Inorganic Particle Coating with Poly(dimethylsiloxane)

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SYNOPSIS

Stable, thick poly(dimethylsiloxane) (PDMS) coatings are formed on iron(III) and aluminum oxide and calcium carbonate particles by impregnating the particles with dimethylsilicone oil and heating at 250–280°C. These coatings are strongly resistant to solvent extraction and to exposure in a water-saturated atmosphere. Coated particles are strongly hydrophobic, as evidenced by their greater stability in apolar solvents. Silicone coating formation on oxide particles is interpreted as a result of two reactions: siloxane chain opening at higher temperatures, followed by the reaction of active chain end-groups with hydroxo groups at the metal oxide or carbonate surfaces and silicone cross-linking by methylene or siloxane bridges. The procedures described in this paper differ from usual silanization or siliconization procedures because it uses stable PDMS and yields thicker coatings. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Composite materials have attracted considerable attention in the past decades, and many current important industrial products are made with them. A composite is the result of the combination of two or more distinct components,[1] which often belong to different classes of materials. Many composites are natural (e.g., bone), but there is a large number of synthetic composites. Most often, composites are made of a continuous phase, or matrix, interspersed with particles, fibers, tissue, or other form of a second phase.[2] The interfacial regions are very important in composite materials, and they have a decisive role in the ultimate mechanical properties.

Composite (or encapsulated) particles are special and important reinforcing materials. They are interesting because of the properties that may be obtained, both as particulate materials or as precursors of bulky solids. There are many interesting examples of encapsulated particles from the recent literature. Hasegawa et al.[3–5] studied the encapsulation of $BaSO_4$, $CaCO_3$, and TiO_2 with poly(methyl methacrylate), obtained by emulsion polymerization. In this case, monomer adsorption on the particles is

followed by its polymerization. Chambers et al.[6] studied the polymerization of many monomers over the surface of inorganic particles, using γ-ray initiation. TiO_2 particles coated with polymers have been described; paint coatings in which they are used have a longer useful life. This same method has been used for a variety of substrate–polymer systems.[7–10]

Oyama et al.[11] coated well-defined silica particles with alumina and then polymerized divinylbenzene over the particles and dispersed in an organic medium. The coating polymer is cross-linked, which should strongly affect its mechanical and adhesion properties.

Silica particles coated by "decomposition of adsorbed silicones" is described in the chromatography literature.[12] In this case, the objective is the preparation of chromatographic supports. In a recent work from this laboratory,[13] the formation of stable poly(dimethylsiloxane) (PDMS) coatings on borosilicate glass surfaces was presented. There is also a related large body of literature on the silanization of inorganic surfaces.[14–20] This is usually done by reaction of a silane derivative and silanol or other hydroxo groups on the surface. Alkoxysilanes are widely used; they undergo hydrolysis, thus forming silanol groups.[18,19] These may undergo condensation reactions with other oxanol groups, forming an oxane bond between each silane and the surface, which is now coated with a layer with physicochemical characteristics as determined by the other chemical

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groups from the silane. Amino-alkyl alkoxy silanes, for instance, will create a positively charged surface.

In our recent work,[13] the starting siloxane is a chemically stable PDMS, e.g., silicone oil or rubber. That means it is a polymeric reagent, activated by being heated to 250–300°C. Under these conditions in the presence of air, there are two concurrent transformations in PDMS. First, there is chain heterolytic scission, which creates reactive Si— and O— terminated groups. These may react further with oxanols from neighboring surfaces and Si—O groups from the same or from other chains, forming branches and olygomers, both linear and cyclic. Second, there is methyl group oxidation leading ultimately to cross-linking by methylene or siloxane bridges.

