Fabrication and properties of CNTs reinforced polymeric matrix nanocomposites for sports applications

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Abstract. The polymeric matrix composites have found extensive applications in sports because of high strength to weight ratio, ease of processing, and longer life. This work was carried out to study the properties of different sections of composite field hockey sticks and the influence of carbon nanotubes on their properties. The samples were fabricated by compression molding process. The increase in mechanical properties by the incorporation of carbon nanotubes is correlated with the process parameters to consider enhancement in the overall performance of the stick sections.

1. Introduction
The polymeric matrix composites can be a better choice for production of sports and other items owing to high strength to weight ratio, ease of processing, and longer life [1]. A comparison of the properties of wood, fiber reinforced polymeric matrix composite, and nanocomposite is shown in Table 1. The performance and durability of sports materials is enhanced in recent years by replacing traditional wood with advanced polymeric matrix composites and nanocomposites [1]. In sports items particularly field hockey sticks are now produced by a mix of glass fibers (GF) and carbon fibers (CF) reinforced polymeric matrix composites [2]. The carbon nanotubes (CNTs) are used in advanced polymeric matrix composites to further improve the properties. CNT/epoxy nanocomposites were previously fabricated and studied for creep behavior [3], thermal and mechanical properties [4], morphology [5], cure behavior [6], effect of interfacial chemistry on molecular mobility [7], damping capacity in a broad temperature range [8], doping of nano-particles (titania) for synergistic effects in the multiphase nanocomposites [9], electrical and thermal conduction mechanisms [10], influence of cup-stacked CNTs [11], and effect of silane functionalization on the properties of CNT/epoxy nanocomposites [12].

In glass-fiber/polymer composites, addition of CNTs can increase the cyclic delamination crack propagation resistance significantly. It also shows improvement in interlaminar fracture toughness. The fatigue life can be improved up to three times in case of in-plane cyclic loading. The CNTs can decelerate the delaminating crack propagation by CNTs pull-out and fracture, and crack bridging [13]. Glass fiber reinforced epoxy and epoxy based vinyl ester composites were modified with CNTs and studied for interfacial [14] and interlaminar shear strength [15]. CNTs can also improve the Z-axis properties of composite laminates remarkably by direct reinforcing the matrix, fiber bridging mechanism, and toughening effect [15]. The flexural strength of glass fiber reinforced epoxy
Table 1. Comparison of mechanical properties of wood, composite, and nanocomposite used to manufacture field hockey sticks.

| Property                      | Wood (Mulberry) | Composite (GF/Epoxy) | Nanocomposite (CNT/GF/Epoxy) |
|-------------------------------|-----------------|-----------------------|-------------------------------|
| Density (g/cm$^3$)            | 0.64            | 1.17                  | 1.20                          |
| Flexural strength (MPa)       | 75              | 99.8                  | 154.9                         |
| Ultimate tensile strength (MPa) | 4               | 5.7                   | 11.3                          |
| Young's Modulus (GPa)         | 4.9             | 6.2                   | 8.1                           |
| Ref.                          | Relevant websites | [12, 14]               | [16, 17]                      |

Composite modified with SWNTs treated with dispersing agents Volan and BYK-9076 (proprietary) showed enhancement up to 16% mainly caused by better dispersion of SWNTs in the composite [18].

The CNTs have also improved the properties in carbon fiber/polymer composites. Carbon fiber/epoxy hybrid nanocomposites modified with amine functionalized SWNTs were fabricated and studied for crack resistance at cryogenic temperature [19] and quasi-static strength and fatigue properties [20]. Carbon fiber/epoxy hybrid nanocomposites modified with cup-stacked carbon nanotubes (CSCNTs) were fabricated and studied for mechanical properties [21] reporting three times higher fracture toughness than that without CSCNTs [22].

This work was carried out to examine properties of fiber reinforced polymeric matrix composite field hockey sticks and sheet samples produced by compression molding process. The influence of carbon nanotubes on the properties of stick samples is studied. The role of varying volume fractions and number of fiber plies of carbon and glass fiber reinforcement is determined to assess the overall performance of field hockey sticks.

