POSS® COATINGS AS REPLACEMENTS FOR SOLAR CELL COVER GLASSES

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I. Introduction

Presently, solar cells are covered with Ce-doped microsheet cover glasses that are attached with Dow Corning DC 93-500 silicone adhesive. Various antireflection coatings are often applied to the cover glass to increase cell performance. This general approach has been used from the beginning of space exploration. However, it is expensive and time consuming. Furthermore, as the voltage of solar arrays increases, significant arcing has occurred in solar arrays, leading to loss of satellite power. The cause has been traced to differential voltages between strings and the close spacing between them with no insulation covering the edges of the solar cells. In addition, this problem could be ameliorated if the cover glass extended over the edges of the cell, but this would impact packing density. An alternative idea that might solve all these issues and be less expensive and more protective is to develop a coating that could be applied over the entire array. Such a coating must be resistant to atomic oxygen for low earth orbits below about 700 km, it must be resistant to ultraviolet radiation for all earth and near-sun orbits and, of course, it must withstand the damaging effects of space radiation. Coating flexibility would be an additional advantage.

Based on past experience, one material that has many of the desired attributes of a universal protective coating is the Dow Corning DC 93-500. Of all the potential optical plastics, it appears to be the most suitable for use in space. As noted above, DC 93-500 has been extensively used to attach cover glasses to crystalline solar cells and has worked exceptionally well over the years. It is flexible and generally resistant to electrons, protons and ultraviolet (UV and VUV) radiation; although a VUV-rejection coating or VUV-absorbing ceria-doped cover glass may be required for long mission durations. It can also be applied in a thin coating (< 25 μm) by conventional liquid coating processes. Unfortunately, when exposed to atomic oxygen (AO) DC 93-500 develops a frosty surface. Such frosting can lead to a loss of light transmitted into the cells and destroy the essential clarity needed for a concentrator lens.

Thus, the investigation has turned to a new class of materials. These materials must be glass-like in their final state, resist AO, UV/VUV and be resistant to electron and proton radiation. Flexibility would be a benefit, but is not essential. The initial investigation of these new materials has been directed toward determining their resistance to proton irradiation. Many space missions are only possible by flying through the heart of the Van Allen radiation belts. One mission in particular is a solar electric propulsion mission that moves a satellite from low earth orbit (LEO) to another location. The location may be geosynchronous earth orbit (GEO) as for a communications satellite, a lunar orbit like ESA's Smart 1. While these missions take more time than using a chemical kick motor, the costs are substantially lower. Another class of missions that is of interest is those that would benefit from observing the earth and that fly either elliptical orbits that pass through the belts or that stay within the belts. This initial focus is on the resistance to 2 MeV protons because they are absorbed in glass-like materials in about 75 μm. Protons are exceptionally damaging because most of the damage occurs at the end of their path, thus causing maximum damage in a very narrow region of the material. If the new materials can withstand this punishment, the next step will be to assess their resistance to VUV/UV illumination.

The New Option

A new class of materials has recently been discovered during the search for improvements in optical plastics. These new polymeric building block materials are called "polyhedral oligomeric silsequioxanes". They were developed by the Air Force Research Laboratories at Edwards Air Force Base in 1998. The technology is exclusively manufactured by Hybrid Plastics Inc. (Hattiesburg, MS) under the acronym POSS® nanocomposites. This technology has several significant advantages that are relevant to solar cell use. The glass-like composition of POSS

provides excellent resistance to UV and much reduces or eliminates degradation by atomic oxygen. POSS nanobuilding blocks can be incorporated into all known plastics using conventional polymerization or compounding techniques to afford customized, optically transparent materials with and entirely new performance levels.

