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Mechanical Properties of Electrospun CNF/PVA Nanofiber Mats as Reinforcement in Polymer Matrix Composites

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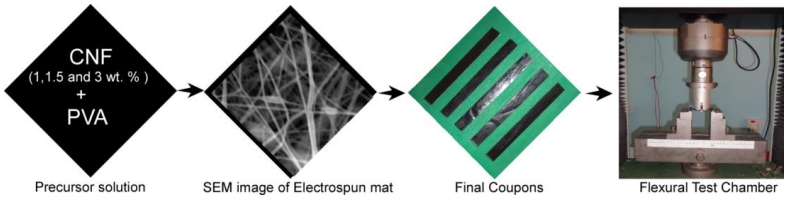
Abstract



Carbon nanofiber (CNF) reinforcement in the resin matrix composites is one of the effective methods which improve the overall performance of the composites. In this work, we have investigated the influence of electrospinning to obtain nanofiber composites of carbon nanofiber (CNF)/polyvinyl alcohol (PVA) by varying the percentages of CNF (i.e., 1, 1.5 and 3 wt %). CNF incorporation has been confirmed by X-Ray diffraction and SEM analysis of nanofibers revealed that the fiber diameter increased with respect to CNF percentage. Then, we fabricated flexural coupons utilizing CNF/PVA nanofiber mats as laminates and epoxy resin (ER) as matrix. A total of fifteen coupons, five for each CNF weight percentages, were finally obtained. The fabricated coupons had smooth surfaces. Ultrasonic testing (UT) provided information about the defects present in the coupons. Three point flexural tests performed through a 10 ton universal testing machine (UTM) following the ASTM standard showed significant improvement in the flexural strength of the CNF loaded polymer composites. The maximum flexural strength of 137.28 MPa was obtained with the 3 wt% CNF loaded coupons (i.e., C_3P-4), compared to the pure epoxy coupons (65.31 MPa from NC-2). The flexural strength was compared with direct-

mixed CNF/ER composite coupons (dM-CPs) and found to increase as much as 46%. The uniform dispersion of CNF/PVA with tunable nanofibers, their higher surface area and load bearing characteristics could be attributed for this enhanced strength and these composites may open up numerous possibilities for industries like defense and automobile.

Keywords: Carbon nanofiber (CNF), poly-vinyl alcohol (PVA), ultra-sonic scanning, flexural strength and epoxy composites

1. INTRODUCTION

Epoxy resin (ER) based matrices have been extensively studied for their tremendous applications. In the polymeric field, epoxy resins are well predictable thermosetting matrices presenting a series of remarkable characteristics like excellent stiffness, specific strength, dimensional strength, chemical resistance and also strong bonding to the reinforcement [1]. It has been extensively used in the areas such as electronics and astronautics industries. Still, there is a big space for research to enhance the overall performance of the epoxy resin matrices by introducing new reinforcements. The emergence of nanotechnology gives positive approaches which could solve the existing problems faced in macroscale levels. Especially, the use of nano-fillers such as Carbon nanotubes (CNTs) and Carbon Nanofibers (CNFs) can provide improved properties for the epoxy resin matrix.

Carbon nanofibers (CNFs), due to their better tensile strength, thermal, mechanical and electric properties, have been widely used for polymer reinforcement techniques [2]. CNFs have been used as the reinforcement materials in polymers like polyethylene [3], nylon [4], and polycarbonate [5] and are preferred for their high temperature resistance, good thermal and mechanical properties. CNFs are widely preferred for high load bearing applications. Many studies have demonstrated the bare inclusion of CNFs onto the resin matrix but little effort has been made to electrospun the CNFs and thereby evaluating its performance.

Electrospinning is a simple and economical process for making ultra-fine fibers, first Patented in 1934. At first, a droplet of polymer solution forms at the needle's tip due to gravity and is held in place by surface tension. Subsequent formation of nanofiber begins when the electrostatic force applied between the electrodes is greater than the surface tension of the droplet. The fiber is formed as a result of the ejected jet stream and narrowed by whipping itself due to an increase in surface charge density and evaporation of the solvent [6-10]. The electrospun mat collected on the grounded surface will contain continuous or discontinuous fibers ranging from microscale to nanoscale in size [11]. Figure 1 shows the working principle of an electrospinning setup.

