Coating of a stainless steel tube-wall catalytic reactor with thermally treated polysiloxane thick films

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Abstract:

Homogeneous polysiloxane films were deposited on a 316L stainless steel by plasma assisted chemical vapour deposition process. Thicknesses up to 10µm were developed. The organosilicon films were then thermally treated under air and the influence of calcinations conditions was investigated by infrared spectroscopy, Raman microscopy and XPS.

On all films, it appears that the structure varies according to the thermal treatment parameters. Indeed the surface composition appears to be $SiO_{1.8}$ which might represent a structure close to amorphous silica whereas the deepest layers retain a variable organic nature. Under the severer treatments, the nature of the deposit evolves toward a low reticulated glass-like silicon oxide but cannot be related to an amorphous silica structure. At 1273K the steel remains coated and hidden despite visible but non penetrating cracks of the upper layer of the physical barrier.

Key-words: PACVD, TDMS, stainless steel, surface passivity.

1. Introduction

The use of tube-wall catalytic reactor for exothermic reactions, such as the Fischer-Tropsch synthesis or partial oxidations, may offer a better thermal control of the chemical reaction (Babovic *et al.*, 2001). The problematic of the grafting of a catalyst on a metallic substrate has been extensively studied on metals such as aluminium (de Sanctis *et al*., 1995) (Thompson, 1997) or modified steels (for example Fecralloy® (Haas-Santo *et al*., 2001)). Basically, the active phase is grafted on the oxidized surface of the metal. This bond layer can be obtained in various ways such as thermal oxidation for Fecralloy®, or anodization for aluminium based alloys (Thompson, 1997). Except for modified steels, such pre-treatments are not always sufficient to allow a strong bonding of the catalysts onto the metal in the case of stainless steels.

On stainless steels other techniques were applied such as flame spraying or plasma spraying (Dalai et al., 1990). Less aggressive methods based on the use of dip-coating from a sol-gel preparation have proved their efficiency too. But these methods have an impact on the deposit morphology which can highly influence its inner activity or the further grafting of any active compounds on its surface (Giornelli, 2004).

This work deals with the preparation of such a bonding layer whose characteristics should allow the further grafting of a wide range of catalysts such as metal clusters or oxides: polysiloxane films were retained as a basic material. Their deposition on 316L stainless steel was done by plasma assisted chemical vapour deposition process (PACVD). Process conditions were tuned in order to obtain thick and non-porous deposits from decomposition of an organosilicon precursor. The organosilicon films were then thermally treated under air and the influence of calcinations conditions on film properties was investigated by infrared spectroscopy, Raman microscopy and XPS.

2. Experimental

2.1. *PACVD apparatus*

The PACVD process used consists in a polymerization of a selected compound induced in the cold remote nitrogen plasma discharge zone (CRNP). This reactive medium is obtained from a flow of nitrogen ionized by a microwave discharge upstream of the CRNP zone. Reactivity is obtained by breaking of monomer chemical bonds by the excited nitrogen. Activated monomers might then be rearranged in a condensed form such as a polymeric film, depending on the hydrodynamic in the deposition chamber (Callebert *et al.*, 1994). Polymer on SS316L anchors and growths at the surface of the substrate from Cr-N and Fe-O sites created during pre-treatment and deposition (Gheorghui-de La Roque *et al.*, 1998). Such a method allows many advantages such as:

- High deposition rate
- No or little etching due to low aggression of N_2 under cold remote plasma conditions
- Increased adhesion property of the deposited layer on the target surface
- Good deposition homogeneity control induced by an accurate control of flow scheme in the PACVD reactor, even on large and complex target surfaces

The figure 1 shows the experimental setup, the PACVD reactor. The plasma is induced from nitrogen (1,8slpm, industrial grade) introduced in the reactor at a pressure of a few mbars. Discharge plasma excitation is created with a 433 MHz excitation using a coaxial coupling device. The discharge useful power is 200W at 2450 MHz.

Monomer is 1.1.3.3-tetramethyldisiloxane 97% (TMDSO, ABCR). O_2 is Air Liquide (industrial grade) and is injected in the CRNP area as a transport gas for TMDS.

