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Research Article

Design and Study of Epoxy Composites based on Polycaprolactone and Nanodiamond Functionalized Carbon Fibers

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Abstract

In this study, the carbon fibers were coated with polycaprolactone (PCL) through *in-situ* polymerization. During this process, different content (1-10 wt. %) of functional nanodiamonds (NDs) were added to form PCL-CFs-NDs. The affect of NDs on the polymerization and molecular weight of PCL was deliberated through gel-permeation chromatography. The weight average molecular weight of PCL was decreased from 42×10^3 gmol^{-1} to 18×10^3 gmol^{-1} when the polymerization was carried out in the presence of 10 wt. % NDs. The fractographic study showed the formation of polycaprolactone and nanodiamonds coating over the surface of modified carbon fibers. The fiber pullout was found to decrease with the filler loading due to better interface bonding and interaction with epoxy. DSC results revealed an increase in the melting temperature with higher NDs content. Epoxy/PCL-CFs-NDs 10 with 10 wt. % filler acquired the tensile strength of 1226 MPa and tensile modulus of 891 MPa.

Keywords: Epoxy; polycaprolactone; carbon fiber; functional nanodiamond; in-situ polymerization

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1. Introduction

The recent progress of growing industrial technology depends in numerous ways on the development and utilization of new engineering materials which are able to perform their functions under severe conditions. One successful candidate fulfilling the many demand is the carbon fibers owing to its superior characteristics and rapid progress and utilization [1, 2]. Synthesis of carbon fibers can be accomplished from various basic raw materials such as gas (methane, ethane and benzene), polymer (cellulose (rayon), polyacrylonitrile (PAN), polyvinylchloride, phenol resin), and pitch (isotropic and mesophase pitch). The three basic raw precursors are for example rayon; PAN and pitch are utilized in the commercial production of carbon fibers [3-5]. Conventionally, carbon fibers can be characterized by atypical diameter of 5-10 mm [6, 7]. In comparison to ceramics and metal-based traditional engineering resources, carbon fibers possess lower density and superior mechanical properties in terms of their higher stiffness and high strength [8]. Carbon fibers are also candidate for higher temperature applications owing to their low thermal expansion, ablation resistance, thermal stability, higher thermal conductivity and thermal shock resistance. Due to above mentioned outstanding characteristics, carbon fibers find applications as reinforcement material for the synthesis of primary and secondary structural composites, in the civilian construction projects, in the manufacturing of military and civilian aero planes, in wind turbines for generating clean and renewable energy, off-shore tethers for the deep-sea oil platforms, medical and sporting goods, and, pressure tanks in automotive industry [9, 10].

Polymeric materials because of their modified physical characteristics are recently in increasing demands for high technology applications. Further polymeric materials can be efficiently modified by the incorporation of filler or reinforcement (such as carbon fibers) into the matrix of polymer. Fibrous fillers play a crucial role in preservation of stiffness, frictional characteristics, strength, and thermal stability of composite materials [11]. This second phase filler will considerably control the wear resistance of composite material. Literature highlights the effect of reinforcement such as fibers on the wear resistance of composite materials [12-14]. Carbon, aramid and glass fibers are the main candidates as fiber reinforcement. Carbon fibers reinforced polymer composites exhibit high strength, high modulus and conductivity, which are required for light weight applications. Researchers attempted to understand the modification in wear resistance and reduction in co-efficient of friction of fiber reinforced polymer composites [15-17]. Except a few one [18], addition of carbon fibers may lead to an improvement in wear resistance even with low content [19, 20]. This can be attributed to the reduced ability of ploughing which provide good interfacial adhesion between the matrix and fiber reinforcement, tearing, and other non-adhesive components of wear [18]. Carbon fibers incorporated polymers have various applications (owing to its astonishing characteristics) such as satellites, aerospace structures, missiles, lightweight structural materials for aircraft radiators, directed energy mirror structures, and also as heat sinks for cooling of aircraft microelectronics [21]. In this effort, the carbon fibers were first modified as amine-functionalized carbon fibers. Afterwards, the amine-modified carbon fibers were coated with *in-situ* polymerized polycaprolactone. During the coating process, 1-10 wt. % of nanodiamonds was added to form homogeneous covering over the fiber surface (PCL-CFs-NDs). Diglycidyl ether of bisphenol A was opted as matrix material and was reinforced with the modified carbon fibers. The molecular weight of the polycaprolactone was studied using GPC to see the effect of nanodiamond addition on the synthesized

PCL. Fractographic, melting and tensile behavior of Epoxy/PCL-CFs-NDs composites were also investigated.

