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Shawn Phillips et al., "Hybrid Inorganic/Organic Reactive Polymers for Severe Environment Protection"

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HYBRID INORGANIC/ORGANIC REACTIVE POLYMERS FOR SEVERE ENVIRONMENT PROTECTION

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ABSTRACT

Leading-edge, fundamental research in polymer technology is often directed towards those applications requiring dramatic improvements in temperature or oxidation resistance. While non-reactive polymers systems are often desired, many benefits can be realized by utilizing inorganic, 'reactive' molecules within the polymer matrix. In such systems, a sacrificial layer of the hybrid polymer is destroyed until passivation occurs. Over the last decade the Air Force Research Laboratory has studied how the incorporation of Polyhedral Oligomeric Silsesquioxanes (POSS), which are nanostructured chemicals, can be used for protective coatings in oxygen rich environments. This talk will detail the strategy employed for using sacrificial nanocomposites along with applied research in the areas of solid rocket motor insulation and space-survivable materials.

KEY WORDS: atomic oxygen, POSS, silsesquioxane, insulation, space

1. INTRODUCTION

Two of the most common goals for synthesizing high performance polymers are increased use temperature and improved oxidation protection. Over the years, researchers have been successful in synthesizing many new polymers which have resulted in significant improvements in these key areas. Although there have been many creative solutions for overcoming polymer limitations (e.g., thermal sinks, heat dissipation techniques), organic polymers are inherently limited by the strength and oxidation potential of the carbon-carbon bonds. Another approach that has come of age is the idea of incorporating inorganic additives not only for improving thermal stability, but also for *in-situ* formation of a passivating layer. With the recent incorporation of nanocomposites into polymer matrices, the passivation layer paradigm has been realized. Gilman and co-workers have been utilizing passivating techniques by taking advantage of clay nanocomposites to dramatically reduce the flammability of many organic polymers.[1] The concept involves burning away sacrificial layers of the hybrid organic/inorganic polymer, with the concomitant formation of an inorganic silica-like layer by the clay nanocomposites.

A similar approach of passivating layer formation has been successfully used for POSS-polymer applications in severe environments found in both space and rocket motors. Over the years, the hybrid polymer research program at the Air Force Research Laboratory at Edwards (AFRL/PRSM) has focused on the incorporation of Si-O containing frameworks into traditional polymers. This research has shown that addition of POSS monomers via copolymerization, grafting, or blending (1) results in numerous property enhancements, including increased modulus and temperature stability, oxidation resistance, and ceramic-layer formation.[2] These enhancements are obtained without adversely affecting the density or processibility of the polymer matrix, which will be discussed. Flammability studies, rocket motor insulation testing, and atomic oxygen results have shown that upon degradation, the hybrid organic/inorganic nanocomposites form a passivating Si-O layer.[3]

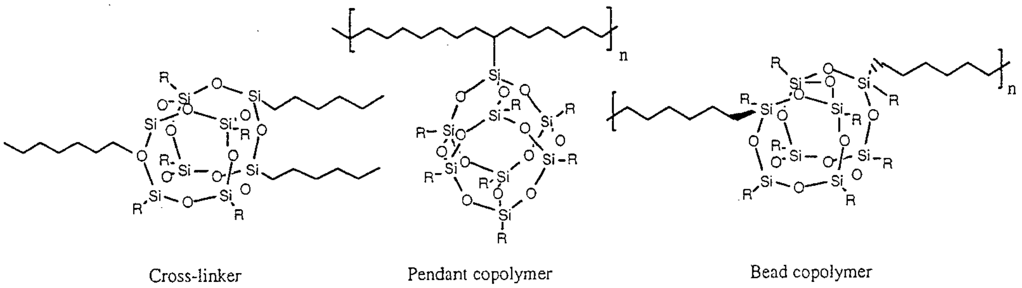
Cross-linker Pendant copolymer Bead copolymer

Figure 1: POSS-polymer Structures.