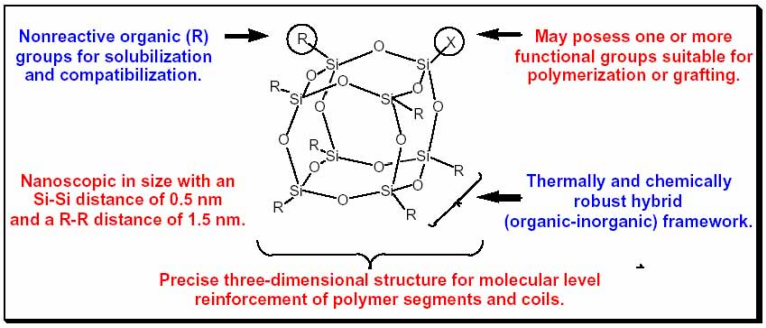

Figure 1: Anatomy of a POSS® nanostructured® chemical

POSS® building blocks contain hybrid (organic-inorganic) compositions in which the internal frameworks are comprised primarily of inorganic silicon-oxygen bonds. As shown in figure 1, the exterior of the nanostructure is covered by both reactive and non-reactive organic functionalities (–R) which ensure both compatibility and the ability to tailor the nanostructure with organic polymers. The resulting nanoscopic chemicals have low density, range in diameter from 0.5 to 3 nm and can be tailored through variation in the –R groups and the size of the nanocage reported by Gilman[1] and more extensively by Gonzalez[2], the molecularly dispersed POSS readily forms a passivating silica layer when attacked by atomic oxygen. This layer in turn protects the virgin material from degradation. Furthermore, the silica-like composition of POSS provides enhanced UV and VUV resistance. The UV and VUV resistance provided by POSS can even be enhanced further through replacement of metals like Ce for the silicon atoms at the vertices in the nanocage.

II. Experimental Description

Sample Formulation

In this study, several different compositions of POSS based adhesives were used. Those POSS based adhesives are manufactured by Hybrid Plastics, Inc. under the product name of FireQuench PM1287 and MA8000. Variants of PM1287 and MA8000 were produced for this research. FireQuench PM1287 has a cyclic silicon-oxygen structure. It can be cured through a hydrosilation method. The MA8000 is a methacrylic adhesive reinforced by functional POSS

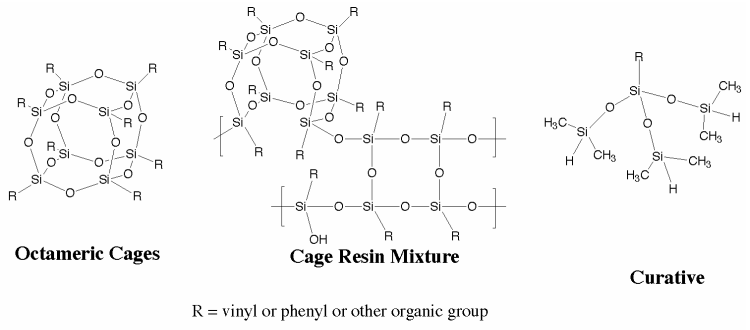

Figure 2a: PM1287 structure

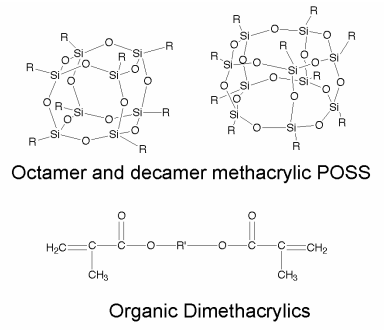

Figure 2b: MA8000 structure

molecules. Figure 2 shows a drawing of the cyclic silicon-oxygen structure in FireQuench PM1287. The –R groups can be either vinyl groups or phenyl groups. In addition, PM1287 and MA8000 are found to be compatible with POMS (Polyhedral Oligomeric Metal Silsesquioxane). The metal is added directly into the POSS cage and is very stable. The addition of POMS can further improve the overall performance of those POSS based adhesives.

The samples were coated onto standard 3.5 cm by 2.5 cm Thales CMG200 Ce-doped microsheet glass slides. PM1287 samples were thermally cured using platinum catalyst. MA8000 samples were cured under UV light. The POSS layer was deposited by brush. Optical transmission of the samples was measured between 200 and 1200 nm with a Shimazu UV3600 UV-VIS-NIR Spectrophotometer using an uncoated Ce-doped slide as the background reference. Because an uncoated slide was used as the reference, the data do not take into account transmittance differences due to reflection at the interfaces. After initial characterization samples were sent for irradiation.

