SURFACE MODIFICATION OF PARTICLES ASSISTED BY CO$_2$

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The paper reports feasibility studies of coating or binding oxides particles, in order to design hybrid of new surface properties.

The coating technique uses CO$_2$ as antisolvent, with a polymer organic suspension that is sprayed in (semi-continuous mode) or expanded with (discontinuous mode) carbon dioxide; the coating is a polymethyl methacrylate, and the substrate is either silica of 5µm, or titanium oxide of 50 nm. For TiO$_2$ samples produced by discontinuous route, microscopy shows aggregates or even fibers, whereas for larger silica, the coating is evidenced but still with a high degree of particle agglomeration. The spray mode is a good way to prevent such agglomeration, and the so-produced TiO$_2$-PMMA particles were further characterized by TGA; a quick test of dispersion in various solvents allowed to confirm that the surface modification indeed occurred.

The second way of surface modification deals with binding organic molecules at oxide surface. The technique is based on batch contacting the species under atmosphere of CO$_2$, with a CO$_2$-soluble specie contacted with particles suspended by stirring. The organic molecule is salicylic acid, and the particles are titanium oxide of 20-30 nm. Although TGA, infrared spectroscopy and the bright yellow color indicate interactions, the products need to be thoroughly characterized to discern covalency to surface adsorption .

INTRODUCTION

Modification of particle surface is of considerable interest in materials design since it allows for controlling physical and chemical properties of the new device : supported metal catalysts prepared by gold or iridium coating of TiO$_2$ [1], improved compatibility between filler and host polymeric materials obtained by modify SiO$_2$ surface with organic [2], improved dispersability in solvent provided by the grafting of PMMA at ZnO surface [3], PEGylation of silica surface to reduce protein adsorption in drug-delivery applications [4], grafted SiO$_2$ with C$_{18}$ surface as chromatography stationary phases, coating of drugs, biomolecules or food ingredients by polymers for bioavailability, stability or taste masking. The functionalization (coating or binding) can be performed by vapor deposition or in solution, but with the increasing demand for nanomaterials, the agglomeration inherent to the wet route is difficult to overcome. Supercritical-based routes seem thus promising, owing to the low viscosity and absence of surface tension that allows the wetting of complex substrates.

MATERIALS AND METHOD

Titanium dioxide (TiO_2) was P25 (Degussa) and PC50 (Millennium Chemicals); Salicylic acid ($C_7H_6O_3$, purity of 99%), Polycaprolactone (PCL, 14000 Da) and Poly methyl-metacrylate (PMMA, 120000 Da) were from Sigma Aldrich.

Details of the batch and continuous equipements can be found elsewhere [5,6]. Trials of binding organics and TiO_2 were carried out in the batch set-up. The powderous components were put in the vessel and CO_2 was added until the desired pressure; the system was maintained under stirring for 3 hours, and a flushing by fresh CO_2 was further carried out before depressurization. Coating experiments were carried out by antisolvent precipitation from suspensions, either in batch or continuous set-ups; in the continuous set-up, the pre-mixed suspension of the dissolved polymer and the inorganic particles was sprayed into the flow of carbon dioxide. Polymer-coated or organic-modified particles were characterized by SEM (morphology), with a solid-state backscattered probe for energy dispersive X-ray spectrometry (EDS) analysis (Ti monitoring) and by DSC/TGA for thermal events (polymer monitoring).

I. COATING PARTICLES BY POLYMERS

I.1. by batch

Few trials were carried out on TiO_2 (P25) or glass beads as oxides and PMMA as polymer, but since most of them produced pastes rather than powder, the technique was rapidly discarded; Table 1 however reports some investigated conditions and the overall aspect of the product, whereas the product morphology is detailed in Fig.1.

Table 1. Experimental conditions and produced material for coating TiO2 by PMMA in batch set-up. (acetone, 500 rpm, 36°C and 10 MPa)

Species concentration (mg/mL)	Volume of solution	Product aspect
TiO_2 (12) + PMMA (12)	85 mL	Coarse powder + paste
TiO_2 (5) + PMMA (25)	40 mL	Fine and white powder
TiO_2 (5) + PMMA (5)	40 mL	Small amount of coarse powder

