



GEOPOLYMER: ULTRA-HIGH TEMPERATURE TOOLING MATERIAL FOR THE MANUFACTURE OF ADVANCED COMPOSITES

Joseph Davidovits and Michel Davidovics
Geopolymer Institute, Cordi-Geopolymere SA
16 rue Galilée, F -02100 Saint Quentin, France

ABSTRACT

Geopolymers of the Poly(sialate-disiloxo) type (-Si-O-Al-Si-O-Si-O-), very-low viscosity inorganic resins, harden like thermosetting organic resins, but have use-temperature range up to 1000°C (1830°F). High-temperature techniques are no longer necessary to obtain materials which are ceramic-like in their properties. Geopolymers provide faithful reproduction of mold or die surface and allow for precision and fineness. Geopolymer composite-tooling and geopolymer castable-tooling offer direct replication, on-site construction capabilities and very short cure-cycle. They enable product designers and tool makers to envisage the use of ceramic type materials with the same facility as organic polymers. Geopolymer composite and castable tooling have been fabricated and are in use, processing APC-2 thermoplastic materials as well as PMR-15 polyimides.

KEYWORDS: Composites; Geopolymer; Manufacturing/Fabrication/Processing; Tooling.

1. INTRODUCTION

Advanced thermoset and thermoplastic composites require high processing temperature. Polyphenesulfide (PPS), linear polyimide (KIII) and polyether ether ketone (PEEK) reach temperatures of 330°C (625°F), 345°C (650°F) and 400°C (750°F) respectively during manufacture. Due to these high temperatures, careful attention to the thermal expansions is required during manufacture. The coefficient of thermal expansion (CTE) for composites comprised of graphite fiber with matrices of PPS, KIII and PEEK ranges from 4 to $8 \times 10^{-6} / ^\circ\text{C}$ ($2-4 \times 10^{-6} / ^\circ\text{F}$). It would be most desirable, especially when molding very large parts to use mold material with a CTE equivalent to that of the material being molded [1,2]. They have been difficulties in setting up dedicated tooling to manufacture aircraft parts made of advanced composites. Ceramic tooling, "once considered a bright hope for ultra-high-temperature applications, is now very much in doubt" [3]. The applications of geopolymer resins in very high temperature tooling were presented at the

last 1990 SME Tooling Conference [4]. Most of our presentation dealt with the chemical make-up of the geopolymers and their physical properties. Our young experience, in terms of tooling for advanced composites, started in 1989, when French aerospace companies like Marcel Dassault, Aerospatiale and Hispano-Suiza decided to carry out comparison tests involving American ceramic tooling materials and our geopolymer compounds. Previously, advanced geopolymer tooling materials had been successfully introduced in the thermoforming of glass, use-temperature 500-700°C (932-1292°F), and the casting of aluminum, use temperature 800°C (1472°F) [5,6].

Geopolymer resins produce tools with properties superior to those of monolithic graphite, castable ceramic and chemically bonded ceramic. The geopolymer composite formulations, Geopolymer, and the castable geopolymer resins, Geopolymite, were used to make tooling for fabrication of parts from APC-2, PEEK carbon-fiber thermo-plastic composite (ICI) and PMR15 polyimide prepreg.

2. CHEMISTRY AND PROPERTIES

Geopolymers, inorganic polymers, are semi-amorphous three dimensional networks of polymeric sodium-, potassium-, calcium- *SIALATES* (silico-oxo-aluminate). Our target with this paper is not the discussion of the chemical mechanism involved in geopolymerization, but to provide basic information. In 1978, looking for inorganic-polymer technologies, we were struck by the similar hydrothermal conditions which were controlling the synthesis of thermosetting organic phenolic resins on one hand, and the geo-chemical synthesis of mineral feldspatoids and zeolites on the other hand. Both syntheses require high pH values, concentrated alkali, atmospheric pressure, and thermoset at temperatures below 150°C. [7,8] Geopolymite, water soluble geopolymer resins, harden at room temperature, between 20°C (68°F) and 120°C (250°F) and are rather similar to thermo-setting organic resins, but are stable up to 1000°C (1830°F). It is assumed that the geo-chemical syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structures of the three dimensional macromolecular edifice, as displayed in Fig. 1.