2. Experimental

2.1. Materials

Diamond nanopowder (<10 nm particle size), Araldite® 506 epoxy resin (diglycidyl ether of bisphenol A), Araldite® M hardener 964, triethylenetetramine (≥ 97.0 %), and ε-Caprolactone (97 %) were obtained from Aldrich. T-300 carbon fibers were obtained from Toray co. containing 6000 filaments per tow.

2.2. Measurements

Infrared (IR) spectra were recorded using Fourier transform infrared (FTIR) Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD (4 cm^{-1} resolution). The number average and weight-average molecular weight (M_w) was measured using Viscotek TDAmax. For the phase morphological studies, samples were cryogenically fractured in liquid nitrogen and the morphology was investigated by FEI Nova 230 field emission scanning electron microscope (FE-SEM). Differential scanning calorimetry (DSC) was performed by a METTLER TOLEDO DSC 822 differential scanning calorimeter at a rate of 10 °C/min under nitrogen atmosphere. The mechanical properties were measured by universal testing machine H50KS (Hounsfield) using a load cell of 50 kN and cross head speed of 0.5 mm/min. The total length of the composites was 200 mm and the gauge length was 150 mm.

2.3. Purification of NDs

The detonation soot contained some sp^2 carbon species (such as amorphous carbon, some heteroatoms and fullerene like carbon) and certain metallic impurities. Purification of NDs from non-diamond sp^2 by product was performed by subjecting it to thermal oxidation in nitric acid at elevated temperature i.e. 200 ℃ under a pressure of 80-100 atm in a titanium alloy reactor. Removal of metallic impurities from the detonation soot was acquired by boiling it with HCl (100 ℃) followed by washing with deionized water until neutral pH was attained [22].

2.4. Functionalization of NDs

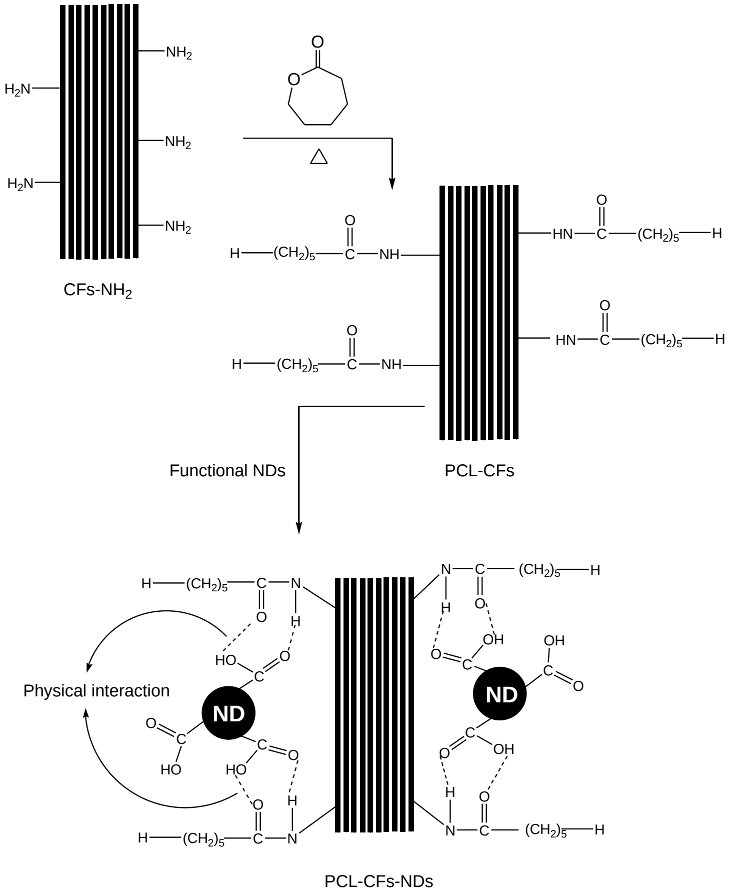
The purified NDs were treated with the mixture of strong acids (H_2SO_4 and HNO_3 in the ratio of 3:1, respectively) at 30 ℃ with constant stirring of 24 h. The resultant mixture was poured into 200 mL hot water (70 ℃) and again stirred for 10 h (at room temperature). The product obtained was filtered and washed repeatedly with deionized water and dried at 80 ℃ [23]. FTIR (KBr, cm^{-1}): 3479 (hydroxyl O−H stretch), 3003 (aromatic C−H stretch), 1720 (carboxylic acid C=O stretch), 1190 (S=O stretch), 1040 (symmetric SO_3H stretch).