N_2, O_2 and TMDSO gas flows are regulated via MKS mass-flow regulators. The gaseous mixture is extracted at the bottom of the reactor by a primary pump (Alcatel).
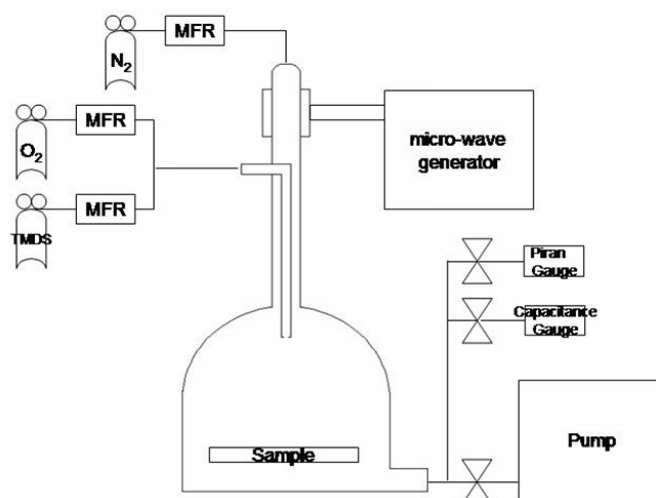

Figure 1: PACVD apparatus

2.2. *Thermal treatment oven*

The polysiloxane films deposited on stainless steel were treated in air under a natural convection regime with a Maton programmable oven. Power and temperature ramp were

controlled with a Nabertherm C6 thermal regulator. Thermal treatment protocol was validated with thermo gravimetric analysis.

2.3.   *Characterizations*

Selected samples were characterised before and after thermal treatment by FT-IR, Raman microscopy and XPS analysis. Thicknesses were measured using a Foucault current probe. Each given thickness is a mean value obtained from five thickness measures, one in the middle of the sample the others at each corner of a virtual 1 cm large square centred on the first measurement point (Azzouz *et al*., 1999). Measurement precision is +/- 1µm.

FT-IR apparatus was a Perkin-Elmer Spectrum one. Spectrum acquisition was done under reflexion.

Raman microscopy was done with magnification x50, laser used was 532,18nm. Exposure time was 2 minutes with 1 accumulation and D0.6 filter. Degussa (Aerosil 100) fumed silica was used for Raman comparisons with amorphous silica.

Mass loss was measured for thermally treated samples before and after exposure to a tangential air flow (50L/minute).

2.4.   *Experimental conditions*

Stainless steel samples (20x2 and 40x20mm) were cut into a 2 mm thick laminated foil. Samples were degreased in acetone (VERBIESE 99.5%) and dried in a drying oven at 110°C for 12h. samples were stored in desiccators until their use.

PACVD treatment was carried out at room temperature under mbar. N_2 flow was 1,8 slpm. TMDS and O_2 flows were 5sccm and 25sccm, respectively. Samples were first kept under N_2 CRNP exposure for 15minutes. This treatment allows a deeper cleaning of the substrate and strengthens the mechanical properties of the coating through nitrogen grafting onto Fe and/or Cr sites (Gheorghui-de La Roque *et al*., 1998). These points act like strengthened anchorage sites for the polymer growth. Then samples were treated under N_2 and TMDSO+O_2 for various exposure times.

Some samples exposed for 10 minutes were thermally treated under air. These 5µm thick films were treated at 450, 650 and 900°C respectively. The temperature programmed ramp used was 5°C/min. Final temperatures were hold 1 hour in the two latter cases. For the 450°C final temperature program, the final value was hold 1, 2, 3, 4 and 5 hours respectively. Thermo gravimetric analysis was done on a stripped plasma deposited polymer film with a temperature programmed ramp of 5°C/min. 1 hour long temperature steps were applied at 450°C, 650°C and 900°C. Event gases were analyzed by mass spectrometry.

3. Results and interpretation

3.1.   *PACVD films characterisation*

The influence of sample exposition time to the PACVD spray on the thickness of the deposited film was monitored at constant flow and fixed sample position. Both flow rates and height were selected in order to obtain a polymer under a film form (Callebert *et al*., 1994).