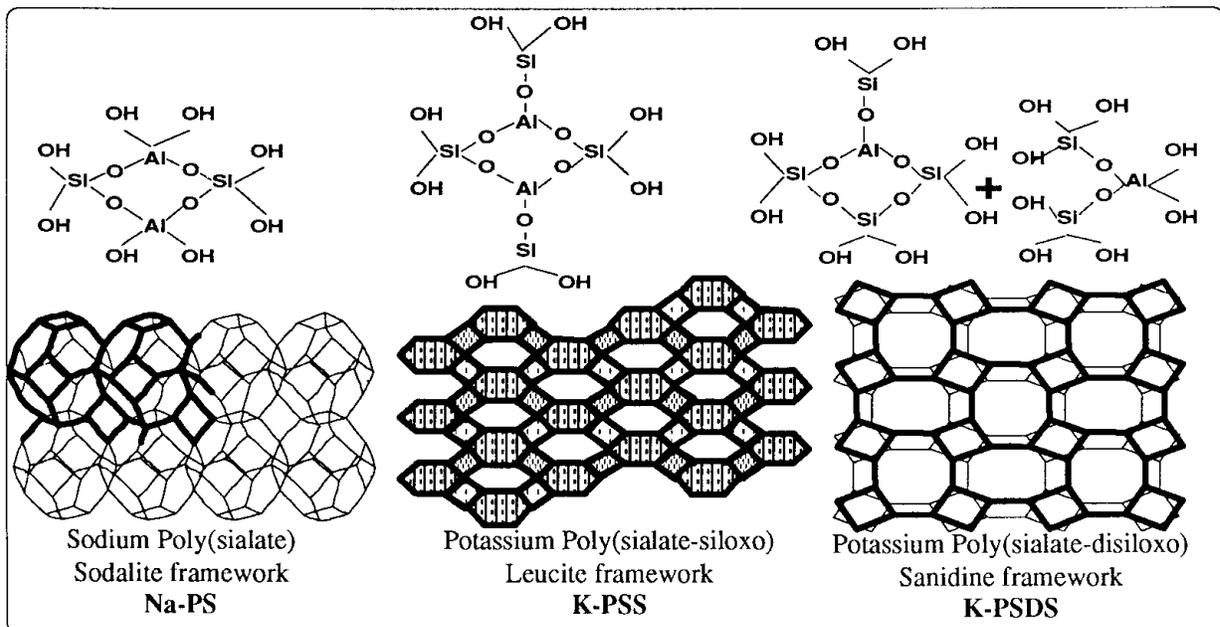


Figure 1: Computer molecular graphics of sialate oligomers and related frameworks.

Tab. 1 displays the geopolymer resins (Geopolymite) commercially available in 1990. State of the art geopolymer-tooling materials are poly (sialate-disiloxo), M-PSDS, and fluoro-poly(sialate-disiloxo), F,M-PSDS Geopolymite resins. F,M-PSDS Geopolymites, the most promising tooling resins for advanced composites with organic matrices, result from the conjunction of two advanced techniques: geopolymerization and sol-gel technology. F,M-PSDS Geopolymites [Patents Pending] comprise a geopolymeric network made of poly(sialate-disiloxo) associated with molecular silicon oxide SiO₂ embedded within the matrix. The trapped molecular SiO₂ yields a low-porosity, highly-packed microstructure, with higher density. As displayed in Fig.2 and Fig.3, physical properties of geopolymers, such as fusion temperature and CTE, are a function of the Si/Al ratio. Fig.3 displays a comparison between the coefficient of thermal expansion CTE for common tooling materials and for geopolymers (K-PSS, K-PSDS, F,M-PSDS types). CTE values measured for geopolymers are those of commercially available Geopolymite resins, without any additional filler. In the case of F ,M -PSDS formulations, CTE values increase with the amount of molecular silicon oxide SiO₂ packed inside the geopolymeric tri-dimensional network (type 1,2, 3).

GEOPOLYMITE [®]		Utilization
PS2 <i>Na-PS</i> <i>poly(sialate)</i> $M_n-(Si-O-Al-O)_n$ <i>M-PS</i>		thermal insulation, fire-resistant board,
GP 711 <i>K-PSS</i> <i>poly(sialate-siloxo)</i> <i>M-PSS</i> $M_n-(Si-O-Al-O-Si-O)_n$		refractory for aluminum casting, high-performance cements, toxic wastes, fire-resistant composites, fire-resistant composites, GEOPOLYCERAM composites,
GP 50	<i>(K,Ca)-PSS</i>	
GP 70	<i>K-PSS</i>	
GP 140 <i>K-PSDS</i> <i>poly(sialate-disiloxo)</i> <i>M-PSDS</i> $M_n-(Si-O-Al-O-Si-O-Si-O)_n$		refractory for aluminum casting, fire-resistant composites, GEOPOLYCERAM composites, tooling and structural composites for use-temperature range 650-1000°C
HTF 1 HTF 2 HTF 3 <i>(F,K,Na)-PSDS</i> <i>fluoro-poly(sialate-disiloxo)</i> <i>(F,M)-PSDS</i> $F,M_n-(Si-O-Al-O-Si-O-Si-O)_n$		fire-resistant composites, GEOPOLYCERAM composites, tooling and structural composites for use-temperature range 300-650°C

Table I: Geopolymer resins. Terminology and uses.