2.5. Amine-functionalization of carbon fibers (CFs-NH_2)

The fiber tow was dipped into 70 % nitric acid at 115 ℃ for 2 h. The fibers were then rinsed with a slow and continuous flow of distilled water until the neutral pH was obtained. Portions of both the HNO_3 treated and the untreated (as-received) carbon fibers were reacted with triethylenetetramine to introduce amine groups onto the fiber surfaces. Fiber specimens (50 g) were placed in a large excess of dimaine (500 mL) and heated at 190 ℃ for 12 h. After cooling, the fiber specimens were washed with distilled water until neutral pH was attained. FTIR (KBr, cm^{-1}): 3398, 3339 (Primary N−H stretch), 2935 (C−H stretch), 2246 (C≡N stretch), 1737 (C=O stretch), 1362, 1219 (C−O resonance), 1170 (methacrylate C−O).

2.6. Polycaprolactone and nanodiamond functionalization of carbon fibers (PCL-CFs-NDs)

The modified fiber tow was dipped into 500 g of ε-caprolactone and 1000 mL of THF. The mixture was heated at 140 ℃ for 12 h and the mixture became viscous. After the reflux, 1-10 wt. % of functional nanodiamonds were added and mixture was refluxed at 120 ℃ for 2 h (Scheme 1). The heating was further continued for 0.5 h until the mixture became viscous. Afterwards, the fibers were removed and washed with distilled water. FTIR (KBr, cm^{-1}): 3377 (N−H stretching), 1593 (N−H bending), 2998 (C−H stretch), 2212 (C≡N stretch), 1736, 1654 (C=O stretch), 1345 (C−O).



Scheme 1 Schematic route to PCL-CFs-NDs.

2.7. Synthesis of Epoxy/PCL-CFs-NDs composites

For the composite preparation, the modified fiber tow was dipped into the molten resin maintained at 80 ℃ and drawn through a wire drawing die of 1 mm diameter. The fiber tows were stretched between two ends using weights to avoid bulging of filaments. The matrix was allowed to cure at 80 ℃ for 12 h using the hardener. After that, the weights were removed and the samples were post cured at 120 ℃ for 8 h [24]. FTIR (KBr, cm^{-1}): 3422 (hydroxyl O−H stretching), 3201 (N−H stretching), 1597 (N−H bending), 2962 (C−H stretch), 1650 (C=O stretch), 1276 (C−O).

3. Results and Discussion

3.1. Influence of nanodiamond addition on molecular weight of PCL

In this study, polycaprolactone was *in-situ* polymerized to form a coating layer over the surface of carbon fiber. During the *in-situ* process varying nanodiamonds contents were added to coat the carbon fibers. The influence of nanodiamonds loading on the molecular weight of polycaprolactone was studied using gel-permeation chromatography technique (Table 1). To comprehend the effect of nanofiller on the molecular weight of the synthesized polymer, dilute samples were prepared. A decrease in the molecular weight of PCL was predictable due to the addition of NDs. Neat polycaprolactone obtained through *in-situ* technique showed higher M_n and M_w of 23×10^3 and 42×10^3 $gmol^{-1}$ respectively. Addition of 1 wt. % NDs decreased the M_n and M_w of PCL to 21×10^3 and 40×10^3 $gmol^{-1}$ respectively. However, the values were significantly higher to represent a reasonable molecular weight. With the increasing filler content, the number average molecular weight was decreased and reached the value of 17×10^3 $gmol^{-1}$ in PCL-CFs-NDs 3 with 3 wt. % nanofiller. Similarly, M_n was decrease for PCL-CFs-NDs 5 and PCL-CFs-NDs 10 to 14×10^3 and 10×10^3 $gmol^{-1}$. Comparable decreasing trend with increasing NDs addition was observed in the case of the weight average molecular weight of PCL. The PCL-CFs-NDs 3, PCL-CFs-NDs 5 and PCL-CFs-NDs 10 had M_w of 32×10^3, 26×10^3, and 18×10^3 $gmol^{-1}$.