Results obtained are gathered on figure 2a. Film thickness appears to vary linearly as a function of exposure time. Film growth rate is therefore constant under the conditions used.
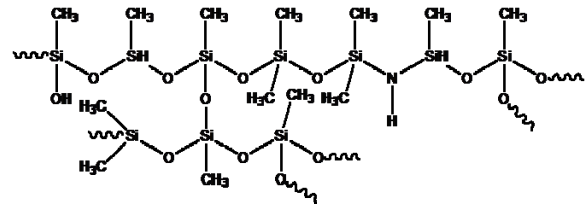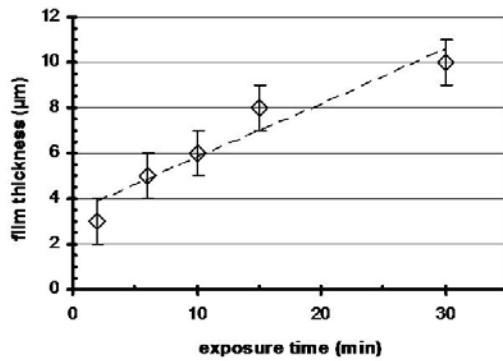
Figure 2: characterisation of PACVD deposits
a. film growth (left)
b. polymer expected structure (right (Callebert *et al.*, 1994))

Spectral characterisation under FT-IR (figure 5) and Raman microscopy (figure 4) gave results similar to the ones traditionally observed for polysiloxane films (Anderson, 1974). The 2145cm^{-1} peak observed for the monomer and related to the Si-H bond disappeared on the Raman spectra which indicates a fully solid deposit and not a possible liquid condensate form from an incomplete polymerisation of TDMSO. On the FT-IR spectra the double peak observed in the 1000-1200cm^{-1} area of the spectra is characteristic of the Si-O-Si asymmetric stretching from a linear form of $((CH_3)_2SiO)_x$ polymer. A reticulated form of polymer would induce a shift of these peaks toward the 1200cm^{-1} area. 2950, 1400 And 1250cm^{-1} peaks correspond to multiple –CH$_3$ stretching and deformation modes (symmetric and asymmetric). On the basis of this spectroscopic evidence the film form is likely to correspond to the one proposed in figure 2b (Callebert *et al.*, 1994).
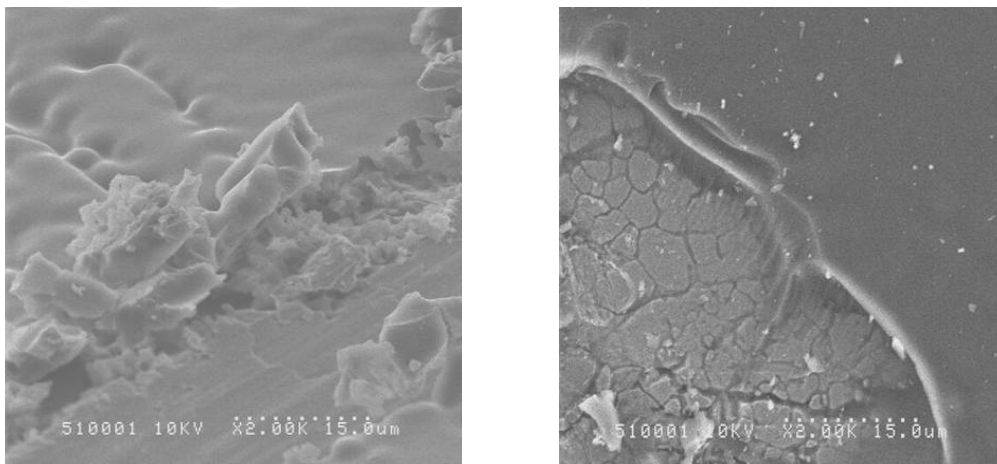

Figure 3: Tilted upper views of SEM micrograph of coated stainless steel (magnification x2000)
a. fresh PACVD deposit, blade scratched (left)
b. 5 hours treatment at 450°C, blade scratched (right)