Ablation reduction tests were done using a proprietary solid rocket motor test stand, with the insulation samples placed in a conical section in front of the nozzle. POSS-polymer samples were tested side-by-side with SOTA insulation provided by Pratt & Whitney Space Propulsion. The effect of atomic oxygen (AO) on material degradation was studied using a novel electron stimulated desorption (ESD) atomic oxygen source combined with *in-situ* XPS analysis before and after incremental exposures.

2. EXPERIMENTAL

2.1 Materials

2.1.2. Preparation of POSS-EPDM Polymer In a typical sample, the proprietary POSS monomer (5-50%) was blended into the EPDM pre-polymer using a standard braebender, followed by extended curing in a standard oven. The flexible POSS-EPDM polymer was then cut and fitted into conical phenolic sections for testing.

2.1.2. Preparation of the POSS-dianiline and POSS-Polyimide copolymer The POSS-dianiline and POSS-polyimide synthesis and characterization have been reported elsewhere.[4] The synthetic procedure is shown below.

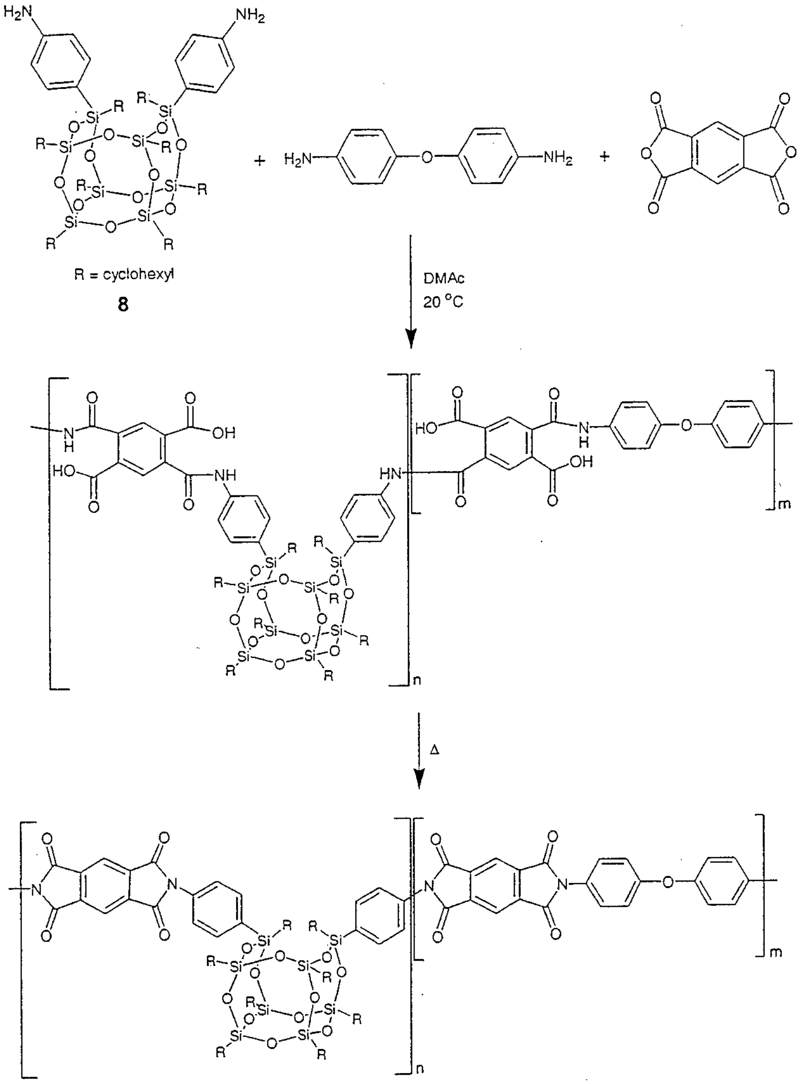

Figure 2: Synthetic scheme for synthesis of the POSS-Kapton® copolymer.

