Thermomechanical characterization of state-change materials used in a tooling system for composite materials

Shahidur Rahman
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THERMOMECHANICAL CHARACTERIZATION OF STATE-CHANGE
MATERIALS USED IN A TOOLING SYSTEM
FOR COMPOSITE MATERIALS

by
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August 2003

A dissertation submitted in partial fulfillment
of the requirements for the

Doctor of Philosophy Degree in Mechanical Engineering
Department of Mechanical Engineering
Howard R. Hughes College of Engineering

Graduate College
University of Nevada, Las Vegas
August 2007
The Dissertation prepared by
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Entitled
Thermomechanical Characterization of State-Change Materials
Used in a Tooling System for Composite Materials

is approved in partial fulfillment of the requirements for the degree of
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ABSTRACT

Thermomechanical Characterization of State-Change Materials Used in a Tooling System for Composite Materials

by

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Dr. Brendan J. O'Toole, Examination Committee Chair
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A new Reconfigurable Tooling System (RTS) is being developed for use in composite repair and prototype manufacturing. The system utilizes a state-change material that can change from a liquid slurry to a hardened solid and back to a liquid. The material in its hardened state consists of hollow glass microspheres held together by a small amount of binder to form a porous solid. Desirable properties for this material in a tooling application include: low thermal expansion coefficient, high strength and stiffness, good thermal conductivity, and high temperature stability. This is a unique material system and there is very little literature available for comparison. The main purpose of this study is to understand the bulk physical and mechanical properties of the standard state-change material and to evaluate variations from the standard that may improve these properties. Properties of interest include density, porosity, compressive strength, flexural strength, flexural stiffness, coefficient of thermal expansion (CTE), and thermal conductivity. The CTE is consistent for all heat treated specimens with an
average value of $5.7 \times 10^{-6}$ K$^{-1}$ and a standard deviation of 8.4%. The average value of the flexural strength and modulus were 3.94 MPa (571 psi) and 3.18 GPa (461 ksi) with a standard deviation of 9% and 13% respectively. Environmental effects such as thermal hardening and humidity were studied. And finally, the properties were used in a computational model to simulate the expansion and stresses generated in a tool-bed during the heating process.
ACKNOWLEDGMENT

I would like to express my sincere gratitude to my advisor Dr. Brendan J. O'Toole for his continuous guidance, encouragement and invaluable support throughout my Ph.D. studies. I also appreciate his effort to develop my research skills by allowing me to go to different technical conferences and workshop. I am profoundly grateful to him for permitting me to go to an internship.

I express my heartiest gratitude to my committee members Dr. Ajit K Roy, Dr. Zhiyoung Y Wang, and Dr. Linda L Clements for their time, comments and suggestion. My special thanks to Dr. Moses Karakouzian for serving as graduate college representative. I am very grateful to Dr. Linda L Clements for her suggestions after the proposal defense.

I would like to thank Dr. David W Hatchett and John M Kinyanjui for allowing me to use their laboratory.

I am thankful to my colleagues, Kevin Nelson, Stacy Raagas, Julio Malpica, Jogadeep Thota and my friends and family for their support.

I would like to acknowledge 2Phase Technologies and the U.S. Army Aviation Applied Technology Directorate (AATD) for their support.

Finally, I thank to Almighty Allah for giving me the ability to do this research.
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CHAPTER 1

INTRODUCTION

The primary objective of this dissertation is to investigate the suitability of a new "state-change" material for use as a component of a tooling system that can be used for fabricating polymer composite materials. The primary focus is to understand the thermal-mechanical properties of the material in comparison to traditional tooling materials. Specific objectives of the dissertation are stated at the end of this chapter. A thorough discussion of recent advances in composite tooling is presented first to provide the background and motivation for this work.

1.1 Composite Tooling

1.1.1 Traditional Composite Tooling

Composite components are increasingly being utilized in a variety of applications due to their high strength-to-weight and high stiffness-to-weight ratios. The major application areas are aircraft, space, automotive, sporting goods, marine engineering etc. Aerospace is one of the leading industries where high performance composite components are used widely. Initially, composite components were limited to secondary structures such as floorboards and engine cowlings due to limited experience with designing composite structures. However, as the mechanics of composite materials became better understood and higher quality materials have been developed, their use has increased as primary aircraft components such as flaps, wing sections, and even as the entire fuselage.
Military and commercial aircraft use composite materials in many applications because weight reduction is critical for higher speed and increased payload. Currently, there exist commercial aircraft that have a complete fuselage and wings made entirely from composite materials. Commercial airline manufacturers have increased their dependence upon composite materials to meet their ever-increasing demands for improved efficiency and lower costs. Composite materials also are used in military and defense applications, where the performance requirements may be even more demanding.

The use of graphite, carbon and Kevlar fiber composite material has been increased due to their high strength to weight ratio but the manufacturing processes employed in fabricating parts need to improve. A significant drawback to the use of composite structures in aerospace applications, whether commercial or military, is the complicated and expensive tooling required for their fabrication and repair. Many different processes exist for the fabrication of composite structures, and many different demands are placed upon tooling designs and materials. Commonly used carbon fiber-epoxy composites require processing temperature of 177 °C (350 °F). Higher performance composites are processed at 400 °C (~750 °F).

A lot of materials can be used to fabricate tools for composites materials. A vital aspect of affordable composite manufacturing is the ability to fabricate parts within tight dimensional tolerances. Residual stresses invariably arise during the processing of composite structures that can result in dimensional changes of the parts [1]. Some important factors must be considered in the tool design. For instance, the coefficient of thermal expansion of the mold material is of fundamental importance. As the tool is heated, it may change shape at a rate different from that of the composite material if the
coefficients of thermal expansion of the tool and composite material are different. At elevated temperatures, a composite material becomes rigid, whereas, it contracts when cooled. The difference in the coefficient of thermal expansion of the composite and the tool material can create geometrical inaccuracies of composite parts as well as residual stresses can be developed in it [1-17].

Another important property to consider is the thermal conductivity of the tool material. If the tool material has a low thermal conductivity, significant time can be spent simply getting sufficient heat to the composite part. Thus, curing irregularities can develop between areas of thick and thin tooling. These irregularities also translate into geometric inaccuracies and residual stresses.

Due to these restrictions, tools for composite structures are most often comprised of steel, Invar, aluminum, and carbon/BMI. With the exception of Invar and carbon/BMI materials, the tooling materials generally have a much higher coefficient of thermal expansion than the composite material being fabricated, and this expansion must be accounted for in the mold design. Also, metal mold materials generally require complex and time-consuming machining operations in order to create the tool surface, which further contributes to design complexities. For larger components, the time required to generate the surface of the tool can become unacceptable. Additionally, it can be very difficult to make any modifications to metal tooling once made, if changes to a part are subsequently identified. Thus, if part changes are required, it is often easier to make new metal tooling rather than attempt to re-work the original tooling [2]. Steel and aluminum are widely used in composite tooling and they are shaped using conventional metal fabrication techniques [3]. Vagerko [3] also described the problems of the conventional
metal fabrication technique (metal tooling) which included weight of the tool, moving and handling for further investment, justification of the investment in the numerically control (N/C) machined steel or aluminum or rolled metal skin on N/C machined stiffened frames. He also proposed to make patterns using low cost material (wood, plastic, syntactic foam etc).

Repair technology is gaining more attention. Operators of aircraft are discovering that composites are showing a better service life than metals, mainly due to their better fatigue (as reinforcement can be used in loading direction) and corrosion resistance properties. But at the same time composites are more prone to impact damage, which increases the importance of repair. As new generations of aircraft uses huge amounts of composite materials, both commercial and military operators will demand improved repair technology. Both the cost of repairs and the down-time resulting from the complexity and special facility and equipment requirements are putting severe demands on repair technology. Current repair technology is not satisfactory, and improvements are necessary [4].

Tooling costs and complexity increase as the part performance requirements and the number of parts to be produced increases. High-rate production tools are generally made of robust metals, often called hard tooling that can withstand repeated cycles and maintain good finish and accuracy. Metal tooling is extremely expensive for short production runs or prototyping; whereas, soft tooling is more economical. Soft tooling is often the term used for polymer or composite tooling. Polymer tooling is often more vulnerable to wear and typically used for low volume production. In the near future, composite tooling may be able to produce in the medium volume production sector. The
benefits of composite tooling greatly outweigh metal tooling. Composite tooling can typically be produced in half the time of a metal tool. The cost of several tools made of composite materials can often be less than one metal hard tool. [5]

During the last two decades, extensive research work has improved tool design in different areas such as rapid tooling, soft tooling, metal spray tooling reconfigurable tooling etc [1-17]. Some important research is presented in this study. Wimpenny and Gibson [6] demonstrated a metal spray tooling method for the manufacture of composite material with low thermal mass, low mass, a CTE matched to that of the component material and low cost. They also described incompatibility of the traditional release agent (PVA) with high temperature steel. Metal spray tooling gave opportunities to the end user for adjusting the process to suit requirements to manufacture large composite components of carbon fiber composite (CFC). The metal spray tooling process has been successfully employed and it is up-sizable to large aircraft primary structures [6]. Rapid tooling allows best performance in terms of cost and delay for small or medium production of composite materials. It can reduce manufacturing lead time and fabrication costs in some injection molding cases [8, 12]. Brian and Anthony [9] demonstrated selective laser sintering (SLS) to manufacture various elements of modular rapid tooling (RT) systems that include both injection mould inserts and extrusion dies. For small lot production thermal spraying can manufacture metal molds without limitation of pattern size in the rapid hard tooling method [10]. Park and Colton [11] presented a parametric study to determine dominant process parameters of tool life. Sala [13] presented a technique to manufacture hollow components using elastomeric mandrels and glass microspheres. Twigg et al. [14] demonstrated interfacial shear stresses between the tool and part during processing.
1.1.2 Reconfigurable (or reformable) Tooling

Several research organizations are working on reconfigurable or reusable tooling for composite materials. (2Phase Technologies Inc., Cornerstone Research Group Inc. (CRG), Advanced Ceramic Research Inc. (ACR) and Rensselaer Polytechnic Institute/ Northrop Grumman Corporation)

Advanced Ceramic Research Inc. (ACR) has developed water-soluble composite-tooling materials with high thermal stability and good mechanical properties [2]. Water-soluble tooling materials have been developed for complex polymer composite parts and honeycombs manufacturing processes such as filament winding and vacuum assisted resin transfer molding (VARTM). This material is available either in paste (Aquacore™), castable and machinable forms (Aquapour™ and Aquapour™ premium) or in a form that can be packed into a mold (Aquacore™ premium and Aquacore™ 8000 and 9000 series) and consists of a thermally resistant polymer blended with ceramic microspheres and/or quartz sand and plaster in the case of the castable version. After fabrication, the Aquacore™, Aquacore™ premium and Aquapour™ premium materials may be machined to net shape using conventional machine and hand tools [2].

Water-soluble sand or salt mandrels are offering high precision. A metal support rod runs through the center of a mass of bonded sand or salt that forms the mandrel shape. The filament is wound onto the soluble mandrel and then cured. After the composite part has cured, water is injected inside the part to loosen the sand or salt from the cured part. When the soluble mandrel has been flushed away, the supporting rod is removed [5].

Soluble mandrels are also expensive and require disposal of noxious materials. ACR has demonstrated a reusable mandrel system for rapid repair and fabrication of complex-
curved composites. This low-cost mandrel system quickly and easily transforms into various detailed shapes, and then functions as a traditional mandrel that is dimensionally accurate, autoclave-tolerant, rapidly removable, and reusable [5].

Cornerstone Research Group Inc. (CRG) has demonstrated the feasibility of using shape memory polymers (SMPs) for tooling applications, as both molds for external and injection molding and mandrels for filament winding. As to the SMP technology, CRG has been conducting research on SMP since 1998 under the trade name Veriflex™. Under thermal stimuli, SMPs can exhibit a radical change from a rigid polymer to a very flexible elastic state, and then back to a rigid state again. In its elastic state, SMP will recover its memory shape if left unrestrained. Veriflex™ offers several benefits in terms of manufacturing composite parts. SMP can be used to rapidly fabricate molds in its softened state and then return to its rigid state for tooling use. After curing of the composite part, the SMP can be heated above its transition temperature to its softened state and returned to its memory shape, which allows for easy demolding [18].

Daniel et al. [7] proposed a very innovative and interesting process utilizing a computer controlled reconfigurable discrete element mold to incrementally form a compound curvature part shape from a flat lay-up. He demonstrated the tooling system as: “A reconfigurable forming tool refers to a discrete element tool comprised of identical elements, usually square, arranged in a matrix as shown in Figure 1.1. While two-dimensional examples exist (e.g., the contour gauge used by handymen to transfer complicated curves), most discrete element tools are three-dimensional and capable of reproducing surfaces. Within some geometric constraints, a reconfigurable forming tool
is capable of forming an infinite variety of part shapes. Changing the vertical displacement of each element controls the shape of the surface.”

2Phase Technologies Inc. has developed and patented a rapid tooling system that provides nearly instant manufacture of detailed tools of any size. With the 2Phase system, tools can be made for fabrication or forming of any shape that can be processed at 177 °C (350 °F) or lower and at less than 689 kPa (100 psi). Higher temperature and pressure formulations are also in development. The tooling can be formed to 0.127 mm (0.005 inch) tolerance in less than 15 minutes. The technology is applicable to approximately half of the 16 billion dollar per year US tooling industry that produces non-metallic parts, from aircraft components to hearing aids [19].