A SEM micrograph reveals a film more or less smoothed (figure 3a). These irregularities are to be seen as under-printing of the substrate: sample is a SS316L 2mm thick laminated foil. During lamination some parallel stripes are impressed on the metal and correspond to the parallel irregularities of the film. Nodule shaped irregularities are more likely some polymer powders formed by early polymerisation in the TMDSO spray. These

powders fall on the film and are reincorporated in the matrix by further film growth. Indeed some powder deposit is noticeable in the upper area of the PACVD reactor.
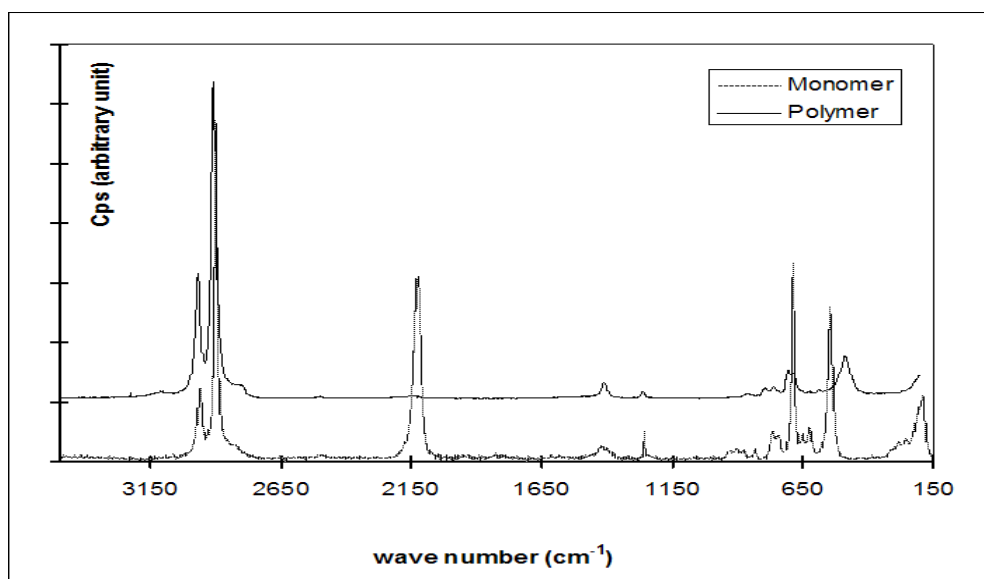

Figure 4: Raman spectra of TDMS (dashed, below) and deposited polymer (plain, above)
(polymer spectrum was vertically shifted for improved legibility)

3.2. Thermal treatment influence

The presence of methyl (-Me) groups on the polymer is likely to confer strong hydrophobic properties. These are potentially an obstacle to any further catalyst impregnation from aqueous precursor solutions. Moreover polysiloxane films are known to be degraded under thermal stress. This property which is used to retard fire propagation on coated polymers will induce a modification of the deposit under thermal effect (Quédé *et al.*, 2002). The stability of the coating is therefore not adapted to any heated application. An adapted thermal treatment of the coating is considered as being a way to stabilize and to inert the polysiloxane polymeric film.

XPS analyses of the thermally treated samples show a surface composition close to $SiO_{1.8}$, which would correspond to structures approaching silica (Table 1). But spectral data show a slightly different material (figures 5 & 6).

Table 1: surface formula calculated from XPS data

Sample	Surface formula (from XPS results)
Fresh polymer	$SiC_{1.08}O_{1.15}N_{0.04}$
After thermal treatment (450°C)	$SiC_{0.12}O_{1.67}$
After thermal treatment (650°C)	$SiC_{0.05}O_{1.8}$
After thermal treatment (900°C)	$SiC_{0.01}O_{1.82}$

Spectral results for 450°C are reported in figure 5. Whatever the calcinations final step duration is, the overall aspect of the spectrograms does not differ. Below 1450 cm^{-1}, the area is changed mainly for peaks relatives to Si-O-Si asymmetric stretching and -Me symmetric deformation. Spectra are smoothed and characteristic peaks for polysiloxane tend to disappear. However an organic participation from –Me groups remains: the symmetric and