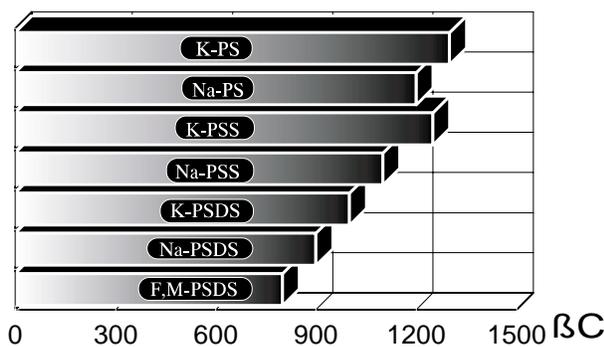


Figure 2: Fusion temperature of geopolymers

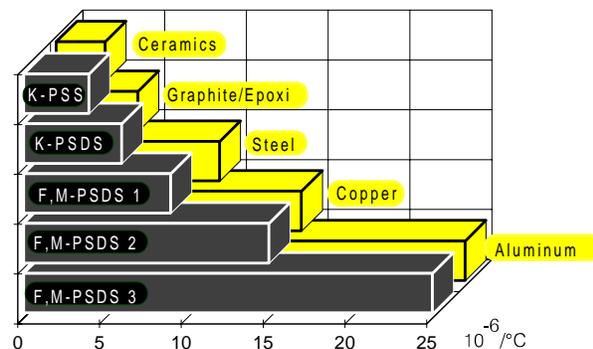


Figure 3: Coefficient of Thermal Expansion for geopolymers and tooling materials

Geopolymite resins are designed to match the CTE of steel, enabling them to be used with steel inserts or frames, or have a CTE matched to that of other metal, carbon-fiber epoxy parts, monolithic graphite, or any organic resins. The addition of low CTE ceramic fillers yields geopolymeric castable compounds providing CTE in the $2-4.10-61^{\circ}\text{C}$ ($1-2.10-61^{\circ}\text{F}$) range. The very low viscosities, in the range of 300-600 centipoises, of Geopolymite GP 140, HTF 1, HTF 2, HTF 3, advanced geopolymer resins, are very suitable for a successful impregnation of any type of fabric, sheet or non-woven reinforcement. Due to their low dehydroxylation shrinkage, Geopolymite HTF resins have been successfully implemented in castable formulations, with tailored aggregates, providing very low shrinkage at 400°C (752°F) use-temperature and flexural strength in the range of 40-45 MPa (5.8-6.5 KPSI) as displayed in Fig.4 and Fig.5.

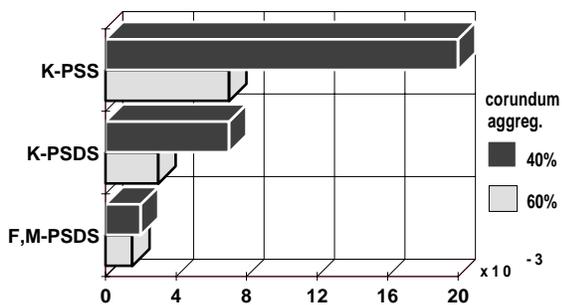


Figure 4: Shrinkage in % after heating at 400°C for Geopolymite resins containing 40% and 60% of corundum aggregates

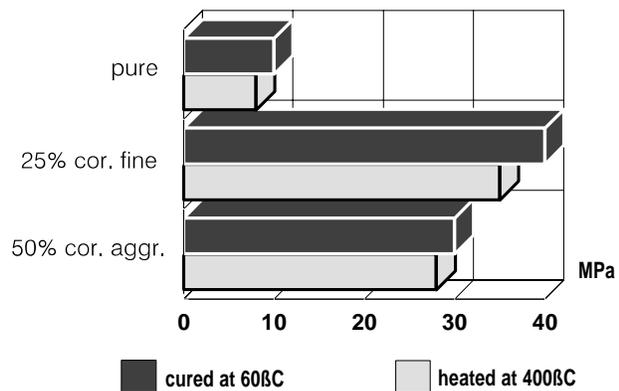


Figure 5: Flexural strength of F,M-PSDS Geopolymite HTF1 with and without fillers

3. CASTABLE GEOPOLYMER-TOOLING

Tool shapes that have a complex curvature or that include fine details, can be quickly and easily produced from geopolymer castable material. Geopolymer tools are cast under vacuum, vibration or sedimentation, over a pattern or mandrel. Geopolymite resins provide faithful reproduction of mold or die surface and allow for precision, fineness, polish and brilliance. The final tool will incorporate every detail, including the surface finish, of the pattern. Painted wood, castable epoxy patterns produce excellent results. Those made from metals or metal-filled epoxies should be avoided as the alkali-sialates in the Geopolymite will react with aluminum and some of the softer metals and can create bubbling on the surface. The cast specimens are generally cured over night at 40°C (104°F)- 60°C (140°F), demolded, then dried for one day at the same temperature.