Figure 1.1 Reconfigurable forming tool comprised of an array of discrete elements [7]
1.2 Detailed Description of 2Phase Technologies Reconfigurable Tooling System

The 2Phase tooling system allows master pattern shapes to be pressed into a forming bed while the tooling material is in a liquid state, which is then consolidated, and converted into a rock-like hard state. Figure 1.2 shows the 2Phase tooling system and its functionality has been described in section 1.3. The tool is now ready to be used for making parts. Once part fabrication is complete the tool may be returned to its liquid state, readying it to create a tool for a different part. This can be considered as a state-changeable tooling system – from the liquid-like state to the solid state, and back again to the liquid-like state. It is a new class of material formulations that can undergo a reversible room-temperature transition – going from liquid-like to solid with no change in volume. Use of the 2Phase system significantly reduces the cost of tooling since the tool created is reformable and thus reusable when the tool is no longer needed. The technology also removes the necessity to store bulky tools for possible future use.

The tooling systems can be rapidly configured for layup of composite parts, filament winding and production of other types of trapped parts, capture of part configuration for creation of repair patches or replacement parts, vacuum thermoforming, or open- or closed-molding of liquid resins.

Reconfigurable tooling can take the contour of any shape pressed against it. Prototype tooling can be prepared in five minutes or less and can be repeatedly transformed into different contours for different parts. The tooling can take a splash or negative that can be turned into a positive on another reconfigurable tool. After thermal hardening at moderate temperature of 126 °C (260 °F) for minutes or a few hours, depending on the size of the
tool, it can be 177 °C (350 °F) capable, can be given a CTE to match most materials system, and will be capable of use under vacuum and up to 689475 Pa (100 psi). [19]

Figure 1.2 2Phase Tooling System

A state-change material can take on the properties of nearly any particulate filler material used in its formulation. It can have the stiffness, thermal stability and CTE of hard tooling materials or the elastomeric properties of soft tooling. Transition materials will be tailored to a user's exact specification to include CTE and mechanical properties.
Since the change is accomplished at ambient temperature, a 'splash' can be taken from any stable material, such as foam block, wood, the part to be replicated, or a rapid-prototyped part from stereolithography (STL), fused-deposition modeling (FDM), laminated object manufacturing (LOM), or any machined or hand-worked material.

Concept tests of 'quasi-stable' transition materials have also been made, showing that the development of 'toolable' transition materials is possible, with the material being progressively sculpted to shape. A large, variable volume tool bed was also used to create a tool directly from a large composite helicopter component at University of Delaware. As shown in Figure 1.3, a tool (mold) was successfully completed, demonstrating the applicability of the redesigned tool bed to replacement of damaged composite components. When transition materials with three properties are developed (liquid, solid, quasi-stable state), the option will exist to go directly from 3D CAD to a formed pattern or tool without resorting to rapid prototyping, machining or hand fabrication of patterns.

Figure 1.3 Tool created from large helicopter component
Early tests have been made on tailoring the physical properties of these materials and utilizing them for both dimensional capture ('splash' tools) and the creation of male and female molding tools. Light fill can be used to create large-scale universal splash tools— including sectional tools—that can be manually transported and positioned, with 'limpet' application under partial vacuum to conform the liquid-stage tool to a surface before transition to the solid stage. In like manner a variety of 'melt-out' mandrels can be produced for wide-ranging applications as tool inserts.

In the future the prospective user will be free to specify a desired set of physical properties, such as a CTE matching that of the composite structure to be produced. The materials should be tailorable so that properties including CTE's and dimensional stability match those of all current tool materials. Potentially infinite variations of the physical and chemical properties, including tailored CTE, stiffness, elastic properties and temperature resistance are possible. The materials can be contained permanently within elastic membrane elements or can be transferred in a liquid-like state from flexible containment to holding tanks and back.

2Phase Technologies advances the following concepts:

- Modifications of tool – add or subtract contours; blend two shapes into one; form controlled-thickness offset; instantly create matched-tool set.
- Transfer from positive to negative repeatedly with no loss of accuracy.
- Reinforcement – make patterns over properly sized plug; lay, form and consolidate preforms between male and female tools; apply light tack-release forces to develop patterns with actual materials.
• Rapid hard-shell forming – thermoform and thermal hardened prepregs in one operation.
• Form over honeycomb or core material; foam between skins & cure under pressure.
• Scale complex parts up or down by transferring dimensions. See Figure 1.4.

Figure 1.4 Master of vehicle grille (left). Tool created (right) from vehicle grill master

• Perform a wide variety assembly tooling functions, holding, positioning, clamping and pressing operations.
• Use in rapid field repair tooling kits – patch tools can be formed quickly without the use of chemicals and temperature controlled materials.

Potential tooling forms, in either hard or soft tooling, include:

  o 'Splash' tooling of any scale, including segmented exterior and separable mandrel elements. These can be tools that are pressed against a surface by
partial vacuum, or they can be internally pressurized to capture interior contours.

- Open molds of any size, including multi-part designs. These can be suitable for VIP, VARTM and 'Light RTM' applications, with permanent bags or caps being formed by matched tooling. These can be temperature-controlled with liquid lines or heater elements embedded beneath the tool surface.

- Collapsible mandrels & core tools for hollow body forming. These can be used for a wide variety of applications including filament-winding, hand- or machine-layup, or co-curing.

- Trapped tooling can be fabricated in one piece without multi piece jigsaw puzzle metal tooling. This reduces not only tooling cost but also tool assembly and disassembly.

- Rapid prototype tooling of multiple part configurations can be made from one tool, vastly reducing cycle time in prototyping or fabrication on R&D parts or materials.

- Matched tooling for pressure forming and thermoforming. Temperature-controlled tools can also be produced.

- Closed molds with two or more mating components are available, and a variety of internal mandrels can be developed for use in conjunction with these molds. While initially offering 'light' pressure molds, continuing transition material development will provide RTM-capable tooling and eventually injection-mold tooling.
Autoclave tooling for a variety of applications.

Bonding fixtures can be formed to fit individual parts contours and part-to-part variations to ensure that pressure can be applied uniformly over entire surfaces.

NDI inspection part holding fixtures can be formed.

1.3 Reconfigurable Tooling Overview

1.3.1 State-change Material

The state-change material consists of a unique combination of constituent materials that make it suitable for reconfigurable tooling. Consisting of glass microspheres in a water soluble refractory binder, the tooling material, when in a fully hardened state, displays refractory characteristics and is capable of sustaining high temperatures. However, the binder is water-based, and thus can very easily be dissolved to return the tooling material to its liquid state for the purpose of reforming the tool. Additionally, when in a slurry state, the tooling material is adept to the formation of complex shapes with a high degree of surface detail.

The solution is enclosed in a frame with flexible membranes of silicon or latex on the top and bottom. A master part is pushed against the top membrane and into slurry and a vacuum cap is applied. Vacuum is then applied between the vacuum cap and the top membrane which draws the slurry up, with the top membrane, to exactly take the shape of the master. Then a second vacuum is applied to the state-change material between top and bottom flexible membranes. This removes the small liquid excess from the slurry and stiffens the tool. At this point the master part may be removed. Heat is then applied to the
tooling material while it is still under vacuum to produce a hard, stiff tool that can be used for making composite or polymer components.

The process is illustrated schematically in Figure 1.5 and a compression test specimen of the solid material is shown in Figure 1.6. The resulting tool can be used repeatedly but once it is no longer needed for part fabrication, moisture may be reintroduced into the tooling material, allowing the material to return to the original, liquid state. The process can now begin again and a new mold can be made. The tool is shown in Figure 1.7.

Figure 1.5 Reconfigurable Tooling Concept: (a) the state-change material starts as a liquid slurry, (b) the part master is pressed into the liquid tooling material and held down with vacuum, (c) excess liquid is removed using vacuum (d) heat is used to convert the molded material into a hard, rigid tool, and finally, (e) the process can be reversed to make a new tool.
1.4 State-Change Material Description

1.4.1 Glass Microspheres

The microspheres may be glass, carbon, ceramic, or metallic. The microspheres should be spherical, non-cohesive, strong, intact, moisture and chemically resistant, and hydrolytically stable. The currently available tooling material consists of readily available glass microspheres. The main technological advantage of microspheres is that the viscosity of systems with spherical fillers is always less than that of a system with fillers of any other shape, because a sphere has the smallest surface. Moreover the isotropic materials with the best strength properties are those with spherical glass inclusions. Hollow microspheres are 1-500 μm in diameter, have a wall thickness 1-4 μm, bulk densities 70-500 kg/m$^3$ (4.37 lb/ft$^3$ – 31.23 lb/ft$^3$) and apparent densities of 50-250 kg/m$^3$ (3.12 lb/ft$^3$ – 15.61 lb/ft$^3$) [20]. Solid microspheres are also available.
Shutov [20] and Sokol et al. [21] described the procedure of microsphere production where glass microspheres are manufactured in vertical tube furnaces heated by gas, e.g. a propane-butane mixture. A finely dispersed powder containing glass and porofore is sprayed into the bottom of the tower. The porofore (a chemical blowing agent) evolves gas at the melting point of the glass and inflates the partially fused monolithic particles. The microspheres thus formed are carried by the hot gas to the top of the tower where they are cooled. They are then treated with acid to improve their chemical resistance and raise their softening temperature, and finally washed with water to remove defective microspheres. Sodium and borosilicate glasses are generally used to manufacture microspheres.

Microspheres are widely used in various industries from aerospace to oil to electronics. Microspheres are used as a light-weight filler for composite polymeric material of different kinds, protective surface layers to prevent evaporation of toxic highly volatile liquid, cryogenic technology, fabrication of industrial explosives, fabrication of acoustic and thermal insulating materials, filler for paints and varnishes, targets for laser thermonuclear synthesis, fabrication of abrasive material, fabrication of polymeric composites with special properties for electronics and electrical engineering, fabrication of composites polymer putties and compounds for filling in technological surface defects etc. [22]. Addition of microspheres to a composite material enhances the properties and increases the glass transition temperature [23, 24]. Soo-Jin Park et al. [25] analyzed that hollow glass microsphere-filled composites showed higher surface free energy, higher fracture toughness, lower coefficient of thermal expansion, and lower dielectric constant than those of neat epoxy matrix. And, the glass transition temperature
and mechanical interfacial properties of hollow glass microsphere-reinforced composites studied were significantly higher than those of neat epoxy resins.

1.4.2 Sodium Silicate Binder

Sodium silicate, also called water glass or Soluble Glass, is any one of several compounds containing sodium oxide, Na₂O, and silica, Si₂O, or a mixture of sodium silicates varying ratios of SiO₂ to Na₂O, solids contents, and viscosity. Traditionally, sodium silicates are classified according to the acid from which they are derived as Orthosilicate Na₄SiO₄; Metasilicate Na₂SiO₃; Disilicate Na₂Si₂O₅; Tetrasilicate Na₂Si₄O₉. They are also classified by an X-ray diffraction method according to their crystalline structure. All these compounds are colorless, transparent, glasslike substance available commercially as a powder or as a transparent, viscous solution in water. They can be dissolved in water to form a syrupy liquid. Some forms are slightly soluble, and some are almost insoluble; they are best dissolved by heating with water under pressure. The solutions are strongly alkaline.

A binder can be a liquid or solid that forms a bridge, film or matrix filler that causes a chemical reaction. This definition is very applicable to sodium silicate since silicates can be either liquids or solids. The diverse chemistry of silicate means that it can bond by forming a film, react to form a matrix or chemically, bond with the material being agglomerated. Dissolved or liquid silicates are the most popular commercial form of sodium silicate for agglomeration applications. The most important property of sodium silicate is the weight ratio of SiO₂:Na₂O. Silicates are commercially produced in the ratio range of 1.5 to 3.2. There is not one ideal silicate ratio for use in agglomeration applications. Having said that, high “3.2” ratio silicates tend to be the most commonly
used. The selection of silicate ratio will be based on such things as: type of binding mechanism, set-up time needed, material being agglomerated, etc. Sodium silicate is unique in that it can undergo four very distinct chemical reactions. These reactions have been defined as: hydration/dehydration, gelation, precipitation, and surface charge modification. These reactions allow silicate to act as a film binder, matrix binder and chemical binder. Silicate can be adhered to an agglomerated material by one or more of its chemical reactions. Sometimes silicate-based formulations achieve their best performance by taking advantage of more than one of these adhesion mechanisms. The diverse chemistry of sodium silicate along with the many commercial varieties of silicates presents a complex choice for those who wish to agglomerate with sodium silicate [26].

Sodium silicate is used to manufacture the state-change material syrupy liquid. Serving a dual purpose, the binder lubricates the microspheres when in a slurry state and glues them together when hardened. When wet, the binder material individually coats each microsphere; however, when a vacuum is applied, due to capillary action it remains only at contact points between the spheres.

1.4.3 Polyglycol Plasticizer

Plasticizer is added to a polymer to modify its properties making it easier to process and/or meet application requirements such as improved toughness or flexibility. Plasticizers function by internal solvation of the polymer chains. Plasticizers are chemicals that modify the physical properties of a basic polymer. Plasticizers are chemically and thermally stable compounds, ranging from solids to liquids. They are used in plastics to impart flexibility, resilience, and softness to various polymers, and to
reduce brittleness [27]. Propylene glycol is used in some of the state-change material formulations as a plasticizer to increase the state-change material's ductility.

When plasticizers are used in the correct proportion to the polymer, they impart flexibility by relieving the molecular rigidity of the material. The type of plasticizer, or combination of plasticizers, and its ratio to the polymer can be optimized to obtain the desired properties. The plasticizer and the polymer must be at least partially soluble or miscible in each other.

Propylene glycols play a significant role in industry due to their wide range of practical application, such as antifreezes, coolants and aircraft deicing fluids, heat transfer fluids, solvents, food, flavors and fragrances, cosmetics and personal care products, pharmaceuticals, chemical intermediates, hydraulic fluids, plasticizers, thermoset plastic formulations, etc. Propylene glycol industrial grade (PGI) from Dow is the preferred propylene glycol for manufacturing high-performance, unsaturated polyester resins for many uses such as reinforced plastic laminates for marine construction, gel coats, sheet molding compounds (SMC), synthetic marble castings etc [28].

