High Temperature Polymer Nanocomposites

K. Balasubramanian and Manoj Tirumalai

Abstract The chapter on High Temperature Polymer Nanocomposites mainly covers the advancements made in the research on varied composite materials and their novel innovations for high temperature applications. The chapter begins with a prelude on existing polymers of thermoplastic or thermosets and also a combination of the two to exploit the dual advantage of both high temperature thermoplastics and thermosets. The polymer composites are developed and implemented for varied temperature regimes in the range of 120–250°C, 250–350°C specially suited for aerospace applications. Further research work is under progress to explore the material suitable for temperatures above 350°C. The initial section explains on the applicability of polymer composites having matrices such as either liquid crystalline polymer, cyanates, polyimides or bismaleimides which are reinforced with either the carbon, glass or aramid fibres especially continuous fibre which provides improved material and physical properties. The polymer-composites are assessed for performance of the matrices and the composites not only for their strength or stiffness but also for their resistance to cracking, minimum loss of weight, brittleness due to cross-linking and other properties that may degrade the performance of the composites over the long period of high temperature applications. This section mentions on the literature reviews having come up with research in progress on other types of resins for high temperature applications namely the oligomers such as the acetylene terminated polyimides or the norbornene terminated polyimides. The second section is concerned with the polymer-nanocomposites for high temperature applications. In this section, the role of nanofillers in the enhancement of composite properties is discussed. The various forms of nanofillers are the nanoclay, nanofibres, carbon

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nanotubes, Polyhedral OligoSilsesquioxanes (POSS) and nano-oxides where they reinforce polymer chain at molecular scale as against the carbon fibres of macroscopic scale seen in polymer-composites. In a nanocomposite the thermal properties depends on the filler's nature, rate and dispersion in a matrices. The applications have been as fire retardant materials or for re-entry applications in aerospace vehicles. Research on nanofillers is still at its nascent stage that ample scope is available for exploring the potential of various nanofillers for high temperature applications and as fire retardant materials. Some polymer thermosets such as PMR-15 (Polymerization from Monomeric Reactants) are the most extensively used resin for applications where long term thermal stability is required at 300°C. This section dwells on other progress under way in the field of nanocomposites as high temperature nanocomposites. The last section presents a review on advanced materials for high temperature applications, especially applicable for the next generation aerospace vehicles. The issues concerning adhesives for joining of surfaces exposed to high temperatures, the effective role of nano-fillers for improving fracture toughness at high temperature etc. It is seen that the most promising resin for high temperatures has been the polyimides (315°C). This resin has high Tg (400°C) and other good characteristics such as good micro cracking resistance, low moisture absorption and low toxicity. There are various grades of polyimides under development. Overall, the chapter provides a glimpse on the effective developments in the field of polymer-composites and nanocomposites for high temperature applications especially for aerospace vehicle and automotives.

1 Prelude on Polymer Composites for High Temperature Applications

1.1 Introduction

1. The appearance of polymers in 19th century and the popularity of composites since last decade has revolutionised the scope of materials with substitution of metals and non-ferrous alloys by polymer-composites. The area of application has been from the least significant parts of aerospace vehicles, medical equipments, household equipments, technology equipments for automobiles, and other science and engineering products to the most significant parts [1]. The application has been progressively being made for high temperature requirements [2–7].
2. The application of fibre reinforced composites has been mainly seen on aerospace vehicles where the parts are subjected to a temperature range of 150–400 °C. The parts affected with such temperature range are the airframe skin, the aero-engine parts and the surrounding areas, and the parts exposed to hyper velocity or supersonic speeds. The commonly used matrices are the liquid crystalline polymers, cyanates, polyimides and bismaleimides [2, 8, 5, 6, 9]. The

matrices are reinforced with carbon, glass or aramid fibres especially continuous fibre which provides improved material and physical properties [2, 8, 9]. The epoxy based carbon or the glass or the aramid composites have been extensively used for load bearing structural applications on the aircraft. The future generation aircraft or any other high temperature applications of the range of 120–400 °C [5] would require the matrices to withstand the brunt of the high temperatures based on the area of application. In case of aircraft the high temperature zones have been the aircraft skin of supersonic/hypersonic aircraft, the leading edges of the wing and control surfaces and around the aero-engine regions even at the exhaust end where high exhaust plumes are exposed on the exhaust plates which are subjected to temperature stresses and strain.

1.2 High Temperature Composite Specialty

3. The matrices which are most popular will be the polyimides. The polymer matrices-composite behaviour depends on the interfacial bondage. The composite needs to retain properties at high temperatures, maintain glass transition temperature ($\sim$300 °C) without being affected by the presence of the moisture i.e. low moisture absorption of nearly 4 %, retain thermal stability, overcome ageing affects and do not get affected by oxidation. The polymer matrices are developed in the high temperature ranges viz, 120–250 °C, 250–350 °C and 350 °C and above [5].
4. The polymer matrices such as the cyanate esters (CE), BMI, phenolics, polyimides have been used for temperature application between the range 120–250 °C, for the range 250–500 °C the polyimides are found suitable and for temperatures beyond 350 °C the research is in progress to find the required material [5].
5. The epoxies were found to mostly suit for a temperature application of 135 °C limits. The BMI has been found to be thermally stable and having thermo-oxidative stability [6]. The various mechanical properties of a Polymer Composite Matrices as applicable to mainly aircraft structures have been the tension providing the longitudinal modulus (GPa)/strength (MPa), transverse modulus (GPa)/strength (MPa), the compression also providing the longitudinal modulus (GPa)/Strength (MPa) and transverse modulus (GPa)/strength (MPa). The carbon fibre has the Young's Modulus given in the range 220–230 GPa, Ultimate Tensile Strength 3 GPa. Over the period the advancement in polymer composite research has been in improving these properties by performing structural modifications in the polymers like the bismaleimides by reducing the cross-link density and having cross-linking through chain extension. The properties are further refined for damage tolerance by adding fine particles of polyimides which are high temperature materials. The primary structures which are subjected too high temperatures due to kinetic heating during flight have such composites of carbon/bismaleimide that can sustain a temperature of 180 °C.