Geopolymer tools are machinable; therefore, modifications to the mold, the part, or the process can be made during development of prototype parts or manufacturing processes. Tooling holes can be cast in situ or, to ensure accurate positioning in the stabilized tool, can be located after the tool has been cured. Damage to a geopolymer tool can be repaired. Compounds are available to repair holes, cracks, or abrasion wear. In some cases the tool can be machined or a metal insert can be installed to remove damage. Geopolymer tools displayed in Fig.6, made of F ,M PSDS Geopolymite resins and ceramic fillers, thin shell or mass cast can be used to form thermosets or thermo-plastics up to 450°C - 650°C (850°F - 1200°F). They are vacuum tight.

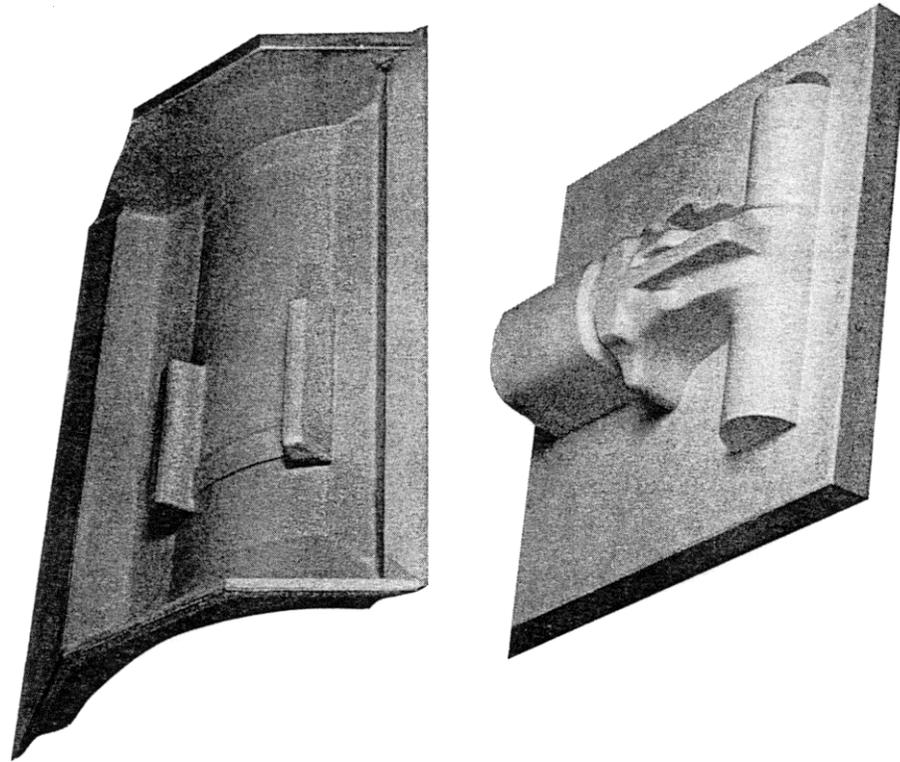


Figure 6: Autoclave and press molding tools made of castable F,M-PSDS Geopolymite resin and corundum aggregates with tailored grain size for Gel-Coat and core.

4. GEOPOLYMER COMPOSITE-TOOLING

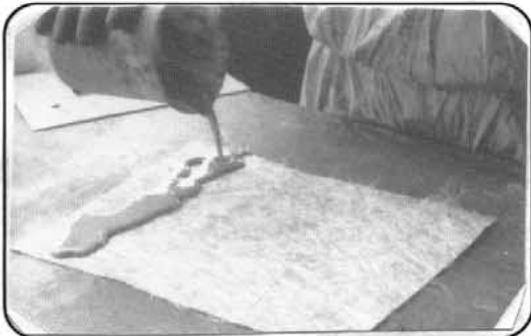
The relationship between operating temperature, flexural strength and fiber type for Geopolyceram composite tooling material, is displayed in Fig. 8. E-glass and Carbon fabrics should be used up to 450°C (842°F) with the F,M-PSDS matrix. Higher temperatures require ceramic fibers such as SiC, Nicalon fabrics, or Safil aluminum oxide fibers. In all cases, a use-temperature higher than 700°C (1292°F) implies a M-PSDS matrix. The values displayed in Fig.8 were obtained with pre-impregnated Geopolymite composite tooling material, GeopolyPreg, which offers more uniform resin content throughout the tool, reduced chance of delamination between plies, lower water content. Increased consistency can be translated into thinner, more reliable laminates, reduced labor costs, higher heat transfer, easier handling and higher mechanical properties. Vacuum integrity requires appropriate gel-coat.