The present work describes the formation of silicone, (Fe,Al) oxide and calcium carbonate composite particles, by using a procedure based on the ab-
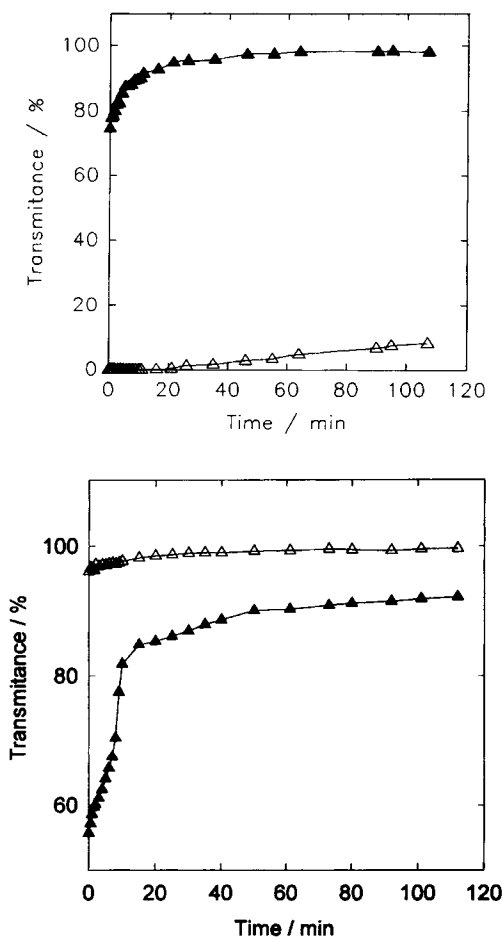

Figure 2 Transmission electron micrograph of Fe_2O_3 (a) and silicone-coated Fe_2O_3 (b).

sorption of PDMS silicone oil, followed by heating. The result is the formation of hydrophobic particles, coated with a stable and adherent layer of silicone.

EXPERIMENTAL

Reagents

PDMS is a 1000 cSt fluid from Dow Corning. Iron(III) oxide is from Bayer. X-ray difractogram shows that this material is α-Fe_2O_3 mixed with non-crystalline oxide. Alumina is a Merck product for chromatography (90 active neutral grade) and calcium carbonate is also from Merck. Other reagents are analytical grade.

Particle Coating Procedure

Powdered iron and aluminum oxide powders were subjected to silicone treatment following these steps: powder impregnation with silicone oil (the powder was mixed with oil at a 1/1 mass ratio, heating of

