NASA/TM—2009–215901

NASA Materials Research for Extreme Conditions

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July 2009

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Space Administration

Marshall Space Flight Center • MSFC, Alabama 35812

July 2009

Acknowledgments

Special thanks to Donald Frazier (ED10) for reviewing this Technical Memorandum for scientific accuracy.

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443–757–5802

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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ARC	Ames Research Center
$C_2H_4(NH_2)_2$	ethylene diamine
CNT	carbon nanotube
CVD	chemical vapor deposition
HRSI	high-temperature, reusable surface insulation
ISS	International Space Station
LCA	lightweight ceramic ablators
$MeSiCl_2$	dichlorosilane
MSFC	Marshall Space Flight Center
MWNT	multiwalled nanotube
N-H	amino functional group
PICA	phenolic-impregnated carbon ablator
Pol	polymer chain
R1	methyl radical
R2	phenyl radical
RCC	reinforced carbon-carbon
Si	silicon
SILC	Shuttle ice liberation system
SWNT	single-walled nanotube
TPS	thermal protection system
X	hydrogen, halogen, alkyl or aryl radical

TECHNICAL MEMORANDUM

NASA MATERIALS RESEARCH FOR EXTREME CONDITIONS

1. INTRODUCTION

Since its birth, NASA has faced the challenge of developing materials suitable for the harsh environment that space travel presents. These environments run the gamut from various atmospheric pressures to extremes of hot and cold to reentry into Earth's atmosphere. With each mission NASA has undertaken (Mercury, Gemini, etc.), scientists have confronted new and unfamiliar materials development issues. However, out of these challenges have risen some of the most important innovations in science and technology of the modern age.

Chemistry and materials science have played a major role in these innovations. For example, experimentation in stable and efficient organic polymers yielded results in developing materials resistant to extreme temperatures and pressures. In addition, carbon fiber/phenolic composites, developed in the late 1990s, have proven useful in structural aspects of mission programs. Such vital research supports and ensures the continued success of the American Space Agency.

The NASA technical reports server provides an extensive archive of such advancements in materials development. This Technical Memorandum outlines a brief survey of significant materials developments over NASA's history, explains the basic development of these materials, and discusses their use and importance.

2. MATERIALS RESEARCH IN THE 1960S

The Space Race pitted the USSR and the United States against each other in launch vehicle development. NASA scientists faced the problem of producing a vehicle powerful enough to leave Earth's orbit (the Saturn V rocket) while also developing the Apollo capsule that would carry Americans to the Moon. The materials with which the launch vehicle and spacecraft would be built needed to meet specific qualifications of resistance to temperature, pressure, and durability.

