Mechanical behaviour of graphene and carbon fibre reinforced epoxy based hybrid nanocomposites for orthotic callipers

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ABSTRACT
The current analysis examines the efficiency of a composite with polymer matrix reinforced with carbon fibre and graphene at the micro and nano level respectively as an alternative material for aluminium components of Orthotic callipers. An attempt has been made to use both the carbon fibre and graphene as hybrid reinforcement with the matrix as epoxy resin. The addition of graphene and carbon fibre was 2% and 10% respectively by weight of epoxy. Dispersion of graphene was carried out using an ultrasonic sonicator and carbon fibres were reinforced using hand lay-up technique. The total fabrication was carried out under vacuum to ensure void-free test samples. The samples were tested under tension and 3 Point Bending condition to estimate the Tensile and Flexural properties, under permissible load and deflection criteria. The results found were then compared with presently used material for orthotic callipers extensively used by amputees suffering from the locomotive, gait issues, and polio-affected survivors. The proposed composite showed higher strength, lower deformation and higher stiffness with a lower weight-to-volume ratio as compared to presently used material, i.e. aluminium.

1. Introduction
As the population is increasing at a faster rate in the same way more cases of disability is also being observed. There are different types of disability which are categorised into various type related to body parts like eye, ear, legs and many more. Here in this paper authors are really concerned about those people who are suffering from problems related to legs, i.e. who are not able to walk properly, sit and move from one position to another. The reason can be amputation, disfigurement or underdevelopment of legs. These people are always in need of device or an appliance which are designed to provide assistance for their movement. Orthotic Callipers was the solution provided by scientists/researchers toward the problems of the amputees. Orthotic callipers (Figure 1) are appliances that are brought up by an orthopaedist to improve the situation for affected polio survivors and patients suffering from disability related to locomotion [1]. With the help of callipers, it
becomes easy for the patients to keep their weakened joints straight and incorrect position [2]. They provide stiffness and strength to those joints which are feeble or are paralysed and do not function properly. Hence selecting proper callipers is of utmost importance for the patients which provides a solution to all their specific requirements such as it controls the undesirable movement due to which they can walk, sit and move in right manner without any distractions. Orthotic callipers consist of side metallic braces which are made up of metals attached to it, leather knee straps and shoe. The side metallic braces of orthotic callipers are nowadays made up of aluminium alloy. Orthotic callipers being

Figure 1. Commercially available orthotic braces/callipers.
designed by the researchers/scientist to inherit certain qualities like it should have a lower weight-to-volume ratio, less costly, provide higher firmness and durability, reliable, environment-friendly etc. They are also planned according to the patient’s age group, their problem, occupation, and body weight. After a certain age, upper body fatigue increases in case of polio patients due to which they find difficulty in walking and moving and then callipers are not strong enough to sustain the individual weight and unfortunately they have no option but to change their callipers again [3]. Not every individual is capable enough to afford new callipers and replaces it as per their requirement. So, the callipers designed should be adjustable and moulded as per the requirement. They are made accessible to the patients in nearby hospitals and rehab centres [4].

As presently manufactured callipers are made up of aluminium hence weight of the same is still an issue which needs to be reduced. The physically challenged patients are in need of such material which is lighter in weight, provides required strength and stiffness when compared to other materials (ferrous and non-ferrous), should be long-lasting, cost-effective and environmentally inert. One such material could be a polymer-based hybrid composite comprising of epoxy as matrix reinforced with graphene and carbon fibre as additives. Presently these are the emerging material in the field of engineering, science, and technology. Both the materials (graphene as well as carbon fibre) have come into picture due to its extraordinary and unique properties which makes it a phenomenal material for being used in designing orthotic callipers.