2.1.3. Preparation of Thin Films A film is cast from the resulting POSS-poly(amic acid) on a clean glass plate and placed in a clean oven under a nitrogen blanket at 80 degrees Celsius for 4 hours. The temperature of the oven is then slowly raised to 300 °C at which point the film is let cure for approximately 1 hour. The films were dried at room temperature for 24 hrs. The aluminum substrates were cleaned with Boraxo® soap and water, rinsed with deionized water, followed by ultrasonic cleaning in toluene, acetone, trichloroethylene, acetone and ethanol successively.

2.2 Atomic Oxygen Exposure and XPS Analysis of Polymers

2.2.1. O-Atom Source Characteristics The ESD source used in this study was developed by Hoflund and Weaver (17), and is commercially available through Atom Sources, Inc. It is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature, and produces a high-purity, hyperthermal (>1.0 eV), AO flux with an O atom: O^+ ratio of about 10^8. These sources are superior to plasma sources in that they produce primarily ground-state O atoms and operate at UHV pressures (~10^{-9} torr) while producing negligible amounts of other species, including ions, and UV and IR radiation. The operational concept of the hyperthermal oxygen atom generator is shown in Figure ~~4~~ 3.

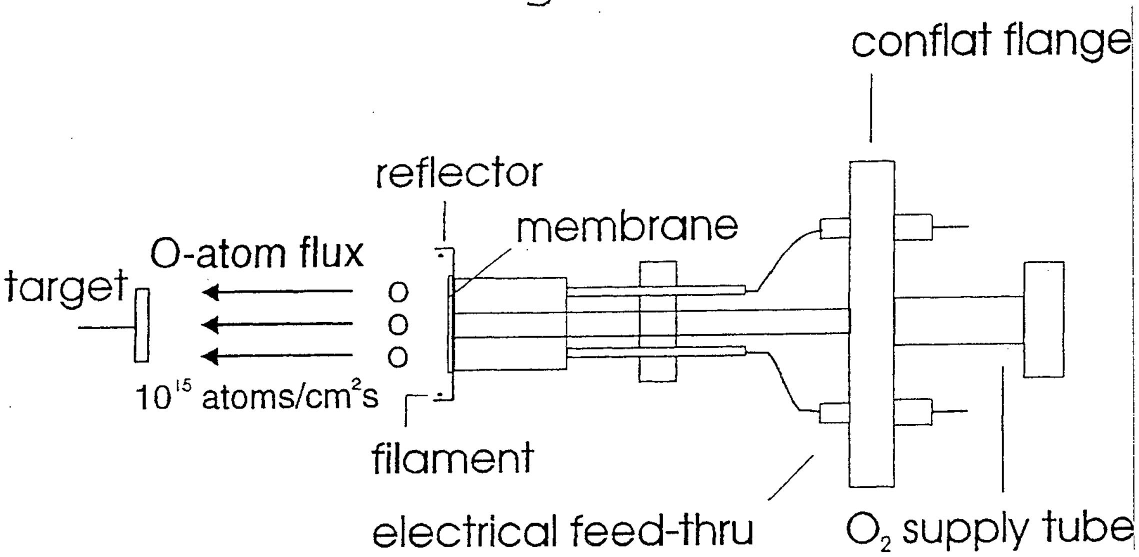

Figure 3 Schematic diagram of the atom source.