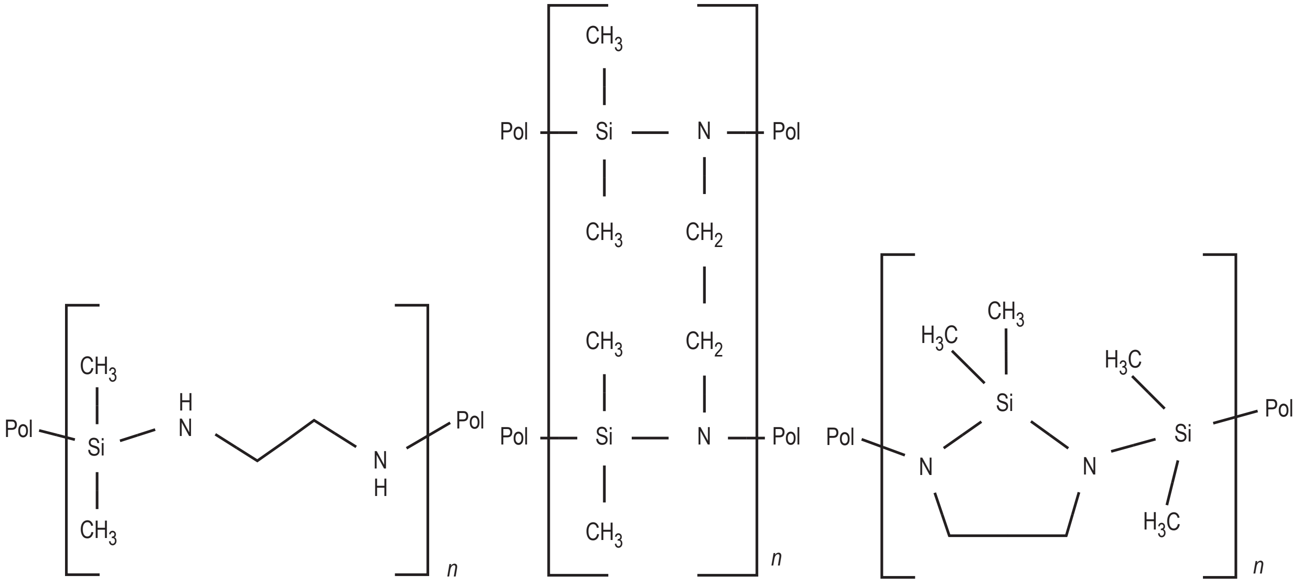
2.1 Silazane Polymers

During the mid-1960s, James Byrd and James Curry, materials scientists at Marshall Space Flight Center (MSFC), Huntsville, AL, proposed the use of silazane polymers in their research for the applications of heat-sensitive portions of spacecraft.[1] Byrd pointed out in his paper "Studies in Silazane Chemistry" that silicones and their traditional compounds, while particularly useful at room temperature, broke down at temperatures in excess of 482 ºF (250 ºC). However, when silicone (Si) bonds with amino functional groups (N-H), the physical properties of these materials become much more durable. The product is known as a silazane, and when this material undergoes polymerization, its characteristics make it a viable candidate for materials needed for successful space flight.

Byrd and Curry noted that in the chemical reaction between ethylene diamine ($C_2H_4(NH_2)_2$) and dichlorosilane ($MeSiCl_2$), there were three possible polymeric structures—the linear form, the ladder form, and the five-membered, cyclic form. Their structures are given in figure 1.

Further research showed that this concept of forming polymers with the silicone-nitrogen (N) bond linkage would be useful in developing materials resistant to high temperatures. In addition, due to its high elasticity, silazane polymers were found to have applications as seals and gaskets under high temperature. Today, silazane polymers are used as a tool for patching reinforced carbon-carbon (RCC) surfaces on the Space Shuttle before returning to Earth.[2] The polymer is mixed with a silicon carbide and various other metal carbides to form a paste that can resist temperatures up to 3,500 ºF (1,927 ºC).

This innovation, amongst others, illustrated the incorporation of research in organic chemistry into the Space Agency during the 1960s; Curry and Byrd's work served as a springboard in the development of new, stronger materials for use in the Space program.



(a) Linear Structure (b) Ladder Structure (c) Cyclic Structure

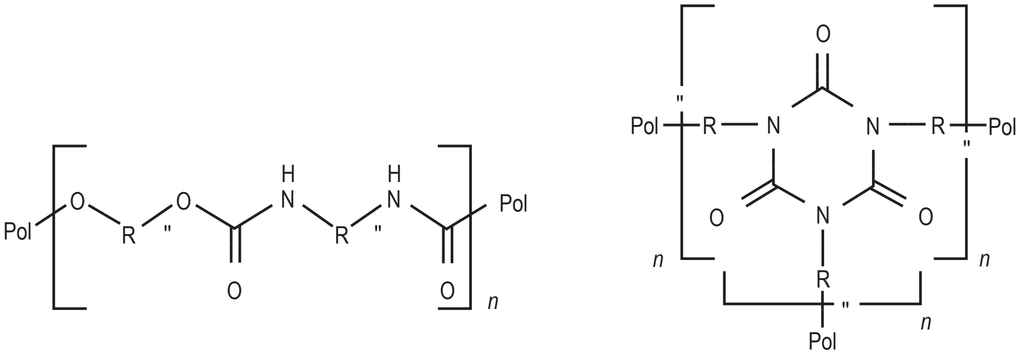
Figure 1. Structures of the three forms of products of reaction between ethylene diamine and dichlorosilane: (a) Linear structure, (b) ladder structure, and (c) cyclic structure.