asymmetric stretching peaks for -Me around 2950 cm^{-1} are not fully eliminated by the thermal treatment steps at 450°C. Raman microscopy does not allow, in absence of any internal standard, a direct quantification from the peaks area. However the ratio of peak intensities in the same spectrum may give some information about the relative participation of bonds in the analyzed polymer. Here, two peaks may be considered: the first one at 2950cm^{-1} and the second one at 1000cm^{-1}; they are related to the organic (-Me) and mineral (Si-O-Si) character of the film respectively. The ratio of their intensity gives information on the mineralization rate of the considered film sample after treatment. Whatever the duration of the final thermal treatment step, this intensity ratio does not evolve in a significant way: at 450°C the combustion kinetic of the organic part of the film is quite limited and cannot be complete even after 5 hours. This may be due to strong gas diffusion limitations in the material. Mineralization may be observed on an SEM micrograph: the aspect of the film is glass-like in surface (figure 3b). A mechanical scratch reveals another structure for the deepest layers: underneath the glassy surface the polymer seems not to have been dramatically influenced by the thermal treatment.
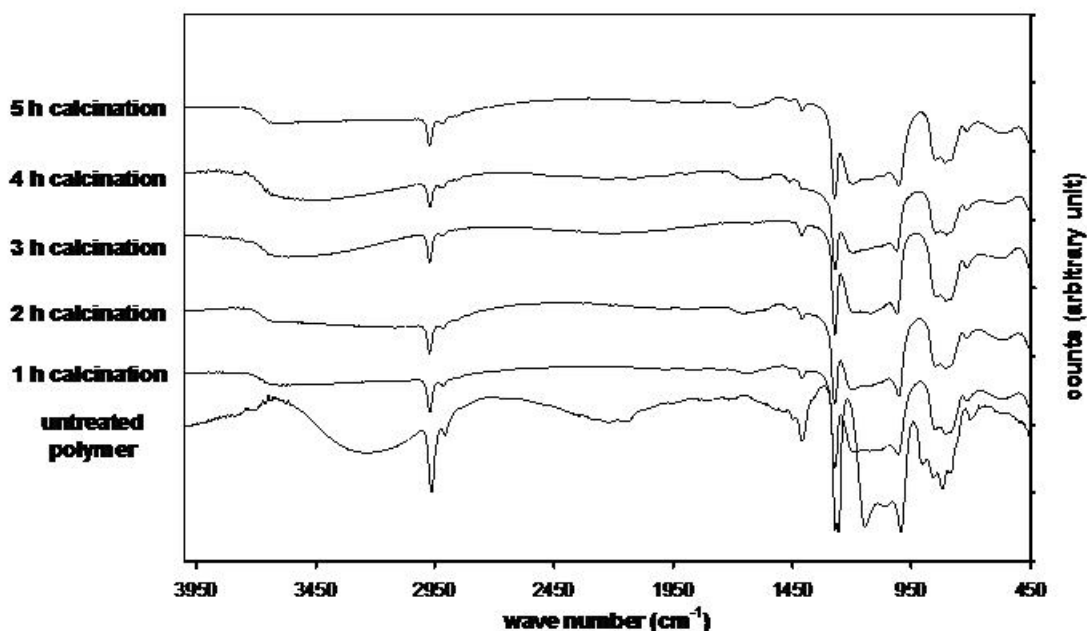

Figure 5: FT-IR spectra of fresh and treated polymers (450°C, variable treatment durations)
(polymer spectra were vertically shifted for improved legibility)

At 650°C and 900°C, after a one hour long final step, the film is fully mineralised and does not show any –Me related peak (figure 6). The spectra between 650 and 900°C evolve: peaks below 500cm^{-1} tend to disappear whereas 550 and 680cm^{-1} peaks tend to shift to the lower wave numbers. In all cases, the spectra are not related to amorphous silica: the linear polymer, once mineralised, is not reticulated. However the 900°C thermally treated sample shows a tendency to shift its spectrum toward a spectrum which may recall amorphous silica.

No mass loss was recorded on thermally treated samples before and after exposure to a tangential air flow (50L/minute).
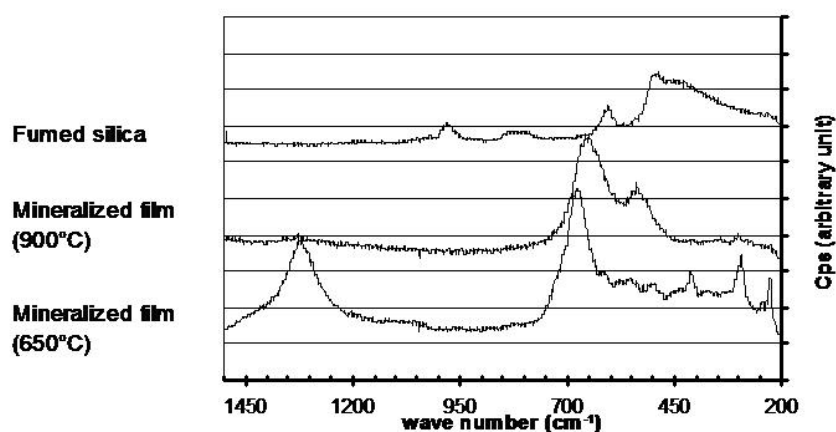
Figure 6: Raman spectra of treated polymers (650°C & 900°C) and fumed silica
(polymer spectra were vertically shifted for improved legibility)