Ultrahigh purity molecular O_2 dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature (~400 °C) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of O atoms forming a continuous flux. The O atoms produced by this source have been shown to be hyperthermal, but their energy distribution has not been measured. Corallo et al. (18) have measured the energy distribution of O ions emitted by ESD from a Ag(110) surface and found that this distribution has a maximum at approximately 5.0 eV and a full-width at half maximum of 3.6 eV. This ion energy distribution would set an upper bound for the neutral energy distribution because ESD neutrals are generally believed to be less energetic than ESD ions. This point has been discussed often in the ESD literature but not actually demonstrated. A mass spectrometer has been used to characterize the flux produced by this ESD source. The ion acceleration potential was set at 0.0 V in these studies. Since calibration studies demonstrated that the ions entering the quadrupole section had to have a minimum kinetic energy of 2.0 eV to reach the detector, the ESD neutrals have a minimum energy of 2.0 eV. Therefore, the

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hyperthermal AO produced by this ESD source have energies greater than 2.0 eV but less than the maximum of the ion energy distribution.

2.3.2. Surface Characterization Solvent cast POSS-Kapton® films were wiped with isopropanol and inserted into the UHV chamber (base pressure $<10^{-10}$ torr). XPS was performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-270AR) and a Mg K□ X-ray source (PHI Model 04-151). XPS survey spectra were taken in the retarding mode with a pass energy of 50.0 eV. High-resolution XPS spectra were taken with a pass energy of 25.0 eV. Data collection was accomplished using a computer interfaced, digital pulse-counting circuit followed by smoothing with digital-filtering techniques. The sample was tilted 30 deg off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 ± 6 deg off the DPCMA axis.

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XPS spectra were first obtained from the as-entered, solvent-cleaned samples. The samples were then transferred via a magnetically coupled rotary/linear manipulator into the adjoining UHV chamber that houses the ESD AO source. There the surfaces were exposed to the hyperthermal AO flux and re-examined *in-situ* after total exposure times. The approximate normal distance between the sample faces and source in this study was 15 cm, at which distance the flux was about 2×10^{13} atoms/cm^2-s for the instrument settings used. Substrate temperatures were determined using a chrome-alumel thermocouple attached to the Al substrates. The samples remained at room temperature during the AO exposures. However the sample temperatures did increase to 50 °C during XPS data collection. After the final AO exposure, the samples were exposed to air (room temperature ~22 °C and relative humidity ~60%) and reexamined using XPS.

3. RESULTS AND DISCUSSION

The testing of POSS-EPDM samples for ablation performance was achieved using standard tactical and boost rocket motor propellants. Both the insulation standard and the POSS-EPDM sample were present in the same rocket motor firing, thus insuring consistent comparisons. Post-firing analysis of the samples involved the use of industrial standard scraping of the formed char layer followed by measurements of the remaining polymer at various stages in the sample, which represent different mass fluxes (i.e., mach number regions) the sample was exposed to. As one can see from Figure 4, there is a significant amount of scatter in the low mass flux regions of the samples. This is expected in typical rocket motor firings. With Mass fluxes greater than 0.200 it is clear that the POSS-EPDM sample performs significantly better than the standard, with ablation rates of up to 50% less than the industrial standard. These results are very significant, since a 50% reduction in the ablation rate of current SOTA materials can results in up to a 7.4% increased in payload to orbit.