Graphene also denoted as GA, is a two-dimensional rectangular array of a carbon atom which is arranged in a structure of small hexagonal cells. Two derivatives are derived from graphene which is named as graphene oxide (Go) and other is known as reduced graphene oxide (rGo) [5]. Graphene is an exciting material and has numerous numbers of beneficial properties which helps in creating composites of superior qualities. It can be easily added to different materials such as metals, polymers, and ceramic to create composites that are conductive and resistant to heat as well as pressure [6]. There are many materials which perform only one function at a time but graphene is multifunctional. Graphene is very light, thin, strong, large surface area, great heat and electrical conductivity due to which it is also stated as a ‘miracle material’ [7]. Ball milling is the process being used for the production of graphene. The process allows a change in fillers structure which helps in increasing the characteristics of fillers with polymer blends. Earlier this process of milling was used to mix polymer blends and filler nano-material in definite shape and volume [8,9]. It is mostly done at room temperature and the process of fabrication is environment-friendly and is capable of being sustained economically. It has limitless applications in the field of aerospace, transport, sports, purification of industrial and pharmaceutical products, anti-corrosion coating, fuel cells, flexible electronics, food packaging and are also being used in sports gadgets like tennis racquet [10,11]. For water filtration, derivative of graphene that is graphene oxide is used. Graphene inherent attributes opened up completely new opportunities such as building structures, design components that researchers never thought of [12].

Polymer matrix composites, also known as PMC finds use in the many facets of applications. Generally, two types of polymeric matrix exist, thermoplastic and thermosetting. Materials that soften when heated above glass transition temperature and becomes hard on cooling are thermoplastic materials. Examples of the same are polyethylene, polycarbonate, polystyrene, polypropylene etc. Thermoset materials cannot be recycled and are
hard, brittle in nature and do not soften with heating. Thermoset materials consist of epoxies, polyesters, phenolic, Bakelite, etc. For fabrication of thermoplastic based composites, use of injecting moulding, extrusion etc. are utilised whereas, for thermoset based composites, compression moulding equipment’s like Carver Press are used. The properties of polymer-based composites are determined by the properties of the fibre and the resin, geometry, and orientation of the fibres in the composite and above all the fibre volume fraction [13,14].

In the present study, graphene and carbon fibre were embedded in a polymeric matrix (Epoxy) for designing side metallic braces of orthotic callipers for polio-infected survivors and patients suffering from locomotion problems and gait movement. The mechanical performance was studied after the experimentation and strength obtained were compared to the presently used aluminium based callipers.

2. Materials and experimental details

2.1. Materials

In the present work, the epoxy-based thermosetting polymer was used as matrix and was reinforced with Graphene (2% by wt.) and Carbon fibres (10% by wt.). The standard epoxy matrix has a two-component with bisphenol A, based resin, AW 106 and an amine-based hardener, HV 953IN. The standard epoxy resin was chosen as matrix material owing to its greater mechanical strength, higher thermal stability, and negligible dimensional shrinkage on curing, high viscosity and density than the other thermoset polymer resins like polyester [15]. Graphene, with properties such as flexibility, transparency, ultra-strength, elastic nature, scalable, transferable, corrosion resistance, electrically conducting etc., has evolved and dominated the materials world. GA has a high tensile modulus, strength, low density and large surface area when compared to materials like aluminium and steel [16]. Carbon fibre is relatively new sophisticated material that has found many uses in the world of sports, i.e. tennis racquets, skis, high jump poles etc. Its light and flexible yet strong boosting performances give the object desired strength and flexibility suitable for its function [17,18]. The properties of carbon filler like high stiffness, firmness, low weight-density-to-volume ration, high reliability, better chemical resistance, heat tolerance and low coefficient of thermal expansion make it usable in construction and building components, products in industrial, military, sports and others [19,20]. The properties, as per the suppliers’ documentation, of graphene and carbon fibre used for the present experimentation, is stated in Table 1.