Proton Irradiation Facility

Auburn University has a NEC Pellatron 2 MV Dual Source Tandem Accelerator shown in figure 3. This accelerator can provide a beam of protons from a SNICS ion source with energies from 100 keV to 4 MeV. It can also provide a beam of alpha particles ranging in energy from 100 keV to 6 MeV. In addition, a range of heavier atoms including nitrogen, aluminum, and phosphorus can be provided for ion implantation. The ion implantation energies range up to 12 MeV. The facility is also used for Rutherford Backscattering Spectroscopy and ion beam channeling.

Figure 3: NEC Pellatron 2 MV Dual Source Tandem Accelerator

For this work, all irradiations were done in vacuum, $5x10^{-7}$ to $1x10^{-6}$ torr at room temperature. The dose rate was kept constant for each irradiation, with the exception the last dose, the rate was tripled. The initial irradiation was a dose of 10^{12} protons/cm^2. After each irradiation the samples were visually inspected for damage and another transmission spectrum was acquired. The following irradiation total dose schedule was used, second irradiation 10^{13} protons/cm^2, third irradiation 10^{14} protons/cm^2 and finally a fourth irradiation 10^{15} protons/cm^2 (p^+/cm^2). Beam currents ranged from 55 nA at the lower doses to 190 nA at the highest dose. The proton beam was scanned over a 5 cm diameter area with the samples at room temperature. Scan rate was 517 Hz in the x-direction and 64 Hz in the y-direction. Two samples were irradiated at a time.

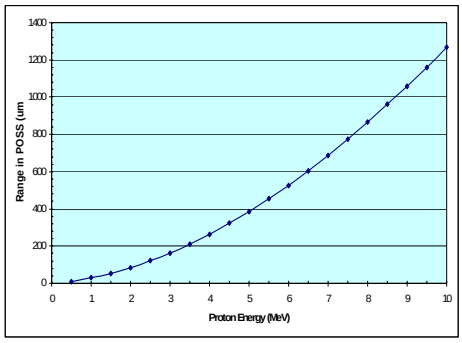

Figure 4: Proton range-energy curve in POSS with 1.2 g/cm^3 density

The range-energy calculation[5] for the POSS materials is shown in figure 4. This was obtained using the density of the POSS. At 2 MeV, the range of the protons in POSS is 85 µm with a straggle of ~2 µm. Thus the entire proton beam is absorbed within the 300 µm thick POSS layer, creating maximum damage within the layer.

III. Experimental Results

PM1287 Samples

The PM1287 resin was tailored to have different phenyl contents. The phenyl percentage used in this paper indicates the mole percentage of the phenyl groups compared to the vinyl groups that are attached to the POSS cage (Fig. 2). A total of 4 samples were made: 10% phenyl, 15% phenyl, 20% phenyl and 50% phenyl. The 50% phenyl PM1287 demonstrated the best proton radiation tolerance as shown in figure 5. The presented data are limited to the region of interest between 300 and 600 nm. Below 300 nm the CMG200 slide has limited transparency and above 600 nm the film transmittance does not vary with wavelength. For the 50% phenyl sample, the transmittance did not decrease until the 10^{14} p^+/cm^2 dose and substantial darkening and cracking did not occur until the 10^{15} p^+/cm^2 dose as shown in figure 6.

For the 10^{12} p^+/cm^2 dose, the high concentration of phenyl (50%) provided the best radiation tolerance and the lowest concentration (10%) the least tolerance as seen in figure 7. Because the intermediate samples 15% and 20% do not follow this trend there may be additional factors (i.e. catalyst loading) that affect the radiation tolerance.

