to 100 nm. The polydispersities of the samples were high, which confirm the necessity of the utilization TEM to get more detailed information about the polydispersity and morphology of the encapsulated particles.

Table 5: Average particle diameter (DP) and polydispersity of the encapsulated TiO_2.

Reaction	DP [nm]	Polydispersity
1[a]	357.6	0.141
2[b]	408.4	0.230
3[a]	413.8	0.323
4[b]	346.1	0.207
5[a]	287.6	0.190
6[b]	376.6	0.181

a = Batch Process, b = Semi-continuous Process.

Morphology of the particles of encapsulated TiO_2

Figures 2, 3 and 4 show TEM images of TiO_2 before and after encapsulation by batch and semi-continuous processes, respectively. In figures 3 and 4 the presence of free polymer particles in the aqueous medium is verified, which confirms the high polydispersity values obtained by LS and the low encapsulation efficiency determined by TGA. In addition, the occurrence of encapsulation can be easily evidenced by comparing figures 2 and 4 since in figure 4, almost all the pigment particles were completely covered by the polymer. Figure 4 also showes that the encapsulated pigment exhibits a raspberry-like core-shell morphology. Such a morphology can be explained by the fact that the encapsulation reactions were performed at 60°C, whereas Tg of PMMA is much higher. Relevant information in the micrograph of figure 4 is the formation and stabilization of a large number of free polymer particles in the water phase. These particles were probably formed by a mechanism of micellar nucleation, which is of major importance as it indicates that it could be possible to improve the efficiency of encapsulation by avoiding the particles nucleation and their stabilization in the water phase. Higher values of efficiency could be attained by optimizing the recipes (reduction of the SDS concentration) as well as the process conditions (monomer feed rate).

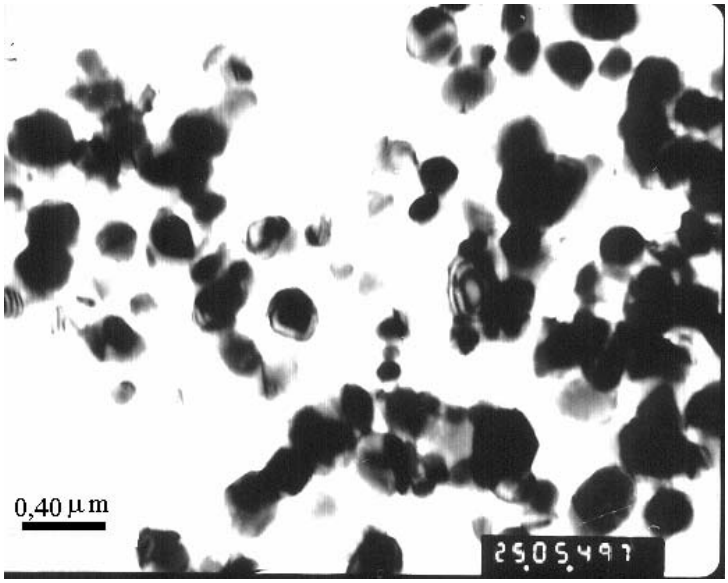

Figure 2: TEM micrography of the pigment before encapsulation.