Figure 1 Transmittance of the supernatants of Fe_2O_3 ($\triangle$) and coated Fe_2O_3 ($\blacktriangle$) dispersions. (a) Dispersions in acetone, 1.0% solids; (b) dispersions in carbon tetrachloride, 0.9% solids.
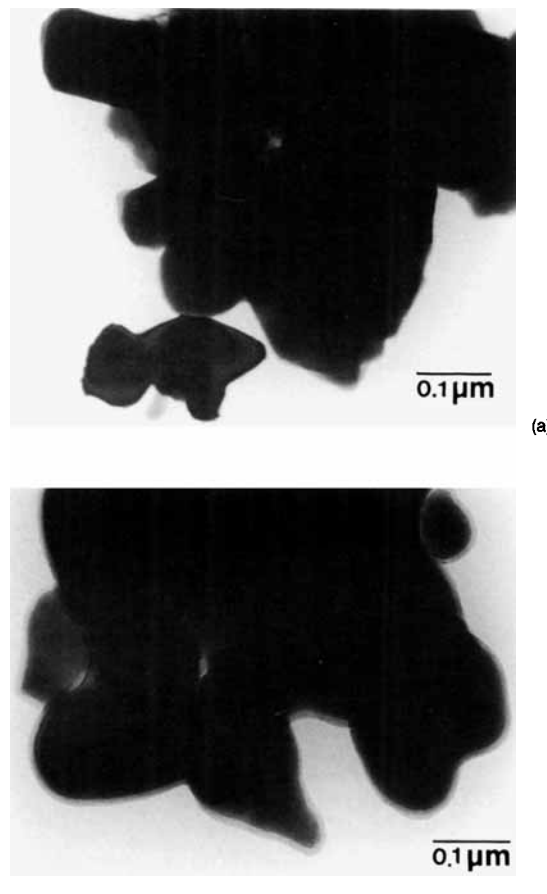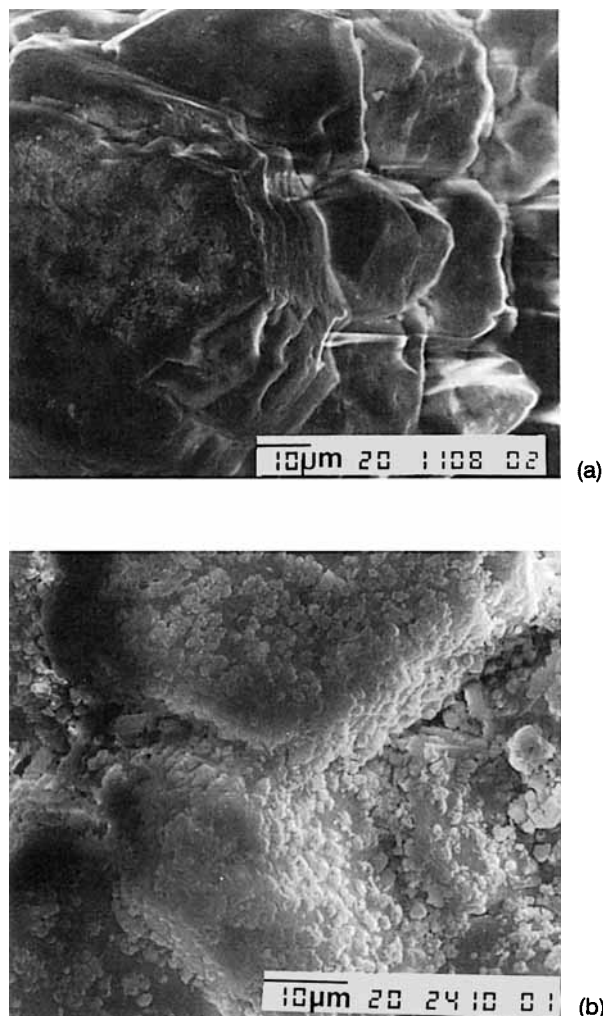
Figure 3 Scanning electron micrographs of alumina (a) and silicone-coated alumina (b).

the impregnated powder (280°C for 60 min); extraction with toluene (at 80°C for 3 h), and drying in an oven at 100°C for 60 min.

Evaluation of Particle Dispersion Stability

The stability of particle dispersion in liquids was evaluated in the following way. Powder samples were weighed in capped vials and solvent was added. The dispersions were vigorously shaken for 30 min and then allowed to stand for 30 s. An aliquot of the supernatant was then transferred to a spectrophotometer cell, within a Micronal 382B spectrophotometer. Transmittance readings were taken at 650 nm.

Sample Preparation for Electron Microscopy

Scanning electron microscopy preparation was done as follows. Powder samples were sprinkled over the

sample holders coated with a conductive adhesive. The samples were coated with gold by sputtering and observed at 20 kV in a JEOL T300 microscope fitted with a Noran X-ray analyzer. Samples for transmission electron microscopy were dispersed in isopropanol and applied onto parlodium-carbon–coated copper grids and examined in a CEM-902 Zeiss instrument, fitted with an electron monochromator and image analysis system.