Tripropylene glycol regular grade (TPG) is typically used as an initiator for urethane polyol synthesis from epoxides and as the polyol in some polyurethane foam systems. TPG from Dow is an excellent solvent in applications where high solvent power is needed. Its water solubility, solvent power, low volatility, and high boiling point make it a material of choice for textile soaps and lubricants, cutting-oil concentrates, and many similar products. TPG is also used as an initiator for urethane polyols [28, 29].

1.5 States-Change Family of Materials

Very little literature was found on the 2Phase state-change material. However quite
extensive research has been done on a similar type of material known as syntactic foam. Some of the useful research work for this dissertation is mentioned in this section.

1.5.1 High Void Content Syntactic Foam

Syntactic foams are a special kind of particulate composite material made by a matrix (binder) and a gas-filled aggregate (filler) consisting of hollow spherical microspheres. These composite materials are classified as foams since they possess a structure formally similar to that of a cellular, gas-expanded, solidified liquid. Syntactic foams are normally tertiary systems, since matrix and gas-filled aggregate are usually made of different materials: thermosetting polymers such as epoxy and phenolic resins, polyimides, sodium silicate, polyurethanes and silicones are often used as binders; glass, carbon, metal, and resin made of microbubbles are frequently taken as fillers. However, syntactic foams are basically classified as two-phase systems, when they do not contain dispersed air bubbles between binder and filler (vacuum manufacturing), or as three-phase systems, when air bubbles are included, in some cases on purpose, in view of lowering the foam density.

The binders used to make syntactic foams must have low viscosities, easily controlled gelation times, small exothermal effects during curing, small curing shrinkages, and good adhesions and wettabilities to the filler, and they must be compatible with modifiers and fillers such as diluents, plasticizers, dyes and antipyrogenes. Syntactic foams are processed using free pouring, molding, casting, or extrusion, depending on the binder and filler fraction. A typical manufacturing process consists of the mixing of the microspheres and binder and then filling of the mold or structure, with mixing and curing. The binder/filler ratio determines the fluidity and hence the process technology for a given syntactic composition. The lower limit of apparent density is at the concentration at
which the filler is most densely packed; at this point the material has its highest specific strength. The closest packing of the spheres within the binder is obtained when the material is mixed and cast or molded under vacuum. Lower apparent densities can be obtained by allowing air intrusions into the binder.

Extensive research work has been conducted [30-62] on syntactic foam and some important points are discussed in this section. The properties and densities of the mixtures and their resultant syntactic foams not only depend on the binder/filler ratio but also on the microspheres themselves, their size, sphericity, polydispersity, apparent and bulk density, thickness and uniformity of their shells. The bulk density of microspheres increases the final strength of the material. The larger spheres have lower apparent densities because they have thinner walls. If they could be made with thicker walls, the resultant syntactic material would be stronger.

Presence of hollow spheres in the matrix material makes syntactic foams a two-phase material, as shown in Figure 1.7 A. Existence of significant amount of voids in the polymer matrix of a two-phase syntactic foam gives rise to three phase structure (Figure 1.7 B). Sometimes, depending upon the application, a three-phase structure is derived intentionally, with a view to obtain lower density but higher specific strength foams. Hence, entrapment of voids due to mechanical mixing of raw materials in syntactic foam structure is considered beneficial where structural applications are concerned.

Low degree of water absorption is one of the peculiar properties of syntactic foams; it mainly depends on the chemical and physical properties of filler and binder and their volume ratio. Thermal properties are normally dominated by the matrix characteristics; among polymers, polyimides show the best mechanical properties at increasing
temperature. Syntactic foams are also characterized by good thermal insulation and dielectric properties. Concerning the mechanical behavior, syntactic foams display at best uniaxial compression strengths of about 100 MPa (14.5 ksi), hydrostatic compression strengths around 150 MPa (21.75 ksi), uniaxial tension strengths of about 25–30 MPa (3.62 – 4.35 ksi), tensile Young’s modulus around 2500–3000 MPa (362 -435 ksi) and the behavior in compression is quite ductile, whereas tensile response is rather brittle [30].

Figure 1. 7 A representative sketch showing (A) the two-phase structure involving micro balloons and the matrix material, and (B) three phase structure due to the presence of voids.

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The spectrum of engineering applications of syntactic foams is quite broad. First and more significant applications of syntactic foams date back to the 1950s in the area of naval and marine engineering, where they have been used for structural elements such as hulls, ribs and decks, for components at deep depth (up to 12,000 m (3937 ft)) such as submarines, submerged buoys, deep sea platforms and pipe joints, and for shielding and repairing submerged apparatuses. Syntactic foams are often used in civil and industrial engineering, in construction and as an imitation of wood and marble; often they are employed as core materials due to good shear stiffness and strength, fatigue and impact resistance [30-62]. Syntactic foams made with glass and more often carbon microbubbles are widely used in aeronautical and aerospace engineering as fillers of alveolate structures and as protection shields for space vehicles and missile heads. In the automotive industry, syntactic foams have been used for spoilers, dashboards and roofs. They are also employed in the electronics and telecommunication fields for shielding electronic components or cables from vibrations, electromagnetic fields, radiations and high temperatures.

The most significant research during the last two decades on syntactic foams is pointed out here. The specific properties of syntactic foam depend on the types and volume fractions of microspheres utilized in the syntactic foam; an increase in microsphere density and the thickness-to-radius ratio leads to an increase in specific tensile stiffness [31]. The strength of syntactic foam decreases with increasing void content in it [32]. Compressive properties and the fracture characteristics of syntactic foams have some dependence on the wall thickness of microspheres [33]. Fiber inclusions improve the mechanical properties of syntactic foams [34-36]. Koopman et al.
[37] studied the microstructural failure mode after three point bend tests and compression tests and found that strength and interface strength of the microspheres play big role on foam performance. Song et al. [38] showed that with confinement the syntactic foam has a higher modulus of elasticity and yield strength, both of which are sensitive to strain rates. In multiaxial loading conditions (with confinement), the capability of energy absorption of the syntactic foam is significantly increased through the elastic–plastic-like responses. The lateral confinement restricted the evolution of cracks in specimens. Instead of forming large and long cracks, small and short cracks connected glass-microspheres in specimens that collapsed under one dimensional strain loading, resulting in a continuation in load-bearing capability to large strains. Ho Kim and Plubrai [39] presented a unique technique to manufacture syntactic foams as well as failure mechanism of the syntactic foam. Prabhakar [40] measured effective elastic modulus of syntactic foams. Songn et al. [41] showed the temperature effect on the dynamic compression of syntactic foams. The syntactic foam underwent softening with increasing (or decreasing) temperature when the temperature was above (or below) the transitional value. The syntactic foam has a transitional value of environmental temperature. Glass transition temperature, Tg, varies with neat resin in the foam [42]. Sauvant-Moynot et al. [43], Gupta and Woldesenbet [44] studied hygrothermal/hydrolytic aging of syntactic foam and they showed that modulus and strength decreases notably with water absorption in syntactic foam at some temperature close to 70 °C (158 °F). Hybrid insulation manufactured using syntactic foam and aerogel gives high thermal resistance, and low compressive strain with varying hydrostatic pressure makes it attractive for potential wetsuit and underwater pipeline insulation [45]. Heat diffusion within the syntactic foam.
is inhibited by the hollow microspheres and the crosslinking of the resin at their surface is hindered [46]. So homogeneous curing is generally not achieved by normal heating. In contrast, microwave curing energy directly activates the polymerization, excluding the heat conduction. Palumbo and Tempesti [46] showed the different mechanisms of failure of syntactic foam between normal heating and a microwave curing system due to a greater homogeneity of the microwave-cured syntactic foam. Fine et al. [47] discussed high temperature syntactic foam and concluded that syntactic foams exhibit good performance at 150 °C (302 °F) as expected from the matrix selection. Besides all the above research, Engin and Raman [48] studied closed-cell silicon carbide foams and characterized the mechanical and thermal properties. Ho Sung Kim and Mitchell [49] studied impact performance of syntactic foam. Gupta and Maharsia [50], and Maharsia et al. [51] studied syntactic foam with nanoclay and rubber inclusion, Palumbo and Tempesti [52] studied hybrid composite beam with fiber reinforced syntactic foam cores. Balch et al. [53], and Balch and Dunand [54] studied aluminum matrix / hollow ceramic microsphere syntactic foams. Chavez et al. [55], Gladysz et al. [56] studied carbon microballoon (CMB) syntactic foam for high strength foam and Shabde et al. [57] analyzed thermal conductivity of syntactic foam. Bardella and Genna [58] examined syntactic foam analytically, experimentally and numerically and the results showed that the technique has the capability of predicting the elastic moduli of real syntactic foams. Gupta et al. [59] showed that the aspect ratio (height/width) has some effect on the compressive strength and modulus of syntactic foam. Medhat and Hareesh [62] studied dynamic fracture behavior under low velocity impact loading on functionally graded syntactic foam.
Some cases syntactic foam is manufactured in a similar fashion as 2Phase material as its requirement. All the information found from the research discussed above can be utilized for 2Phase material to control or improve its utilities.

1.6 Objectives of the Dissertation

There is still a need for a better fundamental understanding of the behavior of the new state-change tooling material and system. The primary objective of this dissertation is to develop a fundamental understanding of the thermal-mechanical properties and behavior of the hardened state change material. The objectives of this dissertation are to:

1) Determine the mechanical and thermal properties of state-change materials
2) Investigate the effect of individual components on the properties of the state change material. Components of interest include:
   • Microspheres
   • Binders
   • Plasticizers types
3) Determine the environmental limitations of the state-change material (temperature and humidity effects)
4) Unit cell modeling of state-change materials to estimate overall tooling material properties based on the individual component properties
5) Use the experimentally determined material properties to simulate the deformation and stress distribution of a typical composite mold subject to normal handling loads and temperature changes.
CHAPTER 2

BASELINE CHARACTERIZATION OF STATE-CHANGE MATERIAL PROPERTIES

A series of experiments were conducted to measure the properties of the proposed tooling material. First the properties of the baseline material were needed to serve as a standard and to check its worthiness as a composite materials tooling system. These properties were also required as a reference for comparison when the base materials or processing methods are changed. Thermo-mechanical analysis (TMA), thermo-gravimetric analysis (TGA)/differential scanning calorimetry (DSC), flexure tests, compression tests and scanning electron microscope (SEM) images of the baseline material are reported in this chapter. TMA tests were performed to determine the coefficient of thermal expansion (CTE), which is a big issue for the dimensional accuracy of tooling materials. TGA/DSC tests were conducted to measure the mass lose and find the glass transition (Tg) temperature of the material. Flexural and compression tests give information about the strength of the material and SEM images help to analyze the structure and failure mode of the material microscopically.

2.1 Brick Making

Making material characterization test specimens directly from a tool bed is difficult because the material becomes stuck in places to the membrane. Besides that, the tool bed
can be damaged if whole pieces of solid-state material are taken out of the tool bed. It also wastes a lot of material if a big chunk of material is collected to perform a few tests. For these reasons several small tool beds have been made to make small bricks for the material property experiments. The brick is fabricated in a similar fashion to what the tool bed material experiences during tool formation. The small tool bed material is processed and tested to find the results best suited to matching the program objectives.

A microsphere-based material with a matrix of sodium silicate binder is used to make a test bar. The test-bar processing technique permits to preparation of appropriate mixtures of microspheres and binder with known composition and processing conditions. This information can be fed back into future system designs and to address particular customer needs. A separate system is used to make test bars. The equipment for the test bar making consists of four major components: 1) a tool bed frame with standard “active-vacuum” seal and an aluminum frame with plumbing, 2) a flexible silicone test bar mold with screen at the bottom that allows easy removal of the thermally hardened test bar, quick cleaning and fast turn-around for the system, 3) a removable box furnace for rapid heat curing, and 4) a vacuum/liquid control system and liquid reservoir filter housing to introduce and extract custom binder solutions independent of the standard tool bed tank. The vacuum source is provided by a standard base station.

Sodium silicate solution (77.7% sodium silicate and 22.3% water by volume) is poured into microspheres. The binder solution in the mixer is 15% by volume or 25% by weight of total volume or total weight. Usually PQ Extendospheres SG type microspheres are used to make test bars. The microspheres are washed and pre-wetted with sodium
silicate of specific gravity 1.3. In some test bars 0.7% propylene glycol is used as plasticizer. The specific gravity of extracted liquid is 1.15.

2.2 Baseline Brick Characterization

2.2.1 Thermal Mechanical Analysis (TMA)

A NETZSCH TMA202 was used to determine the linear coefficient of thermal expansion (CTE) of the state change material. Cylindrical specimens with a height and diameter of 7.3 mm (0.287 inch) were tested with a nitrogen purge and the data was calibrated with a sapphire test standard. The tests were performed after curing the state-change material at several different temperatures from 150 °C (302 °F) to 500 °C (932 °F). Specimens and equipment set up for the TMA test are shown in Figure 2.1

2.2.2 Flexural Strength

A four-point flexural configuration was used as shown in Figure 2.2. Aspects of three ASTM test standards were used to prepare a flexural test procedure for this unique material. No single standard was found appropriate for this material, although several standards were observed to contain information specific to a number of the individual desired testing requirements. As a result, a “composite standard” was created, taking appropriate and compatible preparations, procedures and analyses from ASTM standards for mortars C580-98, glass-fiber reinforced concrete C947-99, and unreinforced and reinforced plastics D6272-02.