The technique proceeds by suspending the oxide particles in a solution where the polymer was dissolved, and by submitting the suspension to an addition of CO_2 up to a desired pressure. It is expected that CO_2 will induce the polymer precipitation by antisolvent effect onto the available surfaces, which are the oxide particles. By batch, the technique is challenging since extra surfaces are provided by stirrer, vessel walls and baffles and since it is difficult to drive the system far from equilibrium, besides the fact that polymer precipitation proceeds by L-L demixing before solidification. Results in batch set-up indeed point out such difficulties, since most trials led to chewing-gum like pastes, excepted when smaller volume of solvent was used, or when the suspension was diluted in TiO_2. SEM pictures (**Fig. 1**) show a high degree of particles aggregation, with TiO_2 particles forming spherical aggregates or fibers under the presence of PMMA in the product.
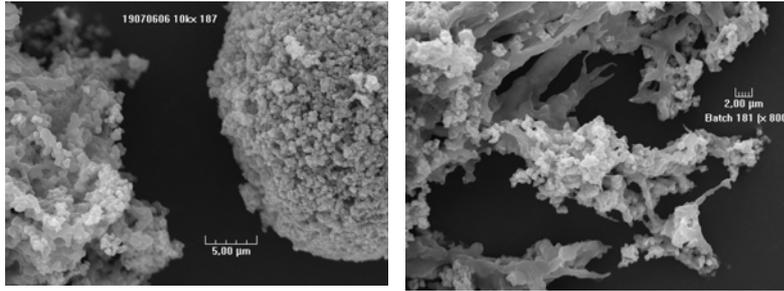
Fig. 1: Batch processing TiO_2 + PMMA from acetone at concentration of 5:5 (left) and 12:12 (right) mg/ml

I.2. by SAS

By SAS, the solution that contains dissolved PMMA and particles of TiO_2 in suspension is sprayed into the CO_2 flow (procedure adapted from Wang et al [7]); selected trials reported in Table 2 emphasize the role of polymer concentration.

Table 2. Experimental conditions and produced material for coating TiO_2 by PMMA in SAS set-up. (methylene chloride, 40°C and 11 MPa; TiO_2 concentration of 3.5 mg/ml).

Run	Polymer	TiO_2/polymer ratio	Yield (%)	Comments
1	PMMA	3.5 / 1	85	Fine, white powder
2	PMMA	1 / 1	56	Fine, white powder
3	PMMA	1 / 4.3	52	Fine, white powder
4	PMMA + PCL	1 / 1 / 1	80	Fine, white powder

Contrary to batch experiments, fine white powders were usually obtained, due probably to the combination of spray efficiency and diluted suspension, besides the change of solvent. Agglomeration of particles still exist (Fig. 2), but at particle level and in a far lesser extend than in batch, with no balloon –like aggregates viewed in left Fig.1. Morover, as seen from the pictures, the increase of polymer concentration leads to the formation of bigger particles.

Fig.2. SAS processing TiO_2 + PMMA from methylene chloride, with variable TiO_2/polymer ratio (same SEM magnification of 20kx)
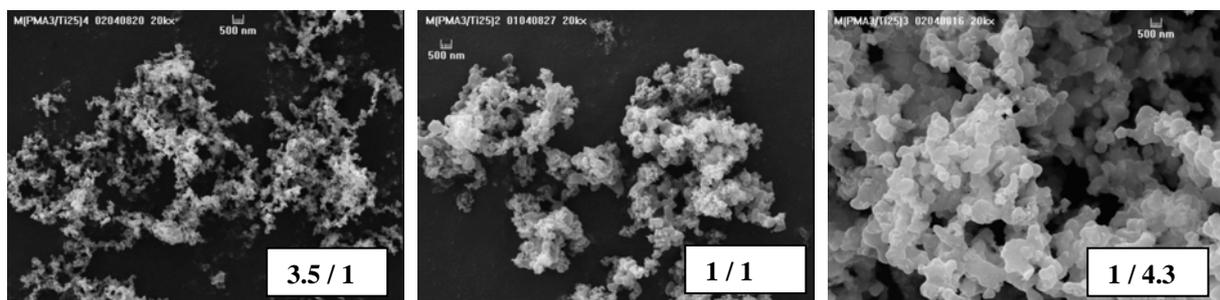

To confirm the existence of both species in the produced samples, a microanalytical characterization by EDS analysis was carried out for tracing TiO_2, and TGA was carried out to trace PMMA via thermal events. EDS analysis performed in different areas of samples indicates that TiO_2 was not segregated in spots, and conversely speaking, was thus dispersed quite homogeneously throughout the powder. Thermogravimetric analysis shows an increased

weight loss of the sample as the polymer concentration in the initial solution increased, indicating an increasing amount of polymer in the product.

