Design and Fabrication of High Strength, High Modulus Polymer Reinforced Metal Matrix Composites for Light Weight Applications

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Abstract

Objectives: The present work reports the possible solution of using the high thermal stability polymer fibres with superior mechanical properties as that of, or, even better than metals for light weight applications like aerospace and automobile.

Methods/Statistical Analysis: The PBO filament fibre was used as reinforcement. The PBO fibres were electroless copper coated to protect the polymer fibre from oxidation during processing and to improve the interfacial properties between the reinforcing polymer and the metal matrix. LM6 aluminium cast alloy was used as a matrix metal. The electroless copper coated PBO fibres preform were unidirectional placed inside a mould and infiltrated by molten liquid metal.

Findings: After casting, it was found that the liquid melt could infiltrate only partially through the first layer of the fibre preform, and could not infiltrate further, which was evident from the infiltrated metal front. This was mainly because of the forced convective heat transfer made by the argon cover gas, which cools the molten metal front and thereby increases the surface tension of the advancing front. It was further noticed that some charring of the polymer fibres after two hours of casting, which reflects that, there was oxidation of polymer fibres after prolonged heating by the hot infiltrating metal front in absence of argon cover gas after first one hour of its use after casting.

Application: The new material proposed for development could find applications in light weight high performance vehicles like aerospace and automobiles.

Keywords: Composites, High-Modulus, High-Strength, Metal-Matrix, Polymer, Reinforced

1. Introduction

Long time since, no great attempts were made in reinforcing polymers¹,² in a metal matrix, mainly, because of the low processing temperatures of the polymers, and its low degradation/melting temperature. This characteristic made them unsuitable to be processed along with metals, especially, by liquid melt infiltration techniques. Though a number of high thermal stability polymer fibres with superior mechanical properties were reported³ they could not withstand such high temperatures as required for the processing of metals. The main advantage of reinforcing a polymer fibre in a metal matrix, is its lower density, compared with the metals; combined with the high strength, high modulus, and high elongation-at-break properties of the super fibres like Zylon, Kevlar, PBI etc. whereby, a...
high specific strength and high specific modulus composite that could serve at a high temperature could be made. Such a metal plastic system offers higher weight reduction and suits in aerospace, automobile, performance sports, and like applications. An attempt was reported in a patent to cast a polymer fibre reinforced MMC (Metal Matrix Composite) with random orientation of fibres, but the work did not quantify the material properties of the composite thus made. Another important challenge in reinforcing the polymer fibre in a MMC is the poor interfacial bonding between the reinforcing the polymer fibre and the metal matrix. Thus one of the present challenges in reinforcing the polymer fibre in a MMC is the poor interfacial bonding between the polymer fibre and the metal matrix. One of the possible solutions is to coat the polymer fibre with a suitable metal such that the coated metal forms a better interface between the polymer fibre and the metal matrix. Hence an attempt was made to reinforce PBO fibres, which are commercially available by the trade name Zylon; in a commercially available Al-Si eutectic alloy namely the LM6, an aluminium cast alloy as a metal matrix with the polymer fibres electroless coated with copper.

The main advantages of the high performance polymer reinforced MMC are:

- To take advantage of the low density of the fibres in reducing weight considerably where metals are fully used.
- To take advantage of the high strength and high stiffness of the super fibres, which are lighter and stronger than the metal matrix used.
- To protect the fibres in a metal matrix, thereby enabling it to be used for high temperature applications.
- To protect the fibres from UV and other light exposed degradations.
- To compensate for the thermal stresses due to negative coefficient of thermal expansion of the polymer.
- To take advantage of the higher Limiting Oxidation Index, so that the polymer fibres can be used for high temperature applications.
- To carry 70% to 90% of the load, depending upon its volume fraction.
- High thermal stability fibres can be used for applications for high service temperatures.

2. Design

The design proposed was such as to fully utilize the superior properties of the reinforcing high performance polymer fibres. Thus, a uni-directionally reinforced polymer perform was devised so as to characterize the composite without coupling effects and for its interfacial properties. Volume fraction of 20% was used. The unidirectional fibre perform was prepared on a SS grade 304, steel frames of 0.25 mm thick, on which the fibres were wound manually, with an approximate spacing of 0.5 mm. The fibre wound frames were separated from each other by the empty stainless steel frames alternatively as spacers. The perform was secured in place inside the mould by a cast iron block, which was mechanically constrained by six bolts with clamps. The block also forms a reservoir for the molten metal for infiltration. The infiltration was gravity assisted, and the mould was kept inside a steel chamber that used Argon as a cover gas during casting, to prevent oxidation of the polymer fibres.