A span length (L) of 203 mm (8 inch) and a height of 14.2 mm (0.559 inch) provided a span-to-depth ratio of 16. The edges of some of the specimens had been damaged during cutting; these were tested at a smaller span to ensure a minimum of 25 mm (0.984 inch) of overhang on each support rod. Special fixturing for uneven, rigid specimens was
developed and utilized, as per ASTM standard C947-88, to prevent eccentricity of loading (see Figure 2.3).

All flexural tests were conducted on a United SSTM-1 universal testing machine with a 4.4 kN (989 lbf) load cell and an LVDT mounted underneath the specimen at the centerline for measuring deflection. A rate of crosshead motion was calculated, with a value of 1.4 mm/min (0.055 inch/min) for the four-point loading scheme.

Force and deflection data were recorded and the following equations used to produce stress-strain curves. The failure stress was determined from the highest force reading and the modulus of elasticity was determined from the initial linear slope of the stress-strain curve.

2.2.3 Thermal Conductivity

A Mathis Instruments TC Probe™ was used to determine the thermal conductivity of the state change material. Tests were carried out with specimens of interest in direct contact with probe sensors. When a test begins, a small amount of current passes through the wires in the sensor. Some of the heat generated from the heating wire penetrates into the specimen while some of the heat is trapped within the sensor. The more insulative the specimen, the more heat is trapped and the higher the temperature rise. The probe compares the rate of temperature rise with known specimens to generate the thermal conductivity of the tested specimen. The specific specimen dimensions were 12.7 mm x 12.7 mm x 76.2 mm (0.5 inch x 0.5 inch x 3 inch).
Figure 2.1 TMA test apparatus (A), specimens (B) and test set up (C)
2.3 Results

2.3.1 Coefficient of Thermal Expansion (CTE)

A large number of specimens were tested to determine the CTE value for the state-change material subjected to no thermal hardening (no heating). A minimum of 3 specimens were tested for each thermally hardened temperature. The CTE value is very consistent for specimens that were thermally hardened above room temperature. Figure 2.4 shows a typical elongation curve versus temperature for one specimen from each thermal hardening range. The average CTE value for the specimens with no thermal hardening was $2.65 \times 10^{-6} \text{ K}^{-1}$. The linear range of the elongation curve went from room
temperature up to 53 °C (127 °F) and then the specimen contracts while being heated from 53 °C (127 °F) to 130 °C (266 °F). The specimen expands very rapidly above this temperature. The contraction phase disappears for all the heat treated specimens and the linear range increases approximately 50 °C beyond the thermally hardened temperature for all heat treated specimens. Table 2.1 summarizes the CTE value in the linear range and the maximum temperature in the linear range. The CTE is consistent for all heat treated specimens with an average value of $5.7 \times 10^{-6} \text{ K}^{-1}$ and a standard deviation of 8.4%.

![Figure 2.4 Elongation versus temperature during the thermal mechanical analysis (TMA) experiments for specimens subject to different thermally hardening](image)

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Table 2.1 Thermally hardening effect on CTE and the maximum temperature of the linear range

<table>
<thead>
<tr>
<th>Thermal hardening Temp. (°C)</th>
<th>Average CTE (1/K)</th>
<th>Maximum Temperature of Linear Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.65 x10^-6</td>
<td>53</td>
</tr>
<tr>
<td>150</td>
<td>6.14 x10^-6</td>
<td>200</td>
</tr>
<tr>
<td>200</td>
<td>5.50 x10^-6</td>
<td>250</td>
</tr>
<tr>
<td>250</td>
<td>5.35 x10^-6</td>
<td>300</td>
</tr>
<tr>
<td>290</td>
<td>5.22 x10^-6</td>
<td>340</td>
</tr>
<tr>
<td>500</td>
<td>6.28 x10^-6</td>
<td>500</td>
</tr>
<tr>
<td>Average of all Specimens</td>
<td>5.70 x10^-6</td>
<td>N/A</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>8.4%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

2.3.2 Flexural Strength

Both the modulus and strength show a slight increase with density. The average value of the flexural strength was 3.94 MPa (571 psi) and with a standard deviation of 9%. The average value of the flexural modulus was 3.18 GPa (461 ksi) with a standard deviation of 13%. A typical flexural stress-strain curve is shown in Figure 2.5. The curve is linear up to the point of brittle failure. The specimens break cleanly in one or two places simultaneously at failure as shown in the inset of Figure 2.5.

2.3.3 Thermal Conductivity

All thermal conductivity test specimens were taken from the same brick of state-change material. The average thermal conductivity value was 0.123 Wm^-1K^-1 (0.071 BTU
hr⁻¹ ft⁻¹ °F⁻¹) with a standard deviation of 7.1%. It was a preliminary expectation that the conductivity values would range somewhere in between that of air and glass microspheres, as those are the primary constituents of the hardened 2Phase material. As the material is not perfectly homogeneous and contains numerous air pockets, perfect contact cannot be made with the testing probe. As such, it is not possible that the yielded value should be that of just the microspheres or that of just air. Instead, in places that the test bar makes good contact with the probe a value similar to that of the spheres should be found and in the places where an air pocket occurs on the test bar a thermal conductivity value similar to that of air should occur. As glass microspheres and air carry thermal conductivity values of 1.1 Wm⁻¹ K⁻¹ (0.636 BTU hr⁻¹ ft⁻¹ °F⁻¹) and 0.026 Wm⁻¹ K⁻¹ (0.015 BTU hr⁻¹ ft⁻¹ °F⁻¹) respectively, an average conductivity of 0.1230 Wm⁻¹ K⁻¹ (0.071 BTU hr⁻¹ ft⁻¹ °F⁻¹) is well within the range of expectation.

Figure 2.5 Typical flexural stress/strain curve for baseline material
2.3.4 Density

2.3.4.1 Bulk Density of Flexure Specimens

Baseline properties were determined from four different bricks of material. A minimum of 4 specimens were tested from each brick. The density of the baseline material from these four batches was fairly uniform with an average value of 0.46 g/cm$^3$ and a standard deviation of 2.8%. This slight variation in density can be attributed to small variations in microsphere size, amount of binder material on spheres, and microsphere packing differences.

2.3.4.2 Solid Material Density

A Quantachrome Ultra Pycnometer was used to measure the density of just the solid material within each specimen. It measures the density of porous materials based on the Archimedes principle of fluid displacement and Boyle's law to determine the volume. It measures the material density of each specimen five times. A gradient in the solid material density from top to bottom is observed. The top has the highest density and the middle portion possesses the lowest density. This can be caused by the amount of small spheres floating next to the surface of the brick. In the middle, the brick may contain larger spheres that are not able to fill up all the spaces. Finally, broken spheres, which are not buoyant, are settled at the bottom of the brick along with the largest spheres. This means that debris fills up the cavities present in the bottom portion.

2.3.5 Porosity

The porosity is determined using the following equation:

\[
\text{Porosity} = 1 - \frac{\text{bulk density}}{\text{solid material density}}
\]
2.3.6 Summary of Density and Porosity Data

The numerical values for the bulk density, material density, and porosity are shown in Tables 2.2. The readings from the Pycnometer show us that indeed the top layer, which sits next to the brick surface, is denser than the rest of the brick. It was also shown that the bottom is the most porous layer. There exists a correlation between the density and the porosity. The smaller spheres fill up the cavities present making the material denser, therefore bringing the porosity level down. The data for the Center and Western region are similar so average values for top, middle and bottom layers of both regions are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bulk Density (g/cc)</th>
<th>Solid Material Density (g/cc)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Specimens</td>
<td>0.488</td>
<td>0.806</td>
<td>39.5</td>
</tr>
<tr>
<td>Tops</td>
<td>0.530</td>
<td>0.846</td>
<td>37.4</td>
</tr>
<tr>
<td>Middles</td>
<td>0.468</td>
<td>0.761</td>
<td>41.5</td>
</tr>
<tr>
<td>Bottoms</td>
<td>0.448</td>
<td>0.808</td>
<td>44.6</td>
</tr>
</tbody>
</table>

2.4 Tool-bed Material Characterization Procedures

The objective of this work is to determine the properties of state-change material that had been used for an extended period of time in a medium-sized tool bed. Properties are
evaluated at different locations and in different orientations within the tool bed. The medium-sized tool bed is much larger than the brick maker and thus it is important to verify that the material from the actual tool bed is comparable to the material processed in the form of bricks. The brick maker can be used for the development of new materials with tailored properties for specific applications as long as the brick material properties are similar to those from an actual tool bed.

2.4.1 Tool-bed Description

After measuring the properties of the small brick materials, tool bed material was collected from a medium-sized tool bed for testing. A medium-sized tool bed was used to generate a large block of solidified state-change material for characterization. The tool-bed material was hardened in to a relatively flat block of material. The tooling system has a rigid frame with flexible top and bottom membranes as shown schematically in Figure 2.6. A photograph of the tooling system is shown in Figure 2.7. The thickness of the block of material varied slightly because of the membrane flexibility. The block dimensions were measured approximately 914 mm (3 ft) x 610 mm (2 ft) x 25.4 mm (1.0
in). A photograph of the block after it was removed from the tool-bed is shown in Figure 2.8. The system was not designed for removal of the state-change material in the solid state so there was some cracking in the block from the extraction process.

![Toolbed ready for use, Part master about to be copied, Hardened toolbed, Fabricate part from toolbed](image)

Figure 2.7 a) Toolbed ready for use, b) Part master about to be copied, c) Hardened toolbed, d) Fabricate part from toolbed

2.4.2 Thermal Expansion Testing

Specimens for thermal expansion testing were prepared from rough cylinders cut with a hole saw and a sander with an approximate diameter of 10 mm (0.39 in). The CTE specimens were collected from three regions, center and western as well as an eastern portion of the large test brick. Each cylinder was then divided into three specimens to determine if properties change as a function of thickness as shown in Figure 2.9. All tests
to determine the linear coefficient of thermal expansion were carried out using a NETZSCH TMA202. Specimens were tested with a nitrogen purge and the data was calibrated with a sapphire test standard.

Figure 2.8 Block of material extracted from the tool bed. Cracks were induced by the removal process.

Figure 2.9 Coefficient of thermal expansion (CTE) specimen configuration
2.4.3 Experimental Results

2.4.3.1 Density/Porosity Results

The average values for all specimens are reported in Table 2.3 along with the results for the top, middle, and bottom locations through the thickness. The bulk density was highest in the top layer at 0.530 g/cc (33 lb/ft$^3$) and lowest in the bottom layer at 0.448 g/cc (27.98 lb/ft$^3$). Corresponding to this, the porosity was highest at the bottom and lowest at the top.

Table 2.3 Average bulk density and porosity data for the tool bed material

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Bulk Density (g/cc)</th>
<th>Solid Material Density (g/cc)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Specimens</td>
<td>0.488</td>
<td>0.806</td>
<td>39.5</td>
</tr>
<tr>
<td>Tops</td>
<td>0.530</td>
<td>0.846</td>
<td>37.4</td>
</tr>
<tr>
<td>Middles</td>
<td>0.468</td>
<td>0.761</td>
<td>41.5</td>
</tr>
<tr>
<td>Bottoms</td>
<td>0.448</td>
<td>0.808</td>
<td>44.6</td>
</tr>
</tbody>
</table>

The variation in bulk density and porosity through the thickness is attributed to a gradient in the amount of binder between microspheres in the state-change material. Scanning electron microscopy (SEM) was used to obtain images of the material for qualitative comparison only. It was not possible to measure specific thicknesses of binder between the spheres. Figure 2.10 shows a 50X and 190X image of the state-change material taken from the top half of the block and Figure 2.11 shows the same size images from the bottom of the block. There appears to be more broken spheres and debris in the specimen from the top half indicated more binder and a stronger bond between spheres.
There are fewer broken spheres and the spheres appear cleaner in the specimen from the bottom half of the block.

Figure 2.10 SEM images showing more broken spheres and debris in specimens from the top layer

Figure 2.11 Specimens from the bottom layer are cleaner and have less binder material
2.4.3.2 Thermal Expansion Results

A large number of specimens were tested from the tool bed material for CTE up to 177 °C (350 °F). All of the specimens were cycled through the TMA machine twice because some additional curing still occurred during the first cycle. The elongation versus temperature curves for the first cycles and the second cycles are shown in Figure 2.12 and Figure 2.13 respectively. The slope of the elongation vs. temperature curves is equal to the coefficient of thermal expansion (CTE). Two distinct groups of lines are observed in Figure 2.13. The 4 lines on the upper part of the graph are all from "top" level specimens and have a fairly consistent slope equivalent to a CTE = 6.8x10^-6 K^-1. The rest of the lines in the graph are from "middle" and "bottom" level specimens. It is hard to distinguish between these two levels. The average slope for these specimens is equal to a CTE = 5.4x10^-6 K^-1. There also does not seem to be much variation with respect to the region of the tool-bed. The overall average for all specimens is CTE = 5.9x10^-6 K^-1.
Figure 2.12 Elongation/temperature of tool-bed up to 177 °C (350 °F) during first heat-up cycle
2.4.3.3 Flexural Results

Flexural strength and modulus for the tool bed material was measured at top and bottom layers of the toolbed and it was measured in two directions (north/south and east/west). The top was significantly stronger and stiffer than the bottom and there was a
much higher standard deviation in the bottom. All of the flexure specimens failed in a brittle manner and a typical stress strain curve is shown in Figure 2.14. Table 2.4 summarizes all the flexural properties for the tool bed material.

Figure 2.14 Typical stress/strain curve for an east or west specimen.

Table 2.4 Summary of Flexural Properties from the Tool Bed Material.