Geopolymite composite-toolings offer direct replication, on site construction capabilities, and are easy to repair. Most importantly, they offer coefficients of thermal expansion very close to those of materials they are used to form, minimizing part distortion during cure. Tab.2 compares tool lay-up procedures for composite Geopolymite resin prepreg with typically recommended lay-up procedures for composite/organic thermoset resin prepreg [9]:

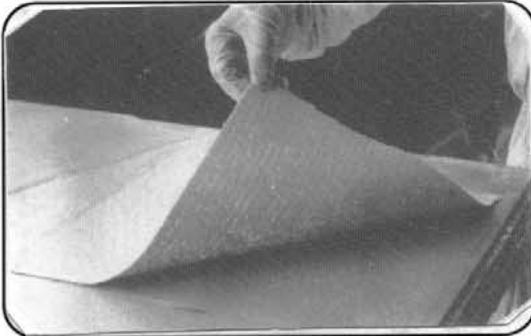
Table 2: Lay-up procedures comparison

Graphite/organic thermoset-resin tools cured by the vacuum bag method (ICI Toolrite).	Composite/Geopolymite resin tools cured by the vacuum bag method.
<p>Step 1 - Apply mold release to PFP Master. Apply wax to PFP and buff.</p> <p>Step 2 - For vacuum bag cure, gel coat is necessary for smooth finish. Apply first gel coat.</p> <p>Step 3- Use thickness gauge to assure recommended thickness of first coat. Let the initial coat take of at room temperature, then apply a second coat.</p> <p>Step 4- Start lay up as soon as second gel coat is applied. Apply three plies of prepreg. Work carefully into all corners and radii with squeegee.</p> <p>Step 5 - Begin second stage of lay up by applying four plies of prepreg.</p> <p>Step 6 - Debulk the tool at this stage. Install one or more thermocouples. Apply nylon fabric peel ply to surface and cover this with hand perfored separator film. Top with a breather layer. Bag, apply a minimum 25 in. (625 mm) vacuum and heat to 150°F(65°C) for one hour. Allow to cool, then carefully remove bag, breather, film and peel play layer .</p> <p>Step 7 - Follow with eight plies of prepreg. Apply peel ply, film, breather layer and bag.</p> <p>Step 8- To cure, heat the tool at a rate of3-8°F (1.5-4.5°C) per minute under a minimum of25 in. (625 mm) vacuum. When part temperature reaches 200-210°F (95-99°C) hold at least 6 hours. Allow cooling under vacuum to 100°F (38°C) before removing from oven.</p> <p>Step 9 - Remove bag, breather, film and peel ply. Cut support templates from egg crate or gusset board.</p> <p>Step 10 - Attach support structure to tool. Allow curing and removing tool from PFP Master.</p> <p>Step 11 - Place tool in oven. Bring temperature to 150°F (65°C) for one hour. Raise to 200°F (95°C) for one hour and then to 275°F (135.C) for another hour. Bring to final cure temperature of 350-375°F (177-190°C) and hold for two hours. Cool to 100°F(38°C) before removing from oven. Tool now ready for 350°400°F (177-205°C) service temperature.</p> <p>Note: If autoclave cure is to be used, application of gel coat is not required.</p>	<p>Step 1- Apply mold release to PFP Master.</p> <p>Step 2 - For vacuum bag cure, gel coat is necessary for smooth finish. Apply first gel coat.</p> <p>Step 3- Use thickness gauge to assure recommended thickness of first coat, apply a second coat.</p> <p>Step 4- Start lay up as soon as second gel coat is applied. Apply three plies of prepreg. Work carefully into all corners and radii with squeegee.</p> <p>Step 5 - First drying of the tool at this stage. Install in an oven to 150°F (65°C) for 10 minutes. Allow approximately 10% of water to dry out then allow cooling.</p> <p>Step 6 - Begin second stage of lay up by applying four plies of prepreg.</p> <p>Step 7- Second drying of the tool at this stage. Install in an oven to 150°F (65°C) for 10 minutes, then allow cooling.</p> <p>Step 8 - Follow with four plies of prepreg, third drying at 150°F(65°C) for 10 minutes, allow cooling and following with four plies of prepreg.</p> <p>Step 9 -To cure, heat the tool at a rate of3-8°F (1.5-4.5°C) per minute under a minimum of25 in. (625 mm) vacuum. When part temperature reaches 150°F (65°C) hold at least 2 hours. Allow cooling to room temperature before removing from oven.</p> <p>Step 10 - Remove bag, breather, film and peel ply. Cut support templates from egg crate or gusset board.</p> <p>Step 11 - Attach support structure to tool. Allow curing and removing tool from PFP Master.</p> <p>Step 12- Place tool in oven. Bring temperature to 200°F (95°C) for one hour and then to 275°F (135°C) for another hour. Bring to final cure temperature of 400°F (205°C) and hold for two hours. Cool to room temperature before removing from oven. Tool now ready for 800°F (425°C) service temperature.</p> <p>Note: If autoclave cure is to be used, application of gel coat is not required and only one drying step is recommended. Wet lay-up, without intermediate drying results in lowering flexural strength by 50%.</p>