Additional Analysis

Thermogravimetric analysis was done in a Dupont 9900 instrument, under an N_2 atmosphere, at a heating rate of 10°C/min. Transmission IR spectra were obtained using powder dispersions in a mineral oil, using a Perkin-Elmer FTIR instrument, series 1600. The adsorption ability of calcium carbonate was evaluated by placing 2 g of powder within 50 mL of methylene blue solution (1.88×10^{-5} mol $\cdot$ L^{-1}) for 1.5 h under stirring. The supernatant was separated using a centrifuge (2000 rpm for 10 min), and its absorbance was read at 668 nm. The solids were washed twice with 10 mL ethanol, dried in an oven (90°C, 24 h), and kept in a desicator, under vacuum. Visible reflectance spectra were recorded in a Macbeth Color-eye 2020 instrument, using 5-mm-thick pellets prepared by pressing adequate amounts of the particles. ^{29}Si solid-state NMR spectra were obtained on a Bruker AC 300/P spectrometer at 59.63 MHz. The samples were spun in the magic angle at ca. 3.5 kHz. The cross-polarization technique was used with contact time of 4 ms, acquisition time of 10 ms, and 1-s pulse interval time. The spectrum shown was obtained with ca. 68,000 fid's.
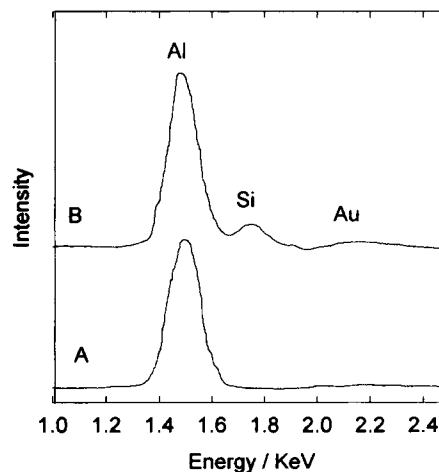

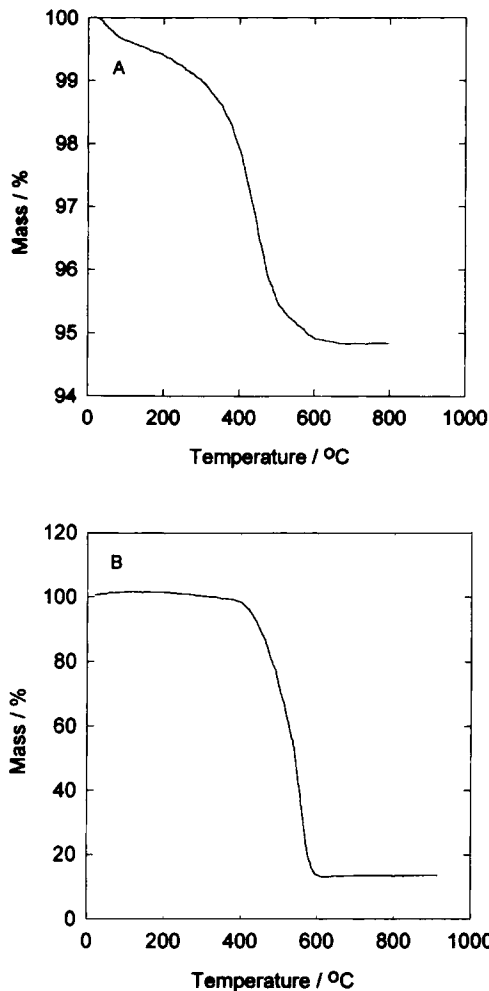**Figure 4** X-ray emission spectra of Al_2O_3 (a) and coated Al_2O_3 (b).

Figure 5 Thermogram from coated aluminum oxide (a) and pure silicone room temperature vulcanisate (RTV) (b).

Figure 6 (a) IR spectra (transmission mode) from coated Fe_2O_3; (b) same as (a) but after exposure to a water vapor saturated atmosphere (72 h at 50°C); (c) same as (b) but after toluene extraction in a Sohxlet apparatus for 3 h.

particle surfaces with a polymer that is strongly soluble in many apolar solvents, particularly hydrocarbons and chlorinated hydrocarbons.

Transmission Electron Microscopy

Clear-field micrographs of silicone-coated and pristine iron oxide particles are shown in Figure 2. These pictures were taken using unscattered and elastically scattered electrons. The first represents a large particle aggregate, in which most particles are surrounded by a low-density regular skin. Because this

RESULTS AND DISCUSSION

The aspect ratios of iron and aluminum oxide powders after impregnation with silicone oil followed by heating, extraction with toluene, and drying are similar to those of the original powders. However, the impregnated powders are strongly hydrophobic.

