

Inorganic Polymers for Space Applications

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ABSTRACT

Spacecraft designers need to find innovative ways to reduce satellite mass. In this direction, a new technology is being developed which has the potential payoff in the difficult subsystem of imaging payloads. A class of inorganic polymers, called geopolymers, is being tested for their use as lightweight mirror materials. Two formulations, one for use as an adhesive and the other one for use as a structural material, are under development and are being space qualified as part of this overall effort. Geopolymers have the advantages of low initial coefficient of thermal expansion, easy preparation at room temperature and atmospheric conditions, castability, and adhesion to a number of common mirror coating materials. If successful, geopolymer based optics have the potential to improve the areal densities of traditional monolithic glass mirrors by a factor of 3 or more. This paper will detail the progress on our formulations of geopolymers for developing lightweight mirrors for space applications, and the status of the space qualification testing at this time, specifically the results of ASTM outgassing tests.

INTRODUCTION

Production of space qualified optics has reached a plateau of performance as defined by mirror diameter, limited by the reduction of areal density of traditional optical materials (i.e. monolithic glass). Efforts such as Air Force Research Laboratories Materials and Manufacturing Directorate's (AFRL/RX) Advanced Mirror System Demonstrator (AMSD) have achieved areal density and processing time improvements such that the cost and development of glass optics was optimized to achieve a mirror fabrication cost and schedule to half of that used to produce the mirror for the Hubble Space Telescope. However, to continue the trend of improvement to even lighter weight space optics with sufficient structural and thermal stability, new materials and fabrication processes need to be developed. Instead of glass, composite materials (metals, ceramics, polymers, or combinations), foams, and microstructured materials would form the basis of the optic structural substrate. Reflecting surfaces can be attached to these substrates in a number of ways, such as direct thick film deposition techniques (cladding) followed by grinding, polishing, and reflective coating application, or by adhesion of a replicated reflecting foil or nano-laminate. Recent work at AFRL/RX using this replication approach has made possible small flat mirrors with areal densities less than 7 kg/m², a 50%

reduction over the best currently available light weight monolithic glass substrates¹.

Thermal stability of these optics is chiefly governed by matching the coefficients of thermal expansion (CTE). The mirror substrate and reflecting surface along with adhesive, when used, need to have close or the same CTE values, otherwise stresses due to materials expanding or contracting at different rates will introduce physical deformities to the optical surface, which will then propagate optical distortions to the reflected image. Next generation substrate and reflecting materials in work at AFRL/RX are close to being matched at the same CTE level (~3 ppm/deg C). Development of an adhesive to match these CTE values has been a challenge. Current space qualified adhesives based on organic polymers have CTE's on the order of 40-50 ppm/deg C and their high cure temperature (> 300 deg C) results in dimensional expansion beyond acceptable limits for optical applications.

Inorganic polymers of the aluminosilicate family, commonly called geopolymers, have been proposed to as a potential solution due to their low initial CTE value, their low curing temperatures compared to organic polymers, and the wide range of materials for which it has been shown to have good adhesive properties. Barely refined geopolymers have been used

for decades in Europe and other locales as “green cements”, and more recently, geopolymers have been investigated as a possible material for radioactive waste containers. Davidovits performed much of the initial characterization of modern geopolymers², but recent work by Kriven³ and Bell et al⁴ have expanded the knowledge base by looking at the adhesive properties of common geopolymers. For an explanation of the chemistry of the geopolymer reaction, please see Davidovits's keynote presentation from 2002⁵.

PROPOSED WORK

The objective of the research performed by the group at the Air Force Institute of Technology Aeronautics & Astronautics Department (AFIT/ENY) for the AFRL/RX effort is a step toward making these materials space qualified. In order to properly characterize geopolymers for use in the space environment, problems have to be overcome in the processing of the materials themselves, determining the response of these materials to basic space environment concerns (such as outgassing, thermal vacuum swings, radiation exposure), and subjecting prototypes of these materials in their application state to a typical space and launch vehicle environment test suite. The AFIT/ENY work is focusing on answering some of the processing questions, as well as proving the basic worthiness of the bulk materials for space applications.

In the past year, our group's research on geopolymers has focused on initial questions related to geopolymer processing such as determining suitable casting container materials, quantifying curing shrinkage and the effects of mitigation techniques, verifying that geopolymers will meet the NASA outgassing requirements for a space qualified material, and discovery of geopolymer curing mechanisms as well as internal geopolymer 3-D structure.