A wet lay-up procedure used in the fabrication of tailored ladles developed for the casting of molten aluminum is illustrated in Fig. 7. However, wet lay up, without intermediate drying, provides lower flexural strength.



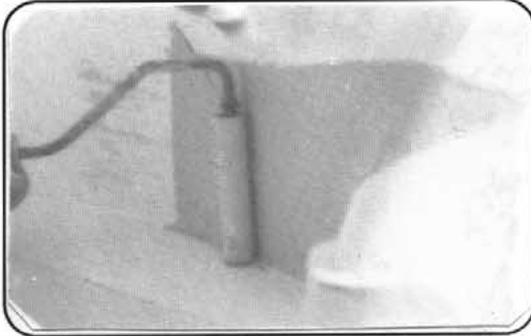
Impregnation with Geopolymite GP 140



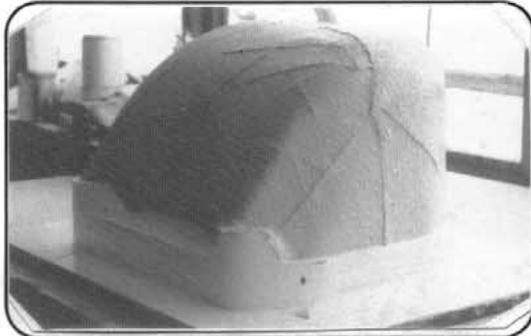
wet prepreg



applying gel-coat on PFP master



first ply



first lay



impregnating last ply



demolding after cure at 60°C

Figure 7: Wet lay-up procedure used in the fabrication of a ladle.

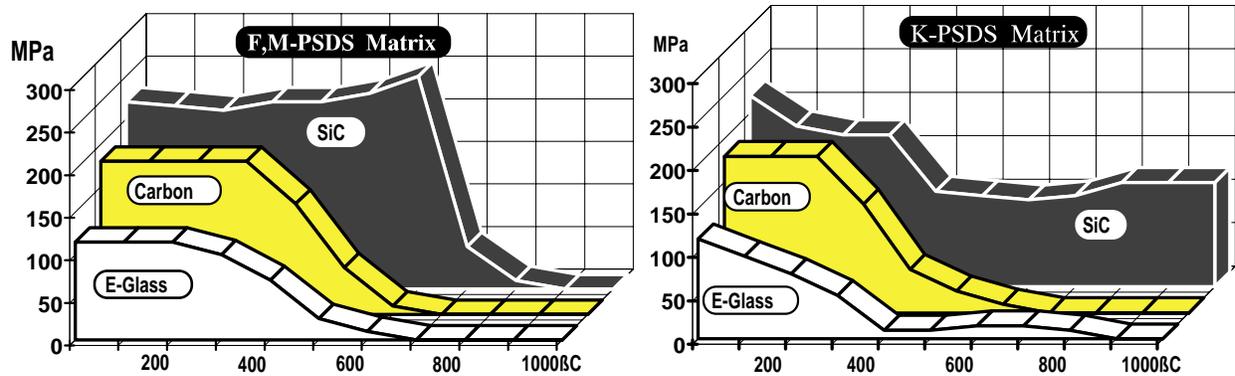


Figure 8: 3-points flexural strength of Geopolyceram composites.
Equilibrated 0-90° wet preregs with intermediate drying before cure at 60°C.