These electrospun fibers and mats have received great attention in recent decades and they can provide emerging opportunities for reinforced composites. Though some reports are available on the mechanical performance of CNF reinforced epoxy resin, electrospun CNF and its effect on the microstructural and mechanical properties are still need to be explored. The problem with CNF while making as fibers is that the

direct electrospinning of crude CNF solution does not give uniform fiber networks and spreads only beads. So we have planned to electrospun CNFs using a supporting polymer Polyvinyl alcohol (PVA) and identify the effect of the electrospun CNFs over the conventional mixing of both CNF and Epoxy resin (CNF/ER).
For mechanical strength comparision, direct blending of CNF with Epoxy resin matrix, without PVA, was executed and in order to investigate the efficacy of electrospinning over direct mixing of solutions. So, both the CNF/PVA nanofiber mats and CNF/ER composites have been prepared as flexural coupons (CP and dM-CP coupons respectively) of same dimension and their flexural analysis were carried out in a 10 ton universal testing machine as per ASTM standards. Also, the concentration of CNF loading onto PVA was varied and its effect over the flexural strength was discussed. The microstructure of electrospun CNF/PVA nanofibers, structural features were studied and defects in the fabricated coupons, their effects on final flexural strength of the composites were simultaneously investigated.

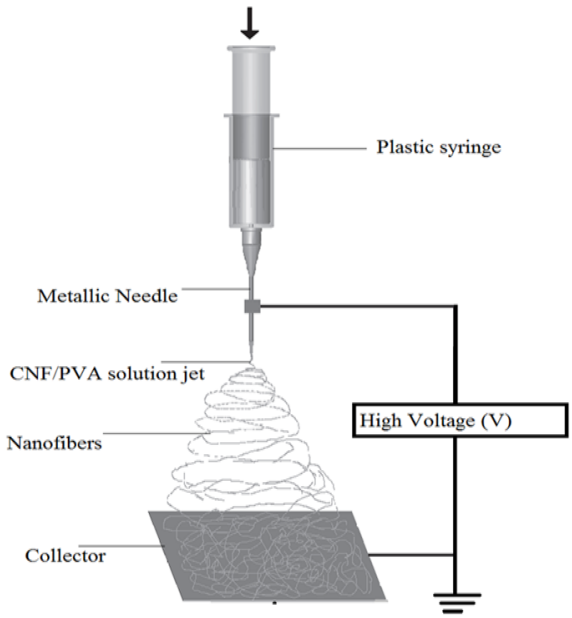


Figure 1: The schematic diagram of electrospinning setup describing its working mechanism

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Polyvinyl alcohol (PVA) of average molecular weight of 85, 000-1, 24000 was obtained (Central drug house (p) ltd) and used without further purification. Araldite standard epoxy resin (CY 230-1, HUNTSMAN) and hardener (Aradur HY 951) were purchased (Leo Enterprises Ltd) and directly used. Carbon nanofibers (CNF) (Sigma Aldrich) used in this study were of 100 nm in diameter, 20-200μm long and of >98% carbon basis.

2.2. Electrospinning of CNF/PVA mat

A homogenous solution of PVA and CNF was obtained by dissolving them in ethanol/water mixture. Different weight ratio of CNF is added with PVA to obtain the final solution. In CNF/PVA mixture, the weight percentage of CNF is varied from 1, 1.5 and 3; and mixed with the respective amount of PVA maintaining the final concentration to 10 wt. % for all samples. The solutions were stirred under a temperature controlled magnetic stirrer at 60˚C for 4 hours. The solutions were further sonicated for 120 s at room temperature. These solutions were utilized as polymer precursors for the electrospinning process using the ESpin-Nano apparatus (PICO India).