3. MATERIALS RESEARCH DURING THE 1970S

The closing of the Apollo program brought about new challenges as NASA scientists sought to establish a temporary home in space (Skylab) as well as develop a reusable space transportation vehicle (Shuttle). These new challenges led to more innovation in the fields of engineering and chemistry. Two major scientific problems and their solutions are briefly outlined in sections 3.1 and 3.2.

3.1 Solvent-Resistant Elastomers for Extreme Environments

A need for materials in fuel tank development encouraged research in elastomeric polymer chemistry in the early 1970s, and in particular, the chemistry of polyurethane and polyisocyanurate. Both of these compounds exhibited strong elasticity and showed a resistance to extreme temperatures.[3] Their structures are provided in figure 2.



(a) Polyurethane

(b) Polyisocyanurate

Figure 2. Structures of (a) polyurethane and (b) polyisocyanurate.

Research on these types of polymers was needed for development of a foam insulator for the proposed Space Shuttle external tank. MSFC materials scientist W.E. Hill discussed in his paper that polyurethane, having a density of 48.06 kg/m^3 and being a material of choice in the coating of the Saturn rocket, was found to be too heavy a material to be acceptable as the insulating foam for the needs of the Shuttle program. Furthermore, he noted that three-dimensional foam polyurethane underwent a decomposition reaction at 302 °F (150 °C). This eliminated three-dimensional foam from serious consideration in the discussion of what could be used to insulate the Shuttle fuel tank, as shown in figure 3.

Polyisocyanurate, however, showed much more promising qualities. Its density of 28.80 kg/m^3 (almost half of the three-dimensional foam) made it a significantly more efficient material for keeping within the weight limits of the external tank. Polyisocyanurate was also found to perform consistently over various temperature range tests.

Figure 3. Space Shuttle external tank.

These properties, along with its elasticity, made polyisocyanurate an excellent candidate for sealant of fuel tanks. Today, this research bears significance in that polyisocyanurates have become the material of choice for the foam coating of the Space Shuttle's external tank.[4] The polyisocyanurate regulates the temperature of the propellants in the external tank, effectively clings to its surface, and minimizes ice formation.

The need for elastomeric materials for Space Shuttle applications became extremely important when the Challenger disaster took place in 1986. The tragedy, which was caused by the failure of an O-ring under unusually low temperature, called for even more innovation in elastomeric polymer chemistry.

3.2 Siloxane Derivatives

Another major problem that NASA scientists faced was the development of effective lubricant systems for spacecraft and launch vehicles. Several lubricants had been used, but none had yet proven to be properly resistant to extensive amounts of radiation from outerspace. MSFC materials scientist Norman Billow developed a organosilicon-based compound with a resistance to radiation.[5] His discovery is outlined below.

Thiophenyl ether siloxanes exhibit several physical properties useful in applications of spacecraft lubricant. The structure of a general thiophenyl siloxane is given in figure 4.

The key feature in the synthesis of the disiloxane compound is a Grignard reaction between the Grignard reagent of a bromo-substituted phenylthiobenzene with a dichlorosilane and then hydrolysis with water. Synthesis of the trisiloxane takes place through a similar Grignard reaction.