It is anticipated that by the end of 2008, our group would provide information about the suitability of geopolymers' for space based mirrors as well as directions and guidelines for future developments and research efforts on geopolymers as a general space qualified material. This project will hopefully provide sufficient information whether the present composite mirror program should revert toward investigating organic polymers that are already space qualified, but with far inferior curing processes and initial CTE properties. If the geopolymers show the potential, the final part of the project would involve producing mirror prototypes for an actual flight opportunity in 2009-2010.

EXPERIMENTAL WORK

Materials Used

The two primary geopolymers used during this experimental work were illite in the form of the commercially available powder and liquid activation agent, and metakaolin which was made from a mixture of metakaolin powder produced in house at AFRL, and a silicate solution made in house at AFRL/RX as well.

Curing Shrinkage

All flowable materials either contract or expand when forming a network of bonds in the transition to a solid state. For polymers that require time and the right environmental conditions, this is typically a contraction and the term “curing shrinkage” is used to describe the phenomenon. Geopolymers are no different than other flowable pre-cured polymers in that when the 3-D network of bonds begins to form, the structure of the geopolymer matrix begins to take shape and the volume of the bulk material reduces. Initial estimates by AFRL/RX showed that geopolymer curing shrinkage for two of the targeted geopolymers (illite and metakaolin) was a significant concern⁶. The need to quantify the amount of curing shrinkage in a controlled manner and determine the key environmental variables that would control the shrinkage was apparent. Our work was to perform a series of experiments where for each geopolymer, the temperature or pressure would be varied during the curing process and measurements would be taken before and after the curing process to quantify the shrinkage.

The general approach was to prepare the geopolymers by mixing the solid powder and liquid reaction initiator chemicals to form the geopolymer paste, pour these samples into molds which had been dimensionally characterized before the testing began, allow the geopolymer to cure and then extract the solid samples for dimensional measurements. By using a linear dimension metric of height plus length plus width (mold shrinkage)⁷, this would allow us to take into account curing across all three dimensions, instead of just trying to monitor the reduction in cross sectional area.

One result that quickly came to the forefront was that the material of the casting mold was extremely important. Initially, we had used simple polystyrene boxes but after the first samples, the buckling of the geopolymers post cure and the residue on the molds themselves after sample extraction suggested that significant adhesion was taking place between the polystyrene and the geopolymer. This is seen in Figure 1, a photo of one of the samples from this first batch of tests. Because of the adhesion taking place, non-optimal

stresses were developing internal to the curing geopolymer causing the sample to “tent” that would make it difficult to accurately measure the curing shrinkage, in addition to causing fractures to develop in the geopolymer itself.

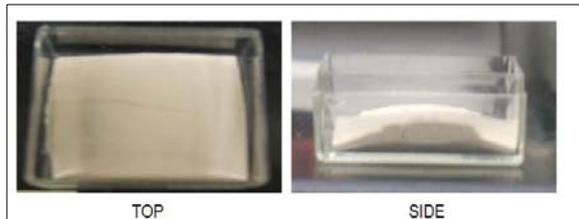


Figure 1: Evidence of adhesion between illite geopolymer and polystyrene mold

A quick review of materials revealed that nitrile rubber would be a good replacement for the polystyrene due to anticipated inertness with the geopolymer, and we had AFRL/RX construct a set of blue nitrile rubber molds for use in future experiments. Each sample chamber of the mold measured 25.23 x 25.23 x 6.32 mm to within 0.1 mm in each dimension.

We then went about preparing the samples to test the curing shrinkage dependence on the two principally controllable environmental variables, temperature and pressure. Unpublished work by AFRL/RX suggested that adding compression force in the form of vacuum bagging samples would be effective in controlling curing shrinkage. The samples were prepared per the chart below (Table 1) and each geopolymer formulation was subjected to one of the following test conditions:

- room temperature and ambient atmosphere
- vacuum bagged and left at room temperature
- vacuum bagged and placed in a 60 deg C oven
- vacuum bagged and placed in a -17 deg C freezer

The samples were left to cure for a period of approximately five days at those conditions. After this period of time, the samples were extracted from their molds, allowed to equalize with room temperature and ambient atmosphere overnight before mass measurements and dimensional measurements were taken.