Table 1. Properties of graphene and carbon fibre (supplier data).

| Material       | Specifications | Dimensions            |
|---------------|---------------|-----------------------|
| **Graphene**  | Diameter      | 10–12 nm              |
|               | Purity        | 95%–97%               |
|               | Specific surface area | 325–594 m²/g        |
|               | Bulk density  | 0.231 g/cc            |
|               | Oxygen content| <4%                   |
|               | Purity        | > 98%                 |
|               | Fibre thickness | 12–20 microns       |
|               | Weight/length | 0.223 g/m            |
|               | Density       | 1.78 g/cc             |
| **Carbon fibre** |              |                       |
|               | Diameter      |                       |
|               | Purity        |                       |
|               | Specific surface area |                 |
|               | Bulk density  |                       |
|               | Oxygen content|                       |
|               | Purity        |                       |
|               | Fibre thickness |                   |
|               | Weight/length |                       |
|               | Density       |                       |
It has already been proved that fillers possess a strong affinity for liquid so they tend to disperse in and mix with them easily because of which it leads to better interfacial adhesion between them. To increase the adhesive property graphene (1%) + resin and graphene (1%) + hardener was mixed separately using ultra-sonication [21]. The mixtures were kept in the ultrasonicator for around 1 h to reach the maximum dispersion [22]. The mixtures were then mixed together with a mechanical stirrer at 100 rpm for 8-10 min to form the matrix. The matrix was then slowly and carefully poured in a rectangular metallic mould containing carbon fibre (10%) placed in proper orientation and spacing. The composite, thus prepared, was kept in a Carver Press at 160 °C and to remove air bubbles vacuum atmosphere was used throughout the process. The material was allowed to rest inside carver press for around 5-6 h at room temperature check for curing. Afterward, the whole mould setup was placed inside a hot air oven at 70 °C for 3 h for post curing purpose. Later on samples were taken out of the mould for investigation.

2.2. Material testing

2.2.1. Void assessment test

The detrimental effect of the presence of manufacturing induced defect like voids makes it a critical issue in the applicability of composite material in engineering structures. The void assessment test is carried out according to ASTM D 2734–94. The theoretical densities of prepared composite material was evaluated by using simple weight additive principle and actual density of the same was determined experimentally by Archimede’s principle, i.e. water immersion method. The difference indicated the void or air content (generally expressed in %age). This must be assessed to investigate the acceptability of developed material and find the allowable amount of void fraction.

2.2.2. Surface morphology

The morphology of the prepared specimens was examined under a scanning electron microscope (JSM-6390LV) using stereo scan 20 kV. Before evaluation, Platinum was used to coat the specimens using a plasma sputtering apparatus to avoid charging under the electron beam. Apart from investigating the nanofiller distribution, SEM study was also performed to establish the nature and trend of mechanical behaviour.

2.2.3. Mechanical tests

Universal testing machine (UTM) was used to test the tensile and flexural behaviour of composite materials. The mechanical tests were undertaken on Instron Universal Testing Machine (Instron Ltd, UK). The tensile test was undertaken as per ASTM D-638 standard using a universal testing machine of 50 kN grip capacity. The typical dimension of the tensile specimen is 63.5 mm × 10 mm × 3.2 mm in a rectangular shape with a gauge length of 7.65 mm at 24 °C and 56% relative humidity. The flexural test was conducted in three-point bending mode following ASTM D 790-03 with sample dimension of 65 mm × 12.7 mm × 3.2 mm with a support span of 50 mm under same testing conditions as that for the tensile test.
3. Results and discussion

3.1. Void content

The assessment of void content that built up due to the trapping of air bubbles during the casting of graphene and carbon fibre reinforced epoxy hybrid composite specimens were accomplished and values are illustrated in Table 2. It can be revealed from the table that experimental data is lesser than the theoretical showing existence of voids at the surface forming the common boundary within the composites. This behaviour can be attributed to the entrapment of the air bubbles due to adhesion to the fibre surface during the curing process. It can also be noted that density of aluminium alloy (presently used orthotic callipers) is more than the epoxy (thermoset) based composites. This ensures the lower self-weight of the orthotic callipers fabricated using the composite.

3.2. Morphological study

SEM images have been used to investigate the dispersion morphology and the interactions between matrix and fibre. From the figure (Figure 2) it can be visualised that the dispersion and the interaction of filler with the matrix are evenly spread.