A dispersion test was further developed as an indicator of the hydrophilic/lipophilic character of the product; dispersion of raw TiO_2 and of PMMA/TiO_2 produced samples was carried out in different solvents, i.e. water (W), toluene (T) and petroleum ether (PE). Fig. 3. illustrates the dispersion tests. Raw TiO_2 can stably suspend in polar water (W), whereas its dispersion in (T) and (PE) is less visible. The PMMA and PMMA/PCL TiO_2 samples were observed to float on the surface of water and to suspend in toluene, indicating that the surface of TiO_2 particles was varied from hydrophilic to lipophilic, consistent with the polymer nature.

Fig. 3. Dispersion tests of initial TiO_2 and precipitated PMMA/TiO_2 and PMMA/PCL/TiO_2 samples, in water (W), toluene (T) and petroleum ether (PE).
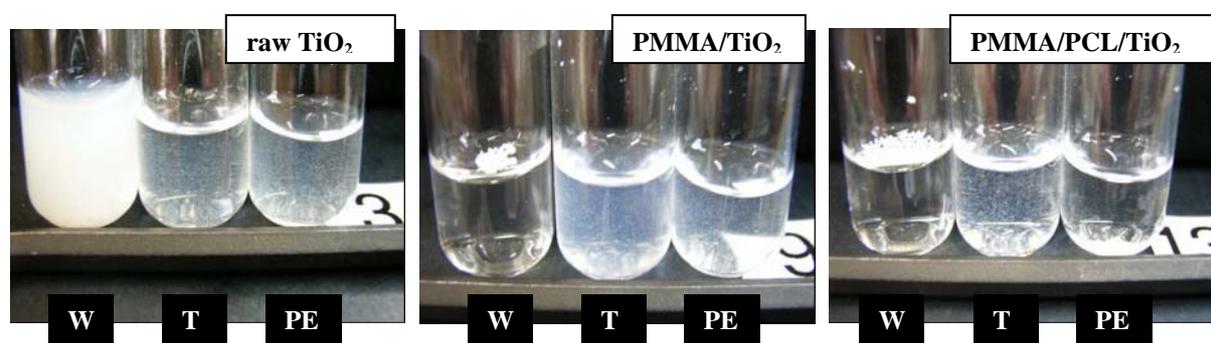
To conclude, several characterization techniques provide indications of successful coating of TiO_2 nanoparticles with PMMA-based polymers, specially when the method involved the spray of the suspension into a continuous flow of carbon dioxide. Extensive trials need to be carried out, to optimize the process regarding the species individual concentration and their ratio, besides the usual SAS parameters known to influence the polymer precipitation (temperature, pressure, molecular weight, flow rates).

II. BINDING PARTICLES WITH ORGANICS

Although surface modification of oxide particles by grafting is largely explored in solution or by vapor deposition, the potentialities of supercritical fluid are still marginally investigated.
Based on the pioneer work from Domingo [8,9] which grafted alkoxysilanes on nanoparticles, we investigated the possibility of modifying TiO_2 surface with salicylic acid. The concept is based on the dissolution of organics in supercritical CO_2 and contacting the formed supercritical solution with oxide particles, suspended in the medium through stirring. TiO_2 was selected owing its high reactivity, since the coordination sphere of Ti atom is incomplete. The molecule to bind should be preferentially CO_2-soluble and should contain reactive functions; salicylic acid (ACS) was selected, owing the presence of a carboxylic group and to its good solubility in $SCCO_2$.
Some selected trials are reported in Table 3.

Table 3: Conditions and results of trials of contacting salicylic acidic with nanoparticles of TiO_2 PC50, with or without cleaning by a fresh CO_2 flow.

Run	Temperature	Final pressure	Cleaning step	Comments
1	40°C	16 MPa	0 min	Yellow powder
2	40°C	16 MPa	30 min	Light yellow powder
3	60°C	20 MPa	30 min	Light yellow powder

Raw powders are white, and most CO_2-produced samples were yellow; although the change of color might sign interactions between the species, it is not specific to the CO_2 treatment, since physical mixtures also turned yellow.

SEM pictures of raw salicylic acid and of TiO_2+ACS powder are given in **Fig. 4**; the TiO_2+ACS samples did not show the rod-like particles of raw salicylic acid, indicating that ACS was at least micronized if not binded with TiO_2; the presence of ACS was confirmed by FTIR spectra.
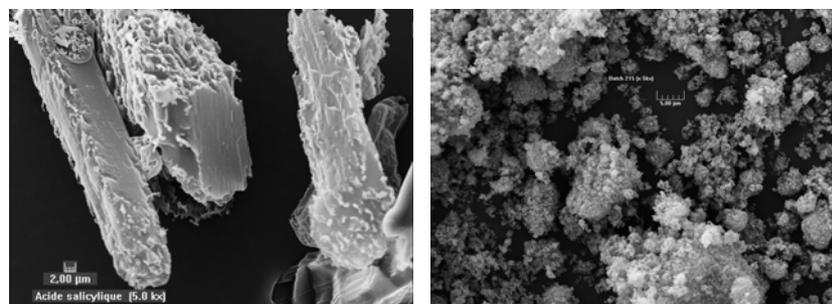

Fig. 4: SEM pictures of raw acid salicylic (on left) and of a CO_2 treated powder of TiO_2 + salicylic acid (run 2, on right), at the same magnification.