1.3 Research Review on High Temperature Composites

6. Promising work is in progress at various countries to improve the thermal stability and curing behaviour of high temperature polymer-composites. In one such example, is the research going on with the addition of amines with bismaleimides/carbon. The other areas of application of high temperature composites have been especially on aerospace vehicles for the radomes, stealth aircraft composites, antennae covers where the surface temperature are high and need to be contained. The Cyanate esters though less superior than the bismaleimides have better dielectric properties and low absorption of moisture. The field has been further expanding from the usage of epoxies as matrice material to thermoplastics. Of the two types of thermoplastics namely the amorphous or the crystalline, it is seen that the crystalline thermoplastics are finding large applications. The crystalline thermoplastic show slow decrease in modulus above T_g (Glass Transition Temperature). The thermoplastics show high fracture toughness (1–2.5 kJ/m^2) and impact strength. Thermoplastics have shown lower compressive strength than the thermosets, however the resistance to environmental effects and better inter laminar shear stress show better applications especially for area of impact and compression. The dual properties of both amorphous and crystalline thermoplastics have been extracted when combined; examples are PEEK, PEI etc [8, 5].
7. The process of improving the high temperature polymer performance is by polymerising more of aromatic heterocyclic units and minimise the aliphatic contents. In the temperature range of 250–350 °C, the groups of polyimides have been used be it the condensation or the addition types. Most of these are commercially available in United States. The condensation type has certain drawback due to volatiles that skill is required to produce low void composites.
8. The polyimides resins obtained through the polymerisation of monomer reactants have been taken for composite applications exposed to high temperatures in the range of 260–288 °C. Therefore in polyimides of condensation types, the reduction in aliphatic content has improved the thermo-oxidative stability and improved toughness due to reduced crosslinking.
9. The thermoplastic matrices under high temperature applications yield to cracking and loss of weight and are subjected to repeat thermal cycling. The compressive and shear properties of the matrices get adversely affected with high temperature exposures.
10. Long term applications of polymer-composites for high temperature applications need to assess the performance of the matrices and the composites not only for their strength or stiffness but also for their resistance to cracking, minimum loss of weight, brittleness due to cross-linking and other properties that may degrade the performance of the composites over the long period of high temperature applications. The high temperature polymer-composites have been extensively researched for applications on aero-space vehicles especially for the skin, aero-engine parts and engine areas (nozzle, liners etc.,)

and the re-entry requirements for the space vehicles (ablative materials) and armament ammunitions (anti ballistic missiles). The research is mainly seen to improve composite composition by improved matrices synthesisation, selection of matrix material with compatible fibre reinforcement, catalysts, additives and solvents to achieve higher glass transition temperature and other mechanical properties useful for prolonged high temperature applications. The degradation due to ageing needs to be considered for improving the materials properties for longer application endurance with time.

11. The other mostly used thermoset-composite will be the phenolics which though are not suitable for load bearing structure are found applicable for high temperature applications especially as ablative and erosion resistance materials in composite form with carbon fibre/silica reinforcements. The other improvement in thermal property will be the char yield which normally is assessed for 70 % at a high temperature depending on the resin composition. Several works are in progress toward this to improve the temperature limits for the char yield of 70 %. The experiments of phenolic-carbon or silica have shown this property at 700 °C with the resin cured by functional groups like maleimides propogylether and phenyl ethynyl while the resin has shown further improvements with cyanates with the temperature limits raising up to 1,000 °C.
12. Literature reviews have come up with research in progress on other types of resins for high temperature applications namely the oligomers such as the acetylene terminated polyimides or the norbornene terminated polyimides which are experimented for suitable replacement as matrices for the phenolics. The process limitations and cost economy has held back the actual applications. As on date, the research still continues on these other oligomers to arrive at cost effective and better polymer-composites for high temperature applications.
13. Therefore polymer-composites have found its usage for various high temperature applications especially connected to aerospace vehicles have been the aircraft skin, engine nacelles, panels, firewalls, engine ducts, nozzle liners, ablative materials, fins for ammunition stores (missiles), cases for helicopter gear box etc. The temperature applications cover a range of 150–250 °C i.e. the aircraft skin areas and 250–350 °C for the engine areas. The thermoplastics such as BMI, CE, and Thermoplastic Polyimides are for lower temperature applications (150–250 °C) and the toughened polymerisation of monomer reactants and the oligomers are for higher temperature ranges (250–350 °C). The latest research on liquid crystalline polymers and phthalonitrile are found to be the latest resins of interest for high temperature applications which are cost effective and less complex in processing with possible adaptation for fine tuning with the autoclave moulding followed for epoxy composites.
14. The applications may be extended to any other field of science and engineering such as the automotives, the ships, thermal and nuclear engineering [10, 11] etc.

2 Polymer-Nanocomposites for High Temperature Applications

2.1 Introduction

1. The polymer composites gave an insight to the various mixtures of polymers with primary reinforcements such as the carbon, glass or the aramid fibres and the silicates for the high temperature applications. The search for improved material properties for varied science and engineering applications gave rise to the birth of nanofillers as substitutes for carbon fibres and other forms of composite reinforcements [12]. The nanofillers are of the size less than 100 nm which are functionalised or surface modified for better interfacial adhesion with the bulk matrices which may be either thermoplastic or thermosets.
2. The nanofillers due to their superior multi-functional properties are being researched as an effective replacement for the exiting carbon fibres and other primary structural reinforcement materials under application for high temperature applications [13, 14]. The drawbacks in polymer–composite mixture of process or synthesisation complexity and cost have been taken care in the use of polymer-nanocomposites. There are several literatures available that describes the nanofiller synthesisation, characterisation and properties [15, 16] along with the [17, 18], various applications of these nanocomposites (polymer-nanofiller) in medical, bio-engineering [17, 18], automotive, civil engineering, nuclear and thermal plants and maximum in aerospace vehicles.
3. The polymer-nanocomposites have been even researched as repair agent for high temperature polymer-composites. One such example is the Bisphenol E Cyanate Ester with alumina nano-particles ($\sim$40 nm) [19]. The repair of laminate composites are undertaken by use of such polymer-nanocomposites by injecting low viscosity polymer-nanocomposites which provides desired toughness and better mechanical properties. The filler will have high T_g (>270 °C) and decomposition temperature which permits the repair of high glass transition temperature composites.

