A review on Graphene Reinforced Composites for Ballistic applications

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Abstract - The review paper emphasizes mainly on the hybridization of coir fiber and spider silk with carbon fiber and different percentage compositions of graphene, with an ultimate aim as to how the strength of these hybridized composites can contribute in the fields of material and manufacturing engineering. Firstly, there is an analysis of different properties of coir, carbon fibers, graphene and spider silk. Secondly, there is an analysis of the ballistic test performed on the specimens. In this review, some very basic yet important information is collected and discussed which will help the future researchers in the preparation of hybrid composites involving graphene. Being a natural fiber, the bristle coir fibers are pre-treated with alkali (NaOH) and then acidic treatment is done to remove the excess alkali. After the fibers become neutral, permanganate treatment is done. In case of spider silk, no pre-treatment is done. These fibers are reinforced with epoxy and different weight percentage of graphene (1wt%, 2wt%, 4wt%, 6wtt %). Carbon fibre is incorporated in between using conventional hand layup technique. The epoxy and graphene mixture is sonicated to make sure that a uniform and good mixture is obtained. The review facilitates to perform ballistic test on the samples as the results from this test can substantiate to deliver a vital improvement in the field of material selection for body armors.

Keywords: hybridization, coir fiber, spider silk, carbon fiber, graphene, ballistic test, alkali treatment, acidic treatment, permanganate treatment, epoxy, hand layup technique, sonicated and body armors.

1. Introduction

In the coming years, a number of industrial sectors will be utilizing natural fibers, including automotive, building, packaging, construction and aerospace industries. Natural fiber composites can be made renewable with comparatively low prices and low material density [1]. Even High Density Polythene (HDPE) which is non-biodegradable can be replaced with the biodegradable natural fibers [2]. However, the challenge still remains to expand the usage of green fibers composites. This can be done only when the cost of production with the properties of these matrixes likes mechanical and heat are parallel to the traditionally used materials [3]. Rural areas have developed their economy by virtue of incorporating natural fibers in various different applications and industries [4]. Natural fibers exhibit an upper hand over man-made fibers as they are cheaper, lighter, smooth with the equipment, safe to the skin, have comparable mechanical properties, less energy consumption and biodegradable [5]. However, having said so, there is still a hybridization of manufactured or artificial fibers such as e-glass fibers and carbon fibers with natural fibers to enhance the properties of the latter in the area of strength. Graphene is often used as reinforcing material to impart strength. From studies, it has been found that interface to volume ratio along with filler size are the governing factors for enhancing the mechanical strength of the composites. Graphene has emerged as outstanding filler for matrix enhancement. The oxygen functional groups in the Graphene oxide impart strong binding to the matrix [6]. Many researches have even shown that the hybrid composites of Carbon fiber and epoxy have better mechanical properties than plain composites [7]. Whenever there is a requirement of a combination of low density and good mechanical property, Carbon fibers (CFs) have an edge over glass fibers due to their high stiffness [8]. From these references (6-8), it is clear that till now there is no such systematic mechanical testing done on fiber composites involving carbon fiber and graphene
with any other natural fiber. Through this review, some very important characteristics of Coir fiber, carbon fiber, Graphene and spider silk are discussed, with a view that in coming future, researchers can think of forming hybrid composites consisting of carbon fiber, graphene and coir fiber (natural fiber).

1.1 Coir

When talked about natural fibers, one of the very potential fibers is the coir fiber. It is the hairy casing of the coconut shell. It possesses about 48% of lignin increasing strength and elasticity of fibre [9]. There is an annual production of around 250,000 tons of coir. One very interesting fact is out of the total production of the white coir in the entire world, 60% is produced from an Indian state- Kerala. Our neighboring country, Sri Lanka too has a significant contribution of 36% in the production of brown coir throughout the world. However, half of the total coir fiber produced in a year across the world is consumed by India alone [10].

1.1.1. Coir hybrid composites

Synthetic fibers if replaced by natural fibers, will contribute towards sustainable development and reduction in greenhouse emissions [11]. When a coir fiber is added into a plastic material its tensile strength, impact strength and hardness increases in comparison with pure plastic specimen because fibers provide strength to reinforced composites.