During the electrospinning process, the as prepared polymer solutions were pumped from a 2.5 ml syringe attached with a hypodermic needle of 0.1mm inner diameter. A voltage supply of 10kV was applied between the two electrodes which accelerated the formation of polymer jet from CNF/PVA polymer solution at the needle's tip (as depicted in Fig.1). The syringe holding the polymer solution was pumped through a microcontroller pump with a feed rate of 1 mlh^{-1}. With the same electrospinning parameters, all the three different CNF/PVA composites had been successfully spun and they are labeled as C_1P (1 wt. % of CNF), $C_{1.5}P$ (1.5 wt. % of CNF) and C_3P (3 wt. % of CNF). A total of 24 CNF/PVA nanofiber mats from three solution compositions were obtained. The length and width of the obtained mats were of 100 mm and 130 mm respectively. The thickness of each mat was of 0.09 mm. The digital images of the as-obtained CNF/PVA nanofiber mats are presented in figure 2.

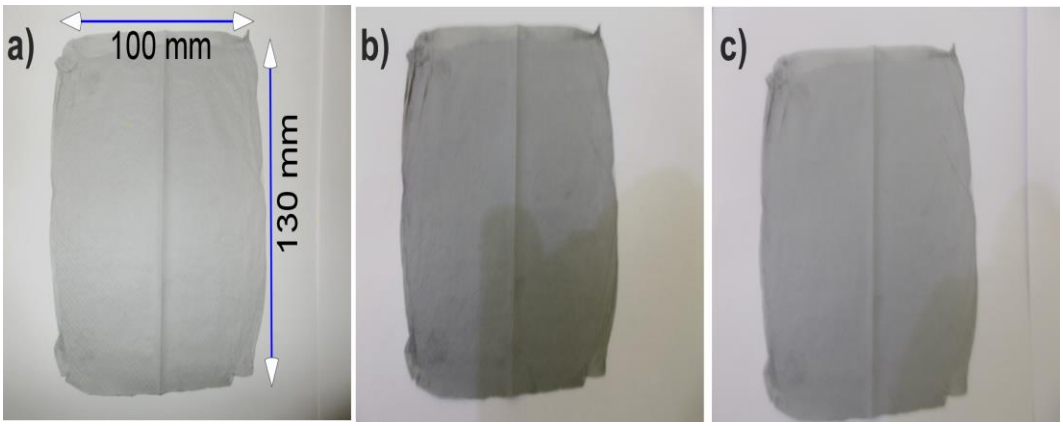


Figure 2: The digital images of CNF/PVA electrospun mats C_1P (a) $C_{1.5}P$ (b) and C_3P (c) (all the three samples possess the same dimension as mentioned in 'a')

2.3. Fabrication of epoxy resin coupon incorporating CNF/PVA nanofiber mats

CNF/PVA nanofiber mats were mixed with epoxy resin matrix through a layer by layer (as laminate materials within matrix by hand lay-up method) technique to make the final flexural coupons. The hand lay-up method is the simplest method for composite molding, which is depicted in figure 3(a).

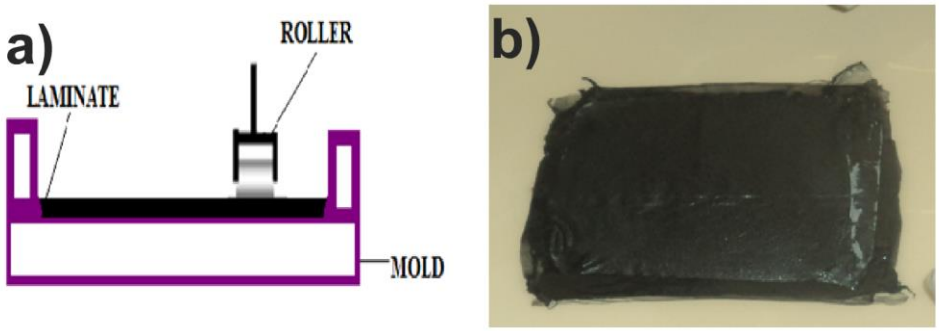


Figure 3: Hand lay-up method for forming the composite (a) and digital image of a flexural coupon ($C_{1.5}P$) during the fabrication process (b)

Pure epoxy resin and CNF/PVA nanofiber mats were utilized to fabricate the flexural coupons and pure epoxy resin coupons (Neat Coupons-NC) were prepared concurrently to be used as control samples. The epoxy resin was fabricated using CY 230-1 epoxy with the hardener HY951. The final matrix was cured at room temperature. For each flexural coupon, total of eight nanofiber CNF/PVA mats from the respective CNF weight percentage was used (depicted in Fig. 3(b)). Finally, three full coupons with the dimension of 100*130*2 mm (length, width and thickness respectively) were obtained. They were cut by using diamond cutter avoiding any edge damage. Each Full coupon was again cut into five small coupons with the dimension of 80*25 mm (length and width respectively). The as-fabricated flexural coupons are shown in figure 4 (a) & (b). The final thickness of the flexural coupons was 2 mm for all the samples. The overall process for obtaining the final flexural coupons is presented as a schematic in Fig. 5.