Table 1 Effect of nanodiamond loading on molecular weight of *in-situ* polymerized polycaprolactone.

Sample	NDs content	$M_n \times 10^3$ ($gmol^{-1}$)	$M_w \times 10^3$ ($gmol^{-1}$)	PDI (M_w/M_n)
Neat Polycaprolactone	0	23	42	1.82
PCL-CFs-NDs 1	1	21	40	1.86
PCL-CFs-NDs 3	3	17	32	1.88
PCL-CFs-NDs 5	5	14	26	1.85
PCL-CFs-NDs 10	10	10	18	1.80

3.2. Fractographic study

The fracture surfaces of PCL-CFs-NDs and Epoxy/PCL-CFs-NDs composite specimens were examined using SEM. The PCL and NDs coated carbon fibers are shown in Figure 1A. In the micrograph, the polycaprolactone and nanodiamonds formed a very fine and homogeneous coating over the surface of modified carbon nanofibers. Here, the surface modification of carbon fibers through NDs addition during polymerization is found to have strong effect on the fiber-matrix interaction and surface morphology of the carbon fibers. 1 wt. % PCL-CFs-NDs loaded epoxy composite is shown in Figure 1 B. The alignment of the modified carbon fibers in Araldite was uniform; however some marks of epoxy matrix were visible over the fiber surface.