![Bristle coir fibers](image)

As the fiber wt % increases in composite interface bonding between fiber and resin keeps on decreasing after a point [12]. An investigation deduced that there is a direct relation between the distance and amount of the fiber with water absorption rate and void content in coir fiber-epoxy composites [13-14]. Arrangement of fibers in the synthesis have a great effect on the composites related to mechanical behavior specially strength, it is observed that longitudinal direction of fibers displayed better mechanical properties than in the transverse direction [15]. Composite is considered good when we have proper interfacial bonding in composite with less dissipation of energy. [16]. Whenever there is an application of tensile load on the short fiber composites, there is a transfer of load to fiber-matrix surface. It takes place by virtue of shear force. The stresses are zero at the end of the composites, while it increases along the fiber length, hence the composite should have a minimum length which is called as the critical length (Lc) so that the tensile loading process is done precisely [17].

1.1.2. Alkali treatment of coir fibers

Raw unprocessed fibers are treated with chemicals in order to be used for any research purpose. The sole aim is to remove the excess lignin content from the fibers. Having said so, there are ill-effects of using excessive alkali. Abundance of oxidant concentration may lead to the loss of the fibrous amount of the fiber which ultimately reduces the crystallinity of the end product. Some researchers have deduced that, when raw fibers are treated with 5% NaOH, composites showed an increase by 34X in tensile strength whereas the load carrying capacity increases 9 folds when compared with composites made from the non-treated fibers. After the alkaline treatment, the strength can further be increased, if the fibers are treated with 3% Permanganate. This increases the load carrying capacity by 1.3X. It also reduces the deflection by 2.9 times with respect to the pure epoxy sample. Surface roughness by virtue of alkaline treatment is the basic reason for the easy bonding of the fibers [18]. As discussed earlier, alkaline treatment helps to remove excess lignin as well as wax and oils. These constituents otherwise contribute in the formation of a weak boundary layer as they reduce the bonding among the fibers with the composite [19]. There has been a substantial improvement observed in the flexural as well as tensile properties of sisal-carbon hybridized composites when alkali treated fibers were used in place of untreated fibers. The reason was again the increase in the surface roughness topography by the action of hemicellulose removal. This topography imparted better adhesion to the fibers which led to enhanced mechanical properties [20].

1.1.3. Coir fiber mass content

Lignin content is high in the case of coir fiber which is contrasting to other natural fibers, which makes it more durable than other fibers [21]. Coir fiber mass content is important in deciding the synthesis properties like mechanical. When coir fiber mass content was taken as 25%, optimum mechanical properties were
obtained as the tensile strength increased by 54.5% and flexural strength by 45.7%, when compared to the pure resin [22]. From various researches, it was concluded that nano-graphite particles when used like strengthening substance, highly increased the synthesis behavioral properties in context to mechanical. [19].

1.2. Carbon fiber

From various studies, it is found that properties of any polymer matrix can be enhanced by hybridization in context to mechanical [23]. For advanced structural applications, plant and synthetic fibers are being hybridized in the nano filler modified polymeric matrix. This interesting research approach has succeeded in obtaining excellent viscoelastic, mechanical and thermal properties. The process of hybridization has reduced the degradation of environment as these have reduced the dependency on synthetic fibers. Carbon fiber has been shown in figure 2.

Figure. 2 Carbon fiber

From studies conducting dynamic and thermogravimetric mechanical analysis, it was observed, at elevated temperatures, Kevlar/epoxy polymeric structures can be efficiently replaced by the hybrid composites [24]. One of the most potential fibers of the hybridization process is carbon nano-fiber (CNF). These fibers, as nano fillers, have found an effective use in enhancing the laminated composite’s shear strength between the laminar. From studies, it has been observed that on addition of organo-clay, properties such as fracture toughness and crack growth resistance underwent significant improvement related to carbon and different polymer matrixes. The mixing of GnPs into epoxy matrix can be done through ultrasonic sonication [25]. Use of natural plant fibers actually positively adds up to the carbon expense as many researches have shown confiscating carbon dioxide nature of these strands of natural fibres [26]. The epoxy resins which are reinforced with carbon fibers are used for many useful purposes such as bridge construction, fuel cells and even aerospace industry [27].

1.3. Graphene

Graphene, two dimensional single atom thick honeycomb material has been considered as a highly reliable substance because of its excellent electrical conductivity, unique thermal and mechanical properties. It has many potential applications in clean energy, sensors, electronic and photonic devices [28]. Graphene is the strongest materials of carbon nanotechnology. Graphene oxide (GO) powder can be shown in figure 3.

1.3.1. Graphene reinforced composites

The thickness of a monolayer of graphene 2D isotropic sheet is around 0.335nm, but still it has an exceptional Young’s modulus of 1 TPa and strength of 125 GPa. With a calculated value of 0.25-0.30, graphene has a very high failure strain [29]. Tensile strength reaches maximum with a small amount of graphene fillers added, beyond that strength decreases [30].