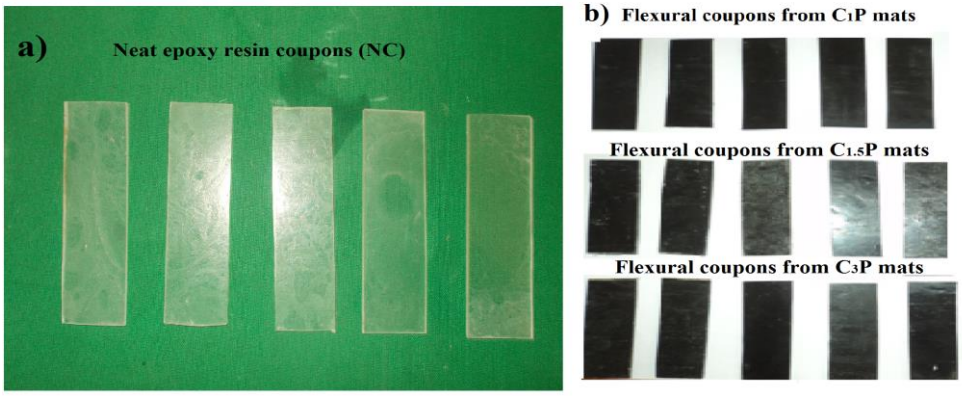


Figure 4: Pure epoxy resin coupons (NC) (a) and the as-fabricated CNF/PVA nanofiber mat reinforced final flexural coupons from various CNF weight percentages (b)

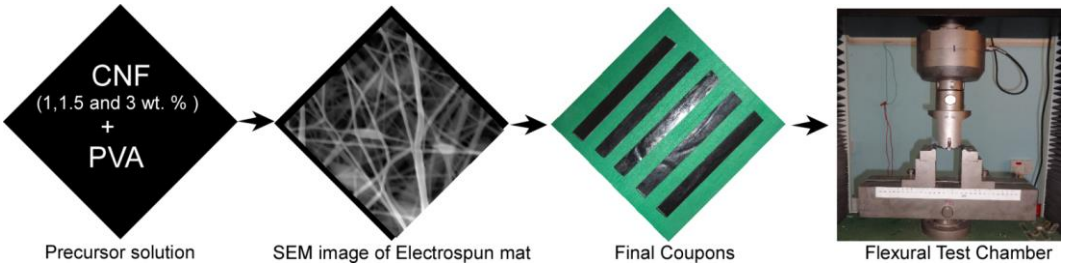


Figure 5: Schematic illustration describing the steps involved in fabricating flexural coupons and their mechanical testing

2.4. Fabrication of direct-mixed CNF/ER coupons

Pure epoxy resin and CNFs were directly blended to fabricate the flexural coupons (dM-CPs). CNF of 0.1gram is blended with epoxy resin (ER) and total of 5 coupons were fabricated and made sure their dimensions (100*130*2 mm) were consistent with their counterparts (NCs and CPs). The photographic image of as fabricated dM-CP coupons were represented in Fig-S1 (see Supplementary Information)

2.5. Characterization

The crystal structure of the CNF/PVA electrospun nanofiber mats was analyzed by PANalytical X'pert Pro equipment available at the Department of Physics, IIT Madras. The X-ray tube was operating at 40 kV with the Cukα radiation source with a wavelength of 0.154 nm. The scan was done over the range of 10 to 80° degree with the step aped of 0.016° per second.The morphologies of the nanofibers were examined by a FEI-Quanta (FEG) (available at SAIF-IIT Madras). The mats were sputter coated before the analysis.