2. Experimental Procedure

Field hockey sticks of specific compositions are presented in Table 2. The fabrication of composite field hockey sticks involves the use of glass fibers and carbon fibers reinforcement in the epoxy matrix. The sticks were fabricated using compression molding process. The fiber orientation in the field hockey stick is shown in Figure 1. The fiber plies were stacked at alternate 0° and ± 45°. The 0° plies impart stiffness while 45° give strength to the stick. The average length of the hockey sticks used in the current study is 95.5 cm (36.5 in). The height of the head is 11.5 cm. The shape of the hockey stick changes along its length. It is circular at the handle while elliptical at the head. The length of major axis changes from 2.5 cm to 5 cm while the minor axis is fixed at 2.5 cm. The wall thickness changes from 1.15 mm (at handle) to 6.10 mm (at head). There are 8 fiber plies in handle while 24 in head. The stick was divided into three portions; initial circular handle (section-I), central elliptical portion (section-II), and the head (section-III). The length of section-I & II is 40 cm while of section-III is 15.5 cm. The epoxy resin used as matrix for composite field hockey sticks modified with CNTs as provided by the suppliers Honlu Technology Co., Ltd. was used to study the influence of

![Figure 1. Schematic diagram showing fiber orientation in the composite field hockey stick sample.](image-url)
Table 2. Compositions of samples fabricated.

| Sr. | Compositions          | Volume fractions |   |
|-----|----------------------|------------------|---|
|     | Matrix               | Reinforcement    | Vf (%) | Vm (%) |
| 1   | Epoxy                | CF/GF            | 47     | 53     |
| 2   | Epoxy                | CF/GF            | 49     | 51     |
| 3   | Epoxy                | CF/GF            | 46     | 54     |
| 4   | Epoxy                | CF/GF            | 52     | 49     |
|     | **Composite sheets** |                  |        |        |
| 5   | Epoxy                | GWC              | 60     | 40     |
| 6   | Epoxy                | GWC/0.4vol% CNTs | 61     | 39     |

GF = Glass Fibers, CF = Carbon Fibers, GWC = Glass Woven Cloth

CNTs on the properties of composite field hockey sticks. Two composite sheets were fabricated whose composition is provided in Table 2. The processing conditions were maintained to compare results with the field hockey stick samples to assess their properties and performance.

Three point bend test of hybrid nanocomposite samples was conducted to study their flexural stress-strain response. The specimens were prepared according to ASTM Standards D790 and D4476 for rectangular and round specimens, respectively. The specimens were cut using hacksaw and polished along the longitudinal direction. The dimensions were 3.0 mm × 12.7 mm × 70 mm of rectangular specimens and 6.25 mm × 12.5 mm × 120 mm of round specimens. The support span was fixed at 48 mm for rectangular specimens and 100 mm for round specimens. The displacement rate was kept constant at 0.5 mm/min. Five specimens were tested for each composition in longitudinal direction. The test was conducted on Instron 100 kN universal testing machine Model 8501.

3. Results and Discussion

3.1. Field hockey sticks

The flexural stress-strain curves obtained from three point bend test of the samples from section-I, II, and III of the hockey sticks are shown in figures 2-4. The trend shows that the strength increases with increasing volume fraction of carbon fibers.

It can be noted that the trend of increasing strength with carbon fiber volume fraction is not linear which can be explained on the basis of microstructure. The optical micrographs reveal fiber orientation of the transverse sections taken from different locations of the stick samples (Figure 5). Figure 5 (a) shows, mainly, the glass fiber plies while (b) shows the alternate layers of glass fibers and carbon fibers. Porosity was found in the samples. It can be observed that porosity is non-uniform in size and distribution. This non-uniform size and distribution of the porosity result in variation in mechanical properties. The other reason can be non-uniform distribution of glass and carbon fibers. Two optical micrographs taken at same magnification but from different locations of the same stick are shown in Figure 6. Figure 6 (a) shows the optical micrograph of glass fibers while (b) shows carbon fibers. It shows that the fiber distribution is not the same throughout. Another reason could be variation in number of plies and fiber orientation. The optical micrographs of stick head (Sec. III) are shown in Figure 7. The stick is kept underweight throughout the hand lay-up process. It is because that the plies cannot be removed from the stick once applied. However, once the shape of the stick is fixed, the strips of fiber plies can be attached easily to get the desired weight. These strips are unequal in size as difference in weight is different for different sticks. These strips are applied at different regions keeping in consideration the weight balance. These strips can either be of glass fibers or carbon fibers. The fiber orientation in all the strips is also not the same. If these strips are not applied, the required weight would not be achieved which will again produce non-standard samples. Because of all these variables, the trend for strength is non-linear.
The influence of carbon fiber volume fraction on flexural strength of different hockey sections is shown in Figure 8. The carbon fibers varied from 5vol% to 90vol% of total fiber reinforcement. There is increase in strength with increasing volume fraction of carbon fibers. The maximum strength is achieved for head (361 MPa) while minimum strength was observed for handle (296 MPa). The number of fiber plies in handle is 8 while 24 in head. The wall thickness of handle (section-I) is 1.15 mm while that of head (section-III) is 6.10 mm. The carbon fibers are concentrated in head to improve the impact strength. It makes head stronger than handle.