Some interesting observations were noted during the curing process. First, in the vacuum bagged samples, there was a significant color change that occurred after the exposure from the vacuum bags where the illite samples changed from various shades of dark green to the expected grey tone. While definitive results are not completed on this phenomenon, it is speculated that the color change occurring is due to an unfinished curing

process where the water molecules formed during the polymerization reaction couldn't diffuse out of the polymer matrix resulting in a hydrate form of the solid polymer. We think the change to the non-glossy grey color may indicate the easiest path free water had escaped the polymer matrix to equalize with the ambient humidity level. The MK samples from vacuum bags experienced a color change as well but not nearly as pronounced.

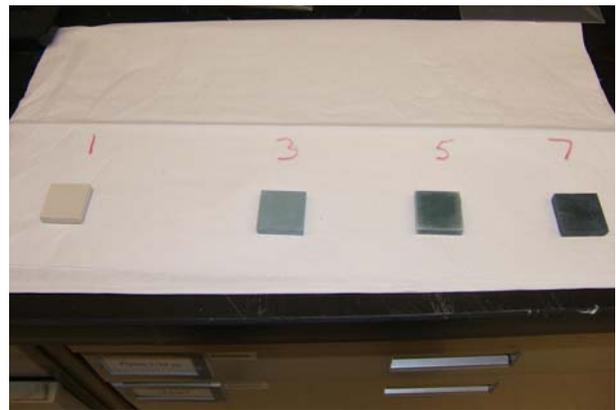


Figure 2: Color change of illite samples from vacuum environment to ambient

Second, little mass change was noted from the time the vacuum bagged samples were opened until after the ambient atmosphere acclimation time was complete. This was an indication that although some water had equalized with the humidity, there was still significant water by-product trapped in the pores of the polymer matrix.

A final observation was noted on the illite and MK samples that were left exposed to the room temperature and ambient atmosphere. Both of these samples showed significant buckling and flaking on the exposed surface and numerous surface cracks were apparent as well. This was a clear indication that a simple room temperature and ambient atmosphere curing process would not be sufficient for any application. It is important to note however, that the sides of the geopolymer sample that were in contact with the mold showed no signs of distortion similar to the exposed surface.

Analyzing the net change in linear dimensions showed that pressure was a dominant effect, although temperature was a contributor to controlling curing shrinkage.

Table 1: Curing Shrinkage Experimental Results

Material	Cure Conditions	Linear shrinkage
Illite	STP	5.08 %

Illite	60 deg C, vacuum bagged	0.49%
Illite	Room T, vacuum bagged	0.72%
Illite	-17 deg C, vacuum bagged	1.17%
Metakaolin	STP	3.32%
Metakaolin	Room T, vacuum bagged	0.25%
Metakaolin	60 deg C, vacuum bagged	0.04%

Coming out of this experiment, it is clear that in order to control curing shrinkage in geopolymers, a pressurized environment is key, even one as mundane as vacuum bagging the molds. Additional work is ongoing at AFRL/RX to determine if higher pressures produce more desirable geopolymer phases by curing geopolymer samples in hydraulic vessels at multiple atms. A higher temperature can also contribute to controlling the curing shrinkage. Compared to other common polymers, it is seen that geopolymers perform favorably⁸.

Table 2: Comparison of geopolymer to other common organic polymer curing shrinkage values

Polymer	Volume Shrinkage
Illite (best experimental performance)	1.2 %
Metakaolin (best experimental performance)	0.2 %
Epoxy	4-5 %
Acrylic	6-9 %
Polyester	9-14 %

Outgassing

One of the defining characteristics of the space environment that separates it from the terrestrial one is the near vacuum atmospherics. This environment wrecks havoc on materials as surface bonded chemicals, liquids trapped inside crystalline solids, and low sublimation threshold materials succumb to release of these substances. These released substances can either re-attach to other spacecraft surfaces creating a coating (possibly disastrous in the case of optical surfaces or electrically conductive materials), or simply releasing to the general local environment causing structural defects in the original material that ages or weakens the original material's strength. All spacecraft launched from Earth will outgas due to atmospheric water vapor that has attached to the spacecraft exterior during shipping and the launch preparation cycle. Organic polymers are particularly susceptible to this problem as the volatile chemicals used in the formulation and released during the curing process

typically are easy to evaporate or sublimate in a vacuum, not to mention upon application of heating due to exposure to the sun while in orbit^{9,10}.

