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AGEING IMPROVEMENT OF SILICON-BASED RESINS SUBJECT TO PROTON IRRADIATION IN SPATIAL GEOSTATIONARY ENVIRONMENT

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ABSTRACT

Study of interactions between charged particles and materials is of prime importance in the aerospace industry. Indeed, these energetic particles can induce damages to any spacecraft whether it be on the external parts of it or on its on board electronics. Silicon resins are materials that play an important role on those devices due to their unique properties. When exposed to proton irradiation, such resins tend to crack and turn yellow. This is detrimental to the proper ageing of the resins, which lose their original properties with time. One of the considered solution for stabilizing such a material is the introduction of charges in the matrix. This paper focuses on the synthesis of a class-I hybrid material where the proton facing side of a polydimethylsiloxane (PDMS) resin is filled with silica nanoparticles in order to limit its premature degradation. Resins bearing silica particles ranging from 230 nm to 2 μ m diameter with total nanoparticles thickness ranging from 1 to 28 μ m were synthesized. The obtained materials were irradiated with 240 keV protons to simulate their ageing and were characterized by UV-Vis-NIR spectroscopy as well as optical and scanning electron microscopy.

INTRODUCTION

Space environment around the Earth is of immense complexity and directly affects the lifetime and performance of satellites. Among all the constraints of geostationary orbit features its radiative environment: highly energetic particles, whether they be charged or not, tend to damage the external materials and electronic components of orbiting spacecrafts and satellites^{1,2}. Silicon resins play an important role on these devices because of their special properties. Their backbone is made of alternating Si-O bonds connecting with a large angle ranging from 140° to 180° and presenting a very low energy of rotation along the chain. This provides PDMS with very low T_g (around -120 °C) and low viscosity. Besides, the energy of the Si-O bond is around 452 kJ mol⁻¹, much higher than its carbon-based

equivalent, allowing silicon resins to be chemically inert, have a high temperature of degradation and be relatively stable upon UV radiations. These properties are the reason why PDMS resins are commonly found in many industrial applications^{3,4}.

When such a resin is exposed to proton irradiation, degradations occur: for increasing fluences, progressive cracking of the resin is observed as well as its yellowing^{5,6,7,8}. Mass loss is also observed due to the outgassing of volatile molecules such as H₂, CH₄, and the very unstable CH₃SiOCH₃. Decrease of the amount of Si-C bonds was proven by infrared spectroscopy concomitantly with an increase of the Si-O-Si bonds due to the loss of organic parts such as methyl groups. These observations lead to the conclusion that the surface of the resin changed for a structure close to inorganic silica (SiO_x).

In this work are presented the elaboration of a class-I hybrid material consisting of a PDMS resin bearing silica nanoparticles at its surface and their effect on the reduction of cracking.

2 EXPERIMENTAL PART

2.1 Materials

PDMS was provided by MAP as a bi-component material: base and curing agent. The base contains predominantly vinyl-terminated PDMS and Pt catalyst (Karstedt). The curing agent is a mixture of vinyl-terminated PDMS, hydride-terminated PDMS. The cross-linked reference PDMS sample was prepared by mixing the base with the curing agent in a 10:1 ratio by weight.

Absolute alcohol (VWR), tetraethyl orthosilicate (TEOS) and L-arginine (Fluka) as well as ammonium hydroxide (28 % NH₃, Alfa Aesar) were used as received without further purification.

SiO₂ nanoparticles were synthesized using the modified Stöber process which consists in the synthesis of germs – SiO₂ nanoparticles of small diameter (around 20 nm) – followed by their growth in a Stöber medium (alkaline hydroalcoholic solution) until obtaining the desired

diameter^{9,10}. Nanoparticles obtained through this method are monodisperse as well as being spherical.

On the one hand, a calculated volume of nanoparticles in their Stöber medium was transferred to a Petri dish of known diameter before evaporation of the remaining solvent in a vacuum oven at 90 °C for 6 h. Through calculation (Equation 1), one is able to predict the thickness of the nanoparticles layers remaining in the Petri dish.