5. TOOLING FOR HIGH TEMPERATURE THERMOPLASTIC COMPOSITES

In a recent *SAMPE Journal*, Morton Kushner, Past President, SAMPE 1969,1970,1971, wrote: "So, here is my challenge to all "young" material and process engineers in aerospace, automotive or "other" hardware producing companies: Develop, with innovative design ideas and innovative processes, away to utilize the best composite materials in the world -thermoplastics- for production hardware." [10]

Laminates and parts can be fabricated from thermoplastics -like APC-2 PEEK, using a wide range of processes ranging from autoclave consolidation to rapid stamping techniques. Thermoplastic composite production is similar in many respects to sheet metal forming processes. Consequently, it should be possible to borrow manufacturing technology from the metal-forming industry, especially superplastic forming of aluminum alloys. Automated lay up processes are believed by many to be the logical approach to labor costs in the thermoplastic prepreg fabrication. However, aircraft manufacturers, unlike automotive manufacturers, may be reluctant to make the new capital investment in equipment required for sophisticated thermoplastic composite production. Autoclave processing is still preferred and remains the most prominent method of manufacture [11]. While autoclaving is versatile, it is expensive in terms of time and equipment. Alternative processing methods were considered by the French aerospace company Dassault Aviation, including rubber press forming, double-diaphragm forming and compression molding [12]. On the premise that thermoplastic advanced composite parts, like superplastic aluminum-alloy parts, will primarily be processed by double-diaphragm forming, we set following objectives:

1. Develop a tooling system that could be molded from painted wood or PFP master
2. Select a mold material with the close CTE match to that of APC-2/graphite advanced composites, and a mold material with the close CTE match to that of aluminum alloys.
3. Develop a mold material capable of repeated use to 425°C (800°F) - 600°C (1110°F).
4. Achieve lightweight molds for ease of transport.
5. Develop a mold material with good thermal conducting characteristics and cooling properties.
6. Achieve mold toughness and high flexural strength.
7. Ease of mold modification or reparability .
8. Obtain dimensional control among the several tooling steps and composite part manufacture.
9. Develop a tooling system that could be constructed "in house" for most composite manufacturing.

The feasibility of geopolymer tooling has been demonstrated with APC2- PEEK parts manufactured

in autoclave at 400°C (750°F) (see Fig.9a) for the French fighter "Rafale", and aluminum alloy parts made with the SPF-AI thermoforming system at 540°C (1000°F) (see Fig.9b).