<table>
<thead>
<tr>
<th>Specimen Description</th>
<th>Average Strength (MPa)</th>
<th>Standard Deviation</th>
<th>Average Modulus (GPa)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>East/West Top</td>
<td>3.79</td>
<td>9.91 %</td>
<td>3.81</td>
<td>5.63 %</td>
</tr>
<tr>
<td>East/West Bottom</td>
<td>2.78</td>
<td>17.2 %</td>
<td>2.52</td>
<td>23.0 %</td>
</tr>
<tr>
<td>North/South Top</td>
<td>3.53</td>
<td>9.90 %</td>
<td>3.4</td>
<td>4.05 %</td>
</tr>
<tr>
<td>North/South Bottom</td>
<td>2.02</td>
<td>28.7 %</td>
<td>1.8</td>
<td>10.05 %</td>
</tr>
<tr>
<td>Top Average</td>
<td>3.66</td>
<td>9.91 %</td>
<td>3.6</td>
<td>4.84 %</td>
</tr>
<tr>
<td>Bottom Average</td>
<td>2.40</td>
<td>23.0 %</td>
<td>2.16</td>
<td>16.5 %</td>
</tr>
<tr>
<td>Overall Average</td>
<td>3.03</td>
<td>16.5 %</td>
<td>2.88</td>
<td>10.7 %</td>
</tr>
</tbody>
</table>
The results show that there is a definite variation in density, strength, modulus, and CTE through the thickness of the tool bed. The material towards the top is denser, stiffer, and stronger and it has a higher coefficient of thermal expansion. This is likely due to the presence of more binder material near the top. The overall average properties of the medium sized tool bed are similar to the properties of the bricks so the brick makers are a valid method for screening new versions of the state-change material. A comparison of properties of common tooling materials is shown in Table 2.5.

Table 2.5 Properties of different tooling materials

<table>
<thead>
<tr>
<th>Property</th>
<th>Brick</th>
<th>Tool-bed</th>
<th>% Diff.</th>
<th>INVAR</th>
<th>Steel</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>0.46</td>
<td>0.48</td>
<td>5</td>
<td>8.13</td>
<td>7.85</td>
<td>2.71</td>
</tr>
<tr>
<td>(g/cc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flex Strength</td>
<td>3.94</td>
<td>3.03</td>
<td>23</td>
<td>675</td>
<td>280-1600</td>
<td>20</td>
</tr>
<tr>
<td>(MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Tensile)</td>
<td></td>
</tr>
<tr>
<td>Flex Modulus</td>
<td>3.18</td>
<td>2.88</td>
<td>9</td>
<td>148</td>
<td>190-210</td>
<td>70</td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Tensile)</td>
<td></td>
</tr>
<tr>
<td>CTE (K⁻¹)</td>
<td>5.7x10⁻⁶</td>
<td>5.9x10⁻⁶</td>
<td>3.5</td>
<td>1.3x10⁻⁶</td>
<td>12.6-13.3x10⁻⁶</td>
<td>24x10⁻⁶</td>
</tr>
</tbody>
</table>

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The binder solution of this tool-bed contains propylene glycol as the plasticizer taken. The SEM photographs were taken of some specimens of this tool-bed which do not vary significantly from those of other bricks. There appears to be a greater amount of debris and broken spheres in the top layer of the tool-bed which is opposite to the bottom layer of the tool bed. This is in agreement with the understanding that there is a greater amount of binder in the top most region of the specimen when compared to the amount of binder in the bottom region. Figures 2.15 and Figure 2.16 show the larger magnification views of the top and bottom regions, respectively. The lack of adhesion due to decreased amounts of binder in the bottom portion of the test material would help in explaining the diminished strength seen in the lower sections of the tool-bed.

Figure 2.15 Top view of specimen_UN0010, x190
Figure 2.16 Bottom view of specimen UN0010, x190
CHAPTER 3

MICROSPHERES AND BINDER CHARACTERIZATION

The components of the baseline material were characterized to determine which constituents influence the tool bed properties the most. Tool bed material properties can be predicted if the properties of constituent are known. Then the changes of tool bed material properties for a given change of in constituent properties can be predicted. The test results of TMA, DGA/DSC, and compression of microspheres as well as binder are reported in this chapter.

3.1 Thermal Analysis of Microspheres

A small cylinder with two tight fitting pistons was used for testing the thermal expansion coefficient of bare glass microspheres. The cylinder and pistons are all made from a low expansion material that looks like the sapphire test standard. One piston is inserted into the cylinder and it slowly slides to the bottom. The air resistance between the piston and cylinder keep it from falling quickly, indicating a tight tolerance. Then, microspheres are placed on top of the bottom piston partially filling the rest of the cylinder. Finally, the second piston is placed on top of the bare microspheres. This assembly is then placed in the TMA test chamber and the loading pin is set on the top piston. The TMA test set up shown in Figure 3.1. The pistons were tested by themselves without microspheres to get a calibration curve for the fixture. There was almost zero expansion of the pistons.
The microspheres tested came from a sample of spheres that were sent to us from 2Phase Technologies. The specimens were labeled M1, M2, M3, etc. Some of these specimens were retested multiple times. Data from the first few tests on the bare microspheres are shown in Figure 3.2. These curves show that the microspheres expand linearly up to 275 °C (527 °F) then it starts to contract step by step (not continuous – see
red curve in the next figure). This appears to be happening because of small spheres or debris from broken spheres blocking the clearance between the piston and cylinder. Some curves show that there is no expansion, rather a little contraction. It appears that debris is blocking the clearance between the piston and cylinder in these cases. The piston can not move freely and the little contraction is from the piston and cylinder. Individual piston-cylinder base line test showed that it contract a little but negligible.

However, the best results where the piston is not blocked are shown in Figure 3.2. The average CTE for these specimens is $5 \times 10^{-6}$ K$^{-1}$. The initial flat region in the rate of elongation vs. temperature curves may be due to settling of the spheres as they heat up.

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests also were performed for microspheres. The TGA curve (Figure 3.3) shows that a little mass change (1.2 %) occurred. Some water might be trapped in the microspheres and that has been evaporated. DSC curve (Figure 3.3) shows a little voltage instability after 280 °C (536 °F) which indicates that something is happening after this temperature.
Figure 3.2 Thermal Expansion results for bare microspheres
Figure 3.3 TGA and DSC curves of microspheres

TMA curves showed contraction after 280 °C (536 °F) and DSC curve showed voltage instability after 280 °C (536 °F). This concludes that microspheres might be softer after this temperature range and crushed or packed each other. As a result the specimen contracts after this temperature.

3.2 Compression Test

A small cylinder of 19 mm (0.75 inch) diameter and 6.5 mm (2.5 inch) height with one tight fitting piston was used for the compression test of bare glass microspheres. The cylinder and piston are all made of steel. The microspheres are placed inside the cylinder to a depth of about one inch. Finally, the piston is placed on top of the bare microspheres. This assembly is then placed in the compression test fixture consisting of two stationary
plates on the bottom and top, shown in Figure 3.4. Compression specimens were tested on the same United SSTM-1 universal testing machine at the rate of 0.0254 mm/sec ($1 \times 10^{-3}$ inch/sec) with 4.45 KN (1,000 lbf) load cell. The engineering strain was determined from both the actuator displacement and a non-contact laser extensometer. Small strips of reflective tape were applied to the specimen. Test results shown in Figure 3.5. Modulus of elasticity values were determined from the linear portion of the stress-strain curve generated with the laser strain data. The calculated modulus of microsphere is around 89.63 MPa (13000 psi).
3.2 Silicate Characterization

A few tests have been performed for sodium silicate diluted with 22% water (thermally hardened 9 hours at 66 °C (150 °F)). Some specimens of sodium silicate before and after heating are shown in Figure 3.6. The rate of elongation vs. temperature curves are shown below in Figures 3.7 and Figure 3.8. In Figure 3.7 the flat region at the top indicates that the material expanded beyond the range of the instrument. A rough estimate
of the CTE in the expansion range can be made as $\text{CTE} = \frac{\text{rate of elongation}}{\Delta T} = 0.164 \ \text{K}^{-1}$, roughly six orders of magnitude greater than the tooling material. The total elongation at 200 °C (392 °F) is about 850 %. However, the elongation is much smaller, and even negative up to about 145 °C (293 °F). Figure 3.8 shows a zoomed in portion of the elongation curve up to 145 °C (293 °F). The negative portion of the elongation curve corresponds to some of the data observed for the state-change material and the spike in CTE is occurring at the same temperature as the spike in CTE of any unheated bar specimens. The expansion of binder specimen above 200 °C (392 °F) went beyond the data acquisition capability of the instrument. So no test data was available after 200 °C (392 °F).

Figure 3.6 Sodium silicate (binder) before heating (top) and after heating (bottom)
Figure 3.7 Elongation/temperature of binder of 2Phase material

Figure 3.8 Elongation/temperature of binder of 2Phase material
The DSC and TGA tests also were performed and test results are shown in Figure 3.9. The TGA (Mass %) shows (blue curve) that the mass is reduced 20 % within 365 °C (689 °F) temperature change. This mass change is due the evaporation of water part of the binder. DSC curve (red curve) shows that the transition of the material occurred at 150 °C (302 °F). The final appearance of the material after the test looks like a solid foam. Initially the material looks like a transparent solid material.

![Figure 3.9 TGA and DSC curves of binder material](image)

3.3 Characterization of Foamy Sodium Silicate

The binder characterization discussed in section 3.2 did not give sufficient information to draw a conclusion. For this reason a different technique was used to make binder specimen for its characterization. In this technique liquid sodium silicate was
heated above room temperature to make a solid sodium silicate plate. Solid sodium silicate was heated and it started to turn into a foamy structure at 140 °C (284 °F). The heating was stopped at 190 °C (374 °F) and TMA and compression tests were performed. During heating the sodium silicate plate, a small amount load of 0.82 kg (1.8 lbs) was applied on the plate. The final shape 179 mm x 179 mm x 25.4 mm (7 inch x 7 inch x 1 inch) is shown in Figure 3.10. Rectangular specimens were made from these plates.

Figure 3.10 Sodium silicate plate (7”x7”x1”) after heating around 185 °C (365 °F)
3.3.1 TMA of Foamy Sodium Silicate

The foamy sodium silicate brick was heated up to different temperatures (210 °C (410 °F), 250 °C (482 °F) and 290 °C (554 °F)) and TMA tests were performed for every case. The test results are shown in Figures 3.11 and 3.12. In the figures specimen number C4_190C was heated up to 190 °C (374 °F) before testing. Similarly 210C, 250C and 290C mean that the specimens were heated at 210 °C (410 °F), 250 °C (482 °F) and 290 °C (554 °F) respectively. Figure 3.11 shows that the specimen started to contract after the curing temperature and after contracting up to some temperature it started to expand again. If the curing time at certain temperature is short, the specimen starts to contract before the curing temperature point (for example C4_190C_2nd_cycle, C5_210C_2nd_cycle and C5_250C_2nd_cycle shown in Figure 3.12). However the contraction rate decreases with increasing the curing temperature. Specimen C5_290C and specimen C6_290C were thermally hardened more than 8 hours at 290 °C (554 °F) and they did not contract before 480 °C (896 °F). The results show that the CTE of linear expansion of sodium silicate varies from $11 \times 10^{-6} \text{ K}^{-1}$ to $13 \times 10^{-6} \text{ K}^{-1}$ (11 parts per million (ppm) to 13ppm).
Figure 3.11 Elongation/temperature curves of sodium silicate with different heat curing

Figure 3.12 Elongation/temperature of second run of some specimens of sodium silicate.
3.3.2 Compression Test of Foamy Sodium Silicate

Rectangular compression specimens were tested on the same United SSTM-1 universal testing machine at the rate of 0.127 mm/sec (5x10^{-3} inch/sec) with 445 N (100 lbf) load cell. The test fixture consisted of one stationary plate on the bottom and a spherically seated top plate, shown in Figure 3.13, to account for any specimen misalignment. Engineering strain was determined from both the actuator displacement and a non-contact laser extensometer. Small strips of reflective tape were applied to the specimen at an approximate gauge length of at least 25.4 mm (1 inch). Modulus of elasticity values were determined from the linear portion of the stress-strain curve generated with the laser strain data.

Figure 3.13 Compression test configuration for sodium silicate
The compression test results are shown in Figures 3.14 and 3.15. The results show that strength of the specimen varies with density. Some high density specimens have lower strength due to non homogeneous density through the specimen. The calculated modulus of sodium silicate is 12.44 MPa (1,804 psi).

![Graph showing Peak Stress Vs Density of Sodium Silicate (Heated up to 185 C more than an hour)](image)

Figure 3.14 Peak stress/ density of sodium silicate
3.3.3 TGA/ DSC of Sodium Silicate

Three different samples of sodium silicate with inclusion of surfactant or without surfactant were tested. The three samples are i) Pure SSN (sodium silicate N), ii) Pure SSN +1% Dowfax 2A1 surfactant and iii) Pure SSN + 1% NIAPROOF 08 Niacet. The specimens were tested using NETZSCH simultaneous thermal analyzer STA 449 C. One TGA/DSC test was conducted from every sample. Only 10 to 15 mg of specimen was tested from each sample as the specimen expands at least three times its original volume. All three test results are shown in Figure 3.16. The TGA curves almost overlap and mass loss is around 24 %. But the DSC curves show some difference for every specimen. Pure SSN (PSSN) has the transition temperature at 155 °C (311 °F) but Pure SSN +1%
Dowfax 2A1 Surfactant (PSSN_2A1_1%) and Pure SSN + 1% NIAPROOF 08 Niacet (PSSN_08_1%) have the transition at 177 °C (350 °F) and 172 °C (341 °F) respectively.