2.2 High Temperature Nanocomposite Salients

4. The various forms of nanofillers are the nanoclay, nanofibres, carbon nanotubes, Polyhedral OligoSilsesquioxanes (POSS) and nano-oxides. The nanofillers reinforce polymer chain at molecular scale as against the carbon fibres of macroscopic scale seen in polymer-composites. One of the significant applications of polymer-nanofiller composites have been as an effective fire retardant material. Nano-composites therefore are a group of nano materials wherein a nanoparticle is dispersed in a matrices resin or multi-phases. The nanoparticle

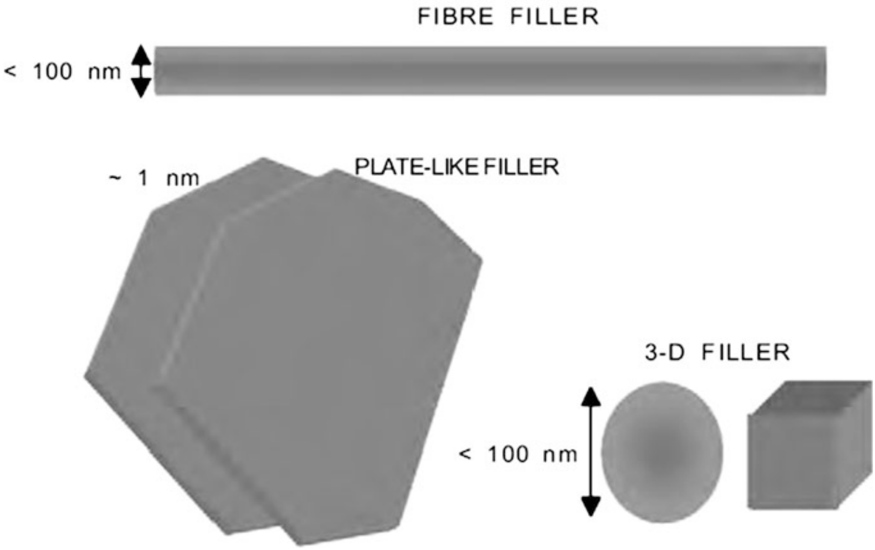

Fig. 1 Nanofiller scale [20]

could be of 1D (a plate) or a 2D (tubes and fibres) or a 3D (nano-metric silica beads) sized nano particle of dimension <100 nm (Fig. 1) [20].

5. The effect in significant properties is achieved by addition of nanofillers in the range of 1–10 wt%. These nanofillers may be mixed in addition to the conventional additives and composite fillers such as carbon black, carbon fibres, silicates etc. The nanoalumina as a filler for repair of composites and the nano antimony tin oxides as good fire retardant material have been found suitable for high temperature applications.
6. The blend of polymers-nanofillers is seen to be better whenever the nanofillers are surface modified or functionalised for good interfacial adhesion and cross-linking. The nanofillers when added either forms regions in the resin matrix forming multi-phases or the polymers intercalates between the nanofillers or exfoliates and disperses throughout the polymer resin (Fig. 2) [21, 20].

2.3 Research Review on Nanocomposites for High Temperature Applications

7. It is seen from the literatures that functionalisation of carbon nanotubes with Poly (acryloyl chloride), PACL reacts well with epoxy monomers that the epoxy grafted CNT adheres well to the epoxy resin matrices that the nanocompsoite formed has better thermal–mechanical properties. This is achieved with low wt% addition of CNTs (i.e. 0.1 to 1 wt%). Experiments have shown

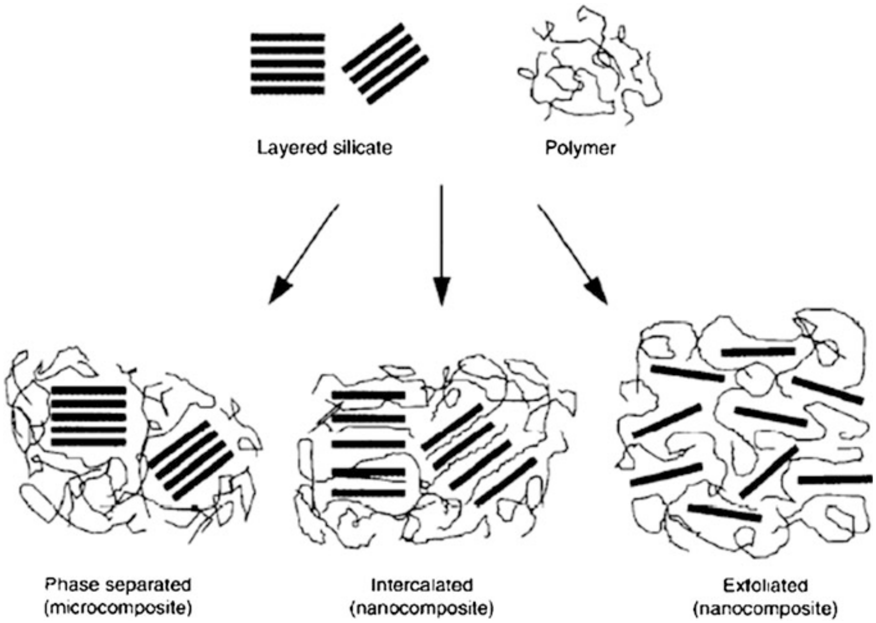

Fig. 2 Three main types of layered nanofiller (say silicates) in polymer matrix [21]

that the addition of Multi Walled CNTs (0.5 %) in epoxy resins have improved the T_g from 167 to 189 °C.