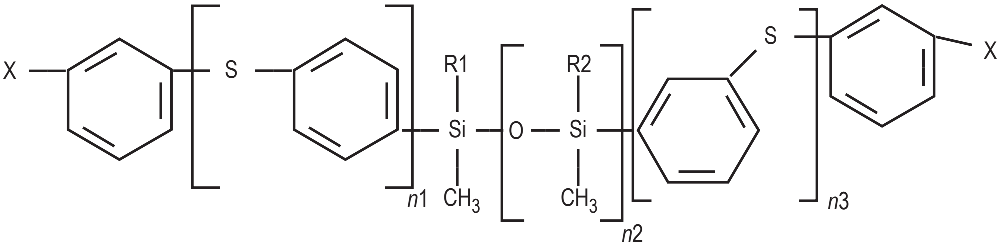


Figure 4. A general siloxane compound (no specific regiochemistry is shown).

Once the compound was synthesized, Billow began to measure its properties; he then discovered that the siloxanes had very low pouring points (the lowest temperature at which a compound will pour or flow) and a strong lubricity. In addition, these siloxanes were resistant to extreme temperature as well as radiation. In practice today, siloxanes are used to prevent ice buildup on the U.S. Space Shuttle.[6] The siloxanes are mixed with ethyl alcohol, ethyl sulfate, isopropanol, and polytetraflouroethylene to form a coating known as the Shuttle ice liberation system (SILC).

This invention was a significant step in materials development in that the problem of radiation had been addressed in the area of lubrication development. Organic/polymer chemistry was at the core of a great deal of research that took place during the early decades of the Space Agency.

4. MATERIALS RESEARCH IN THE 1980S

The advent of a spacecraft that could go into space, return, and be used again brought about an enormous need for new technology in the Space Agency. New systems needed to be developed for launch and reentry, and a new system for propulsion had to be devised. The Shuttle age drew from the knowledge and strategies used in the Apollo program to shift into a higher standard of materials research. One focus of this research, the thermal protection system (TPS) developed by scientists Ian MacConochie, Ashby Lawson, and H. Neale Kelly, is outlined in section 4.1.

4.1 Space Shuttle Thermal Protection System

A reusable launch vehicle called for moving beyond the heat ablation system employed by the Mercury, Gemini, and Apollo programs—designed only to reenter the atmosphere once. Any new material used for regulating temperatures during reentry would have to be lightweight and sturdy while also providing the shielding necessary for the protection of the metal Space Shuttle. Most important was its need to be reusable.

NASA scientists worked to develop a new type of heat-shielding material based on a tile structure rather than the ablation covering that former missions used.[7] The tile would be primarily composed of a layered design with an outer coating that adheres to the surface of the Space Shuttle. A diagram of the tile is provided in figure 5.

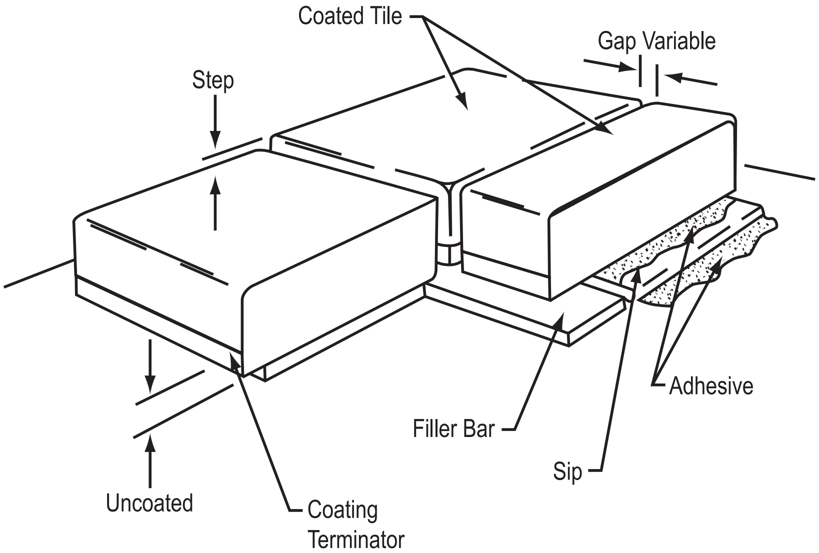


Figure 5. Diagram of the HRSI Space Shuttle tile.[8]