![Mass and DSC Vs Temperature of Sodium Silicate](image)

**Figure 3.16 TGA and DSC curves of sodium silicate**

### 3.4 Simulation of Unit Cell

A unit cell was simulated in ANSYS to predict the coefficient of thermal expansion. Eight hollow spheres are modeled using shell elements. The spheres are stacked close together as shown in Figure 3.17, to form a cube of material. The edge length of the cube and radius of the spheres are 400 μm and 98 μm respectively. Solid elements are used to fill to the space between the shell elements and flat sides of the cube. The solid elements and shell elements are fused together assuming a perfect bond between microspheres and binder. Spheres are considered as microspheres and cubical part is considered as binder.
(sodium silicate) part. So the material properties of microsphere and sodium silicate are assigned to the spheres and the cubical part respectively. The calculated (from experiment) and assumed material properties of microsphere and binder are as follows:

**Sodium silicate:**
Modulus, \( E = 228.57 \text{ psi} = 1.58 \times 10^6 \text{ N/ \mu m}^2 \)
Poisson's ratio, \( \nu = 0.23 \)
Co-efficient of thermal expansion, \( \text{CTE}=12 \times 10^{-6}/\text{K or 12ppm/K} \)

**Microsphere:**
Modulus, \( E = 9000 \text{ psi} = 62 \times 10^6 \text{ N/ \mu m}^2 \)
Poisson's ratio, \( \nu = 0.23 \)
Co-efficient of thermal expansion, \( \text{CTE}=2.8 \times 10^{-6}/\text{K or 2.8ppm/K} \)

Solid45 element type was used for this simulation. Meshed structure is shown in Figure 3.17 and meshed microspheres are shown in Figure 3.18 separately. No void was considered between microspheres and binder as their bulk properties were used where void is already considered. One node was fixed and three faces, parallel to X, Y and Z are constrained in X, Y and Z direction respectively. A temperature difference of 150 °C (initial temperature 25 °C (77 °F) and final temperature 175 °C (347 °F)) was applied as structural load to the entire volume. The contour plot of the deformation in one direction is shown in Figure 3.19. Other two directions have similar results. The maximum deformation from this is 0.466963 µm which gives the maximum \( \text{CTE} = 7.68 \times 10^{-6} \text{K}^{-1} \) but the average CTE will be \( 6.4 \times 10^{-6} \text{K}^{-1} \). The properties of microspheres and binder were also varied to analyze the CTE of unit cell shown in Figures 3.20 – 3.23. Figures 3.20 and 3.21 show that the CTE of unit cell varies linearly with the CTE of microspheres and
binder. The predicted tool bed material properties are very close to the reported properties in the previous chapter.

Figure 3.17 Unit cell
Figure 3.18 Microspheres of unit cell

Figure 3.19 Contour plot of deformation of unit cell under certain temperature change
Figure 3.20 CTE of unit cell/ CTE of glass microspheres

Figure 3.21 CTE of unit cell/ CTE of sodium silicate

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Figure 3.22 CTE of unit cell/ modulus of microspheres

Figure 3.23 CTE of unit cell/ modulus of binder
CHAPTER 4

ENVIRONMENTAL EFFECTS ON BRICK PERFORMANCE

Different environmental conditions were applied to the baseline material and tested to find out the influence of a humid environment and of thermal cycles on the material. The TMA test results of conditioned (placed in humidifier) specimens, multiple cycles of same specimen, and thermally hardened at high temperature specimens are discussed in this chapter.

4.1 Thermal Hardening

4.1.1 Single Cycle

A specimen without any thermal hardening goes through some initial contraction due to water evaporation then it starts to expand quickly due to binder expansion during heating (Figure 4.1 blue curve). When the same specimen cools down it just contracts linearly without any jump. However, it does not come back to its original position (Figure 4.1 red curve) but rather experiences some permanent deformation.
4.1.2 Multiple Cycles

Some specimens were tested multiple cycles to observe if any significant change due to heating or cooling occurred after the 1st cycle (1st thermally hardened). The results (Figure 4.2) show that there is no significant change of rate of elongation between 2nd cycle and 3rd or 4th cycle. There is a little variation in rate of elongation near the final temperature (350 °C (662 °F)). The specimen is heated a few minutes in the final temperature region and it does not have sufficient time to be hardened. These multiple cycles were run within two days so that the specimen did not have enough time to absorb water.
4.1.3 Multiple Cycles with Long Time between the Cycles

A few specimens were tested after a long time sitting in the dry weather (in a room at UNLV) after the 2nd run was completed. Figure 4.3 shows the test results, the first two cycles were performed 7/8 months earlier than the 3rd and 4th run. There is a little variation in the rate of elongation between the 2nd cycle and the 3rd or the 4th cycle. It indicates that in dry weather (weather at Las Vegas) the thermal properties do not change significantly during room temperature storage.
4.2 Moisture Content

4.2.1 Short-term Exposure to Humid Environment

A brick (UN0002) was supplied from 2Phase where it was thermally hardened up to 177 °C (350 °F) and then kept in a 70% humid environment. During the specimen a preparation (rubbed on sand papers) it was found that the lower part of the brick was weaker than the upper part. The upper part also seemed less brittle than the lower part. Due to humid environment the binder in the upper part of the brick absorbed water and
Due to humid environment the binder in the upper part of the brick absorbed water and became ductile. This causes the sticky bonding between binder and microsphere. On the other hand the lower part of the brick contains less binder and in the humid environment some bonding is dissolved. So bonding between binder and microspheres becomes weaker. Thermal expansion experiments were conducted and the data are summarized in Figure 4.4. During heating, this material initially contracted up to 130°C (266 °F) then starts to expand. The contraction occurred more in the top region than in the bottom region. The second run (2nd cycle) for the same specimens provided the same results for all regions. The average CTE for the second run is 5.5x10⁻⁶ K⁻¹.

These data indicate that the material should be heat treated again before using as a tool if it is stored in a humid environment. The difference in contraction and expansion between the top and bottom may be an indication of why the tool beds sometimes crack when stored for lengthy periods of time.
4.2.2 Long Term Exposure to Humid Environment

The brick (UN0002) of state-change material was stored in a relatively high humid environment (Bubble Box) at 2Phase Technologies, Santa Clara. TMA tests were performed and the results are shown in Figure 4.5. Test specimens were taken from three different levels through the thickness of the brick: upper, mid, and lower. The results show that all specimens go through a contraction phase during the first heating cycle, which went up to 300 °C (572 °F). This contraction begins between 50 °C (122 °F) and 90 °C (194 °F). The upper part of the brick contracts more than the middle and lower parts. The brick became very weak in the humid environment. The binder absorbs water and in
some places the bonding in the lower part of the brick is dissolved. As a result the part is
separated easily. The CTE during the second heat up cycle for all specimens was fairly
linear up to 300 °C (572 °F). The CTE varies from 2.63x10^{-6} K^{-1} to 4.04x10^{-6} K^{-1} for all
the specimens in the second cycle with an average value of 3.3x10^{-6} K^{-1}. This is a
decrease from the CTE measured when the UN0002 material was first made. The average
value of the second cycle CTE for UN0002 when it was first fabricated was 5.5x10^{-6} K^{-1}.

Figure 4.5 Thermal expansion of 2Phase material after long time storage in humid
environment
4.2.3 High Temperature Block

Several thermal expansion tests were also performed on specimens of material taken from a block that was heat treated to 399 °C (750 °F) at 2Phase Technologies. The results shown in Figure 4.6 indicate that the CTE is consistent for every test. The CTE varies from $5.5 \times 10^{-6} \text{K}^{-1}$ to $6.3 \times 10^{-6} \text{K}^{-1}$ with an average value of $5.9 \times 10^{-6} \text{K}^{-1}$. The curves of test results are shown in Figure 4.6. Several different specimens were tested from the block of the material but it was a small block and there should be no major differences between them. The data looks consistent although there are a couple of odd curves in the data that are not easy to explain. It was felt during sanding that the brick becomes weaker after thermal hardening. In addition, the lower part of the brick is weaker than the upper part. During thermal hardening the binder becomes foamy. As a result the binder and microsphere bonding becomes weak. The lower part of the brick contains less binder and after thermal hardening some bonding between microsphere and binder may be lost.
Figure 4.6 Thermal expansion data for material heat treated up to 399 °C (750 °F)
CHAPTER 5

VARIATION OF PRINCIPAL MATERIALS IN BRICK MAKING

Several types of microspheres and water-binder composition were used to fabricate bricks; those were water washing with and without filtering, binder-solution washing with and without filtering, and the use of commercially available prewashed spheres. The binder-water was also varied. The materials were characterized using coefficient of thermal expansion tests, uniaxial compression tests, four-point bend flexural tests, porosity measurements and thermal conductivity. This study was conducted because significant differences in material properties were observed between bricks made at different times or in different locations. It was required to determine if the microsphere preparation procedure or water-binder composition were causing these changes in the brick properties.

5.1 Brick Fabrication with Changing Microspheres Type

Seven bricks labeled 0001WT, 0002WT, 0003WT, 0004WT, 0001SLG, 0002SLG and 0001DEL were fabricated in a small rectangular mold using different type of microspheres or microspheres preparation techniques. The microspheres used to fabricate Brick 0001WT were washed in water. For Brick 0002WT microspheres were washed in water and filtered with a 3 micron filter. Microspheres in Bricks 0003WT and 0004WT both were washed in a binder solution and the microspheres in brick 0004WT were
filtered with the 3 micron filter. 0001SLG and 0002SLG bricks were made with prewashed microspheres purchased from a company called Sphere One. The last brick, 0001DEL was made from spheres that were recycled from a tooling system that had been in use for long time. All seven bricks were fabricated with a standard binder solution. Table 5.1 summarizes the above description.

Table 5.1 Seven types of brick using different microspheres

<table>
<thead>
<tr>
<th>Brick</th>
<th>Microspheres Wash Type</th>
<th>Filter Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0001WT</td>
<td>Water</td>
<td>None</td>
</tr>
<tr>
<td>0002WT</td>
<td>Water</td>
<td>3 micron</td>
</tr>
<tr>
<td>0003WT</td>
<td>Sodium Silicate</td>
<td>None</td>
</tr>
<tr>
<td>0004WT</td>
<td>Sodium Silicate</td>
<td>3 micron</td>
</tr>
<tr>
<td>0001SLG</td>
<td>Prewashed by Sphere One</td>
<td></td>
</tr>
<tr>
<td>0002SLG</td>
<td>Prewashed by Sphere One</td>
<td></td>
</tr>
<tr>
<td>0001DEL</td>
<td>Spheres recycled from an old tooling system</td>
<td></td>
</tr>
</tbody>
</table>

5.1.1 Thermal Mechanical Analysis (TMA)

A NETZSCH TMA202 was used to determine the linear coefficient of thermal expansion (CTE) of the state change material. Cylindrical specimens with a height from 6.8 to 7.4 mm and diameter of 7.8 mm were tested with a nitrogen purge and the data was calibrated with a sapphire test standard.

All seven bricks 0001WT, 0002WT, 0003WT, 0004WT, 0001SLG, 0002SLG and DEL, were tested and the results are shown in Figures 5.1-5.7 respectively. All the specimens of 0002WT, 0003WT, 0004WT, 0001SLG, 0002SLG and DEL were prepared from the middle part of the bricks. The figures show that the second cycle of every specimen expands linearly with temperature and the average CTE of 0002WT, 0003WT, 84
0004WT and DEL bricks are $5.2 \times 10^{-6} \, \text{K}^{-1}$, $5.14 \times 10^{-6} \, \text{K}^{-1}$, $5.17 \times 10^{-6} \, \text{K}^{-1}$ and $4.95 \times 10^{-6} \, \text{K}^{-1}$ respectively. The first cycles of the test results varied a little but the second cycles were consistent. The specimens from 0001WT were prepared randomly such as two specimens from lower part, two from the middle and one from the upper part of the brick. Figure 5.1 shows that the result varied through the thickness of the bricks for the 1st cycle or unheated specimen. For the second cycle every specimen expanded linearly with temperature and the average CTE of 0001WT brick is $4.42 \times 10^{-6} \, \text{K}^{-1}$. The first cycle of the tests results of 1SLG (shown in Figure 5.5) varied a little but the second cycle was consistent and the average CTE = $4.74 \times 10^{-6} \, \text{K}^{-1}$. On the other hand the 1st cycle and second cycle both were consistent for 2SLG that are shown in figure 5.6. The average CTE of second cycle of 2SLG is $4.98 \times 10^{-6} \, \text{K}^{-1}$. 

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Figure 5.1 Thermal expansion of 0001WT brick
Figure 5.2 Thermal expansion of 0002WT
Figure 5.3 Thermal expansion of 0003WT
Figure 5.4 Thermal expansion of 0004WT
Figure 5.5 Thermal expansion of 0001SLG brick
Figure 5.6 Thermal expansion of 0002SLG brick
5.1.2 State-Change Material Made with Solid Microspheres

Solid microsphere has much higher strength than hollow microspheres. A block was fabricated with solid microspheres and tested to verify its usefulness in a tool-bed. The test results are shown in Figure 5.8. A total of four specimens were tested and three of them tested for a second cycle. The test results showed that the specimens elongate linearly up to 230 °C (446 °F) during the first cycle, and then they start to expand rapidly up to a temperature of 325°C (617 °F). The specimens expand linearly during the second cycle all the way up to 500 °C (932 °F). The CTE of the linear portion of the first cycle...
varies from $11 \times 10^{-6}$ K$^{-1}$ to $12 \times 10^{-6}$ K$^{-1}$ and for the second cycle it varies from $9 \times 10^{-6}$ K$^{-1}$ to $10 \times 10^{-6}$ K$^{-1}$. The CTE of this block is almost twice the value of the CTE of the regular brick material fabricated with hollow spheres. The quick expansion is also higher in this case. Most probably the binder material proportion is higher in this block than the other blocks. The CTE might also be higher for the solid spheres than the hollow spheres.