8. In a nanocomposite the thermal properties depends on the filler's nature, rate, and dispersion in a matrices. The combination of traditional composite fibres with nanocomposites has proved to be more beneficial with capabilities to sustain larger temperature range than the traditional composites. One such example is the addition of organophile montmorillonite.
9. The high temperature polymers are usually composed of aromatic or heterocyclic rings which are blended by flexible linking groups. The literature studies have brought out that high temperature polymers have high T_g and good mechanical properties. The chemical structures of commonly used high temperature polymers as brought out in the previous sections are shown in Fig. 3a–d [5, 19, 22].
10. PMR-15 (Polymerization from Monomeric Reactants) thermoset polymer is the most extensively used resin for applications where long term thermal stability is required at 300 °C. This polymer has its own disadvantages such as complex processing with high cure temperature needs and toxic starting materials. Group of Cyanate esters is the other popular polymer which is finding applications in the high temperature applications especially for aerospace and microelectronics sectors.
11. The various research objectives on the high temperature nanocomposites have been the following [19]:

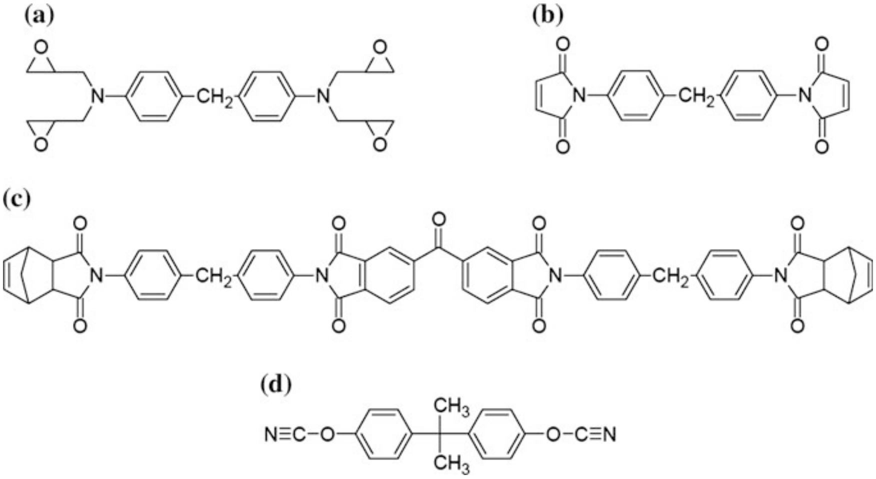

Fig. 3 Chemical structure for high temperature thermosetting polymers. **a** Epoxy resin: MY270. **b** Bismaleimide: 4,4′-bismalimidodiphenyl methane. **c** PMR polyimide: PMR-15 resin. **d** Cynate ester: 2,2′-bis(4-cyanatophenyl)propane [5, 19, 22]

11.1. **Curing Kinetics of Polymer**. This is investigated by Differential Scanning Calorimetry. In this many reaction models are taken to model isothermal curing. The model is analysed for activation energy and reaction orders.

11.2. **The Effect of Nanofillers on the Curing Kinetics of Polymer**. In this the cure kinetics of polymer with varying loadings of nanofiller is tested. The catalyst is not added to the mix. The isothermal curing of the polymer/nanocomposite is determined.

11.3. **Rheology and Dynamic Mechanical Analysis of polymer/nanocomposites**. Nanofillers are functionalised which are characterised by using Fourier Transform IR and Thermogravimetric Analysis (TGA). The dispersion of functionalised nanofillers in the polymer matrices is found to be good. Here, the rheology and rheokinetics of the polymer suspension is evaluated. The Dynamic Mechanical Analysis determines the thermo-mechanical properties for nanocomposites with bare nanofiller and functionalised nanofiller. The change in glass transition temperature is found and the dispersion is seen in a transmission electron microscope.

11.4. **Creep Behaviour of Nanocomposite**. The creep property of nanocomposite is studied through tensile creep testing using DMA. The tensile creep interval is measured at isothermal conditions. The temperature time superposition principle predicts the long term creep behaviour in a high temperature environment.

12. The nanofiller having increased number of hydroxyl groups on the surface will have greater catalytic effects on the cured polymer. The addition of nanofillers will bring about a change in chemistry, curing, crystalline structure, and matrix chain mobility.

2.4 Applications

13. One such application of high temperature conditions will be as ablative materials in nozzles of high speed space vehicles. The selection of filler irrespective of micron or nano size is of importance. The selection of composites/nanocomposite should be such that there is proper bonding of the ablative material with the metal substrate of the nozzle and also serve the purpose of correct transfer of the hot gases of the propellant through the nozzle without damage to the metal structure. The process of manufacture of this ablative material will govern the adequacy of the density, percent resin content, compressive strength, inter laminar shear strength, thermal conductivity, coefficient of thermal expansion, and tensile strength. The example of such a material showing adequate properties for high temperature ablative material is the Carbon-phenolics [23]. This carbon fibre of micron size when replaced by nanofiller will enhance the composite properties many folds due to the better interfacial adhesion between the matrix and the filler with the generation of large surface area and high aspect ratio. Also the thermal conductivity improves due to low percolation thresholds which could be further improved by functionalising the nanofillers. The other ablative materials used depending on the location in the Solid Rocket Motor (SRM) nozzle are the Glass cloth-phenolic and the Silica cloth–phenolic. The ablative properties of C-Ph material can also be improved by adding zirconium diboride particles as additives (Fig. 4) [24].
14. In common a high temperature material especially of nanocomposites show improved thermal stability and high Hot Distortion Temperature (HDT). The thermal stability is improved by commonly incorporating nanoclay into the polymer matrix as it performs as a superior insulator and mass transport barrier to the volatile products generated during decomposition.
15. The research literatures have brought out that the elastic and thermal properties of CNTs vis-a-vis carbon reinforcing fibres have been found to be nearly four times high. The CNTs are uniquely stiff fibres with tensile strength ranging above 50 GPa with the strength to weight ratio being nearly four times larger than the carbon reinforcing fibres. The SWCNT has a greater strain as compared to any other structural material unlike the negligible strain seen in polymer-composite material where the fracture is sudden without prior sign of failure. The thermal conductivity is also high in the range of 1,750–5,800 W/mK.

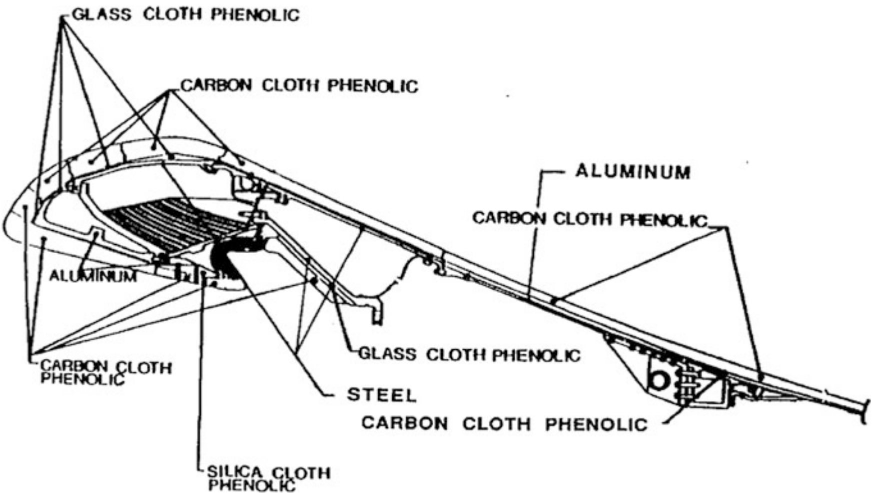

Fig. 4 Ablative materials in a solid rocket motor of a nozzle [24]