The main interior of the tile is a pure silica that is fired at 2,300 ºF (1,260 ºC), and is covered in a borosilicate compound for purposes of waterproofing. The sip layer as well as the filler is comprised of a heat-resistant felt while the adhesive is made from silicone. This high-temperature, reusable surface insulation (HRSI) tile served as the primary material for the underbelly of the Space Shuttle.

However, the nosecone and wing edges of the Space Shuttle called for stronger materials that would need to resist even higher temperatures as they would experience the most heat during reentry. NASA then introduced the RCC. RCC is made in a process that requires laying out the starting material (a carbon fiber) and then infusing it with carbon-forming gas such as acetylene. In today's applications, similar materials are also used in the manufacturing of automotive brake systems.

The TPS for the Space Shuttle brought about a revolutionary concept of reusable materials development that shifted the way NASA viewed the problem of outerspace temperatures. This innovation, along with many others in the age, made the case for the Shuttle as one of the most advanced machines ever built.

5. MATERIALS RESEARCH IN THE 1990S

The 1990s continued the return to flight after the Challenger incident and set in motion the transition of developing a home in space. NASA scientists began to work with other space agencies in order to plan and execute the building of the International Space Station (ISS). Materials innovation became increasingly vital as numerous agencies from across the globe began to assemble separate sections of a space station that would not be assembled until they met in Earth orbit.

5.1 Phenolic-Impregnated Carbon Ablator

Returning to the concept of ablative materials from the Apollo program for heat shielding, scientists at NASA Ames Research Center (ARC) began to develop a family of materials known as lightweight ceramic ablators (LCAs).[9] These materials, known for their durability and low density, served as a springboard into research for future planetary missions.

LCAs consist of a low-density fiber infused with an organic resin. Specifically, phenolic-impregnated carbon ablators (PICAs) use FiberForm as the fiber substrate, a material developed by Fibermaterials Inc., that consists of a rigid, lightweight carbon fiber designed to be resistant to high temperatures in vacuum. The FiberForm is then infused with a phenolic resin. The resin is a product of a polycondensation reaction between phenol and formaldehyde in the presence of a catalyst. The reaction can occur via two routes, which are diagrammed in figure 6. Phenol and formaldahyde structures are given in figure 7.

The route by which the resin is made depends on the ratio of formaldehyde to phenol used in the reaction. If the formaldeyde/phenol ratio is >1, then the process would go through route A, in which the two compounds are mixed, heated, and begin to crosslink with each other in the presence of a base catalyst. If the opposite is true, then the reaction would go through route B, in which an acid catalyzes the reaction, and then a crosslinking agent must be introduced. The final structure of the cured resin is shown in figure 8.

By the end of this research, the result was an extremely durable material that could withstand both extreme temperature and a vacuum environment. In practice, PICA was used as the primary heat shield material for the Stardust spacecraft, whose mission was to collect samples from Comet Wild 2 in February 1999. Due to the fact that Stardust reentered the atmosphere even faster than the Apollo capsule, PICA was a key factor in the mission's success. In addition, NASA scientists are currently experimenting with PICA in their development of the Orion capsule's heat shield for the Constellation program.

It is worth noting, however, that the supply of a key material used to make these composites, rayon, has come under jeopardy due to the prohibition of the method used to make it. This was done due to the harsh byproducts that are released in rayon's synthesis. As a result, research is currently underway to develop an alternative material to replace the rayon cloth.