On the other hand, the PDMS base provided by MAP was mixed with the curing agent in a 10:1 ratio by weight and was homogenized by using mechanical stirrer. This operation leads to the inclusion of air bubbles in the mixture, which were removed under vacuum for two hours.

A calculated volume of the mixture was then poured over the nanoparticles in the Petri dish allowing the PDMS to diffuse through the interstitial spaces in-between the nanoparticles. Once the PDMS has reached the bottom of the Petri dish, that is to say when its content has become transparent, the latter was placed in an oven at 80 °C for 15 h to obtain final material. The thickness of prepared samples was approximately 100 to 1000 µm depending on the experiment carried out.

2.2 Initial characterizations

Differential scanning calorimetry (DSC) measurements of silicon samples (10-15 mg) were performed using a DSC Q100 TA instruments over temperature range from -150 °C to 150 °C, in a heating cooling mode of 10 °C.min⁻¹ in order to determine the best cross-linking temperature. Analyses were carried out under helium atmosphere with aluminium pans.

Silica nanoparticles were first characterized by dynamic light scattering (DLS) at 90° on a Zetasizer Nano ZS90 and the measurement of their diameter was later confirmed by scanning electron microscopy (SEM).

UV-Vis-NIR spectroscopy analyses of materials before irradiation were conducted on a Perkin Elmer lambda 1050 in transmission mode in a spectral range from 250 to 2500 nm. The spectra were obtained with a scanning speed of 400 nm per minute and a resolution of 1 nm acquisition.

2.3 Ageing and post-characterizations

Proton irradiation was conducted in the SEMIRAMIS vacuum chamber coupled with a 2.5 MeV Van de Graff proton accelerator. The vacuum chamber allowed the pressure to be kept under 10⁻⁵ mbar. The incoming protons had an energy of 240 keV. The samples were irradiated with a flux of 1.25 10¹¹ p⁺ cm⁻² s⁻¹ (20 nA cm⁻²). The total fluence was 3 10¹⁵ p⁺ cm⁻² for a total surface dose of 2 10⁸ Gy. The temperature of the sample holder was maintained at 40 °C for the duration of the test.

UV-Vis-NIR spectroscopy was used again to characterize the materials.

Optical microscopy was realized with a Karl Zeiss microscope mounted with a 10 megapixels Canon PowerShot A640 camera.

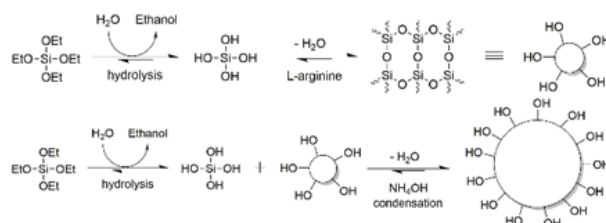
Scanning Electron Microscopy experiments were conducted on a Zeiss GeminiSEM300 in high vacuum mode after metallization of the samples with platinum.

3 RESULTS AND DISCUSSION

3.1 Samples preparation

Silica nanoparticles with controlled shapes and sizes were synthesized following the modified Stöber method^{9,10} (Scheme 1). In this process, silica precursor tetraethyl orthosilicate (TEOS) is hydrolysed in alcohol in the presence of ammonia as a catalyst. The reaction produces ethanol and a mixture of ethoxysilanol, which can then condense with either TEOS or other silanol with the loss of alcohol or water. Various sizes were prepared ranging from 20 to 230 nm. Sizes were checked by DLS at 90° (Figure 1). As can be seen, monodisperse nanoparticles with narrow size distribution were obtained.

Larger micron-sized particles were synthesized following the work of Nakabayashi *et al*¹¹ and were characterized only by SEM as they were too big for DLS experiment to be conducted properly.