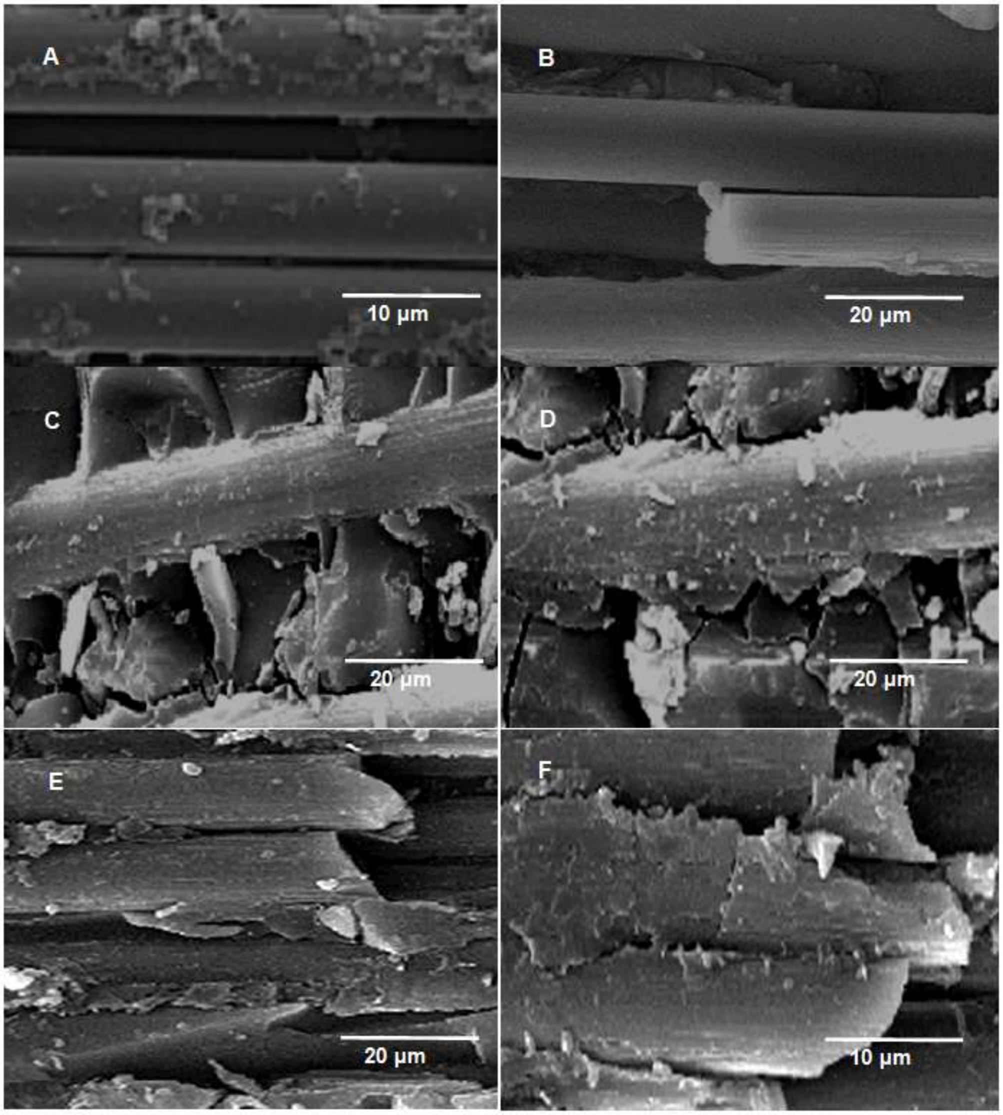


Figure 1 Fractographic images of (A) PCL-CFs-NDs at 10 µm; (B) Epoxy/PCL-CFs-NDs 1 at 20 µm; (C) Epoxy/PCL-CFs-NDs 3 at 20 µm; (D) Epoxy/PCL-CFs-NDs 5 at 20 µm; (E) Epoxy/PCL-CFs-NDs 10 at 20 µm; and (F) Epoxy/PCL-CFs-NDs 10 at 10 µm.

Figure 1 C-F show the fracture surfaces Epoxy/PCL-CFs-NDs 3-10 with higher loading levels of nanodiamonds. In these micrographs, the carbon fibers were seemed embedded in the matrix. Moreover, the epoxy was more attached over the fiber surface compared with the Epoxy/PCL-CFs-NDs 1 composite. The micrographs depicted that the higher loading of functional nanodiamond in the fibers developed better interaction of PCL-CFs-NDs with epoxy. The fiber pullout was observed in almost all types of composites prepared. In Figure 1 C and Figure 1 D, where the nanodiamond content was 3 and 5 wt. % in the CFs, show the greater fiber pullout and matrix debonding at the interface indicating lesser interfacial bonding. In Figure 1C, the pullout along with interface debonding was observed in the case of Epoxy/PCL-CFs-NDs 3. Some fiber pull out was also visible in the micrograph of Epoxy/PCL-CFs-NDs 1 (Figure 1 B). However, the pullout was less than Epoxy/PCL-CFs-NDs 3 and Epoxy/PCL-CFs-NDs 5 composites. For the sample containing 10 wt. % nanodiamond content (Epoxy/PCL-CFs-NDs 10), the pullout decreased obviously due to better interface bonding and interaction with epoxy. The presence of functional nanodiamonds in fact increased the overall interfacial area; thus the bonding with epoxy was increased. The addition of NDs during *in-situ* reaction caused the nanodiamonds firmly attached to the fiber surface and become essential fraction of it. Therefore, the morphology of Epoxy/PCL-CFs-NDs 10 (Figure 1 E & F) with greater NDs content has shown least fiber pull out. Nevertheless, the fiber surface was not smooth due to the increased nanofiller content and polymer coating over the surface. The increased coarseness of the fiber surface also resulted in stronger bonding due to mechanical fastening of the fibers with the matrix. Accordingly, the polycaprolactone and nanodiamonds modified carbon fibers have profound effect in enhancing the mechanical properties of composites through interface strengthening [25].

