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ADDITIVES TO REDUCE SUSCEPTIBILITY OF THERMOSETS AND THERMOPLASTICS TO EROSION FROM ATOMIC OXYGEN

by

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Polymeric materials have many attractive features such as light weight, high strength, and broad applicability in the form of films, fibers, and molded objects. For these reasons synthetic polymers are increasingly being incorporated on orbiting vehicles as the material of choice for thermal blankets, tethers, structural trusses, adhesives, etc. In low-earth orbit (LEO, e.g., 300-500 km) these materials, when exposed on the exterior of spacecraft, have the serious disadvantage of being susceptible to erosion by atomic oxygen (AO).

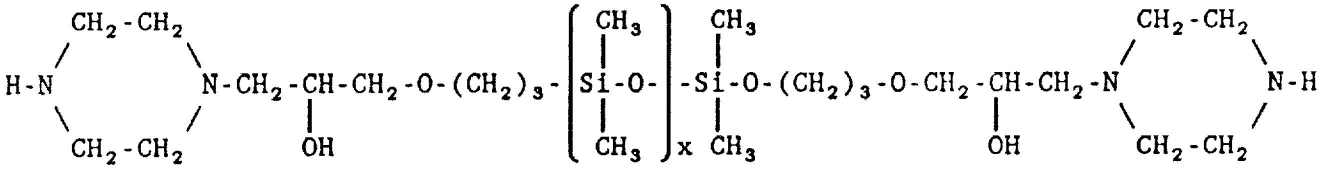
AO is the most common chemical species at LEO altitudes. At typical satellite speeds of 8 km/s, forward facing surfaces undergo 10^{14}-10^{15} collisions/s/cm^2 with AO. AO can be an extremely efficient oxidizing agent as was apparent from the extensive erosion of organic films exposed in STS missions. The mechanism for erosion involves the reaction of oxygen atoms at the surface of the substrate to form small molecular species, sometimes with scission of the polymer backbone. These volatile products escape immediately and the etching of the surface continues as long as it is exposed to AO.

The susceptibility of polymeric materials varies with their chemical composition. Polyethylene and (Mylar) polyester are among the most vulnerable polymers. Experiments in LEO revealed that, for each collision of an oxygen atom with polyethylene or polyester film, an average of 2-3 amu (atomic mass units) of film were eroded. At 10^{14} collisions/s/cm^2, this corresponds to a loss of 0.1 mm from the surface each year. On the other hand, completely fluorinated polymers (Teflon) and polymers with silicon atoms incorporated chemically in their structure are much less susceptible: less than 0.1 amu erodes per collision. The fluorinated films are resistant to AO because the carbon atoms in the macromolecules are already bonded to atoms (fluorine) that are more electronegative than oxygen. Unfortunately fluorocarbon polymers have only limited applicability in space because the carbon-fluorine bond is especially vulnerable to scission by solar UV. More relevant to this work are the silicon-containing polymers. Their resistance to AO is attributed to the formation of a protective coating of inert silicates $(SiO_2)_x$. This quasi quartz-like barrier is generated during the initial period of exposure of the polymer film to AO. Because silicates are nonvolatile, they remain behind on the surface of exposed films blocking the remainder of the material from further erosion by AO.

Films with silicon atoms incorporated in the molecular structures have large coefficients of thermal expansion. This limits their utility. In an alternative approach we have looked for additives to mix physically (as opposed to attaching chemically) that would form a similar protective oxide layer when the film is exposed to AO. A large number of organic compounds containing silicon, germanium, or tin atoms were screened. Most were found to have very limited solubility (<5% by weight) in the polyetherimide (Ultem) films that we are trying to protect from AO. However, one, bis(triphenyl tin) oxide (abbreviated BTO), is miscible in Ultem up to ca. 25%.

Films of Ultem polyimide containing up to 25 wt-% BTO were prepared by evaporation of solvent from a solution of Ultem and BTO. The effects of atomic oxygen on these films were simulated in the oxygen atmosphere of a radio-frequency glow-discharge chamber. Typical results are shown in Fig. 1. Here the degradation rates of polyetherimide with and without BTO are shown as a function of the exposure time. During the initial stage when the tin oxide film is forming, the mass loss of the doped film is considerably greater owing to the greater volatility of the oxidation products involving constituent atoms that are not connected to the long chainlike macromolecules of the Ultem. At longer times after the tin oxide has accumulated on the surface, the erosion rate has decreased to two/thirds that of the undoped polymer. The protective layer on the surface is evident in EDAX studies. Fig. 2 is an EDAX spectrum of an Ultem film containing 20% BTO, before and after a 360-min exposure in the oxygen plasma of the glow discharge chamber. It shows the surface composition changes markedly from predominantly carbon and oxygen to tin and oxygen.

In a second part of this study, we have undertaken to incorporate silicon atoms in epoxy resins by including the following compound and an analogue with



phenyl in place of the methyl substituents at the silicon atoms as part of the curing agent for the epoxy. Experiments are in progress to measure the resistance of films of the cured epoxy to AO in the discharge chamber.

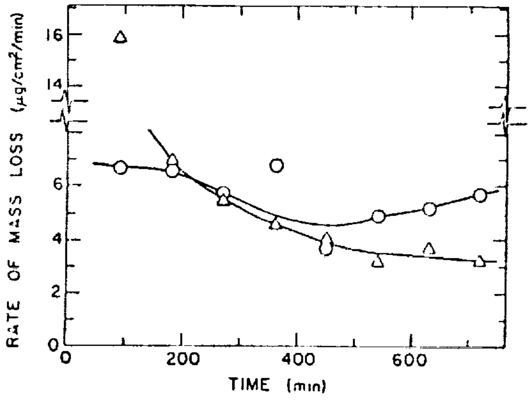


Fig. 1. Erosion rates of polyetherimide doped with 25 wt-% BTO (triangles) compared with those of undoped film (circles).

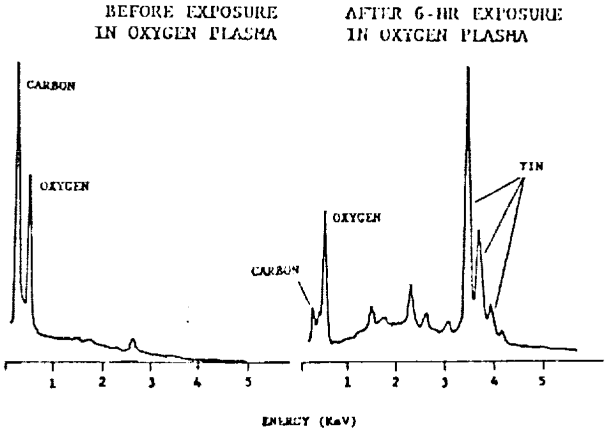


Fig. 2. EDAX spectra of a polyetherimide film with 20 wt-% BTO before and after a 6-hr exposure in the discharge chamber.