Samples were characterized by thermogravimetric analysis, allowing for monitoring both thermal events and weight losses during the heating of samples from room temperature to 750°C; at 750°C, the residue contains only TiO_2, so the weight losses over temperature give an estimates of the sample composition in organic and oxide. **Fig. 5** gives the thermogram of samples processed at 40°C and 16 MPa, with (run 2; green line) or without (run 1; purple line) a cleaning step.
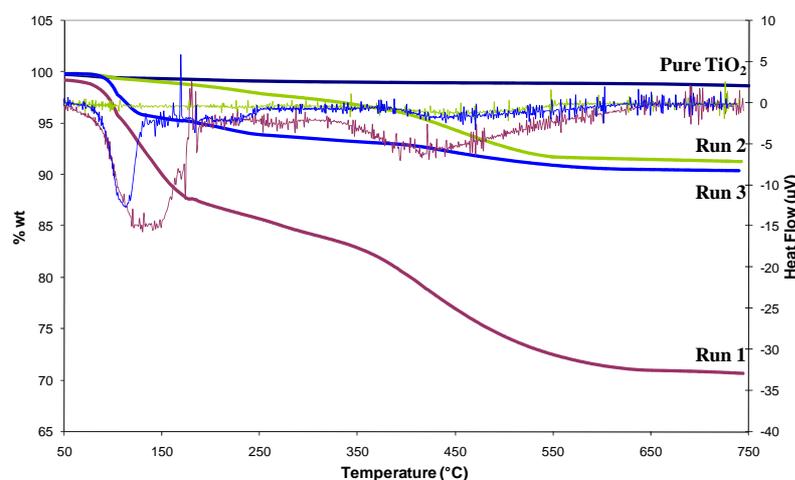

Fig 5: TGA of raw TiO_2 and of CO_2 treated powders of TiO_2 + salicylic acid.
Run 1. with flushing by fresh CO_2
Run 2. no flushing
Run 3. 60°C 20 MPa, with flushing

For the sample processed in a closed atmosphere (run1), two weight losses and two thermal events at 90-170°C and 350-550°C are noticeable, whereas the flushed sample exhibits only

one weight reduction (350-550°C) and no endotherm. The first weight loss that occurs in the range of ACS melting temperature (157-159°C) signs an unreacted fraction of the organic, which is removed upon a fresh flow of CO_2 (no endotherm and no weight loss around 157°C in run2, no endotherm neither in DSC analysis), whereas the weight loss observed at higher T for both samples (but not for raw TiO_2) suggests a strong interaction between TiO_2 and ACS. The TiO_2 content of residues at 750°C were of 92% and 70% for the flushed and unflushed samples, respectively, which, means an ACS content of 8% (binded ACS) and 30% (binded and free) initially in the samples. The sample produced at higher temperature and pressure (60°C, 20 MPa, blue line in Fig.5) contains about the same % of ACS than the sample processed at 40°C/16 MPa; however, the thermal events are slightly different, with a first 4% weight loss at temperature below 130°C followed by a continuous weight loss down to 10%. The behavior could indicate a less stable interaction between TiO_2 and ACS at 60°C, with an additional event of dehydratation that led to an endotherm in the 100°C range.

A dispersion test was also settled to enlight the surface modification via distribution between a polar (Water) and apolar (Toluene) phases. Raw or CO_2-processed pure TiO_2 can stably suspend in water (W); raw ACS remains mostly at the W/T interface although few particles go to the aqueous lower phase. The CO_2 treated powder (run 3) exhibits a different behavior; the totality of the sample remains at the W/T interface, which accredits the reality of an interaction between TiO_2 and salicylic acid that consequently modifies the TiO_2 behavior.

To conclude, first results of TiO_2 modification by drugs are promising, since several characterization techniques point out a different behavior of the CO_2-processed samples compared to raw nanoparticles. However, extensive and more specific characterizations should be carried out to clearly identify the nature of the TiO_2 – modifier interactions (covalently or surface adsorbed) that is a pre-requisite to promote the supercritical dry-route as a very effective approach to functionalize individual particles.

Acknowledgements

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