3.2. Nanocomposite Sheets

The flexural stress-strain curves obtained from three point bend test of CNTs/GWC/epoxy samples are shown in Figure 9. The flexural strength increased from 54 MPa (neat epoxy) to 342 MPa by making composite with GWC as reinforcement. The strength has further increased to 372 MPa with the incorporation of carbon nanotubes. The CNTs act as additional reinforcement thereby improving the strength. The improvement in properties can further be optimized. The optical micrographs of transverse sections of samples taken from composite sheets without and with CNTs are shown in Figure 10 (a) and (b), respectively. Porosity was found that may have due to air entrapment and relative movement of the fibers and resin during compression molding. Another reason for this porosity can be solvent evaporation. The solvent is added in the resin to reduce its viscosity to help
efficient nanotube dispersion. This solvent (along with any other volatiles) gets evaporated while curing at 140 °C leaving behind a huge amount of porosity.

![Efficient nanotube dispersion](image1)

**Figure 5.** Optical micrographs of stick handle (Sec. I)

![Efficient nanotube dispersion](image2)

**Figure 6.** Optical micrographs of stick central portion (Sec. II)

![Efficient nanotube dispersion](image3)

**Figure 7.** Optical micrographs of stick head (Sec. III)

3.3. Fracture behavior

The SEM image of fractured sample taken from composite field hockey stick is shown in Figure 11 (a, b). Figure 11 (a) shows the region where the fibers are bent to give the required curvature to the stick. The fibers perpendicular to the supports were bearing the load and got fractured. Figure 11 (b) shows the intact fibers above which the matrix has sheared. It shows that the interfacial interactions were not strong enough to transfer the load, to the fibers, completely. The SEM image for composite sheet without CNTs is shown in Figure 11 (c, d). The images show delamination among fiber plies along the longitudinal direction. A similar fracture behavior was observed for composite sheet containing CNTs as shown in Figure 11 (e, f). There is no significant difference observed in the fracture mode with the
incorporation of CNTs. However, as the strength was improved by the incorporation of CNTs, the CNTs have delayed the time to fracture by alleviating the stress concentration and by blunting the tip of crack, initiated in the matrix, by CNTs pull-out and fracture i.e. “surface crack bridging” effect.

Figure 8. Influence of carbon fiber volume fraction on the flexural strength of field hockey stick samples

Figure 9. Flexural stress vs flexural strain for CNTs/GWC/epoxy nanocomposites

Figure 10. Optical micrographs of transverse sections of nanocomposite sheets; (a) GWC/epoxy, (b) CNT/GWC/epoxy

4. Conclusions

• In this work, glass and carbon fibers reinforced epoxy matrix composite field hockey sticks and sheets of different compositions were fabricated and main results are presented below:
  • The fiber distribution is not the same throughout the length of the field hockey stick. The carbon fibers are concentrated in the head while the handle is enriched with glass fibers.
  • The strength increases with increasing volume fraction of carbon fibers. The carbon fibers are preferred to increase the strength and to make the stick lightweight.
  • The flexural strength increased from 342 MPa to 372 MPa with the incorporation of carbon nanotubes. The CNTs act as additional reinforcement thereby improving the strength.
  • Porosity was found that may have due to air entrapment and relative movement of the fibers and resin during compression molding. Another reason for this porosity can be solvent evaporation. The solvent is added in the resin to reduce its viscosity to help proper nanotube dispersion. This solvent (along with any other volatiles) gets evaporated while curing leaving behind a huge amount of porosity.
The SEM images of fractured samples showed delamination among fiber plies along the longitudinal direction. There is no significant difference observed in the fracture mode.

Figure 11. SEM images of fractured surfaces of field hockey stick (a, b), GWC/epoxy (c, d), and CNTs/GWC/epoxy samples (e, f). the incorporation of CNTs

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6. References
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