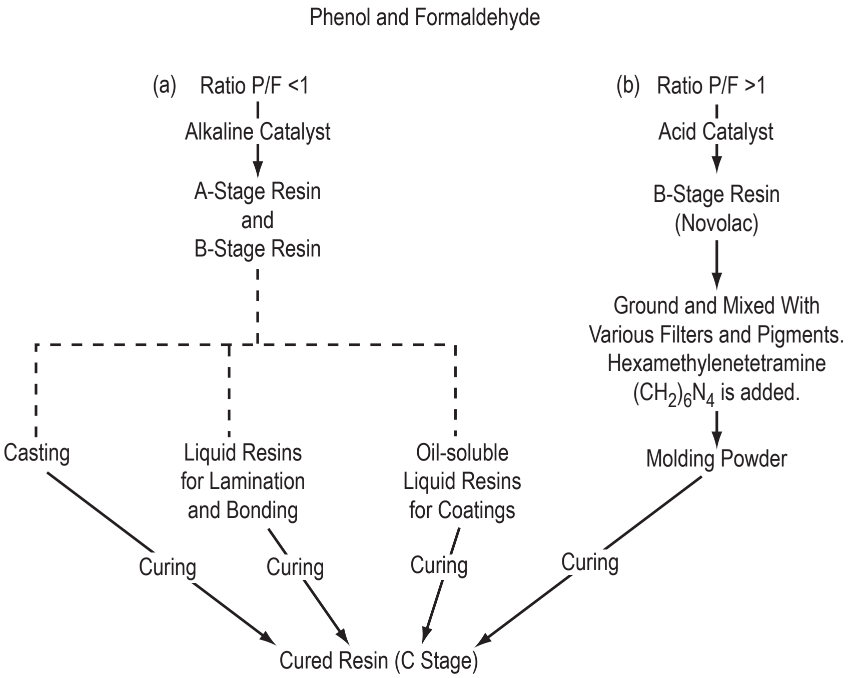


Figure 6. Diagram of the two reaction routes of the phenolic resin polycondensation reaction.

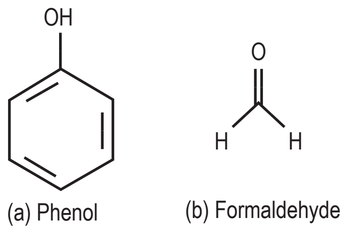


Figure 7. Structures of (a) phenol and (b) formaldehyde.

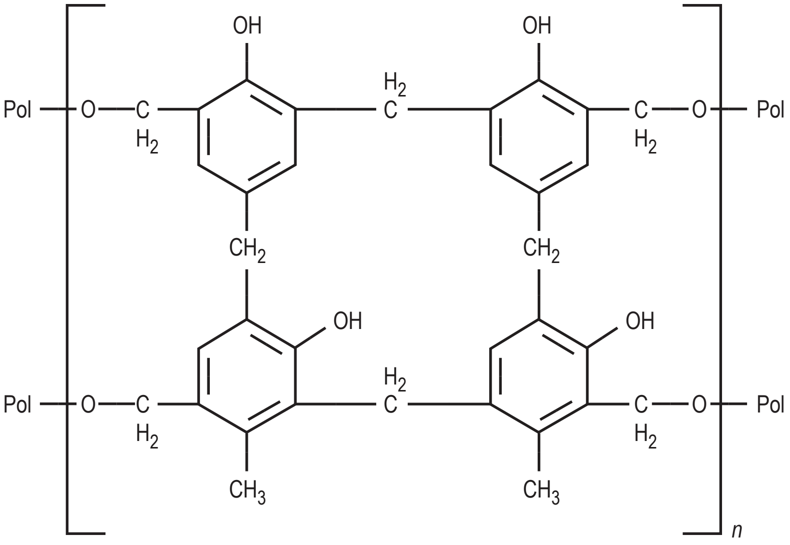


Figure 8. Structure of phenolic resin product.

6. MATERIALS RESEARCH IN THE PRESENT

The 21st century has brought about even more challenges for the Space Agency as production on the ISS continued and as NASA began to answer then President George W. Bush's challenge to return humans to the Moon and Mars. A human mission to Mars requires technology more advanced than has ever been developed before in the history of the Space Agency.