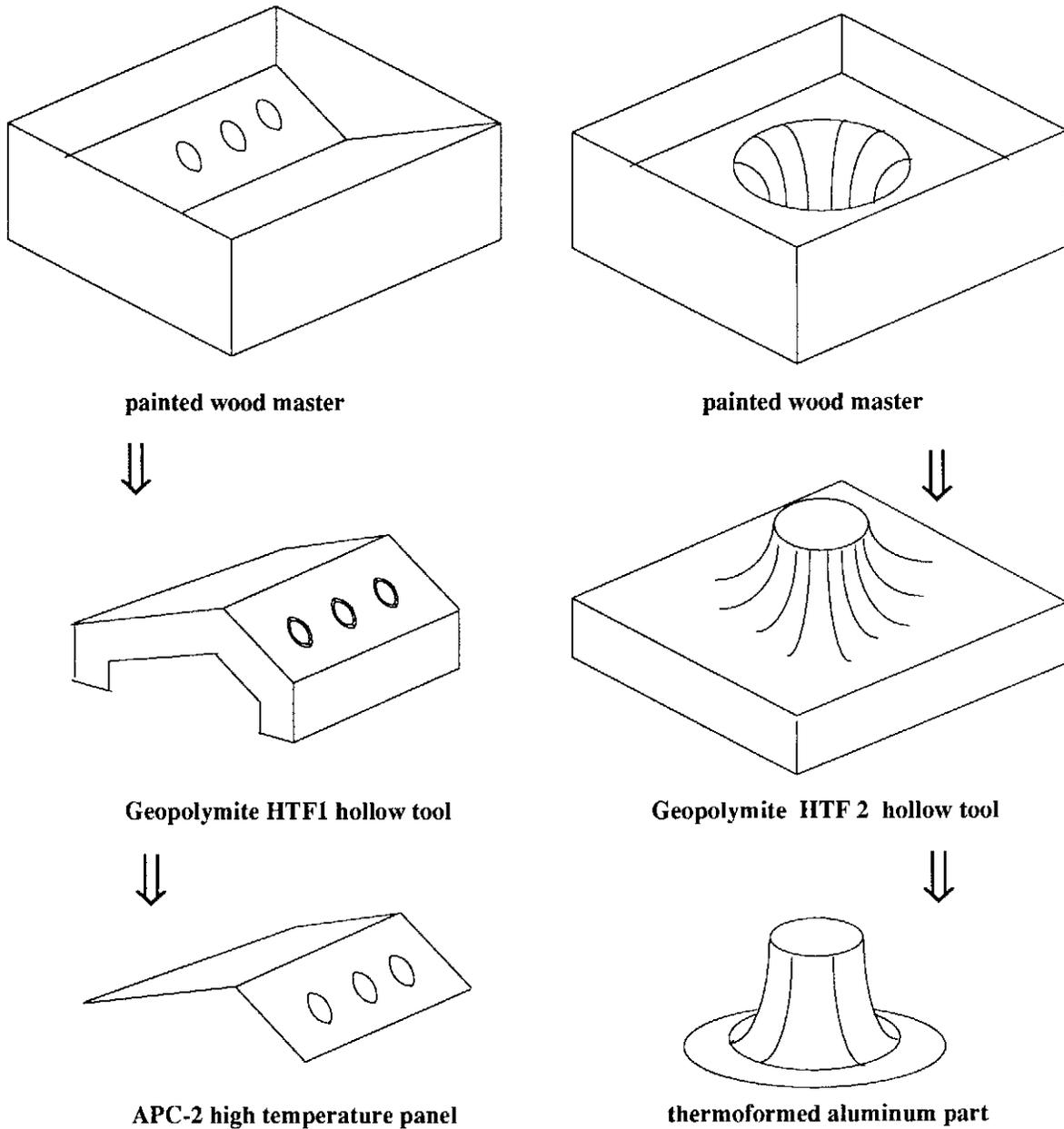


Figure 9: castable Geopolymite tool for
 a) fabrication of APC-2 parts for the French fighter program "Rafale", autoclave at 400°C (750°F)
 b) fabrication of superplastic aluminum alloy parts, thermoforming at 540°C (1004 OF)
 Courtesy Dassault Aviation.

Another form of compressive tool can be built by backing up a geopolymer laminate with "pour in-place" quick-setting Geopolymite syntactic foam. After the two to four-ply laminate over the surface coat is set, a two-part castable syntactic foam could be poured or a froth foam system sprayed over the rear of the laminate to stiffen the master mold surface. The geopolymer foam may be covered with a few more plies of reinforced lay-up material to form a sandwich foam/laminate structure.

This not only reduces the cost to produce the tool, it also reduces the weight of that mold when very large molds are required. It is well to note that the CTE in geopolymer syntactic foams is low, due to reduced amounts of matrix materials and the structural independence of spherical fillers against the matrix material.

6. CONCLUSION

Although geopolymers are more expensive than the most other castable mineral compounds, their superior performances often makes them ultimately more economical. Since they are adaptable, geopolymer resins can be formulated for a multiplicity of processes, such as castable compounds, filament winding, wet lay-up composite or dry lay-up with prepregs.

The material and process will yield the most accurate dimensions in the tool as the tool is being copied directly from PFP masters. As part of the impregnation process, the interface is important in obtaining high translation of fiber properties in the Geopolyceram composite. The interface problem, along with other problems should be studied. It seems clear that the sizings used on carbon fibers and silicon carbide fibers for organic thermosetting prepreg would not be appropriate for geopolymer prepregs.

By functioning as matrix materials in laminated and filament-wound composites for structural molds and parts, Geopolymite resins will serve in a large number of aircraft, space, military and industrial applications. Further developments are necessary.

Geopolymite, Geopolyceram and Geopoly-Preg are trademarks of Cordi-Geopolymere SA, France. Toolrite and Safil are trademarks of I.C.I. Ltd. Nicalon is a trademark of Nippon Carbon and Co.

7. REFERENCES

1. S.R Rogers, *Materials Engineering*, 106, (9), (1989).
2. S.H. Olson, *SAMPE Journal*, 26, (5),31 (1990).
3. D. Stover, *Advanced Composites*, 5, (4) (Jul/Aug), 51 (1990).
4. J. Davidovits, M. Davidovics and J. Orlinski, Tooling for Composites '90 Conference, *Technical PaperEMgO-182*, Soc. Manufacturing Engineers SME, (1990).
5. J. Davidovits and M. Davidovics, *Ceramic Eng. Sci., Proc.*, 9, (7-8),835 (1988).
6. N. Davidovits, M. Davidovics and J. Davidovits, U.S. Patent 4,888,311 (Dec. 19, 1989). 7. J. Davidovits, U.S. Patent 4,349,386 (Sep.14, 1982) and U.S. Patent 4,472,199 (Sep.18, 1984).
8. J. Davidovits, in J. Davidovits and J. Orlinski, ed., Proceedings of the 1st European Conference on Soft Mineralurgy *Geopolymer '88*, University of Technology , Compiègne, France, 1989, Vol. 1 pp. 19-48 and Vol.2 pp. 149-166.
9. Toolrite (I.C.I. Composite Inc.) Tooling Materials System.
10. M. Kushner, *SAMPE Journal*, 26, (5),7 (1990).
11. W. Becker, *SAMPE Seminar* , L.A. Chapter, High Temperature Thermoplastics and Alternate Resin Matrix Composites Producibility Aspects, Long Beach, CA, Aug. 1988. 12. P. Vautey, *SAMPE Quarterly*, January 1990,23, (1990).