16. *Layered silicates as fillers.* Nanocomposites are layered with silicates of a thickness of around 1 nm. The aspect ratio (length to thickness) is high over 1,000 due to the lateral dimension ranging wide. The layer forms gap between them leading to interlayer. The interlayer distances are increased by the exchange of cationic surfactants thereby reducing the action of these layers form stacks with a gap in between them called the interlayer or the gallery. Isomorphic substitution within the layers (Mg^{2+} replaces $A1^{3+}$) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer [20] (see Fig. 5). The inorganic cations within the interlayers can be substituted by other cations. The exchanges with cationic surfactants, such as bulky alkylammonium-ions, increase the spacing between the layers and reduce the surface energy of the filler. Therefore these modified fillers (called organoclays) are more compatible with polymers and form polymer-layered silicate nanocomposites. Montmorillonite, hectorite and saponite are the most commonly used layered silicates [21, 20, 25,26, 17, 18].
17. Nanoclay has been widely researched as potential nanofiller for flame retardancy [14]. The nanocomposite materials such as the organoclay plus aluminium oxide and series of polypropylene plus organoclay have found applications as flame retardant materials. These materials have been commercialised. Even the nanofillers like the CNTs or any other alternatives as the Graphite Oxides or the Graphenes have been experimented to enhance the mechanical, electrical and flammability properties of the otherwise traditional polymer-composites. The graphene nanofillers in range of ceramics have improved their toughness making them suitable for high performance structural applications.

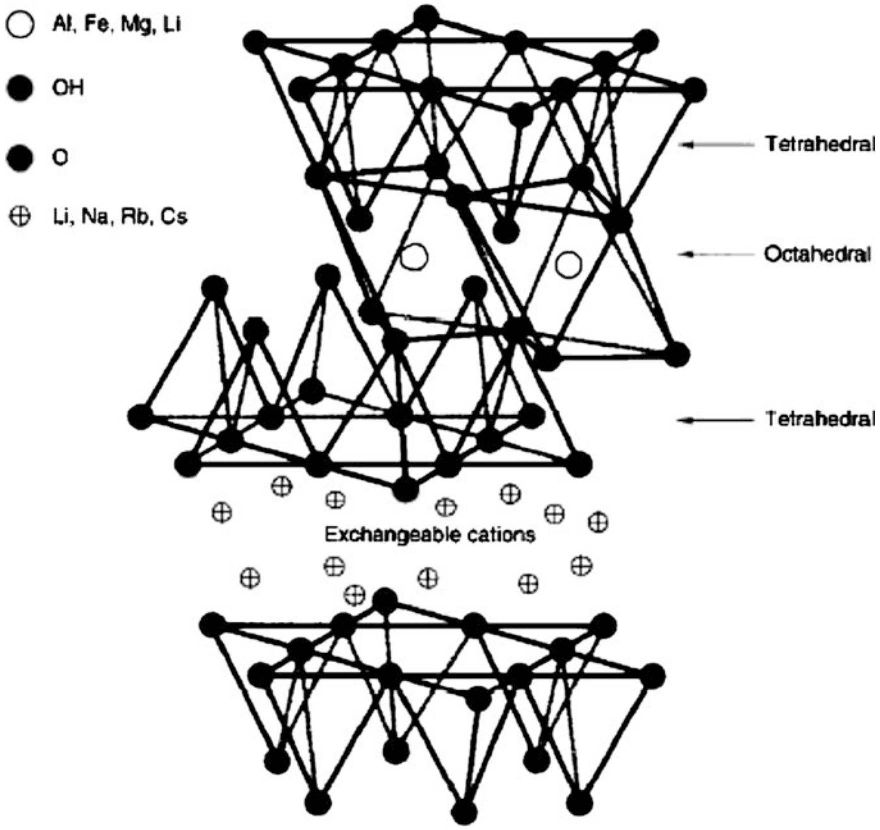

Fig. 5 Layered silicates [21, 20]

18. The nanoceramics are finding its foothold as candidates for high temperature applications. The reasons of having nanocomposites over traditional polymer-composites are for their following benefits: -
    (a) Improved strength, modulus and dimensional stability.
    (b) Higher thermal stability and HDT (Heat Distortion Temperature).
    (c) Better flame retardant properties and low smoke emissions
19. Nanoceramics have shown to have the abovementioned properties and a suitable material for engine applications subjected to temperatures of around 1,400 °C with strength maintained at 300 MPa. The material also exhibits negative creep rate a desirable property for high temperature applications. The other salients exhibited by nanoceramics over the traditional polymer-ceramic composites are the high resistance to oxidation, sub-critical crack growth and thermal shocks.
20. Nanocomposites such as SiC (Silicon Carbide)/Si_3N_4 (Silicon Nitride) composites, are another material exhibiting improved strength, creep and fracture toughness [10, 11, 27–32]. The material retains strength at higher temperatures

and has good resistance to creep. The Fig. 6 shows the microstructure of polycrystalline Silicon Carbide (SiC)-Silicon Nitride (Si3N4) nanocomposites. The structure contains filler Si_3N_4 of 0.8–1.5 μm and the polymer SIC of 200–300 nm. The grain boundary thickness is seen to be around 50 nm. The other similar types of nanocomposites suitable for high temperature applications or under research will be the Graphene or Graphite Oxide/SiC, carbon nanofibres/SiC-Aluminium Oxide (Al_2O_3)/and TiN-Si_3N_4.

21. The ongoing research on nanoceramics at Multiphysics Laboratory at Purdue mainly focuses in understanding the performance of high temperature based nanoceramics especially of nitrides and carbides. The materials so developed will be helpful for power generation applications, nuclear applications, and aerospace applications.
22. The research work is focusing on following areas.