3.3. Tensile and flexural tests

The tensile test was carried out in accordance with ASTM D 638 where the specimens are unit placed within the grips and are unit force till failure. The tensile tests are performed with the best possible load capacity of 1 kN with 50 mm gauge length and 2.5 mm / min crosshead speed. The information regarding the data of tensile modulus and tensile strength are entered on a computer joined in close association with machine setup. The flexural test was executed as per ASTM D 790 standard with loading the sample at the specified rate till the breaking of the specimen. The tests were performed specifying the span as 50 mm and 2.5 mm / min crosshead speed. Flexural stress, flexural strain, and lateral deformation were recorded from the tests. According to the ASTM standard mechanical tests were performed on five samples for both aluminium and prepared composites and average of the results were reported along with the standard deviation. The plots of the various values are depicted in Figures 3 and 4. Figure 3(a) shows the tensile strength values for each of the materials whereas Figure 3(b) illustrates the variation in maximum strain for the same. Figure 3(c) reveals maximum deformation undergone in axial loading condition.

The improvement of mechanical properties of the hybrid composites is primarily guided by the fact that homogeneous distribution of the particulate fillers in the epoxy matrix and formation of a link between the fibre surface and the matrix at the interface. The distribution of filler was uniform as depicted in the SEM images. In this study, the enhancement of mechanical properties of the composite was primarily guided by the

| Material of construction | Density (g/cc) | Void fraction(%) |
|--------------------------|----------------|-----------------|
| Aluminium                | 2.705          | –               | –               |
| Composite                | 1.137          | 1.144           | 0.616           |

Table 2. Density and void content of composite and aluminium alloy.
enhancement of adhesion between the reinforcement and the matrix at the interface due to the presence of graphene. Hence the formation of the primary bond between filler and resin at interface helps the proper transfer of the load from matrix phase to filler phase which increases the mechanical properties.

Figure 4(a) shows flexural strength data whereas Figure 4(b) indicates the flexural strain. The lateral deformation can be viewed in Figure 4(c). From all the graphs it is clear that the mechanical strength of the proposed hybrid composite is more eminent than the existing aluminium alloy. The Equivalent Von-mises strain and Total Deformation is lesser for the composite. This can be imputed to same explanation as for the tensile

![Scanning electron microscopy image.](image-url)

**Figure 2.** Scanning electron microscopy image.

![Comparison of tensile properties with standard deviations](image-url)

**Figure 3.** Comparison of tensile properties with standard deviations (a) equivalent stresses; (b) equivalent strain deviations; (c) maximum deformation.
properties. This shows that the aluminium alloy made callipers can be fancied using graphene and carbon fibre reinforced epoxy based hybrid nanocomposites.

As discussed above and depicted in the figures the maximum deformation and strain also vary in the similar trend as in case of Equivalent Von-mises stress both under axial and lateral loading condition.

4. Conclusions

An alternative material, if chosen, should provide results better than that of the presently used material (aluminium alloy) at a lower cost for acceptability by the manufacturer and users of the lower body orthotic callipers. The present work suggests that one such material can be graphene and carbon fibre reinforced epoxy based hybrid nanocomposites which apart from giving better strength would also provide lower weight to volume ratio. The results indicated that it would provide better strength and stiffness and lower weight to volume ration when compared with the results of presently used aluminium based callipers. Hence, usage of the same would surely decrease the self-weight of the callipers and would increase the ease of mobility of the polio-infected patient.

5. Future work

The callipers should also be tested for Compression and Hardness for evaluation of mechanical properties. Moreover, as, the length of the braces is much more compared to
the cross-sectional dimensions, i.e. slenderness ratio is high, hence a buckling test would also provide a better judgement towards adoption of the alternative material. Since these supports undergo wear and tear and are always subject to adverse climatic conditions hence Tribological testing and Dynamic Mechanical Testing would give a more insight into the material selection. A complete lower body orthotic calliper is required to be fabricated and to be clinically tested under actual usage before replacing the aluminium alloy made callipers with proposed composite ones.

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No potential conflict of interest was reported by the authors.

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