2.5.1. Pulse-echo ultrasonic testing:

Ultrasonic testing (UT) was carried out according to USM 35 specifications. UT is a versatile inspection method to identify the internal and external flaws in the material. In the setup, a transducer sends out a pulse of energy and receives the energy back. Reflection occurs due to the presence of discontinuities and the surface of the test sample. The amount of reflected sound energy is displayed with the change of time, which provides the inspected information about the size and the location of the flaws as shown in figure 6.

UT is conducted on all coupons to identify the defect. The defects identified from the surface and interior of the coupons are represented as a table (table-2).

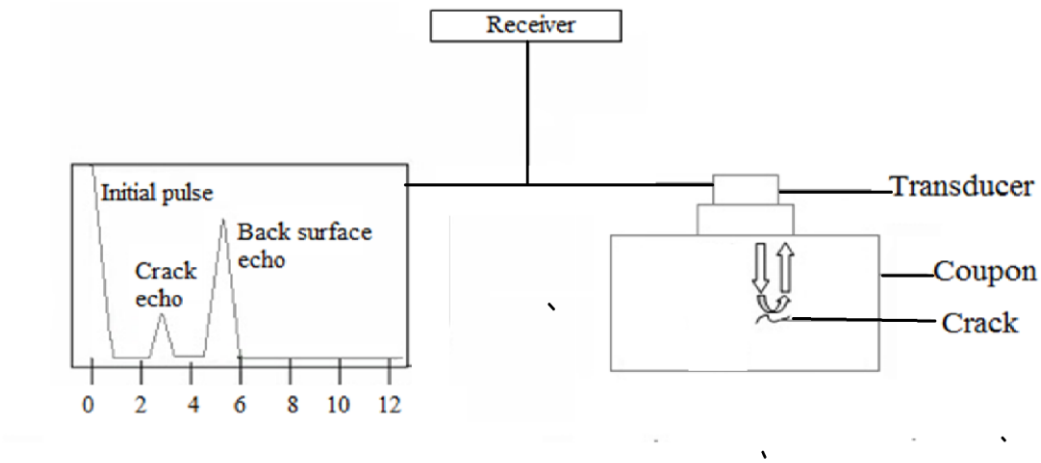


Figure 6: Working principle of an ultrasonic testing

2.5.2. Flexural testing:

The flexural strength of CNF/PVA/Epoxy resin coupons according to ASTM D70 was measured by DAK-UTB 9103 universal test machine (UTM). All the twenty coupons were tested. The spans were of 60 mm and the support length is 10 mm each side. The feed rate of 5 mm/min was maintained throughout the testing. The test specimens were loaded with a three point bending test as per ASTM D790 standards. The schematic view is presented in Fig. 7.

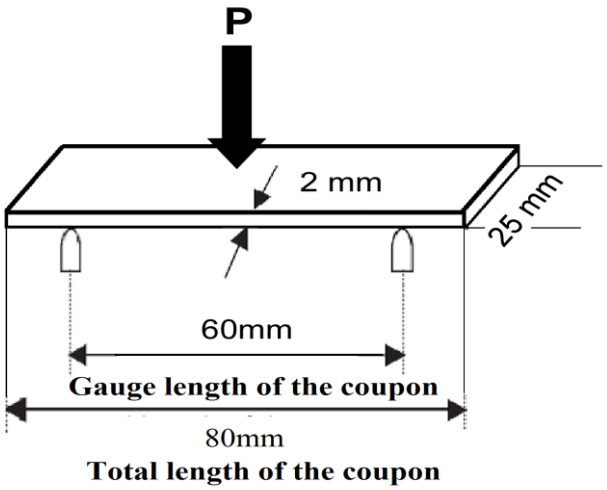


Figure 7: The configuration of the flexural test setup with the coupon

The load was gradually applied in the middle of the flexural coupon. The load was applied until the coupon failure and repeated for all coupons as shown in figure 8.