Figure. 3 Graphene

In addition to this, graphene doesn’t intensify the resistance to the flow of resin in comparison to what carbon nanotubes do, empowering the consolidation of higher concentration into the arrangement. [31]. Graphene can reinforce the compound; however, this fortification stays restricted in view of the huge surface vitality that is created by the solid van der Waals bond [32]. Studies have likewise demonstrated that Graphene oxide (GO) sheets have upgraded the interfacial just as rigidity of carbon fiber fortified composites [33].

1.3.2. Graphene integrated with epoxy
In the current scenario, nano-particle-reinforced polymer composites are most promising and reliable in the field of future tech designing applications with a negligible scattering of nano-particles. Another important component of a composite is epoxy (as shown in figure 4). Right now, improved adhesive saps are widely utilized in the manufacture of natural fiber-fortified composites and in making its diverse modern items because of their predominant properties in the field of mechanical, thermal and electrical [34].

It is a versatile thermosetting polymer. However, due to its inherent hardness and brittle nature, it cannot provide good strength required for high performance applications. To overcome this, epoxy resin can be modified using potential nano-materials such as graphene oxide (GO), graphite nano-platelet and graphene with natural or synthetic fiber as a reinforcing agent. This enhances the strength and stiffness of the composites. This process of nano modification can lead to several enhanced properties which are model dominated such as mechanical, electrical and physical. For the proper mixing and interaction of GO with epoxy resin and fibers, Cetyl trimethyl ammonium bromide (CTAB) treatment is done, which brings about upgraded mechanical properties of the matrix. From recent studies, it has been observed that 5.0 wt. % GO composites, when contrasted with flawless epoxy structures showed greater mechanical properties because of fine scattering of GO in epoxy matrix by CTAB [35-36].

1.3.3. Graphene volume content

It is also seen that graphene volume fraction has a linear relation with the toughness of the amalgamation. When the volume division is high, it results in graphene aggregation which ultimately leads to a dramatic decrement of both the modulus and strength [37]. With this new and effective approach of using GO, various opportunities can be created to develop various good potential high-performance composites for industrial applications [38]. There was an enhancement in vitality retention of the 9 layered Kevlar texture based epoxy combination on addition of graphene nano-platelets (GnPs) [39].

1.4. Spider Silk

Another potential synthetic fiber is silk. It is a protein containing fiber. It is normally created by numerous spineless creatures that incorporate web spinners (Embioptera), trichopteran hatchlings, some Hymenoptera, and all creepy crawlies (Araneidae) [40].

Among these, the most impressive silk toolkits are of web builders. Silks and especially spider silks are exceptionally tough. This durability is principally a result of the amino acid grouping and turning process [41]. Research on spider silk in the course of recent decades has begun to uncover the sub-atomic components that produce its mechanical properties. Spider silk proteins are comprised of many couple rehashes of explicit, exceptionally saved amino acids themes. Distinctive amino acid themes contribute explicit mechanical properties to the fiber. Major Ampullate silk, the most grounded kind of silk, is
comprised of two proteins: Major ampullate Spidroin 1 (MaSp1) and Major ampullate Spidroin 2 (MaSp2). These two proteins each loan quality and flexibility to the fiber through extraordinary tandemly rehashed amino corrosive themes, which are profoundly rationed all through the sphere web weaving creepy crawly species [42]. Some important literature is shown in Table 1.