6.1 Carbon Nanotubes

Discovered in 1991 by Japanese scientist Sumio Iijima, carbon nanotubes (CNTs) have been a topic of great interest due to their remarkable strength and durability.[10] CNTs are another configuration of carbon molecules in which a cylindrical shape is formed. CNTs have since been discovered to exist in the two following types: (1) The single-walled nanotube (SWNT), in which only one layer of atoms is rolled together and (2) the multiwalled nanotube (MWNT), in which multiple layers of atoms are rolled together with a constant spacing of 3.4 Å. CNTs have also been found to have practical applications both in the electrical/circuitry fields as semiconductors and in the structural fields for armor and spacesuits.

Regarding their formation, CNTs can be synthesized via several different means, one of which involves bombardment with an argon laser in the presence of a transition metal catalyst. Another method that has drawn recent interest is the process of chemical vapor deposition (CVD) of nanotubes. In a process similar to the argon laser method, a growth apparatus featuring a quartz tube with a transition metal catalyst is placed inside a furnace. The furnace is heated to temperatures of about 1,292–1,652 ºF (700–900 ºC) at atmospheric pressure while hydrocarbons are fed into the tube (usually ethylene for MWNTs and methane for SWNTs). This process produces in good yield, and scientists at ARC have speculated the possibility of using this method to synthesize CNTs much more selectively.

CNTs have been used by the Space Agency in the application of chemical sensors. Research is currently underway in the structural application of nanotubes with the potential of developing a composite with applications in a large range of structural materials. Their remarkable strength-to-weight ratio (several hundred times that of steel) make them attractive in numerous areas of materials science research.

7. CONCLUSION

These materials developments, amongst many others, have worked to effectively shape both the present and future of American space exploration efforts. Each advancement cited has served in some way to motivate the next, and to this day, NASA continues to rely on its past research in order to ensure its bright future. As the Agency brings the Shuttle program to a close and the Constellation program into focus, more advancements will be required. But with a history in which the successes far outnumber the failures, the Agency continues to move forward in its conquest of outerspace.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
01–07–2009

2. REPORT TYPE
Technical Memorandum

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE
NASA Materials Research for Extreme Conditions

5a. CONTRACT NUMBER
SEC 51

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
R.J. Sharpe* and M.D. Wright

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
George C. Marshall Space Flight Center
Marshall Space Flight Center, AL 35812

8. PERFORMING ORGANIZATION REPORT NUMBER
M–1260

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITOR'S ACRONYM(S)
NASA

11. SPONSORING/MONITORING REPORT NUMBER
NASA/TM—2009–215901

12. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified-Unlimited
Subject Category 23
Availability: NASA CASI (443–757–5802)

13. SUPPLEMENTARY NOTES
*The University of Alabama, Tuscaloosa, AL
Prepared by the Public and Employee Communications Office, Office of Strategic Analysis & Communications

14. ABSTRACT

This Technical Memorandum briefly covers various innovations in materials science and development throughout the course of the American Space program. It details each innovation's discovery and development, explains its significance, and describes the applications of this material either in the time period discovered or today. Topics of research include silazane polymers, solvent-resistant elastomeric polymers (polyurethanes and polyisocyanurates), siloxanes, the Space Shuttle thermal protection system, phenolic-impregnated carbon ablator, and carbon nanotubes. Significance of these developments includes the Space Shuttle, Apollo programs, and the Constellation program.

15. SUBJECT TERMS
materials, silazane, polyurethane, polyisocyanurate, siloxane, thermal protection system, phenolic-impregnated carbon ablator, carbon nanotube

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			STI Help Desk at email: help@sti.nasa.gov
U	U	U	UU	24	19b. TELEPHONE NUMBER *(Include area code)* STI Help Desk at: 443–757–5802

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

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