Thermo-gravimetric analysis was performed on 9.58 mg of striped polymer; thermal profile and mass variation are reported in figure 7. Event gases were analyzed by mass spectrometry. The results from the temperature program show a first combustion of the film at 350°C with the release of CO, CO_2 and H_2O. At maintained 450°C, mass variation occurs, which comforts the slow kinetic of the polymer degradation. A second degradation step appears from 450°C to 600°C; the same degradation products are found at outlet. Above 650°C, no significant mass variation is observed as seen elsewhere (Quédé *et al*., 2002). From 800°C, the sample shows a slight mass increase. This mass increase is considered as being due to oxygen incorporation into the material. This phenomenon increases the reticulation between chains of $-(Si-O)_x-$ and explains the shift of spectral behaviour toward the one of amorphous silica (figure 6).
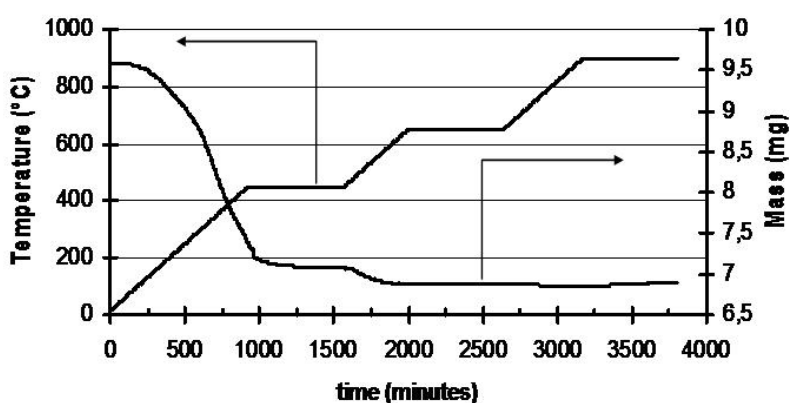

Figure 7: Thermo gravimetric analysis:
Temperature vs. time (left axis) and mass variation vs. time (right axis)

Some samples were treated at 900°C with the same temperature ramp (5°C/min). Temperature was kept 30 minutes, and then samples were retired and exposed to the air at room temperature. This thermal shock was repeated up to 4 times (Guillou, 2004). Raman microscopy revealed cracks of the films. Analyses in the cracks and on the surface did not show a different spectrum. Crack sizes and numbers did not change for more than one

thermal shock. Under this stressful treatment, the film remains on the surface of the substrate and fully masked it.

4. Conclusion

Polysiloxane thick films were deposited on a stainless steel substrate. Under the conditions used, the film is composed of tangled linear polymers. The methyl groups exhibit a high hydrophobic character. A thermal treatment removes these –CH$_3$ fromf the surface but deeper layers remain unaffected at low temperature due to the slow kinetic of gas permeation in the film. At low temperature the obtained materials present a multilayered structure: on the metallic substrate is grafted an organo-silicon layer. The latter is covered with a mineral form of silica-like structure, more likely under a linear form.

At higher temperature the whole PACVD deposit is mineralized. The structure is composed of a single inorganic layer on the metallic substrate. At very high temperature (above 800°C) reticulation occurs and a cross-linking phenomenon appears. Moreover, even if high mechanical stress is applied by thermal shock and high velocity tangential gas flow, the film still covers the substrate which remains fully hidden.

For a use as a catalyst support, these films require to be treated in such a way that they are fully mineralized (thermal treatment at 600°C). The stainless steel is covered and will not take part in the applied chemical reaction (for example in undesired secondary reactions). Hydrophobic character is removed and the film can be directly impregnated with catalysts, precursors or catalysts may be grafted on the silicon oxide rich surface by another technique such as sol-gel coatings for example (Barrera *et al*., 1996).

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