3.3. DSC Analysis

Figure 2 shows the DSC melting curves of Epoxy/PCL-CFs-NDs composites. The data given in Table 2 shows that there was notable influence of nanodiamond inclusion on the melting temperature. The neat polycaprolactone was found to have the melting temperature of 218 ℃. The composites showed increase in crystallinity with the NDs addition compared with the neat polymer. Epoxy/PCL-CFs-NDs 1, Epoxy/PCL-CFs-NDs 3, Epoxy/PCL-CFs-NDs 5, and Epoxy/PCL-CFs-NDs 10 had melting curves around 265, 266, 268 and and 272 ℃ respectively. The melting peaks were found to have broad consistency for all the Epoxy/PCL-CFs-NDs 1-10 composites. The broad peak and higher melting suggested the presence of smaller and defective crystals in the composite samples. There was 17 % increase in crystallinity of Epoxy/PCL-CFs-NDs 1 composite and 20 % increase in crystallinity of Epoxy/PCL-CFs-NDs 10 composite relative to neat polymer.

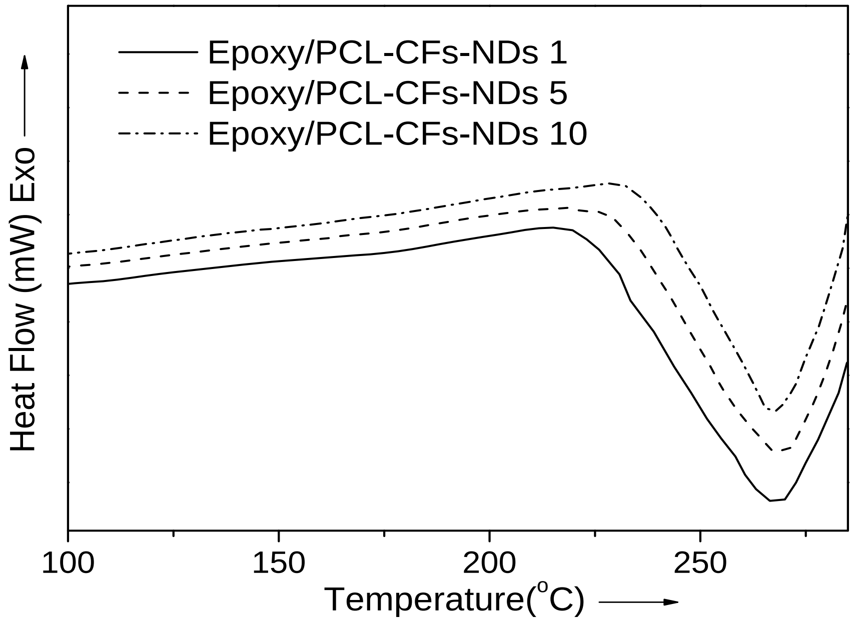


Figure 2 DSC melting curves of Epoxy/PCL-CFs-NDs composites.

Table 2 DSC results of Epoxy/PCL-CFs-NDs composites.

Sample	**Melting Temperature (°C)**
Neat Polycaprolactone	218
Epoxy/PCL-CFs-NDs 1	265
Epoxy/PCL-CFs-NDs 3	266
Epoxy/PCL-CFs-NDs 5	268
Epoxy/PCL-CFs-NDs 10	272

3.4. Tensile Testing

The mechanical properties of the novel composites are tabulated in Table 3 and Figure 3. The tensile strength and modulus of the composites were found to increase considerably compared with the neat PCL. The 1 wt. % PCL-CFs-NDs loaded composite had tensile strength of 980 MPa. The tensile strength was enhanced with the addition of 3, 5 and 10 wt. % NDs-based fibers in matrix. Consequently, Epoxy/PCL-CFs-NDs 3, Epoxy/PCL-CFs-NDs 5, and Epoxy/PCL-CFs-NDs 10 had the tensile of 1121, 1196 and 1226 MPa respectively. The enhancement was attributed to the modified structure of the carbon fibers. Furthermore, the increase in the properties was credited to the orientation of fibers along the fiber axis when samples were stretched. Tensile modulus of the composites followed the same increasing trend as the tensile strength. Tensile modulus of the Epoxy/PCL-CFs-NDs 1, Epoxy/PCL-CFs-NDs 3, Epoxy/PCL-CFs-NDs 5, and Epoxy/PCL-CFs-NDs 10 composites was found to be 254, 365, 512, and 891 MPa respectively. There was 20 % and 71 % increase in the strength and modulus of Epoxy/PCL-CFs-NDs 10 relative to that of Epoxy/PCL-CFs-NDs 1. Moreover, the data showed the percentage decrease in the strain of the composite with the NDs addition. Epoxy/PCL-CFs-NDs 1 had the elongation at break of 20 %, whereas it steadily decreased due to structural stiffness of the material with NDs in the composites. Epoxy/PCL-CFs-NDs 3, Epoxy/PCL-CFs-NDs 5, and Epoxy/PCL-CFs-NDs 10 had strain values of 18, 13, and 10 % respectively [26, 27].