The stability of dispersions prepared with silicone-treated iron oxide in different solvents is very different from that of the pristine powder in the same solvents. The transmittance of the supernatants of some of these dispersions was determined, as a function of time. The results presented in Figure 1(a) and (b) show that silicone-treated Fe_2O_3 is more stable in the apolar carbon tetrachloride than the untreated powder. The opposite happens in the polar solvent, acetone. These results agree with the expected behavior, considering that silicone treatment leads to a total or partial coverage of iron oxide
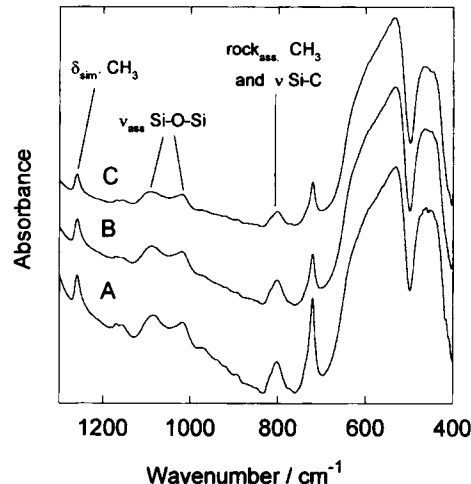

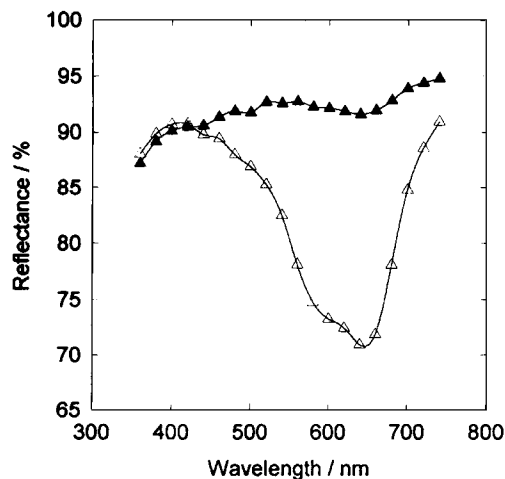**Figure 7** Visible light reflectance spectra of calcium carbonate pellets (△) and silicone-coated calcium carbonate pellets (▲). Both powders were immersed in methylene blue aqueous solution, dried, and pressed into pellets.
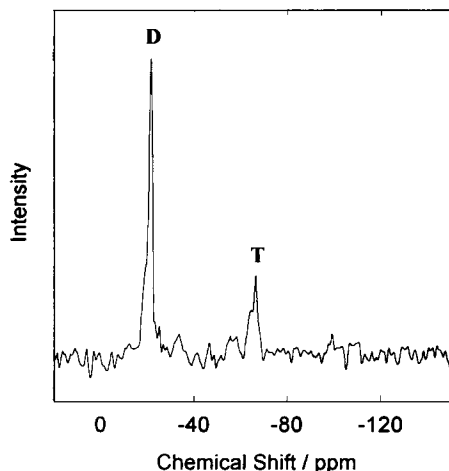
Figure 8 ^{29}Si-NMR spectrum of silicone-coated calcium carbonate. D and T siloxane peaks are indicated.

skin is not seen in the pristine particles, we conclude that it is made of silicone.

Scanning Electron Microscopy

Aluminum oxide particles used in this work are large and can be conveniently seen using a standard scanning electron microscope. Figure 3 shows pictures of both silicone-coated and uncoated aluminum oxide particles. The surface of the platelets of the latter are smooth. On the other hand, most surface areas of the silicone-coated oxide are covered with small semispherical shapes which are assigned to silicone droplets deposited on the oxide surface. These silicone droplets become adherent and cross-linked due to heating. This is not uniformly observed on every particle and may result from particle surface heterogeneity. In a previous work from this laboratory,[21] a related observation was also made and discussed concerning the coating of alumina particles with iron hydroxoacetate. The iron oxide particles were also examined in a similar manner, but the particles used in this work are much smaller and strongly aggregated which obscured surface details.