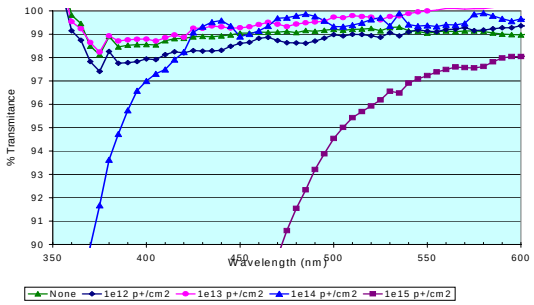

Figure 5: Spectral transmission curves of PM1287 with 50% phenyl

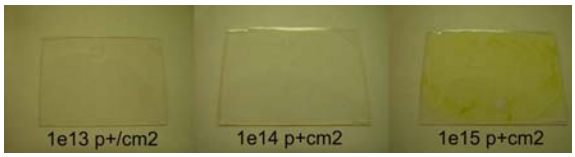

Figure 6: Images of PM1287 with 50% phenyl

In addition to darkening, the sample films showed evidence of structural stress at large total dosages. The damage typically started as micro-fractures on the surface which then developed into long cracks, followed by delamination and separation from the cover glass substrate. The 10% and 15% phenyl films cracked during the 10^{13} p^+/cm^2 irradiation,

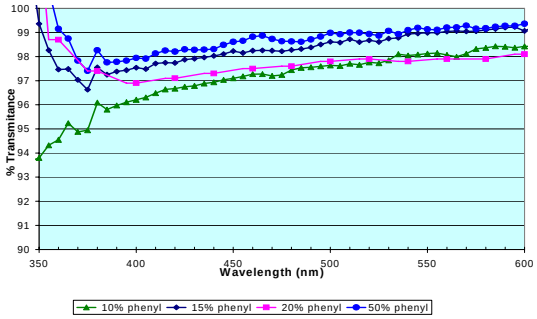

Figure 7: Spectral transmission curves of PM1287 with 10 to 50% phenyl additions at 10^{12} p^+/cm^2

the 20% cracked 72 hrs after the 10^{13} p^+/cm^2 test, and the 50% phenyl film developed one long crack after 10^{15} p^+/cm^2. The mechanism for this internal stress is currently under investigation.

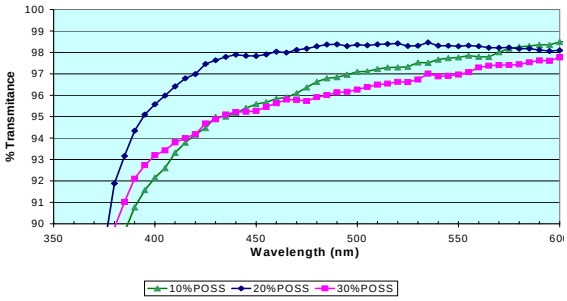

Figure 8: Spectral transmission curves of MA8000 with various POSS additions

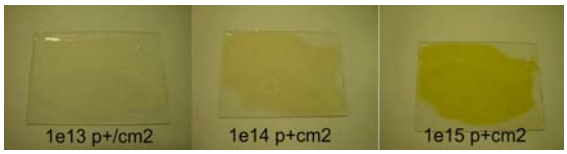

Figure 9: MA8000.2 with 20% POSS images

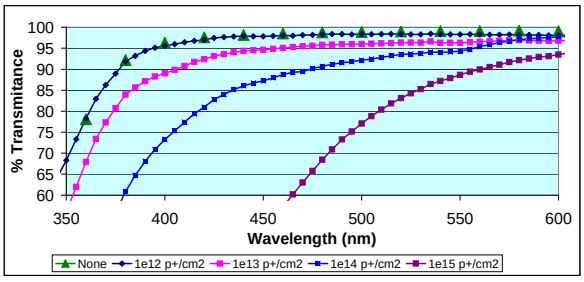

Figure 10: Spectral transmission curves of MA8000.2 with proton fluence

MA8000 Samples

The same procedures noted above were followed for the MA8000 samples. For MA8000 samples, the amount of functional POSS molecules dissolved in the polymer was directly related to the films' radiation tolerance. Three samples, 10 wt%, 20 wt%, and 30 wt% POSS-reinforced MA8000 (MA8000.1, MA8000.2 and MA8000.3, respectively) were made. These samples had greater opacity below 500 nm than did the PM1287 samples. The sample with the 20% POSS concentration showed the least radiation induced darkening in the visible spectrum as shown in figure 8. Layers based on MA8000 also showed indications of stress within the film after irradiation.