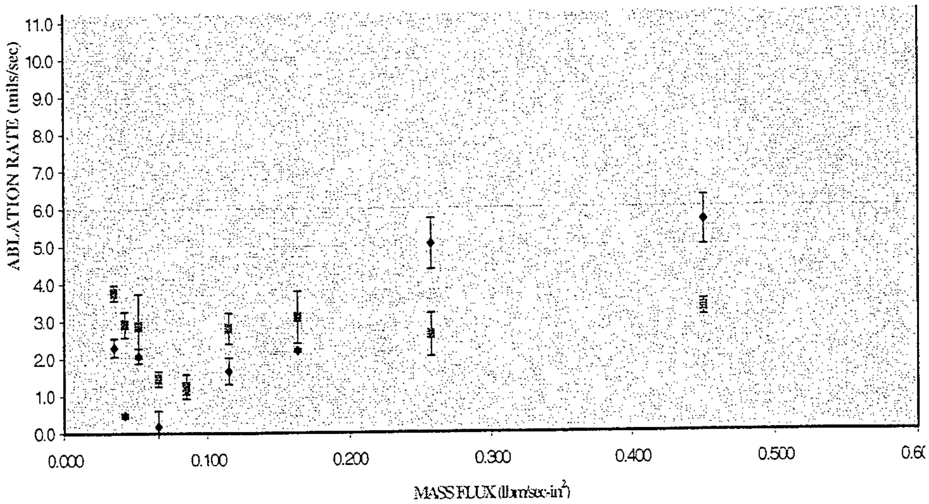

Figure 4: Measured ablation rate versus mass flux for standard (box) and POSS-EPDM (oval) samples.

The structure of the POSS-Kapton® is shown in Figure 5. As can be seen, the difunctional POSS molecule is covalently bonded into the backbone of the polymer chain. Polymerization of POSS into the chain backbone virtually guarantees true "nanodispersion". There are no visible changes in the color or transparency of the polymer with POSS loadings of up to 30 wt%, as compared to a Kapton® standard.

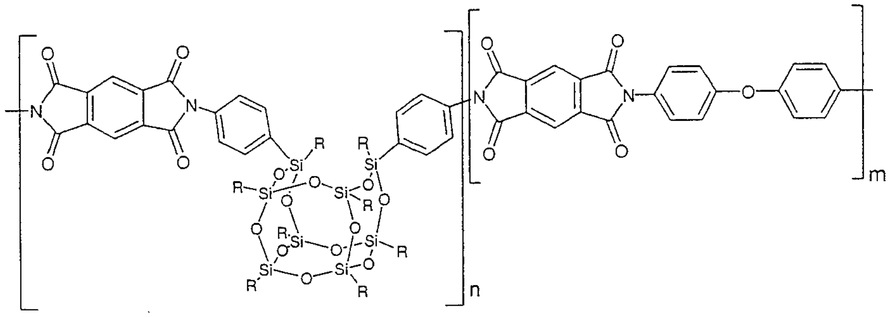

Figure 5: Structure of 10 wt% POSS-Kapton®

XPS probes the near-surface region of the sample and yields a weighted average composition with the atomic layers near the surface being weighted more heavily because these photoemitted electrons have a lower probability of scattering inelastically. The sampling depth is ~4-6 nm, and about 10% of the signal originates from the outermost atomic layer. This near-surface region is inhomogeneous because the AO reacts with the outermost few atomic layers. Therefore, the outermost surface region which is affected to the greatest extent due to reaction with AO also makes the largest contribution to the XPS signal. This fact implies that XPS is an excellent technique for studying AO erosion of spacecraft materials. Even though the distribution functions involving the depth of chemical reactions in the near-surface region and the XPS where ?

determination of the weighted average composition of the near-surface region are complex, the compositional values, determined using the homogeneous assumption and shown in Table 5-3 as a function of AO fluence, provide a trend which is indicative of the chemical alterations occurring during AO exposure. This data is shown in Table 1, which indicates that the O/Si ratio changes almost immediately on exposure to atomic oxygen. It is important to note that the O/Si ratio changes upon exposure to the atmosphere-the surface apparently has reactive species which could occlude ex-situ analyses. This O/Si ratio becomes consistent with the formation of a silica (SiO_2) layer on the surface which protects the surface. The nanocomposite nature of the polymer ensures that if the silica char layer were to be degraded, virgin POSS should remain in the bulk which could then reform the silica layer. The existence of silica is confirmed in Figure 6, where the high resolution XPS signals are plotted. The Si 2p and O1s peaks have binding energies that are very sensitive to the chemical environment of the atoms. A peak shift away from a silsesquioxane ($RSiO_{1.5}$) to silica (SiO_2) occurs after initial exposure to AO, and the peaks do not continue shifting, thus indicating that the silica overlayer is very stable.