3. Selection of Metal Matrix Material

A major criterion in selecting the metal matrix material was its melting and processing temperature. It was noted that eutectic temperatures of Al-Mg, Al-Si are worth considering. Though Al-Mg eutectic has very low melting point, the cast eutectic alloy was found to be highly brittle and seems could not be used directly. Moreover, the processing of eutectic or near eutectic Al-Mg alloys also poses difficulty due to high oxidative nature of magnesium element at eutectic composition. Hence commercial aluminium cast alloy, LM6 was chosen as a metal matrix whose eutectic melting point is 577±1 °C. The chemical composition of the supplied LM6 is presented in the Table 1; and the mechanical properties of the LM6 alloy nominal values are presented in the Table 2.
4. Selection of Reinforcing Material

There are number of high thermal stability polymer fibres with superior mechanical properties are available commercially, of which PBO (poly-benzobisoxazole) is available commercially by the trade name Zylon, manufactured and supplied by Toyobo Co. Japan. This filament fibre has superior mechanical properties than aramid fibre and has a degradation temperature of 650 °C, which was approximately 100°C higher than that of aramid fibre. Table 3 shows the useful properties of the used Zylon AS 110 dtex fibre. It was observed from the TGA that the Zylon AS could safely withstand a temperature of 500°C without significant loss of weight even in air; and loses only around 20% of its weight in air at 700°C and less than 10% in argon atmosphere.

Table 1. Chemical composition (weight per cent) of BS 1490:1988 alloys (LM6 nominal values) against that supplied by Sargam Metals P. Ltd. Chennai

| Alloy element | LM6 (BS) | LM6 (Sargam Metals P. Ltd.) |
|---------------|----------|-----------------------------|
| Cu            | 0.1 Max  | 0.03                        |
| Mg            | 0.1 Max  | 0.07                        |
| Si            | 10.0-13.0| 11.38                       |
| Fe            | 0.6 Max  | 0.23                        |
| Mn            | 0.5 Max  | 0.03                        |
| Ni            | 0.1 Max  | 0.003                       |
| Zn            | 0.1 Max  | 0.015                       |
| Pb            | 0.1 Max  | <0.001                      |
| Sn            | 0.05 Max | <0.001                      |
| Ti            | 0.2 Max  | 0.023                       |

Table 2. Typical mechanical properties of BS-1480:1998 alloys (as cast for LM6)

| Tenacity | Modulus | Elongation | Density | Freezing range |
|----------|---------|------------|---------|----------------|
| GPa      | GPa     | %          | g/cm³   | °C             |
| LM6      | 0.17    | 71         | 5-10    | 2.65           | 575 – 565    |
5. Electroless Copper Coating

The PBO fibres could be Copper/Nickel/Gold coated by electro less coating technique. This was mainly done to make them electrically conductive for electronic applications and also for textile use. The coating procedure was reproduced here for the purpose of protecting the polymer fibres against oxidation, against thermal degradation of its properties, and to improve the interfacial properties between the fibre. The metallization of the PBO fibres was restricted to copper, as copper forms good inter-metallics with aluminium. Figure 1 to Figure 3 shows the SEM images of the uncoated, chemically treated, and electroless coated Zylon fibres. The EDS of the coated fibre shown in Figure 4 reveals that copper was coated and some palladium and tin were also present, which is used for the chemical coating. The TGA of the copper coated fibre shown in Figure 5, reveals an increase in the degradation temperature of 708.95°C as opposed to 650°C against the uncoated fibre.

Table 3. Zylon AS fibre properties

|                | Tenacity | Modulus | Elongation | Density | Heat Resistance |
|----------------|----------|---------|------------|---------|----------------|
|                | GPa      | GPa     | %          | g/cm3   | °C             |
| Zylon          | 5.8      | 180     | 3.5        | 1.54    | 650            |

Figure 1. Zylon AS filament fibres.

Figure 2. Zylon AS filament-chemical treated.
Figure 3. Zylon AS filament – Electroless Cu coated.

Figure 4. EDS of Cu coated Zylon.

Figure 5. TGA of Cu coated Zylon.
6. Composite Properties Calculation

Calculation of Elastic modulus and tensile strength:\[E_{1}\text{comp}} = V_f E_f + V_m E_m\] (1)
\[\sigma_{1\text{comp}} = V_f \sigma_f + V_m \sigma_m\] (2)

Where:
- \(E_{1\text{comp}}\) is the Young's Modulus of the composite along the fiber direction.
- \(\sigma_{1\text{comp}}\) is the Tensile strength of the composite along the fiber direction.
- \(V_f\) is the Volume fraction of the fiber used.
- \(V_m\) is the Volume fraction of the matrix material.
- \(E_f\) is the Young's Modulus of the fiber.
- \(E_m\) is the Young's Modulus of the matrix material.
- \(\sigma_f\) is the Tensile strength of the fiber.
- \(\sigma_m\) is the Tensile strength of the matrix material.

% increase in \(E_{1\text{comp}}\) = ((92.8 – 71)/ 71)* 100 = 30.7%.
% increase in \(\sigma_{1\text{comp}}\) = ((1.29 – 0.17)/ 0.17)*100 = 662%.

This shows that a 20% volume fraction of fibers results in 6.6 times more tensile strength than the matrix metal alone.