Figure 8: Digital image of the flexural test setup (during coupon failure)

3. RESULTS AND DISCUSSIONS

3.1. X-ray diffraction (XRD)

XRD was used to determine the structural properties of the CNF/PVA nanofiber mats. The mat exhibited a major peak at 2θ 19.7°, which arose from the (101) plane of semi crystalline PVA molecules. This broad peak indicates that the PVA nanofiber mat was not only of pure PVA but uniformly mixed with CNFs. Electrospinning technique could also have contributed to the uniform dispersion of CNFs. The color change of the nanofiber mat to black after electrospinning and this broader peak from XRD studies clearly justifies the incorporation of CNF in the PVA mixture as shown in figure 9.

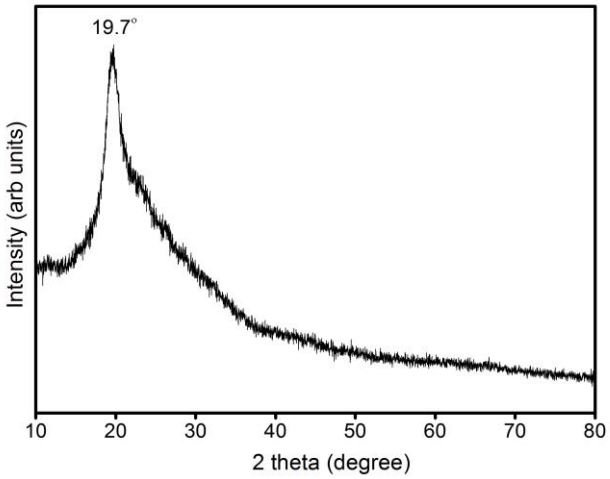


Figure 9: XRD pattern shows semi crystalline nature of the CNF/PVA nanofiber mats

3.2. Scanning electron microscope (SEM)

Figure 10 (a), (b), (c) shows the fiber morphologies of the CNF/PVA nanofiber mats prepared from 1, 1.5 and 3 wt. % of CNF respectively. The diameter of the CNF mat

is measured using the ImageJ software and found between the ranges of 210-987 nm for all the three concentrations. The table-1 clearly indicates that the increase in CNF weight percentage resulted in increase of fiber diameter. The fiber morphology becomes thicker with increase in CNF addition and could possibly help in improving of mechanical properties. Moreover, the cut section views of the PVA/CNF reinforced composites bonded with epoxy resin are depicted in Figure 11 (a). The top view and bottom view of the CNF coupon shows the presence of cavities and a smooth surface respectively as shown in Figure 11 (b) and (c).

Table 1: SEM observation revealing the diameter of nanofiber for each CNF composition

Sample	CNF (wt.%)	Diameter of nanofibers (nm)
C_1P	1	210-225
$C_{1.5}P$	1.5	216-248
C_3P	3	505-987

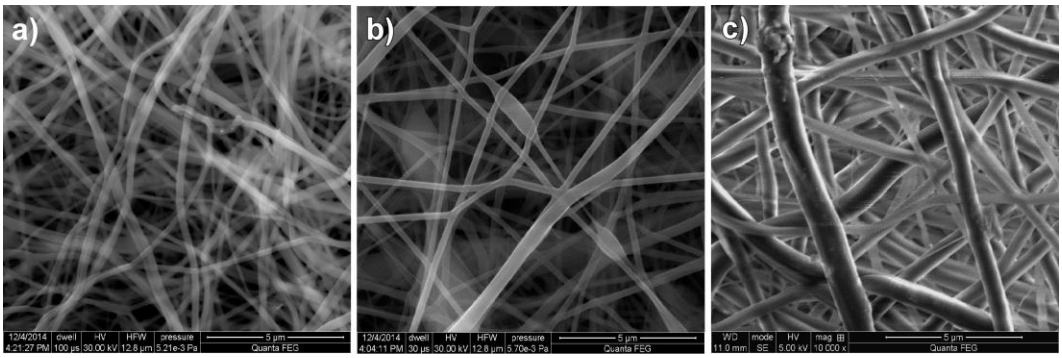


Figure 10: (a), (b) and (c) show the fiber morphology of C_1P, $C_{1.5}P$ and C_3P respectively.