Sample Treatment	O	C	N	Si	O/Si
As entered	15.9	74.5	4.9	4.6	3.4
2.0-hr	14.3	72.6	8.2	4.9	2.9
24.0-hr	11.1	79.6	4.9	4.4	2.5
40.0-hr	9.1	81.5	5.6	3.7	2.4
Air exposed	13.9	76.8	5.8	3.5	3.9

Table 1: XPS results of 10 wt% POSS-Kapton® after atomic oxygen exposure

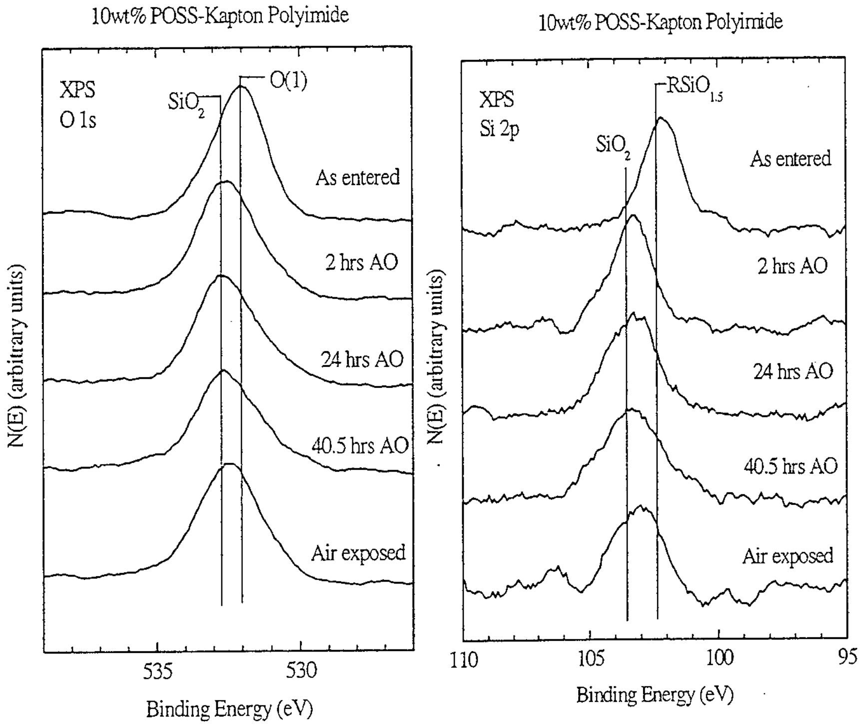

Figure 6: High Resolution Si 2p and O 1s XPS spectrum of POSS-Kapton®, showing formation of a SiO_2 layer.

4. CONCLUSIONS

Hybrid inorganic/organic polymers containing POSS monomers were synthesized, characterized and tested for oxidation protection in either a solid rocket motor or atomic oxygen environment. For the solid rocket motor tests, analysis of the post-fired samples showed the formation of a glass SiO_2 layer. Furthermore, significant reduction in ablation rates was reproducibly demonstrated when compared to state of the art rocket motor insulation. Previously, we had shown that POSS-polymers (e.g., POSS-PDMS and POSS-Polyurethanes) form a passivating SiO_2 when exposed to an atomic oxygen (AO) flux. In this paper, POSS-Kapton®, which had recently been synthesized and characterized, was studied for the effects of AO on the resulting polymers. As expected, the POSS-Kapton® formed a passivating SiO2 layer upon exposure to AO. This protective ceramic layer was shown by Tim Minton at Montana State University to result in a greater than 9x reduction in erosion, as compared to space-certified Kapton® samples. The promising results contained herein when combined with the numerous property enhancements previously reported make POSS-polymers leading candidates for use as in-situ ceramic-forming nanostructured polymers. Future work will focus on studying the physical and mechanical properties of the POSS-polymers after sever environment exposure.

5. ACKNOWLEDGMENTS

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