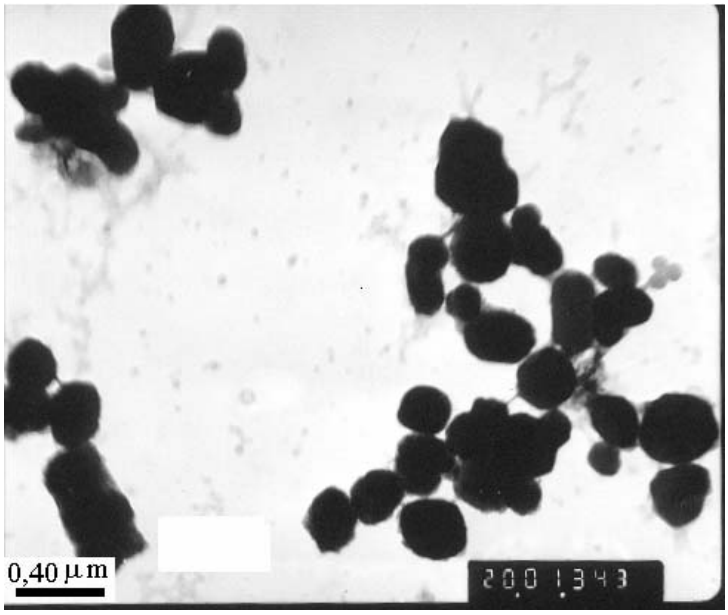

Figure 3: TEM micrography of the pigment encapsulated by batch process (reaction 1).

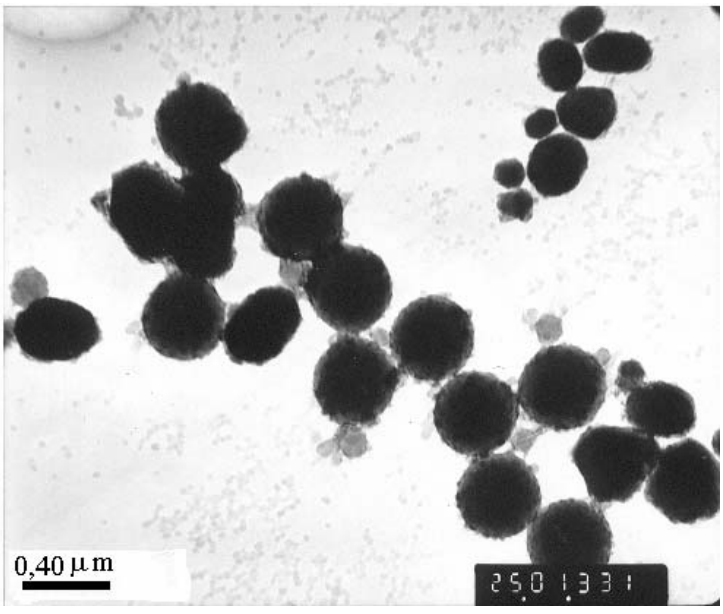

Figure 4: TEM micrography of the pigment encapsulated by semi-continuous process (reaction 2).

CONCLUSION

The semi continuous process was the best polymerization process for the encapsulation of the modified TiO_2. The efficiency values obtained in the semi-continuous process was always higher than those from batch process. The AIBN showed a better performance in the encapsulation reactions. The increase of the monomer concentration improved the efficiency of encapsulation when the reaction was realized by semi-continuous way. The technique of LS was not efficient in the evaluation of the TiO_2 encapsulation. The results obtained by this technique showed only one family of particles. However, TEM technique showed the presence of free polymer particles in the aqueous phase, which confirmed the high values of polydispersity obtained by LS. The technique of TEM was of fundamental importance because it allowed to confirm the encapsulation of the TiO_2. In addition, by this technique it was possible to observe that the encapsulated pigment exhibits a raspberry-like core-shell morphology.

ACKNOWLEDGEMENTS

The authors thank FAPESP to the financial support (Process 99/10299-4), IPIRANGA S.A., DuPONT and IPEN by the TEM analysis.

REFERENCES

1. Mark J E, Lee C Y C, Bianconi P A, (1995) Americam Chemical Society Symposium Series 585 Washington
2. Caris C H M, vaan Elven L P M, van Herk A M, German A L, (1988) 19th FATIPEC Conference book 3: 341-354
3. Janssen R Q F, Phd thesis (1995) Eindhoven University of Technology Eindhoven The Netherlands
4. Caris C H M, Kuijpers R P M, van Herk A M, German A L, (1990) Makramol Chem Makromol Symp 35/36: 335-348
5. Haga Y, Watanabe T, Yosomiya R, (1991) Angew Makromol Chem 189:23-24
6. Caris C H M, Phd thesis (1990) Eindhoven University of Technology Eindhoven The Netherlands