Table 1. Important conclusions from literature survey

| Sr. No. | Authors | Year of publication | Main findings | Uncertainty |
|---------|---------|---------------------|---------------|-------------|
| 1.      | Sean J. Blamires¹, Chung-Lin Wu¹, Todd A. Blackledge⁴, and I-Min Tso¹,² | 2012 | Post-emission handling causes variety in the mechanical exhibition of wild MA silk free of protein organization or turning speed crosswise over 10 types of spider. | Post discharge strands get influenced by different factors, for example, hereditary impacts, phylogenetic sign, post-emission physiological and biochemical procedures and variables acting during turning and post-turning. |
| 2.      | Sean J. Blamires⁴,², Todd A. Blackledge⁴ and I-Min Tso¹ | 2016 | Web-developing creepy crawlies produce to seven distinct kinds of silk, every one of which is discharged from various organs, has various capacities, and has diverse substance and physical properties. | It is basic to comprehend the characteristic procedures that reason spider silk properties to differ among species (phylogenetic inconstancy) and inside species (silk versatility). |
| 3.      | Andreas Koeppel and Chris Holland* | 2017 | This audit gives a diagram of the various methodologies for fake silk fiber turning and analyzes all distributed fiber properties to date which has distinguished future patterns and difficulties out and about towards reproducing elite silks. | Each approach has its very own difficulties to defeat encompassing parts of the feedstock/dope, fiber turning, and post processing: for the entrenched wet turning, apparently post processing through the enduring diminishing in fiber distance across close by an expansion in post draw proportion has seen critical upgrades in mechanical properties. |
| 4.      | Fábio de Oliveira Bragaā,b*, Lucas Tedesco Bolzana, Flávio James Humberto Tommasini Vieira Ramosa, Sergio Neves Monteiroa, Édio Pereira Lima Jr.a, Luis Carlos da Silva | 2018 | Among all the sisal fibre-fortified polyester composites considered in the present work, that with 30 vol. % displayed the best outcomes, as far as injury counteractive action and physical honesty after the effect. In this way, it was viewed as the most appropriate material to be considered as MAS second layer. | The loss of physical respectability of both the flawless polyester pitch and the 10 vol. % sisal fiber polyester composite makes them unacceptable to be utilized as a second layer of MAS in multi hit protection. |
| 5.      | R.Yahaya¹,³, S.M. Sapuan¹,²,⁴, M.Jawaid²,³, z. Leman¹ and E.S. Zainudin¹,² | 2015 | Natural fiber composites may endure when the material is presented to antagonistic situations for long periods of time. | A reduction in elastic properties of the composites was illustrated, demonstrating an extraordinary misfortune in mechanical properties of the muggy examples contrasted with the dry samples. |
| 6.      | Navaranjan N and Neitzert T | 2017 | Izod and Charpy techniques were at first produced for metals and A post assessment of morphology of a NFC test after an effect test is essential to portray the material. |
1.5. **Ballistic Test**

Engineering materials possess very important mechanical property—Impact behaviour. This property is governed by various parameters such as strength, length and orientation of fibres, elastic modulus, and fibre-matrix interfacial bond strength. The type of test performed to measure the impact energy is also one important factor. Some simple methods to perform the impact test are Charpy and Izod impact test methods which are also known as pendulum methods. In these methods, the energy absorbed by the notched and the unnotched sample of a material during fracture is taken into account. This absorbed energy acts as a tool to study the ductile-brittle transition temperature. It also gives a measure of a given material’s toughness. One more important test which can be performed on the composites is the ballistic test. This particular test is used to evaluate the impact resistance of the composite panels and products such as composite armors. In this test, a projectile is fired with excessive momentum on the result to be tested. The localized damage is determined after the impact [43].

![Figure 6 Schematic view of the Ballistic Test arrangement](image)

Because of their low density, large fracture resistance, high energy adsorption and excellent stiffness and strength, nano composites are appropriate choice for ballistic armor material. A typical Multilayer Armor System (MAS) is of ceramic from the front side further its accompanied by a layer of fiber layer composite and aluminum is present at last playing a role of back layer [44]. The first layer, which is the harder front of the ceramic plate has deforms, erodes and shatters bullet projectile. The second layer is generally made of composite material such as coir which soaks up the high speed projectile shards and the ceramic’s energy. The third layer which acts as a final barrier normally involves the use of a ductile metallic layer. The second layer if substituted with natural fiber composites reinforced with graphene improves the impact absorption reduces the overall weight and cost of the system [29].

2. **Conclusion**

This review gives many important insights on composites. An attempt has been made to precisely mention all the necessary conclusions in the following points-

- Natural fibers are often hybridized with artificial man-made fibers in order to enhance the strength of the composites.
- Coir fibers contain the maximum amount of lignin content (48%) among all the natural fibers. Hence it is the toughest.
- Longitudinally oriented fiber composites exhibit better mechanical properties than transversally oriented fiber composites.
- Alkali treatment of fibers increases the strength of the composites in every aspect.
The process of hybridization is environment friendly as the dependency on synthetic fibers is reduced.

Use of reinforcing materials such as carbon fibers is known to exhibit excellent viscoelastic, thermal and mechanical properties to the composites.

The strongest reinforcing material of carbon nano-technology which is graphene is mixed with epoxy through sonication process.

Epoxy which is an excellent thermosetting nano-technology acts as a binding agent inside the composite.

Synthetic fibers such as spider silk are potential replacements for natural fibers in the composites. These are comprised of amino acid themes which results in excellent mechanical properties.

Nano composites are highly preferred choices for ballistic application due to their high fracture resistance, low density and high stiffness.

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