(a) To develop materials of low conductivity by studying effects of material morphology changes on thermal conductivity using simulation techniques such as Molecular Dynamics (MD).

(b) To develop ceramic nanocomposites (nitrides and carbide based) capable of withstanding high temperature environments even meant for nuclear applications. The advanced ceramic nanocomposites materials are researched to have the capability to withstand temperatures of the order of approx 1,800 K and

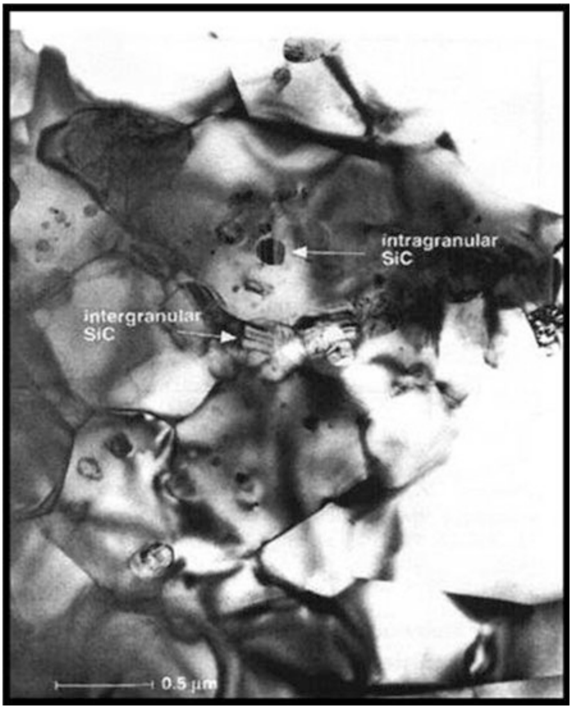

Fig. 6 Actual microstructure of a SiC-Si3N4 nanocomposite [31]

above [33]. The usage of such materials is experimented for various functions like the Multi-functional material or as structures for extreme temperature applications (Nuclear) [10, 11] or as sensors in high temperature zones.

23. The other area of research in nanodomain for high temperature applications have been the nanocomposites of amorphous (Si, O and C) with nano SiC or C fillers [30]. The research has shown that these materials have required properties and characteristics for a wide range of high temperature usage. The nanocomposite exhibits ceramic like properties of negative creep rate and anti-oxidant. The Fig. 7 shows one of the applications of PyroSic. The pyroSic have been found much better than the conventional CFRPs.
24. The pyrolysis of pre-ceramics has been found to be simple as compared to the conventional processing of CFRP. The tooling and process are seen to be less complex as compared to Ceramic Matrix Composites.
25. The other processes evolved for improvement of ablative resistance of composites such as the C-Phenolics has been by introduction of Zirconium diboride particles [34, 35]. Sufficient research is in progress on this subject with various combinations of nanofiller added to C-Ph composites to improve ablation resistive property and also provide reduced smoke emission [23, 35]. The resistance is due to the formation of oxides of Zirconium and Barium. The research in this field has shown that the ablative rate has been higher as compared to Carbon fibres in C-Ph composites. The ablative resistance properties have been improved by adding modified phenolics in the C-Ph matrix [34–39]. The modification is obtained by treating with boric acid or POSS (Poly Oligomeric Silsequioxanes), or H_3PO_4. This treatment gives a reduced erosion rate thereby retarding ablation. Research has seen further improvements in linear ablation rate by having composites of SiC Ceramic, carbon fibres and boron modified phenolics. The Nanosilica powder modified rayon-based composites show better ablation resistance, reduced thermal conductivity and higher ILSS (inter-laminar shear strength) at a controlled quantity. In this, process of improvement involves the modification of either carbon fibres or the phenolics. Researchers find that the effects of ZrB2 on the ablation performance of C–Ph composites are still unclear. The research

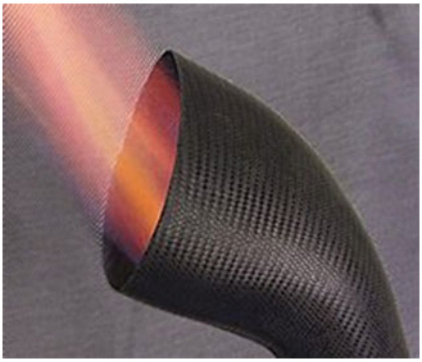

Fig. 7 Exhaust duct made out of PyroSic

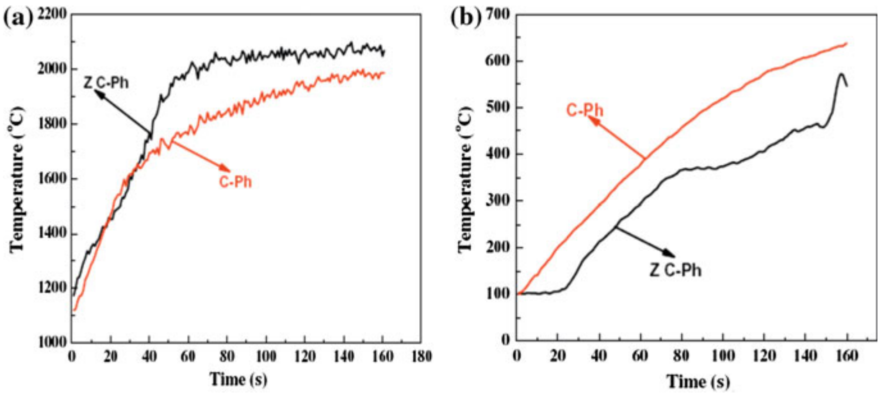

Fig. 8 Surface temperatures of Z C-Ph composites and C-Ph composites (**a**) the ablated surface (**b**) the back surface [35]

papers have shown that the linear ablation rate of Z C-Ph composite has reduced by 79 % compared with the un modified C-Ph composite [35]. The ablation surface though at higher temperature during ablation process the back surface temperature is found to be lower by 100 °C as compared to unmodified composites. This is shown in the Fig. 8. Therefore this material may become the main material for high temperature structural applications.