At 10^{14} p^+/cm^2, both the 10% and 30% POSS samples cracked; the 20% POSS sample did not crack until the 10^{15} p^+/cm^2 irradiation. Photographs of the MA8000 with 20% POSS are shown in figure 9 and the spectral transmission curves are shown in figure 10 (note the scale change). The darkening of the sample seems very great at the 10^{15} p^+/cm^2 dose level. Because spectral transmission curves by themselves do not give any indication of the performance of a solar cell beneath that layer, another study was performed to attempt to quantify this loss.

IV. Relationship to solar cell performance

In order to predict the effect of the observed cover material darkening on the performance of a solar cell assembly, the transmittance of each sample was multiplied by the quantum efficiency of a triple junction solar cell[6] (Emcore ATJ) to determine the short circuit current, I_{SC}. The ATJ quantum efficiency is shown in Figure 11. The I_{SC} calculated for this Emcore ATJ cell is 17.1 mA/cm^2. This value agrees well with data provided on their web site. As expected, the InGaP junction controls the short circuit current. Because the transmittance measurements were made using an uncoated cover glass reference, the data do not incorporate effects due to reflective losses at the interfaces. A final solar cell design tailored for the POSS encapsulant would include optimization of the antireflective coating between the cell and the cover material.

As can be seen in figure 12, the PM1287 with 50% phenyl showed no decrease in I_{SC} for dosages up to 10^{14} p^+/cm^2. Even at lower phenyl substitutions, the I_{SC} decrease was less than 5% for the sample containing 10% phenyl with a dose of 10^{13} p^+/cm^2.

Although the darkening of the MA8000 was more substantial, the decrease in I_{SC} for the 30% POSS sample at a 10^{14} p^+/cm^2 dose is only 2% (Fig. 13). This dose is roughly equivalent to the radiation dose received over a 2000 year mission in GEO. Thus the stability of this POSS coating is quite acceptable for that type of mission. However, it is important to note that no cell degradation has been taken into account.

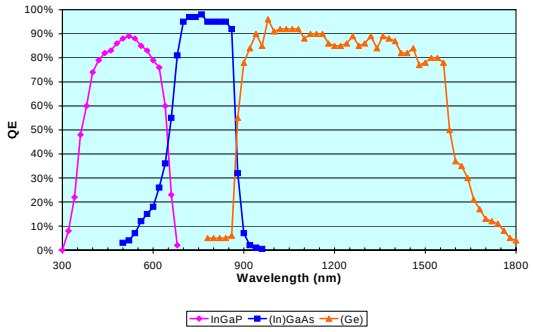

Figure 11: External quantum efficiency, ATJ cell

V. Discussion

The results presented above show that the material compositions studied here show a regular progression in resistance to damage by 2 MeV protons as the phenyl content increases in the PM1287 resin and as the POSS additions increase in the MA8000. It is important to note, that with the calculated Isc of an ATJ cell with these coatings, the PM1287 with 50% phenyl substitutions decreased only about 13% at 10^{15} p^+/cm^2. This is exceptional durability. Furthermore, the MA8000 with 20% POSS showed a 17% drop under the same dose. The mechanisms behind the role of the POSS additives are under study and may lead to even greater resistance. However, we can speculate that the chemical stability of the phenyl group may play a key role in limiting proton damage in these tests. POMS additions may also further increase the durability of these coatings. The inclusion of metallic elements can lead to additional stopping power as has been shown for Gd-POMS and neutrons[7].