Figure 5.8 Thermal Expansion of 2Phase material fabricated with solid microspheres
5.2 Brick Fabrication with Binder Conditioning

Several bricks were fabricated using different water-silicate ratio in the binder solution and they were labeled UN0003, UN0004, UN0006, UN0007 and UN0008. Table 5.2 describes the differences between these bricks.

<table>
<thead>
<tr>
<th>Brick</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN0003</td>
<td>Baseline material with 0.7% propylene glycol</td>
</tr>
<tr>
<td>UN0004</td>
<td>77.7% of silicate type N and 22.3% of water</td>
</tr>
<tr>
<td>UN0006</td>
<td>Diluted mixture of 65.0% of silicate type N and 35% of water</td>
</tr>
<tr>
<td>UN0007</td>
<td>77.7% of silicate type N and 22.3% of water</td>
</tr>
<tr>
<td>UN0008</td>
<td>77.7% of silicate type N and 22.3% of water</td>
</tr>
</tbody>
</table>

5.2.1 Thermal Analysis

Some specimens were prepared from the upper part and lower part of UN0003 and UN0004 bar. The test results are shown in Figure 5.9. In figure UN0003-UP and UN0003-LOWER indicate that specimens are collected from upper part and lower part of the bricks respectively. The results also showed that the upper part was elongated and lower part contracted during heating. This elongation and contraction may cause the crack in the brick during heating.

Several specimens were tested from UN0004 bar, which was prepared without Propylene Glycol and compared with the test results of UN0003 bar which was prepared with 0.7% Propylene Glycol. The test results are shown in Figure 5.10.
Figure 5.9 Elongation/temperature of the brick UN0003, prepared with propylene glycol
UN0006 manufactured at 2Phase contains less Sodium Silicate than UN0003 and UN0004. The first cycle of the tests shows that the CTE of UN0006 is less than that of UN0003 and UN0004 but for the second cycle it is higher than UN0003 and equal to UN0004. Figure 5.11 gives more idea about the CTE of UN0006. The straight lines (approximately) represent 2\textsuperscript{nd} cycle of the tests. The wavy lines represent the 1\textsuperscript{st} cycle of the tests.

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Another bar UN0007 was fabricated at UNLV with the same composition of UN0004. In spite of the same composition UN0007 is stronger than UN0004, the CTE is higher and also there is no negative CTE for the lower part of the bar. The variation of the results might be due to the use of different pump (separate pump), which might exert different pressure and take more time to reach certain level of pressure. The Figure 5.12 and Table 5.3 in the next page depicted the results. The average CTE of 2\textsuperscript{nd} cycle of same specimens of UN0007 is $5.88 \times 10^{-6}$ K\textsuperscript{-1}. 

Figure 5.11 Elongation/ temperature of the brick UN0006
Figure 5.12 Elongation/temperature of the brick UN0007

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UN0008 was one of the three bars fabricated at UNLV. A number of specimens were tested to measure the CTE of the bar. Some cracks were found in the bar after taking off from the tool bed. The curves of the experimental results are shown below in Figure 5.12. The average CTE of the bar during the first test cycle is $2.02 \times 10^{-6} \text{K}^{-1}$. The average CTE of the 2nd cycle of same specimens is $5.96 \times 10^{-6} \text{K}^{-1}$.

The test results of different bricks vary with the binder condition as well as fabrication approach. UN0003 fabricated with plasticizer (propylene glycol) has lower CTE and higher strength compare to UN0004 and UN0006. The CTE and strength of the bricks, UN0007 and UN0008, fabricated at UNLV are found higher than UN0004 fabricated at 2Phase technologies with same ingredient but separate brick maker.

![Figure 5.13 Elongation/ temperature of the brick UN0008](image)
Table 5.3 Summary of Properties to Data

<table>
<thead>
<tr>
<th>Brick</th>
<th>Bulk Density</th>
<th>Flexural Strength</th>
<th>Flexural Modulus</th>
<th>Average CTE (1st Cycle)</th>
<th>Average CTE (2nd Cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN0003</td>
<td>2.82</td>
<td>1.99</td>
<td>3.77</td>
<td>4.98</td>
<td></td>
</tr>
<tr>
<td>UN0004</td>
<td>0.42</td>
<td>2.36</td>
<td>2.26</td>
<td>3.11</td>
<td>6.37</td>
</tr>
<tr>
<td>UN0006</td>
<td>0.46</td>
<td>2.31</td>
<td>2.64</td>
<td>2.56</td>
<td>6.32</td>
</tr>
<tr>
<td>UN0007</td>
<td>0.47</td>
<td>2.97</td>
<td>3.01</td>
<td>4.41</td>
<td>5.88</td>
</tr>
<tr>
<td>UN0008</td>
<td>0.50</td>
<td>3.31</td>
<td>3.26</td>
<td>2.02</td>
<td>5.57</td>
</tr>
</tbody>
</table>

5.2.2 Scanning Electron Microscope (SEM) Analysis

With the assistance of the Electron Microanalysis and Imaging Laboratory (EMIL), the JEOL JSM-5610 scanning electron microscope (SEM) was used to take pictures and analyzed the surfaces of bricks UN0003, UN0004, and UN0006.

Specimen UN0003 is the standard recipe consisting of 77.7% of silicate, 21.6% of water, and 0.7% of propylene glycol plasticizer. Specimen UN0004 contains 77.7% of silicate and 22.3% of water; lastly, specimen UN0006 contains a 35% of water and a 65% of silicate bonding. All the specimens used for microscopy were taken from the flex test samples.

UN0003

The surface of UN0003 seemed to be very irregular, lots of debris was present on and around the spheres as shown in Figures 5.14 and 5.15. There was some type of bonding material present between the microspheres, presumed to be a mixture of the silicate bonding with the propylene glycol plasticizer. In some areas, large plaques of this
mixture were bonding the spheres with flakes of debris and other spheres already broken. The picture below shows some of the material present between the spheres.

Figure 5.14 Large plaques of bonding material were present between the spheres of brick UN0003.

Figure 5.15 This material was present in all levels of the microscopy specimen of brick UN0003.
This specimen was also extracted from a flex test bar. The surface UN0004 was cleaner than that from specimen UN0003 since not much debris was present around the spheres and the spheres were easily visualized. This can be seen in Figure 5.16. Another important aspect was that not much bonding material was present between the spheres linking them together. This was the most noticeable difference from the past specimen, which contained the propylene glycol plasticizer.

Figure 5.16 Spheres surface was cleaner than the specimen with the plasticizer (less debris presents)

Microscopic images of specimens were also taken from the flex test samples from the dilute brick UN0006 shown in Figures 5.17 and 5.18. There are no clear surface differences between these specimens and that past UN0004, they both look very similar.
and not much debris was present. The bonding of the spheres looked quite similar to that found in UN0004; there is not much bonding material between the spheres.

Figure 5.17 Surfaces seem to be free of debris and in some cases large spheres presented corrugated surfaces (UN0006).

Figure 5.18 Surfaces with impurities that seemed corrugated where observed quite often of UN0006.
As seen in Figures 5.17 and 5.18, there seems to be a great difference in sphere bonding with the plasticizer. It is now important to try to correlate the observed surface and bonding characteristics with the results from the mechanical and CTE testing.

Standard Solution Material

SEM images of specimens using standard solution of water and binder with plasticizer conclude that there is an increase in the distribution of the binder at the top portion of the test bricks compared to a relatively low distribution at the bottom. This is evident when viewing pictures of the material, as there appears to be many more broken spheres in the top region compared to the bottom. This would indicate a larger amount of adhesion, which would in turn indicate more binder. See Figures 5.19 and 5.20. The high amount of broken spheres increased binder distribution.

Figure 5.19 Top view of the standard solution.
Next, when comparing the SEM of specimens containing no plasticizer solution in the standard solution, there are many visual similarities. Primarily, the amount of binder visually increases from the bottom to the top. This seems to imply that while there is a lack in plasticizer, the binder distribution is not changed. See Figures 5.21 and 5.22.
The Diluted Solution

Next, using the standard solution photographs as a comparison, it would appear that there is a relatively even distribution of the binder in the diluted solution test samples. It is possible that the increase in the amount of water in the material tends to better distribute and wash the binder throughout the microspheres. Please see Figures 5.23-5.25.
5.4 CTE of Coated Specimen

Some specimens were coated with Sodium Silicate binder material. The specimens were collected from the previous tests and they expanded linearly with temperature before coating. The material’s behavior with temperature after coating is shown in the Figure 5.26. The second cycle of each specimen expands linearly with temperature and
the average CTE of second cycle is $5.37 \times 10^{-6} \text{ K}^{-1}$. So the coating does not have any influence on the second cycle. But for the first cycle coating has remarkable effect. In the figure first cycle of the tests of all specimens (C1, C2, C3, C4, C5, C6 and C7) shows that every specimen has different nature from each other. The most probable cause can be due to water absorption during coating. Some specimens could absorb more water than other. From the figure it seems C1 absorb lot of water on the other hand C5 absorb less water (may be no water absorption for C5).

![Figure 5.26 Elongation/ temperature of coated specimen](image)

Figure 5.26 Elongation/ temperature of coated specimen
CHAPTER 6

FINITE ELEMENT ANALYSIS OF THE TOOLING SYSTEM

The finite element analysis technique is a very effective modeling tool both for design and analysis. It deduces cost during design of engineering structures. Finite element (FE) method was employed to obtain stress distribution in the tool-bed on the basis of experimental data. To investigate the effects of process parameters finite element method was used. All parameters have influence on the stress response of the tool-bed with varying degrees.

6.1 Simulation of the Tool-bed under Pressure Load

A tool-bed with a bath tub shape mold was simulated in ANSYS (the geometry was drawn in Pro-E) using material properties that were found from experiment. The meshed model is shown in Figure 6.1. Solid 95 element type was used in this model. The material properties were used as follows:

State change material: Modulus =2.85 GPa (413 ksi), Poisson’s ratio =0.23
Silicon membrane: Modulus = 8 MPa (1.16 ksi), Poisson’s ratio =0.48
Silicon tube: Modulus = 12 MPa (1.74 ksi), Poisson’s ratio= 0.48
Boundary material: Modulus =1.5 GPa (217.6 ksi), Poisson’s ration=.35

All the side surfaces of the model were fixed (Figure 6.2) in all directions. Different amount of pressure load was applied in the middle (Figure 6.2) of mold to find out the
maximum load that the tool bed can carry. After a series of case study, it was found that 500 KPa (72.5 psi) is the maximum load that the tool bed can carry. Because local tensile stress developed in the slot is equivalent to flexural failure load of the state change material found from the experiment.

Figure 6.1 Mesh of the tool-bed model
Figure 6.2 Boundary conditions and pressure load (red element in the middle)

The contour plot of first principal stress is shown in Figure 6.3.

Figure 6.3 Stress distribution in the tool-bed under pressure load in the middle of the slot

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6.2 Simulation of the Tool-bed under Temperature Gradient

A rectangular block with bath tub like slot in the middle was model to analyze the effect of temperature gradient in the state change material. The simulation gives the idea of residual or peak stress in different places of the tool-bed under a temperature gradient. Solid45 was used as element type. The material properties were as follows:
Modulus = 2.85 GPa (413 ksi), Poisson's ration = 0.23 and CTE = 6x10^{-6}K^{-1}. The mesh of the tool bed is shown in Figure 6.4. All the four side surfaces are fixed in all direction. Initial and final temperatures were applied as 298 K (25°C) and 450 K (175 °C) respectively in the whole volume. One contour plot of Von Mises stress is shown in Figure 6.5. The variation of peak stress with radius of the curvature of the bath tub model is shown in Figure 6.6. Some variation found in modulus of elasticity during experiment. So FEA was performed with different modulus of the material to find the variation of peak stress and the result is shown in Figure 6.7.

![Figure 6.4 Mesh of tool-bed with a bath tub mold](image-url)
Figure 6.5 Contour plot of Von Mises stress of tool-bed under thermal load

Figure 6.6 Stress/corner radius in bath tub model with fixed modulus
Figure 6.7 Peak stress change with modulus of the tool-bed
CHAPTER 7

SUMMARY AND CONCLUSION

This dissertation unearths important information for the new tooling system for composite materials. Extensive experimental work was performed on the proposed tooling materials to verify their usefulness. The results confirmed the worth of the proposed tooling system as the material is strong enough and has very low CTE compared to other traditional composite tooling materials. Several bricks were fabricated with variations of microspheres, binder condition and plasticizer. Thermomechanical, compression, flexural, porosity and thermal conductivity tests of the material were conducted with various testing condition. Constitutive materials were also tested to find out the individual properties. The mechanical and thermal properties of the proposed tooling materials meet requirement for the composite tooling system. Some finite element analysis (simulation of unit cell) was also performed to predict the CTE of the material. Apart from the bricks, the material was also collected from a medium size tool bed and tested in detail. The results from the bricks and tool bed were compared for all kind of testing and the results also gave good comparison. Properties of the material vary with process of the fabrication of material such as improper mixing of binder and microspheres can contain a lot of voids or weak bonding between microspheres. The strength and the CTE of the brick also can be varied through the thickness of the material.
as the amount of binder material varies. The density of the binder material also has some
effects on the strength and the thermal properties. Tripropylene glycol was used as
plasticizer in some bricks and the strength and CTE of those bricks increased. Several
types of microspheres were also used to check their influence in the strength and the
thermal properties. The thermal properties and the mechanical properties both are varied
with the microspheres conditioning or types. So choosing type of microspheres, binder
density and plasticizer are big issues to achieve expected mechanical and thermal
properties of the material.