26. The other promising research for better ablative material or as heat shields for re-entry applications has been the resol type phenolic resin with kaolinite and asbestos cloth nanocomposite [40]. The material has been tested for an external heat flux of 8×10^9 W/m^2 and 3,000 K. The material was tested for its ablation, charr formation and thermal degradation performance for its usage as heat shields. The temperature is withstood by the formation of a strong refractory char on the insulator surface. Insulator later degrades to a char layer at higher temperatures due to pyrolysis. Recent advances in polymer layered silicate nanocomposites are seen as potential ablative materials [41, 42]. The reason being on pyrolysis, the organo–inorgano nanostructure reinforcing the polymer are transformed into a uniform ceramic char, leading to increased resistance to oxidation and mechanical erosion in comparison with composite materials.
27. *Ablation performance.* Experiments on ablation performance of composites (asbestos-Ph) and nanocomposites (Asbestos-Ph-Kaolinite) [40] have shown the following:-
    (a) The back surface temperature of a nanocomposite is found approx 43 % lower than composites (Fig. 9) [40].
    (b) The Heat Release Rate (HRR) and mass loss @ 80 KW/m^2 (Fig. 10) [40] show that to some stage i.e. up to 100 s of the Oxy-acetylene flame test both composites and nanocomposites behave thermally same. After 100 s, with the surface temperature increasing to 1,000 °C the rate of mass loss and HRR reduces for a nanocomposite. The nanocomposites show a reduction of nearly 35 % HRR and 22 % mass loss.

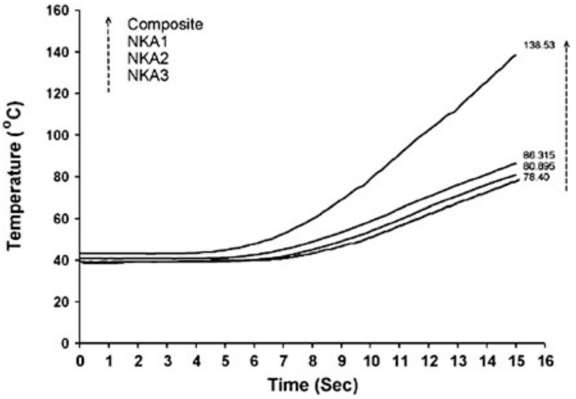

Fig. 9 Temperature distribution of back surface (composite and nanocomposite) [40]

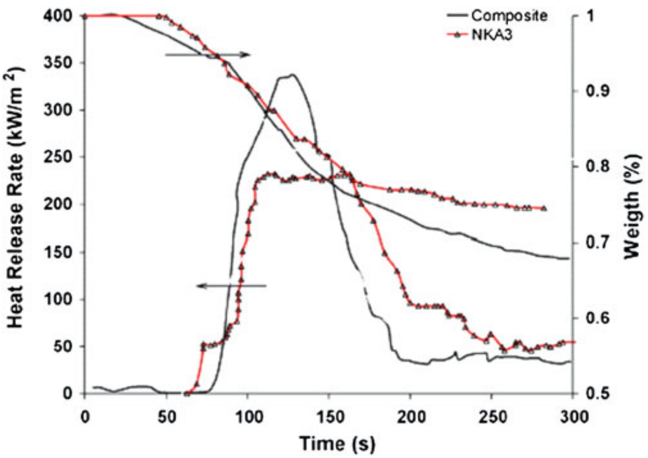

Fig. 10 Comparison of HRR and mass loss @ 80 KW/m^2 [40]

3 Advanced Thermal Protection Materials for Next Generation Aerospace Vehicle Designs

3.1 Introduction

1. The research is under progress at NASA to establish high temperature materials for various aerospace applications such as the structures, adhesives that are used for bonding of composites and the thermal protection system namely fire retardants (coatings). The work is progressing to reduce the thickness of the thermal protection system by having high temperature resistant structures and adhesives.

3.2 Review on Advanced Materials for High Temperature Applications (HTA)

2. The high temperature adhesives are those that have the working temperature ranging from 315–400 °C (600–700 F). The adhesive must also satisfy the bond-line temperature requirement between the TPS-substrate of being above the traditional limit of 250 °C. The adhesive's bond-line (Fig. 11) integrity needs to be maintained for high temperatures and high heating rates [43].
3. The structure which is of honeycomb structure has graphite or aluminium-epoxy face sheet and aluminium honeycomb. This material may be improvised by using nanofillers with low wt% loadings and deriving many fold benefits of thermo-mechanical properties. The thickness of the thermal protection system depends on the allowable temperature for the bond line. The research will be with the aim to increase the bond line temperature (>250 °C) so as to reduce the TPS and hence increase the payload with overall reduction in structural weight. The need for high temperature adhesives will be to withstand high temperatures for short period of time and for one or more loading cycles. The test on adhesive bonding with substrate is carried out to check whether the failure will be due to pure adhesive peeling off from substrate surface which is the adhesive failure or the failure of the adhesive which demonstrates the cohesive failure. The desirable test is to check the cohesive failure which speaks more on the bond line integrity. Some clippings of the NASA tests are shown below at Figs. 12 and 13.
4. The primary requirement of the adhesive is to retain some if not all of its strength at high temperatures. Polymer-composites such as Polyimides group, Cyanate ester group, BMI have shown good strength at high temperatures and the properties profoundly improve when nanofillers such as nanoclay, nanoalumina, nanotubes etc. are added.

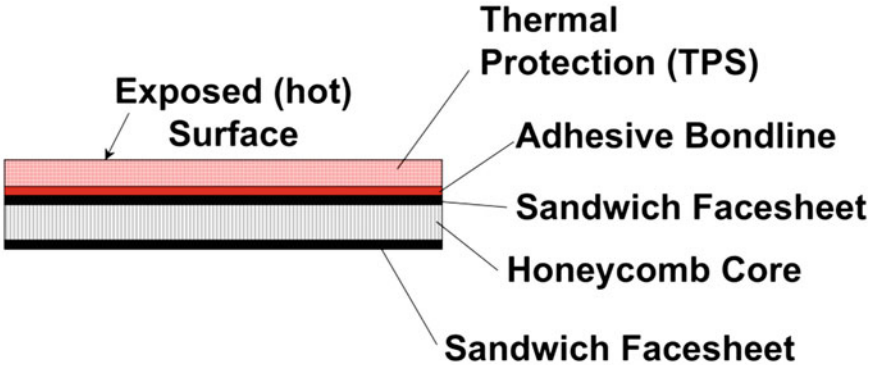

Fig. 11 Aerovehicle structure [43]