Table 3 Average mechanical properties of Epoxy/PCL-CFs-NDs composites.

Property	**Epoxy/PCL-CFs-NDs 1**	**Epoxy/PCL-CFs-NDs 3**	**Epoxy/PCL-CFs-NDs 5**	**Epoxy/PCL-CFs-NDs 10**
Strength (MPa)	980	1121	1196	1226
Modulus (MPa)	254	365	512	891
Strain (%)	20	18	13	10

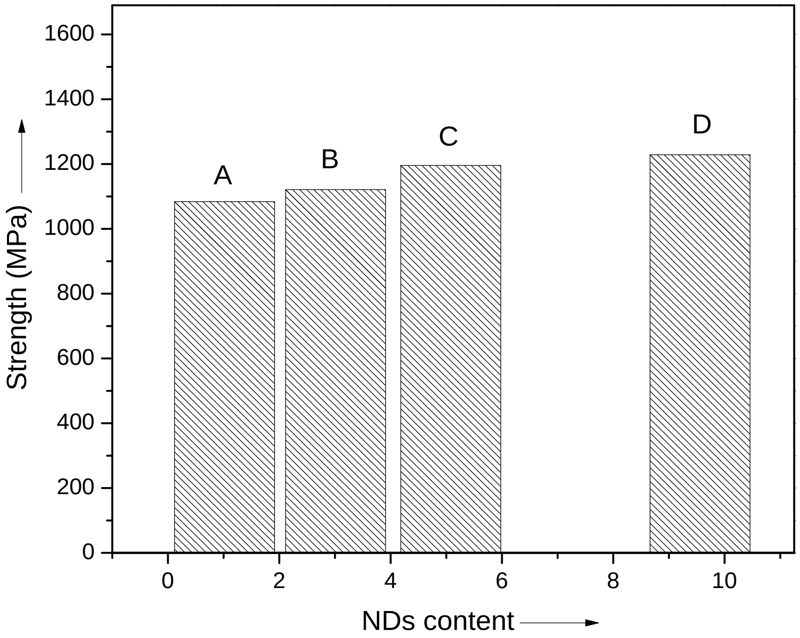


Figure 3 Tensile strength of composite specimens having carbon fibers with different NDs content (A) Epoxy/PCL-CFs-NDs 1; (B) Epoxy/PCL-CFs-NDs 3; (C) Epoxy/PCL-CFs-NDs 5; and (D) Epoxy/PCL-CFs-NDs 10.

4. Conclusions

In novel multi-scale composites, the modified carbon fibers were used as primary reinforcement while NDs acted as secondary reinforcement. The inclusion of NDs during the *in-situ* polymerization of polycaprolactone was found to be very effective to coat nanofiller over CFs surface with out any additional further chemical treatment. The molecular weight of the *in-situ* polymerized polycaprolactone was found to decrease with the NDs addition. A significant increase in the mechanical properties of DGEBA was observed with the addition of PCL-CFs-NDs 1-10. The tensile strength of the Epoxy/PCL-CFs-NDs 10 composite was increased by 20 % as compared with the Epoxy/PCL-CFs-NDs 1. The nanodiamonds were found to improve the mechanical properties due to the high aspect ratios and excellent mechanical properties. DSC studies indicated the increase in melting temperature of Epoxy/PCL-CFs-NDs 1-10. This was attributed to the increased crystallization rate representing the existence of strong interaction between the epoxy and modified CFs. The fractographic study also depicted the enhanced interfacial bonding exposed by less fiber pullout.

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