The thermal expansion data during the heating shows that the material initially
expands and then it contract up to certain range of temperature and finally it expands
rapidly. This rapid expansion gives high CTE which is not good for any tooling material.
During the cooling the material contract linearly but has some permanent deformation.
The second cycle of the same material shows that the material expands linearly and has
low coefficient of thermal expansion which is excellent for composite material tooling
system. The microspheres and binder material (sodium silicate) were tested individually.
The microspheres expand linearly and the CTE is below the second cycle of the tooling
material. The microspheres have linear thermal expansion. But the sodium silicate
expands quickly after certain temperature and this is the main cause of the rapid
expansion of the tooling material. The binder material also expands linearly if it is
thermally hardened up to the point of certain temperature. The DSC tests results of
thermally hardened specimens confirmed that there is no unexpected change or transition
during heating the material up to 550 °C (1022 °F). But TGA shows some mass loss
during heating. TGA/DSC of microspheres does not show any significant transition
except a little mass change. But the TGA/DSC of the binder material shows some
transition at the point where it’s quick expansion starts and a significant mass loss also
was observed. Small bricks were also made using solid microspheres to check their
utility. The strength of material increases greatly but the CTE also increases. In order to
check the releasing effect some tested (TMA) specimen were coated and tested. The
results conclude that the material absorbed significant amount of water which can affect
the tooling system. Some specimens were tested several times to check their property
variation with time. The CTE of the material was not disturbed under repeated heating
and also in normal dry weather (like Las Vegas, NV) they do not change with time. The
material was stored in humid environment in short and long term basis. The microspheres
bonding became weaker in both cases but CTE decreased for the long term storage. Some
variation found in compression and flexure strength for bricks and tool bed but the
average strength and modulus are suitable for composite tooling system. FEA showed
that the peak stress developed in the tool bed directly proportional to the modulus of the
material.

Some important contribution from this dissertation:

- Determination of mechanical and thermal properties of the tooling material.
- It was discovered that material needs to be thermally hardened (heated at elevated
temperature) before fabricating composite materials where high temperature is
exerted.
- The test results for the medium sized tool-bed material supports the earlier results
for the different bricks. There is some difference in density, strength, modulus,
and CTE through the thickness of the tool bed. The material towards the top is
denser and stronger and it has a higher coefficient of thermal expansion. This is likely due to the presence of more binder material near the top. The average properties of the medium sized tool bed are similar to the properties of the bricks so the brick makers are a valid method for screening new versions of the state-change material.

- The material can be tailored according to the properties of manufacturing composite material.
- The tooling system can be used for high temperature composite material fabrication.
- High humidity exposure of the tool bed seems to cause moisture absorption in the material. The tool bed may need to be re-dried before use as a tool.
- The tool bed material thermally hardened to 399 °C (750 °F) appears to have a constant CTE and does not require any additional heating to be used up to that temperature range.
- Solid microspheres can be used where higher CTE is not a problem.
- A coating can be used so that composite part can separate from the mold or tooling material. But it needs special attention during spray coating because it absorbs a lot of water. After coating the mold or tool needs to be heated up to certain level of temperature.
- Slow heating gives less expansion of the material.
- There is also a difference in contraction between top and bottom which may be one of the reasons that some of the tools crack when stored. Liquid suction from the top of the tool bed or brick or a mold can avoid this contraction difference.
• Initial thermal expansion tests on bare spheres indicate a low value of CTE but not that much lower than the state-change material itself.

• Simulation of unit cell gave good comparison of CTE with experimental results. This simulation can be used to predict CTE of the tooling material when new microspheres type is used.

• Plasticizer can play significant role to the material strength and CTE.

• Any corner or sharp edges of any mold for composite materials fabrication needs special attention so that residual stresses do not exceed the limit of compression or tensile stress. Simple computer simulation checks those stresses easily.

Future work:

• The creep effect of the material needs to be investigated as the material distortion has been observed when test specimens sit on a heated surface or with the unbalanced support of some beam shaped flexural specimen.

• Some of the fiber reinforcements increased the strength by as much as 50%. Fiber reinforcement increased the coefficient of thermal expansion. But more research is needed to draw a conclusion because another type of fiber may decrease CTE.

• The present tool bed at UNLV is not large enough to fabricate any effective composite material in it. A bigger tool bed is needed to manage and fabricate composite parts.

• Check the quality of the fabricated composite materials in the proposed tooling system and test those to compare with standard data.

• If the tooling system needs higher strength some nano particle can be used.
• Some work is required on the rubber materials used in the tool bed to check their effect on the whole tooling system.

• Some research is needed on maintenance of the tool bed to make it available to use at any time.
APPENDIX A

SYSTEM HARDWARE

A.1 Plumbing

Six important tubes are used to control the whole system and they are shown in Figure 1.8. One tube (A) is used to transmit the liquid into the tool bed and another (B) is used as outlet. One tube (C) is used to maintain the vacuum so that the membrane of the tool bed sticks to the tooling material. Two tubes (D and E) are used to control the vacuum cap. And the last tube (F) is used to pull down the vacuum cap.

Figure A.1 Tool-bed tubing
A.2 Vacuum Cap

The vacuum cap covers the tool bed master and allows vacuum to cause the state-change material the flexible top membrane to exactly replicate the shape of the master. It consists of an aluminum frame and elastic silicone membrane.

A.3 Heater

A heater is used to harden the mold material and in some cases, to perform in-situ cure of composite materials.
APPENDIX B

UNCERTAINTY ANALYSIS

This section presents the uncertainty of experimental measured and derived quantities. Kline and McClintock equation was used to calculate the uncertainties and the equation is as follows:

\[ U(R) = \left[ \left( \frac{\partial R}{\partial x_1} U_1 \right)^2 + \left( \frac{\partial R}{\partial x_2} U_2 \right)^2 + \cdots + \left( \frac{\partial R}{\partial x_n} U_n \right)^2 \right]^{\frac{1}{2}} \]  \hspace{1cm} \text{B-1}

where, \( U(R) \) = the uncertainty in the results
\( R = \) the given function of the independent variables \( x_1, x_2, \ldots, x_n \)
\( R = R(x_1, x_2, \ldots, x_n) \)
\( U_1, U_2, \ldots, U_n = \) the uncertainty in the independent variables

B.1 Uncertainty of TMA Results

Every week the TMA machine was calibrated for precise measurement of coefficient of thermal expansion. Still it might have some uncertainty. The accuracy of TMA 202 machine is about ± 0.03% in measuring \( \Delta L \) and \( \Delta T \) both. The coefficient of thermal expansion is given by:

\[ \alpha = \frac{1}{L} \frac{\Delta L}{\Delta T} \]
where $\alpha$, $L$, $\Delta L$ and $\Delta T$ are coefficient of thermal expansion (CTE), specimen length, change of length and temperature change respectively. Using equation B-1 the uncertainty of coefficient of thermal expansion, $U(\alpha)$ is given by:

$$U(\alpha) = \left[ \frac{1}{L \Delta T} U(\Delta L) \right]^2 + \left[ \frac{\alpha}{\Delta T} U(\Delta T) \right]^2 + \left[ \frac{\alpha}{L} U(L) \right]^2 \right]^{\frac{1}{2}} \quad \ldots \quad \text{(B-2)}$$

where $U(\Delta L)$, $U(\Delta T)$ and $U(L)$ are uncertainty with associated with measurement length change ($\Delta L$), temperature change ($\Delta T$) and length ($L$).

**Sample calculation:**

$$U(\Delta L) = 0.0003 \times 0.1825 = 54.75 \times 10^{-6}$$

$$U(\Delta T) = 0.0003 \times 400 = 0.12$$

$$U(L) = 0.01$$

$$U(\alpha) = \left[ \left( \frac{1}{7.3 \times 400} \times 5.475 \times 10^{-5} \right)^2 + \left( \frac{5.7 \times 10^{-6}}{400} \times 0.12 \right)^2 + \left( \frac{5.7 \times 10^{-6}}{7.3} \times 0.073 \right)^2 \right]^{\frac{1}{2}}$$

$$U(\alpha) = \pm 1.88278 \times 10^{-8}$$

The uncertainty of the specific CTE value (5.7x10^{-6}/K) is only $\pm 0.3\%$. One example of finding uncertainty of TMA test results is shown in this section. This technique can be utilized to calculate the uncertainty for all the TMA test results.

**B.2 Uncertainty in United Testing Machine Results**

Stress and strain relationship of materials was found from the test results using united testing machine and extensometer and from the stress-strain data modulus of elasticity was calculated. Every united load cell is factory calibrated to insure that it meets required accuracy standards. The accuracy of load cells is $\pm 0.05\%$ and the accuracy of the extensometer is $\pm 0.03\%$.
B.2.1 Uncertainty in Compressive Stress $U(\sigma)$

Using equation B-1 the uncertainty of stress can be derived as follows:

$$U(\sigma) = U(P/A) = \left[ \left( \frac{\partial \sigma}{\partial P} U(P) \right)^2 + \left( \frac{\partial \sigma}{\partial A} U(A) \right)^2 \right]^{1/2}$$ ........... B-3

and the uncertainty of area is:

$$U(A) = \left[ \left( \frac{\partial A}{\partial D} U(D) \right)^2 \right]^{1/2} \text{ (for circular cross section)}$$

$$U(A) = \left[ \left( \frac{\partial A}{\partial L} U(L) \right)^2 + \left( \frac{\partial A}{\partial w} U(w) \right)^2 \right]^{1/2} \text{ (for rectangular cross section)}$$ ........ B-4

Sample calculation for rectangular specimen (2Phase material compression):

Uncertainty in load-cell of united testing machine = ± 0.05%

Maximum uncertainty of optical extensometer =± 0.03%

Uncertainty in slide calipers = ± 0.01 mm.

For yield stress (YS) = 7.63 MPa , load, P=1258.85 N

Uncertainty in load $U(P) = ± 0.0005 \times 1258.85 \text{ N}$

$= ± 0.629 \text{ N}$

Uncertainty in cross-sectional area $U(A)$ for the compressive specimen:

Length = 38.1 mm, width = 12.7 mm.

Uncertainty in length or width or height measurement $U(L \text{ or } w) = ± 0.01 \text{ mm}$.

Uncertainty in area, $U(A) = \left[ \left( \frac{\partial A}{\partial L} U(L) \right)^2 + \left( \frac{\partial A}{\partial w} U(w) \right)^2 \right]^{1/2}$

$U(A) = 40.16 \times 0.01 \times 10^{-6} \text{ m}^2$

$= ± 0.4016 \times 10^{-6} \text{ m}^2$
Uncertainty in stress, \( U(\sigma) = \left[ \left( \frac{\partial \sigma}{\partial P} \cdot U(P) \right)^2 + \left( \frac{\partial \sigma}{\partial A} \cdot U(A) \right)^2 \right]^{\frac{1}{2}} \)  

\[
\sigma = \frac{P}{A} \\
\frac{\partial \sigma}{\partial P} = \frac{1}{A} \\
\frac{\partial \sigma}{\partial A} = -\frac{P}{A^2} \\
= 2066.67 \\
= -5.367 \times 10^9
\]

Now providing all the numerical values in Equation B-5 obtained from the calculation, it is found that,

\[
U(\sigma) = \left[ (2066.67 \times 0.629)^2 + (5.367 \times 10^9 \times 0.4016 \times 10^{-4}) \right]^{\frac{1}{2}} \\
= 2520 \text{ Pa} \\
= \pm 0.0025 \text{ MPa}
\]

**Sample calculation for circular cross-section (microspheres compression):**

\[
U(A) = \left[ \left( \frac{\partial A}{\partial D} U(D) \right)^2 \right]^{\frac{1}{2}} \\
\frac{dA}{dD} = \frac{\pi D}{2} \\
= 0.0299
\]

Uncertainty in area, \( U(A) = \left[ \left( \frac{\pi D}{2} U(D) \right)^2 \right]^{\frac{1}{2}} \)

\[
U(A) = 0.0299 \times 0.00001 \\
= \pm 2.99 \times 10^{-7}
\]

Uncertainty in stress, \( U(\sigma) = \pm 13699 \text{ Pa} \)
\[ U(\sigma) = \pm 0.014 \text{ MPa} \]

This is an example of calculating the uncertainty of compression test result. Similar fashion can be utilized for other compression test results.

B.2.2 Uncertainty in Flexural Stress \( U(\sigma_b) \)

\[ \sigma_b = \frac{Mc}{I} = \frac{PL}{(wh)^2} \]

\[ U(\sigma_b) = \left[ \left( \frac{\partial\sigma_b}{\partial P} U(P) \right)^2 + \left( \frac{\partial\sigma_b}{\partial L} U(L) \right)^2 + \left( \frac{\partial\sigma_b}{\partial w} U(w) \right)^2 + \left( \frac{\partial\sigma_b}{\partial h} U(h) \right)^2 \right]^{1/2} \]

\[ U(\sigma_b) = \left[ \left( \frac{L}{wh^2} U(P) \right)^2 + \left( \frac{P}{wh^2} U(L) \right)^2 + \left( \frac{\sigma_b}{w} U(w) \right)^2 + \left( \frac{2\sigma_b}{h} U(h) \right)^2 \right]^{1/2} \]

\[ \frac{0.153 \times 0.017795}{0.0142 \times 0.0142^2} + \left( \frac{35.95 \times 10^{-5}}{0.0142 \times 0.0142^2} \right)^2 + \left( \frac{3.94 \times 10^6 \times 10^{-5}}{0.0142 \times 0.0142^2} \right)^2 + 2 \times \left( \frac{3.94 \times 10^6 \times 10^{-5}}{0.0142 \times 0.0142^2} \right)^2 \]

\[ = 6279 \text{ Pa} \]

\[ = \pm 0.0063 \text{ MPa} \]

The uncertainty of the flexural test result is \( \pm 0.16\% \). This is an example of calculating the uncertainty of flexural test. This method can be implemented for the case of the other flexural test results.
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