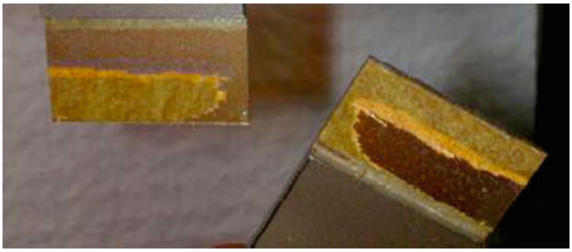

Fig. 12 Adhesive failure [43]

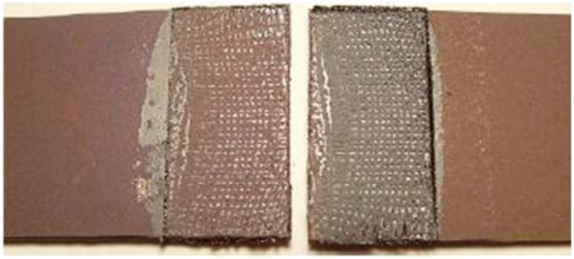

Fig. 13 Cohesive failure [43]

5. The high temperature structures mainly of carbon reinforced fibres with resin for polymer-composites may be replaced with nanofillers or additionally added to the existing phases for strength improvement. The limiting factor at high temperatures is the performance of matrices and their interfacial binding with the nanofillers or the composite fibres. The most promising resin for high temperatures have been the polyimides (315 °C). This resin has high T_g (400 °C) and other good characteristics such as good micro cracking resistance, low moisture absorption and low toxicity. There are various grades of polyimides under development.
6. The applicability of a material depends on its performance during the coupon tests which are carried out for determining the tensile strength/modulus, shear strength/modulus (Fig. 14), for laminates the de-lamination at high temperatures which is seen in case of CFRP composites [43],
7. The other type of resin which is less complex for processing will be the modified polycyanates. The ablators for advanced temperature systems have been the silicon based or the phenolic based with nanofllers or high grade of fibres to increase the stiffness and strength.
8. The potential impact of advancing composites will replace the usage of metals to composites for high temperature applications especially in the field of aerospace vehicles. A typical impact of materials is given in Fig. 15 [44].
9. The use of high temperature composites/nanocomposites will definitely reduce the weight of the structure and increase the payload capacity for useful requirements of space research. The high temperature capabilities will make it possible to have entire aerospace vehicles to be of composites. An example of a

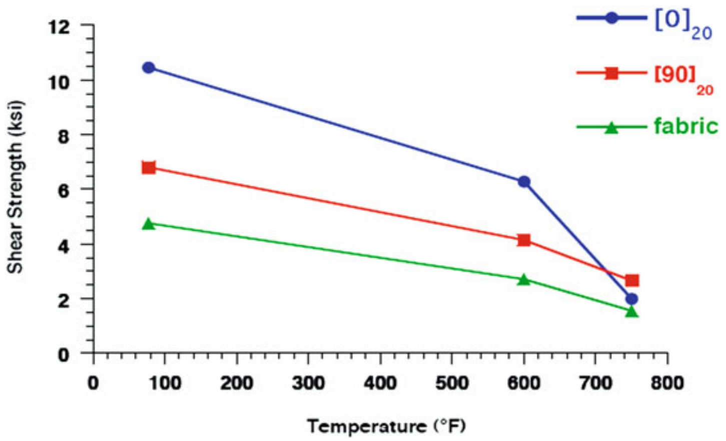

Fig. 14 Effect of temperature on shear strength on three different laminates [43]

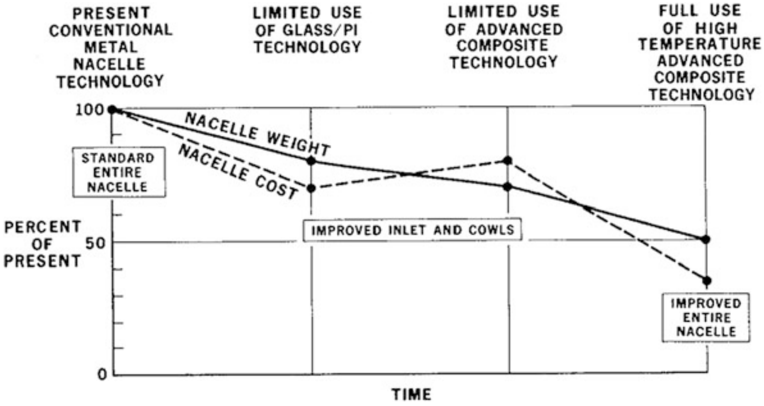

Fig. 15 Impact of change in materials with time [44]

engine nacelle of an aero-vehicle of becoming fully composite is shown in Fig. 16 [44].

10. The challenge ahead is to select the right material for the required high temperature applications. The nanocomposites/composites/hybrid materials etc. are the various many options available which will replace the position of metals in a structure and systems in all fields of science and engineering.

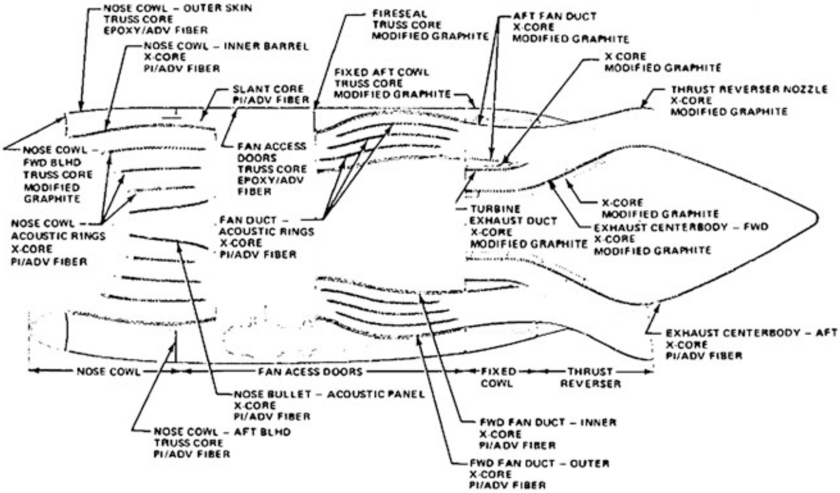

Fig. 16 Impact of advanced composite materials [44]

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