Sch. 1. Synthesis of silica nanoparticles via modified Stöber process

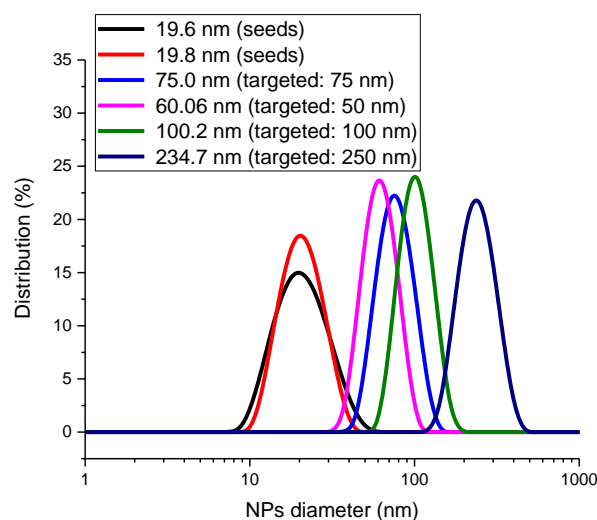


Fig. 1. characterization of silica nanoparticles sizes by DLS

In order to create a layer of nanoparticles with controlled thickness h , a volume V of colloidal solution of mass concentration C_{SiO_2} was collected then transferred into a Petri dish of known radius r . This volume was calculated using Equation 1 below:

$$V = \frac{\rho_{SiO_2} \times 0.74 \times \pi r^2 h}{C_{SiO_2}}$$

Eq. 1. Volume to be collected to obtain multiple layers of total thickness h in a recipient of radius r

Due to their size and self-assembly into a photonic crystal, 230 nm nanoparticles presented a green colour in reflection and a pink colour in transmission¹³ (Figure 2a and 2b) whereas 1 μm and 2 μm particles looked whitish. The PDMS samples were prepared by mixing the base with the curing agent in a 10:1 ratio by weight with the help of a mechanical stirrer. Traces of solvents as well as air bubbles were removed *in vacuo* then the not yet cross-linked PDMS was poured in the Petri dish containing the nanoparticles. Due to the very close refractive indexes of both silica nanoparticles and PDMS – respectively 1.45 and 1.42 – the content of the Petri dish became transparent (Figure 2c).

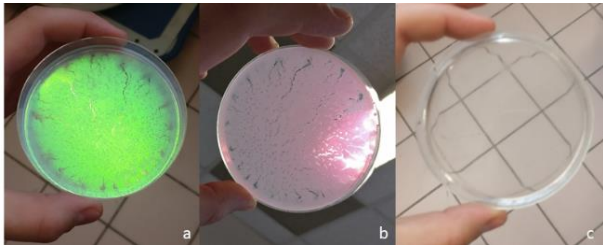


Fig.2. a) and b) 230 nm silica nanoparticles in a Petri dish c) same nanoparticles covered with PDMS

The curing process took place in an oven at 80 °C for 15 hours.

3.2 Optical characterization

The samples were peeled out of the Petri dish and characterized by UV-vis-NIR experiments proton irradiation was conducted on the silica-containing side of the material. The optical characterizations of the materials are reported in Figure 3. Samples are named as follows:

SizeOfParticles(nm)_ThicknessOfSilicaLayer(μm).

One can see that for large particles, the UV-cut appears at higher wavelengths and is detrimental to transparency. This is most obvious for materials containing 2 μm particles where the UV-cut appears at around 1700 nm. These materials were later abandoned. On the contrary, materials with smaller particles were almost as

transparent as the blank materials containing no nanoparticle, comforting the idea that those materials are of interest for the targeted application as long as the silica layer is not too thick. Indeed, it is clear as well that the thinner the silica layer is, the better the transparency reached is.