The X-ray emission spectrum of the coated alumina particles is shown in Figure 4. Using this data and the ZAF correction of the microanalyser software, we found the Al/Si ratio was 9.2 for the sampled volume. This is the lower limit for the overall Al/Si mol ratio in the coated particles, because the alumina particles are typically 10 μm thick and the microprobe sampling depth is ca. 1 μm (under the conditions used) from the particle surfaces.[22]

Thermal stability of the silicone coating on aluminum and iron oxide was evaluated from thermogravimetric runs [see Fig. 5(a) for an alumina

sample]. Temperature of maximum weight loss is 440°C (compare with 492°C in plain silicone rubber). Consequently, the thermal stability of the coating silicone is lower than that of the pure polymer [Fig. 5(b)], but is still high as compared with many other polymers.

Coating stability in a warm humid environment was also evaluated, considering the possibility of hydrolysis of silicone-substrate (oxane) interfacial bonds. This was done by observing IR spectra of (toluene-extracted) powders, before and after exposure to water vapor-saturated atmosphere at 50°C for 72 h (Fig. 6). Peaks at 1260 and 800 cm^{-1} are assigned to vibrations from silicone groups, and their integrated absorbances were used to evaluate the relative residual amount of bound silicone. This showed that less than 50% of the silicone was removed after exposure to warm, humid air, followed by extraction with toluene.

Silicone-coated calcium carbonate particles do not adsorb methylene blue from an aqueous solution, as evidenced by the reflectance spectra of powders immersed in solutions of this dye, at a 1.88 × 10^{-5} mol L^{-1} concentration (Fig. 7). On the other hand, transmission spectra of the respective supernatant dye solutions were also obtained and used for the determination of the adsorbed amounts in the original and coated particles.[23] Pristine CaCO$_3$ adsorbs 4 × 10^{-7} mol dye/g, but silicone-treated CaCO$_3$ adsorbs only 5 × 10^{-9} mol dye/g under these conditions. This decrease in the adsorption capacity of calcium carbonate shows that dye access to calcium carbonate surface is eliminated by coating with silicone. This means the polymer coating layer is continuous, not porous.

There is a large body of information in the literature on the modification of inorganic surfaces using silane derivatives. Very clean well-defined modifications can be accomplished, leading to a host of interesting new surfaces, in which groups with differing chemical properties can be formed. The procedures described in this paper are quite different from those. First, in the present case a stable polysiloxane is used as the surface-modifying reagent, which is only activated at temperatures above 200°C. Second, cross-linked layers are obtained and their thickness is variable within a broad range.[13]

At this time, we cannot say which are the relative roles of silicone-oxide surface binding and of silicone cross-linking in the formation of a stable coating. However, we obtained ^{29}Si-NMR spectra of silicone-coated CaCO$_3$ (Fig. 8), which shows the presence of D and T groups[24-26] (D stands for Si with two neighboring Os; T for Si with three neighboring Os). This means that the polymer in the coating is pre-

dominantly a PDMS, but there is also a significant amount of cross-links or Si—O—Ca groups, which would account for the T band at −66 ppm in the spectrum.

An important aspect of this research is the following. The mechanical properties of silicones can be gradually changed by heat treatments. Upon heating in the 250–300°C range, PDMS becomes brittle. We should thus be able to obtain rubbery or brittle coatings, depending on the extent of the heat treatment. Moreover, a complete silicone decomposition could leave at the particle surfaces a silicate layer that may result in some interesting findings. This could be an alternative to the procedure recently described by Ohmori and Matijevic[27] to obtain silica coatings on iron oxide particles. The coated particles should have coalescence and cohesion properties quite different from the parent particles. Work is now in progress in this laboratory to examine these aspects of silicone-coated oxide particles.

Finally, we may expect that the procedures described in this paper are applicable to any oxide surface, provided it contains sites reactive toward oxisilylene chain ends. These techniques have a much broader scope than simple silica particle silanization by PDMS decomposition, which was described in the literature on chromatography. This may result in a whole new family of organic–inorganic composite particles.

CONCLUSIONS

PDMS undergoes interfacial reactions with iron and aluminum oxides and calcium carbonate at 250°C and above. The particles of these solids are thus coated with a hydrophobic layer, which modifies their adsorption properties. Silicone coatings thus obtained are strongly resistant to both solvent extraction and to exposure to a humid environment.

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