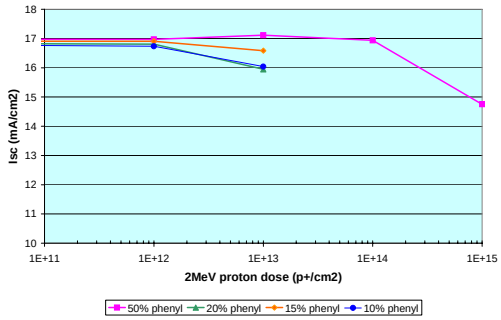

Figure 12: Calculated Isc variation with 2 MeV proton dose for PM1287-coated samples

While these results are very encouraging, many other space durability tests must proceed before any final conclusions can be drawn. First among these is UV/VUV testing which will be underway shortly. The cracking seen in the coatings will also be explored but may well be due to the proton dose rate or other conditions of the irradiation. Because of the inherent adaptability of the material compositions of the POSS, we expect to find solutions to the cracking and ultimately the darkening of these unique materials. While these coatings must be applied to current production cells to confirm that no inherent damage occurs to them, preliminary work with thin film solar cells uncovered no problems[8].

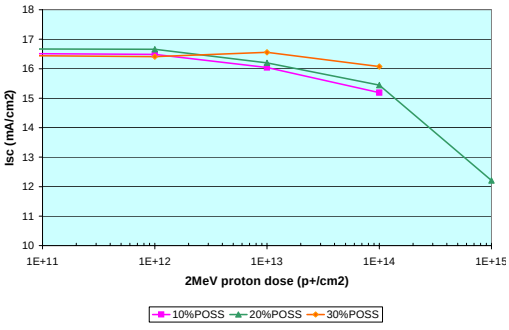

Figure 13: Calculated Isc variation with 2 MeV proton dose for MA8000-coated samples

UV/VUV Preliminary Results

Initial testing was done with four different samples – PM1287 with 50% phenyl addition, MA8000.2, PM1287 with Gd POMS and PM1287 with Tb POMS. The metallic additives were selected to determine if they enhanced stability of the films under this test. The samples were tested for 1024 hrs in the UV/VUV testing facility at the NASA Glenn Research Center. The exposures were made in a vacuum chamber using a deuterium lamp (Hamamatsu L7293) that provides radiation as low as 115 nm. The lamp is outside the chamber to prolong life and the radiation is transmitted into the sample through a magnesium fluoride window.

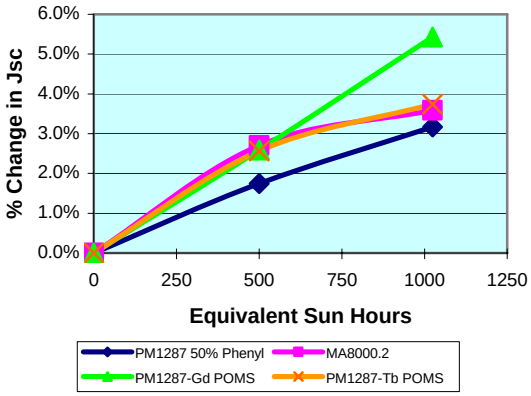

Figure 14: UV/VUV preliminary test results

As it turned out, the samples prepared with the Tb POMS and Gd POMS were quickly prepared using materials at the end of their shelf life. Thus the samples were darkened at the start. In addition the MA8000.2 sample had a green tint that also suggested the materials had gone beyond their shelf life. The transmission spectra were converted into calculated Jsc loss for an ATJ cell. These results are shown in figure 14. It appears that the MA8000.2 and the PM1287 with the Tb POMS showed saturation of the damage. However, because the sample formulation was suspect, we believe these results should be repeated.

VI. Summary and Conclusions

These tests represent preliminary screening of the concept of an easy-to-apply, space durable, conformal encapsulant for solar arrays. The results have shown that some of these coatings are exceptionally resistant to damage by 2 MeV protons, which are completely absorbed within the layers. More materials combinations and modifications will be tested over a range of conditions, not just proton exposure. Furthermore, direct application of these coatings onto production solar cells is an essential next step. If this extensive environmental and radiation testing proves successful, a new approach to totally encapsulating solar arrays will have been demonstrated. With that success, solar array costs should drop and development of high voltage arrays for high power space missions can proceed with confidence. However, despite positive results from diligent ground testing, the ultimate verification will only come through successful demonstration in space.

VII. Acknowledgements

Support by the DOD under Contract #FA9453-05-M-0096 from the Air Force Research Laboratory, Space Vehicles Directorate is greatly appreciated.

VIII. References

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