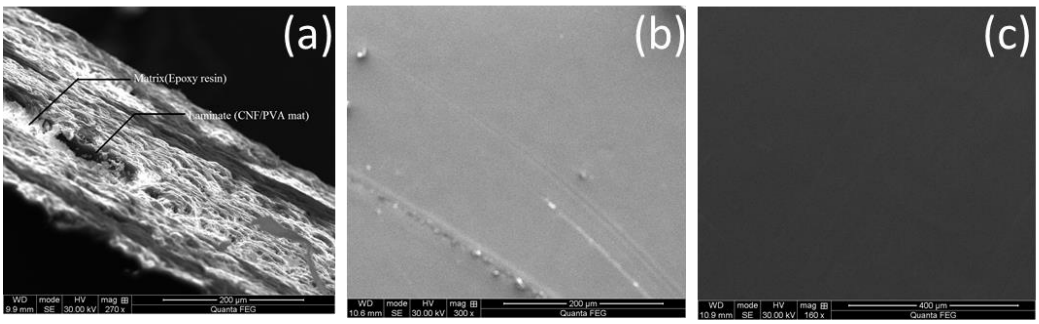


Figure 11: (a) The sectional view of CNF/PVA mat reinforced C_3P coupon (b) Rough surface of the coupon indicating cavities and (c) Smooth surface of the coupon

3.3. Ultrasonic testing (UT)

Ultrasonic testing (UT) was conducted on the coupons to identify the defects. Out of twenty coupons tested total of fifteen coupons were defect free (4 in NC and 11 in CP coupons). The cavities and crack were identified on the surface of the pure resin and the CNF reinforced coupons as shown in table 2. In the pure epoxy resin coupons set (NCs), out of 5 coupons, four were found to be defect free and one coupon (NC-5) was found to have a cavity of 4mm size. In the CNF 1 wt% mat incorporated coupon set, fourth coupon (C_1P-4) was found to have a cavity (4mm) defect. Similarly, $C_{1.5}$P-1 and C_3P-5 coupons both had a cavity of 2 mm each and $C_{1.5}$P-2 had a crack defect of 3 mm. Out of all coupons fabricated, this is the only coupon with a crack defect and others were found to have only cavities. The most important fabrication defect that is likely to occur in practice is cavity (the presence of voids). Some of the other defects occur only very rarely. Cavity can occur because of the air trapped between the surface and the layer during the fabrication of coupons by hand lay-up method. It could also be caused by unstable entrapment of air moieties during the curing of matrix (resin). The ultrasonic testing measures the variation in wave amplitude when passing through the coupons. The amplitude shows the defect size and the area of the defect present. The other defect, crack is not generally expected to be found. Crack will generally lead to delamination growth before a critical stage is reached. Cracks generally reduce the flexural strength which is clearly understood from the flexural examination of coupons.

Table 2: UT analysis revealing the defects present in the coupons

Neat Coupons	Defects Observed	C_1P coupons	Defects Observed	$C_{1.5}$P coupons	Defects Observed	C_3P coupons	Defects Observed
NC-1	Defect Free	C_1P-1	Defect Free	$C_{1.5}$P-1	Cavity (2 mm)	C_3P-1	Defect Free
NC-2	Defect Free	C_1P-2	Defect Free	$C_{1.5}$P-2	Crack (3 mm)	C_3P-2	Defect Free
NC-3	Defect Free	C_1P-3	Defect Free	$C_{1.5}$P-3	Defect Free	C_3P-3	Defect Free
NC-4	Defect Free	C_1P-4	Cavity (4 mm)	$C_{1.5}$P-4	Defect Free	C_3P-4	Defect Free
NC-5	Cavity (4 mm)	C_1P-5	Defect Free	$C_{1.5}$P-5	Defect Free	C_3P-5	Cavity (2 mm)

3.4. Flexural Testing (FT)

The flexural strength of the carbon nanofiber reinforced epoxy resin composite coupons were investigated and found to be increasing while increasing the carbon nanofiber content. A drastic improvement in the flexural strength was observed when there are no physical defects with the coupons. Since the excess reinforcement beyond the optimum level was increasing the porosity of the matrix, the maximum percentage of the CNF loading is optimized to 0.015 wt% (C_3P coupons) as shown in the table 3. It is well known that the reinforced fiber content and fiber strength are mainly responsible for the strength properties of the composites. Therefore the variation in strength properties with respect to CNF nanofiber loading is obvious. The table-3 represents the coupons' flexural strength with or without the defects. When the weight percentages of CNF is varied as 1, 1.5 & 3% and finally reinforced with epoxy resin (matrix), the ultimate flexural strength reaches to 82.37, 92.81 and 137.28 Mpa respectively.