Series Model (Along the transverse direction)

\[E_{2\text{comp}} = 1/((V_f/E_f) + (V_m/E_m))\] (3)
\[\sigma_{2\text{comp}} = 1/((V_f/\sigma_f) + (V_m/\sigma_m))\] (4)

Where, Suffix 2 stands for transverse to fiber direction.

% increase in \(E_{2\text{comp}} = ((80 – 71)/ 71)\times 100 = 12.6%\)
% increase in \(\sigma_{2\text{comp}} = ((0.211 – 0.17)/ 0.17)\times100 = 24.1%\)

The calculations show that the increase in the transverse properties was also significant.

7. Fabrication

The mould for liquid infiltration of electroless copper coated preform was made of die steel, with top pouring facility. Its dimensions were arrived so that three specimens for each test could be made as per ASTM standards in a single casting. The copper coated fibre was wound on steel frames as shown in Figure 6 placed inside the mould. The frames were made of SS grade 304, and empty spacer frames of SS grade 304 placed alternatively with the wound frames as spacers to form the fibre preform. A cast iron block shown in Figure 7 was used to mechanically constrain the fibre preform by means of clamps and bolts. Six ejector bolts were also kept at the bottom for ejecting the mould when needed.

Figure 6. Cu coated Zylon wound on a SS frame.
8. Experiment

The experimental consists of an argon cylinder, connected with the stainless steel chamber, and the mould with fibre preform kept ready for the casting. The LM6 alloy was melted in a muffle furnace to a temperature of 750°C, i.e., super-heated to enable it to be transferred to the mould for casting and also to lose some temperature during transit to the mould. It was poured after passing 30 cc/min of argon cover gas to the chamber. The infiltration was gravity driven. Argon gas was cut off after 1 hour, and the casting was removed after three hours of cooling in atmosphere.

9. Results and Discussion

The SEM images of un-coated polymer shows a very smooth surface, which turns out to be little rough on acid pre-treatment and also a reduction in the diameter of the fibres. The roughness forms interlocks to prevent fibre pull outs. The SEM images of the Copper coated fibre reveals, copper coating of 1.5 µm by the procedure already available, and coated polymer fibre also has rough surface, so that the physical/mechanical interlocking is ensured. The copper coating was also promising that a better interfacial properties will be ensured than the uncoated polymer fibres on a metal matrix. Single fibre pull-out tests has already revealed that friction force created between the fibre and the matrix due to different coefficient of thermal expansion shall be high enough to hold the fibres even when there were no chemical bonding in the interface or formation of interphases. The cast metal reveals that the infiltrating metal front could not proceed further beyond first layer of the fibre preform as show in Figure 8 because of quick solidification by the flowing argon cover gas, which in turn increases the surface tension for the infil-
trating metal front. The charred fibres as shown in Figure 9 reveals that the fibres degrade after prolonged exposure of the fibres in atmosphere when it was in contact with the hot molten metal and in the absence of the argon cover gas which may be because of the thin copper coating or some uncoated regions of the fibre.

10. Summary and Conclusions

Based on the investigation of the results, the following inferences were made:

- The PBO fibres could be successfully electroless copper coated for a thickness of 0.236 µm, so that final coated fibre was 12.9 µm in diameter.
- The SEM images revealed that the coated surface appeared rough enough, so as to enable mechanical interlocking with the metal matrix.
- The electroless copper coated polymer was believed to substantially improve upon the interfacial properties of the fibre and the matrix.
- The copper coated polymer was modified to withstand higher temperatures and thus can be processed at higher temperatures since it was coated with a metal of high melting point ($T_{\text{melt, Cu}} = 1080^\circ\text{C}$) than the metal matrix.
- It was observed with the casting that the liquid melt could infiltrate the fibre preform, only partially, through the first layer of the fibre preform, when cast under open atmosphere, and could not infiltrate further. This was evident from the infiltrated metal front. This was mainly because of the forced convective heat transfer made by the flowing argon cover gas, which cools the infiltrating molten metal front.
- It was further observed that the fibre preform was in place and did not lose all of its strength.
- It was further noticed that, some charring of the polymer fibres took place after two hours of casting when the hot metal was still trying to infiltrate the preform. This was because of the oxidation of polymer fibres after prolonged heating by the hot infiltrating metal front in absence of argon cover gas after the first one hour of its use after casting.

The oxidation was mainly because of the non-uniform coating of the copper metal over the fibre that might have left the polymers exposed for oxidation as revealed by the SEM image.
- Since the molten metal front gets cooled due to the flowing Argon cover gas and the fibre gets charred due to the absence of the argon cover gas, it was suggested/proposed to carry out the infiltration process under vacuum\textsuperscript{15} or in a tubular furnace under argon cover gas, so that the flow rate through the preform was high and consequently the heat lost to the surroundings could be minimum to enable the molten metal front to infiltrate; and also to prevent oxidation of the fibres.

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