National space agencies around the world have realized the danger of high outgassing materials to spacecraft mission success and have established standards to test materials for levels of outgassing. NASA uses ASTM Standard E-595-93 for testing¹¹, and in general (but not all cases) uses a metric of < 1% Total Mass Loss (TML) to qualify a new material as being acceptable for the space environment. TML is calculated by looking at the mass difference after exposure to a 125 degree C vacuum environment.. Water Vapor Regained (WVR) is a measure of how much water vapor is reabsorbed by the material and compares the mass following the two humidity chamber treatments. Taking TML and subtracting WVR gives a "Net Mass Loss" (NML) that measures how much test material mass was lost during the vacuum exposure, excluding the water that was absorbed during the first humidity soak and then released during the outgassing. This is particularly important for hygroscopic materials, the class of materials that readily absorb atmospheric water, as the classic TML value would seem to indicate a huge mass loss, but in reality the majority of that mass loss during the vacuum exposure was the water absorbed immediately before the vacuum exposure. A NML of < 1% for hygroscopic materials can be acceptable for applications where the expulsion of water vapor immediately upon exposure to the space environment is not a large concern.

This ASTM test involves taking a small sample of material and subjecting it to a "soak" in a high humidity (50% relative humidity), elevated temperature environment for 24 hours to simulate storage conditions at the two main space launch sites in the United States, Cape Canaveral in Florida and Vandenberg Air Force Base in California. The mass is measured, and the sample is placed in a vacuum oven for 24 hours at 125 deg C and 1.5×10^{-5} Torr. The specimens are monitored for release of any collected volatile condensable material (CVCM), considered potentially hazardous to manned spaceflight missions. The CVCM value can not be higher than 0.10%. Following the vacuum exposure, the samples are taken out of the oven, measured for mass, returned to the high humidity chamber for a "re-soak" of 24 hours and then the mass is measured again¹².

Inorganic polymers such as geopolymers have, as one of the products of the polymerization reaction, free water molecules that are typically trapped in the voids of the polymer matrix. Since geopolymers also tend to have large molecular surface areas with available Van der Waals bonding sites, they tend to be hygroscopic as

well. This presents the first problem in qualifying geopolymers for the space environment, necessitating the use of NML versus TML for consideration of the materials worthiness with respect to outgassing. If the application can reduce the susceptibility to water vapor absorption and short duration exposure, then geopolymers should be an outgassing friendly material with none of the CVCM problems that are common with organic polymers.

The preparation of the samples was performed at AFRL/RX at Wright-Patterson AFB. The actual outgassing tests were performed at NASA Goddard Space Flight Center (GSFC) Materials Engineering Branch laboratory. The equipment there is based on the Stanford Research Institute developed micro-CVCM apparatus, first built in the 1960's for NASA ¹³.

The first set of samples tested were from the last set of curing shrinkage tests. The illite sample was made on 4 Jan 2008 from a mixture of commercial powder and curing agent in a 5:3 ratio (powder:liquid). Cure was at room temperature in a sealed vacuum bag following an initial setting time of 45 minutes in a nitrile rubber mold. The sample was kept in a vacuum bag for 5 days. The sample was then exposed to ambient atmosphere in AFRL/RXM laboratory facilities prior to shipping. The metakaolin sample was made on 16 Jan 2008 from a mixture of metakaolin powder and sodium silicate in 1:2 ratio (powder:liquid). Cure was at room temperature in a sealed vacuum bag following initial setting time of 60 minutes in a nitrile rubber mold. The sample was kept in a vacuum bag for 6 days. The sample was then exposed to ambient atmosphere in AFRL/RXM laboratory facilities prior to shipping.

A second set of samples was prepared again at AFRL in April and sent off to NASA GSFC as well for testing. The illite sample was made from a mixture of commercial illite powder and curing agent in a 5:3 ratio (powder:liquid). Cure was at room temperature in a sealed vacuum bag following initial setting time of 45 minutes in a nitrile rubber mold. The sample was kept in vacuum bag for 1 day. The sample was then baked at 60C overnight and subjected to 24 hour vacuum bake at 140C for 24 hours (25C for 90 min, 60C for 8 hours, 140C for 24 hours). A final room temperature vacuum exposure was performed for 24 hours prior to shipping.