Likewise, when CNF of 0.1 gram is directly blended with epoxy resin the resulting flexural coupons reach flexural strength of 73.57 Mpa on an average of five coupons (dM-CP). The flexural strengths of Neat Coupons, CNF/PVA nanofiber mat coupons and CNF/ER direct-mixed coupons were averaged and the values were plotted (Fig.12) with standard deviation. The average weight of the coupon sets were indicated on respective bar.

Table 3: Flexural strength of all fabricated coupons with their defects' status

Coupon No.	Neat Coupons (NC)		C_1P Coupons		$C_{1.5}P$ Coupons		C_3P Coupons	
	Defects	Flexural Strength (MPa)	Defects	Flexural Strength (MPa)	Defects	Flexural Strength (MPa)	Defects	Flexural Strength (MPa)
1	-	62.76	-	76.49	Cavity (4mm)	61.78	-	118.66
2	-	65.31	-	82.37	Crack (3mm)	76.49	-	109.83
3	-	61.78	-	78.45	-	89.24	-	122.58
4	-	57.85	Cavity (4mm)	67.66	-	87.27	-	137.28
5	Cavity (4mm)	50.99	-	82.37	-	92.18	Cavity (2mm)	88.25

Figure 12 indicates the respective average of flexural strength from each coupon sets. The direct mixed CNF/ER composite coupons were of around 6 gram in weight but they tend to break very fast when compared to C_1P, which has the least CNF incorporation. The CNF/PVA composite coupons had more or less weight around 5 gram, which is the same case for pure epoxy coupons (NC) too. Though the coupons weights were in similar range, their mechanical properties differ a lot. This essentially gives the confirmation and effect of nanofibrous CNF/PVA reinforcements to yield better mechanical properties.

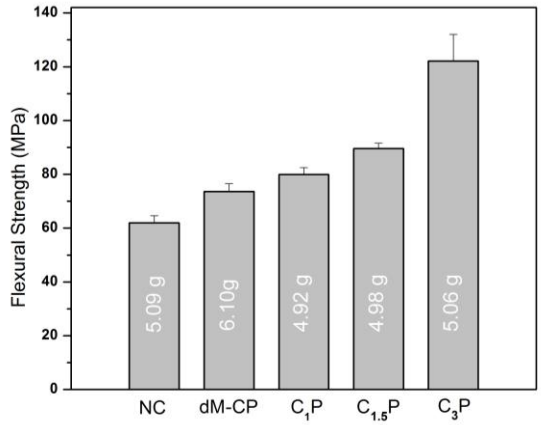


Figure 12: Bar diagram representing flexural strength of different composite coupons with their weight average (values indicate mean ± standard deviation)

CONCLUSION

We have demonstrated that the flexural strengths of Epoxy resin matrixes can be tuned by incorporating CNFs through different methods. Direct blending and electrospinning techniques were compared in order to understand the dispersion mechanism of CNFs on any desired polymer matrix. CNFs have been directly blended with ER and coupons (dM-CP) were fabricated. Similarly Neat coupons without CNF are fabricated to act as control. CNFs were dispersed in PVA to enable electrospinning and weight percentages of CNFs were varied as 1, 1.5 and 3%. The nanofiber mats were characterized by XRD and SEM techniques to understand their structural features and increasing CNF wt% sequentially increased the size of nanofibers. Finally, the flexural strength of all the three different methods suggested that the nanofibrous incorporation of CNF enables the composite to provide the maximum flexural strength of 137 MPa. This value was achieved just by incorporating of 15 mg of CNF in the ER matrix. The weight of CNF/PVA coupons also indicated an average reduction of 1000 mg compared to the direct blend coupons (dM-CP). The results suggest that these lighter but stronger nanofiber based composites will open up more research outcomes in the fields of aeronautics, automobile and defence in the near future.

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SUPPLEMENTARY INFORMATION :

Figure S.1: Digital image of flexural coupons (dM-CP) obtained from direct-mixed CNF/ER composites

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