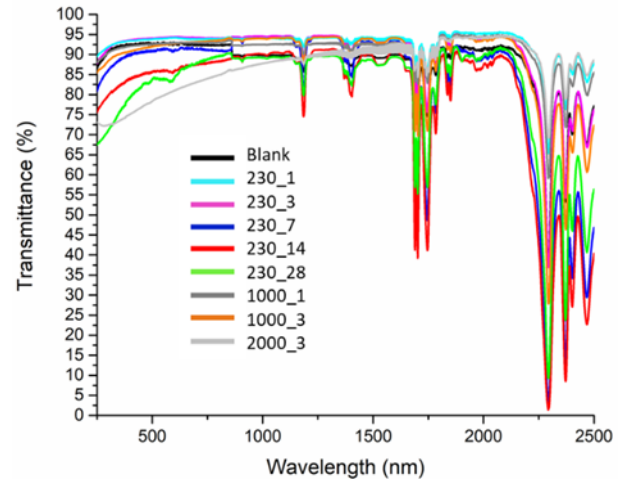


Fig.3. UV-vis-NIR spectra of tested materials before proton irradiation.

Once the materials were optically characterized, they were irradiated in the SEMIRAMIS vacuum chamber described previously.

After the irradiation was completed, samples were optically characterized again following the same process as before irradiation. The results are gathered in Figure 4.

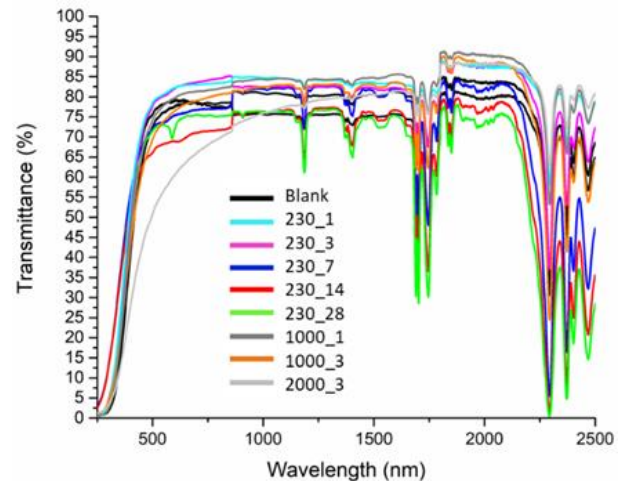


Fig.4. UV-vis-NIR spectra of tested materials after proton irradiation.

All the irradiated materials present a strong loss in transmittance in the [250; 500] nm range due to the formation of UV-absorbing moieties.

The following trends can be observed:

- UV-cut of materials bearing micrometer-sized particles appears at higher wavelength, typically at a wavelength of the same order as their size.
- The thicker the particles layer the lower the transmittance of the materials regardless of the considered wavelength, though this is more obvious in the range [1500; 2500] nm.

Materials presenting a thin layer of small nanoparticles at their surface were the ones for which the absorbance was the lowest and thus were the most transparent.

3.3 Microscopy characterization

One of the goals of the present work being the reduction of cracking in the PDMS coating, all samples were first characterized by optical microscopy in order to qualitatively estimate that reduction. As can be seen on Figure 5, even though every materials have cracked, systems containing nanoparticles have cracked less than the witness systems containing no particles at all: this is certainly due to the minimized amount of organic moieties in the first micrometres of the materials where protons deposit their energy.