The metakaolin sample was made from a mixture of metakaolin powder and a KOH/SiO₂/H₂O solution. Cure was at room temperature in a sealed vacuum bag following initial setting time of 90 minutes in a nylon mold. The sample was then placed in high pressure autoclave for 1 hour. Sample was then baked at 60 C overnight and then 24 hour vacuum bakeout at 140 C (25C for 90 min, 60C for 8 hours, 140C for 24 hours).

A final room temperature vacuum exposure was performed for 24 hours prior to shipping.

The results from all the sets of outgassing tests are presented below in Table 3. As you can see, the first set of samples (labeled "Jan 08") had high outgassing characteristics in addition to CVCM deposits recorded. Our analysis afterward showed these were due to a couple different reasons.

Table 3: Outgassing Test Results

Sample	TML	WVR	NML	CVCM
Jan 08 Illite	19.26 %	9.39 %	9.87 %	trace
Jan 08 MK	20.7 %	8.98 %	11.72 %	trace
Apr 08 Illite	6.15 %	5.61 %	0.54 %	none
Apr 08 MK	8.35 %	7.63 %	0.72 %	none

The poor outgassing performance, from a TML point of view, was due to the fact that the samples sent were not "pre-baked", that is the samples had a lot of free water still trapped in the polymer matrix that was then released when heated under vacuum. This was an easy problem to fix as it required only a change in preparation procedure to bake out before outgassing so as to drive out all the excess free water in the geopolymer before vacuum exposure. This proved to be successful when analyzing our second set of samples which were pre-baked in a vacuum oven overnight, then subjected to a room temperature vacuum overnight as well. This has proven to be the key to controlling outgassing in the geopolymers as exposure to ambient atmosphere will still cause surface absorption of water to occur, but the change in preparation technique has solved the problem of internal matrix water liberating during space like conditions and possibly causing damage to bonded materials as the water attempts to diffuse out of the internal bulk material. This preparation change has been noted for future application work.

The problem with CVCM, apparent in the first set of samples, has been traced to contamination in the activation liquid prior to mixing. Fresh activation liquids were prepared or purchased and used in the mixing of the second set of samples. Using uncontaminated solutions has reduced CVCM traces to levels that do not even register on the NASA GSFC equipment.

One additional interesting observation has been seen during the outgassing sample preparation at AFRL/RX. After the geopolymers were subjected to vacuum oven preparation the first time following curing, the samples were immediately removed from the oven to be weighed once the pressure had equalized. The shock of going from a 125 deg C local temperature to a 70 deg C local temperature caused thermal stresses to be

introduced in the material and surface fissures to form on the geopolymers. These propagated to the point that the samples cracked into small fragments. This result prompted our group to revise our preparation procedure to include a slow cool down time of 6-8 hours following the conclusion of vacuum oven heating with the cooling mechanism inside the oven governed by the entrance of air into the oven through a valve opening and natural cooling to occur. This new procedure resulted in a near flawless set of samples of illite and metakaolin that were then sent to NASA GSFC for testing.

FUTURE WORK

The next set of tasks is to prepare representative samples of the bulk geopolymers and subject them to thermal vacuum cycling and radiation exposure to analyze their response to these two environmental conditions. The thermal vacuum cycling will be performed at AFIT/ENY's in-house chamber, and the radiation exposure tests will use AFRL/RX's SPECTRE facility which can simulate radiation and atomic oxygen exposure levels consistent with many different orbital regimes. Still outstanding as well are questions on the CTE tailorability of the space qualified geopolymers, analysis of the internal structure of the geopolymer matrix and a thorough work up of the relevant material strength parameters of the space qualified geopolymers. We are also planning on constructing application prototypes using the geopolymers as adhesives for composite optics and solar array fabrication as well as using the geopolymer formulations for casting mirror substrates and other spacecraft structural components.

CONCLUSIONS

Our initial work in determining appropriate environmental variables for minimizing curing shrinkage in geopolymers has opened the door to begin postulating application methodologies for geopolymers in optical components. The results from our outgassing tests have shown that geopolymers will meet the minimal standards for surviving the initial space environment exposure, namely exposure to vacuum and heating. While the hygroscopic nature of geopolymers may be a concern for those applications where water vapor evaporation immediately upon entry into space is hazardous, considering the general amount of outgassing of water vapor during shroud release of a typical space launch vehicle, the water release as seen in our geopolymer experiments should be minimal. The results are promising enough to continue work on evaluating geopolymers for space applications.

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NOTE

The views expressed in this article are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the U.S. Government.

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