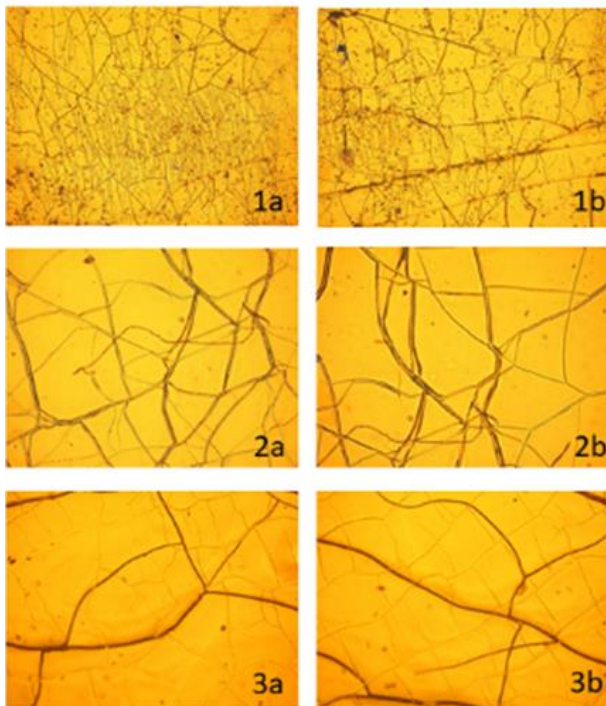


Fig. 5. Optical microscopy (zoom $\times 50$) of irradiated materials. **1a-b:** witness without particles. **2a-b:** 3 μm thick 230 nm nanoparticles layer. **3a-b:** 28 μm thick 230 nm nanoparticles layer.

In order to get a better comprehension of the hybrid materials synthesized, scanning electron microscopy (SEM) experiments were conducted on several samples

before and after proton irradiation. Figure 6a allowed removing doubt about the compactness of the silica nanoparticles layer: it was first supposed that the nanoparticles organized in a compact manner – thus the 0.74 factor in Equation 1 – and this was later confirmed by SEM analysis. Besides, these analyses allowed better characterization of the nanoparticles, layers and cracks dimensions. One can see on Figure 6b the intersection of two cracks in the material after irradiation, showing the good coating of nanoparticles by the PDMS resin suggesting good wetting properties. Figure 6c shows measurements of the silica nanoparticles layer in accordance with theoretical values calculated with Equation 1.

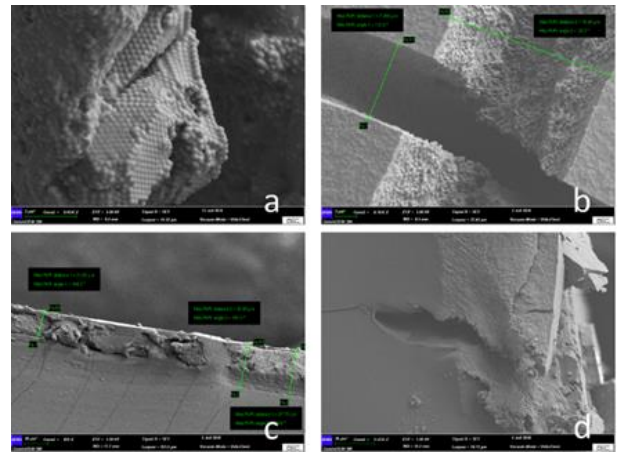


Fig. 6. SEM images of hybrid SiO_2 -NPs-PDMS materials. **a:** side view of a teared PDMS. **b:** intersection of two cracks on an irradiated material. **c:** side view before irradiation of a 28 μm thick silica layer. **d:** zoom on a crack propagating in the PDMS underneath the silica layer.

It is obvious on Figure 6d that simple trapping of the nanoparticles in the PDMS matrix is not enough on its own to disable cracking completely as one can see a crack propagating below the silica layer. Nevertheless, it raises hope that a more cohesive material made of silica nanoparticles covalently bound to the PDMS matrix would be even more resistant to proton irradiation.

CONCLUSION

Polydimethylsiloxane-silica nanoparticles hybrids were synthesized in three steps: 1) silica nanoparticles synthesis using the modified Stöber process followed by 2) blending of the two components PDMS resin then 3) pouring of the pre-resin over the silica colloidal crystal. The obtained materials were characterized by optical spectroscopy as well as optical and electron microscopy. It was shown that the incorporation of nanoparticles in

the PDMS matrix was not detrimental to the transparency of the material as long as the size of the particles and the thickness of their layer were small enough. Control of the nanoparticles size as well as the thickness of the silica layer was reached. Even though fewer cracks were observed in materials containing nanoparticles, the latter is still being damaged by proton irradiation, certainly due to the non-covalent binding between particles and PDMS matrix. Further work will include covalently bound particles to the matrix allowing stronger interactions between them, which should lead to a more cohesive material.

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