

CARBON NANOFIBER HYBRID LAMINATES FABRICATION AND CHARACTERIZATION

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1 Abstract

Multi-walled carbon nanotubes (MWCNTs) are a new class of materials widely used for their unique electrical and mechanical properties related to their nanometric size. MWCNTs are expected to be useful for polymer reinforcement. In the present work, nanofibers are synthesized via electrospinning process. A solution of MWCNT dissolved in ethanol is added with deionized water and Polyvinyl Pyrrolidone (PVP). The solution is ultrasonicated to obtain homogeneous MWCNT-PVP Nanofibers using electrospinning as a high voltage electric field process. The scanning electron microscopy images show that fine MWCNT-PVP nanofibers are clearly synthesized and carbon nanofibers are covered obviously with PVP particles. The produced nanofibers are used to reinforce epoxy resin and to form a composite layer. This layer is combined with some other layers reinforced by woven carbon and Kevlar fabrics to obtain hybrid laminates. Tension tests are performed to characterize the mechanical properties of the laminates. The experimental results show that the thin nanofiber layer has low reinforcing effect on the laminate properties. This is attributed to the improper method of nanofiber fabrication used in this work resulting in discontinuous fibers.

2 Introduction

Carbon nanotubes are well known to have extremely high elastic modulus and strength. Exceptional properties of carbon nanotubes and their homologue, carbon nanofibers, have led to the development of polymer nanocomposites containing nanotubes and nanofibers [1]. The nanoscopic diameter of the carbon nanofibers has resulted in a significant increase of the carbon surface area per volume unit compared to that of traditional carbon

microfilaments. Eitan et al. [2] have reported that the contact surface was about 150 times higher when going from carbon microfilaments with 5 μm diameter to carbon nanotubes with an outer diameter of 30 nm. This leads to a much larger percentage of interphase between the filler and the polymer matrix, and thus a more efficient load transfer. The better nanofiller reported up to now is single-walled carbon nanotube (SWNT) with a small diameter and high aspect ratio. However, these materials are generally hard to separate and infiltrate with a matrix [3]. A better alternative is to replace SWNTs by multi-walled carbon nanotubes (MWCNT) with higher diameter, lower aspect ratio and specific surface area, but with a much better dispersibility.

Xu et al. [4] studied the elastic modulus of multi-walled carbon nanotube reinforced epoxy composite thin films. They showed that dispersing a very low volume fraction of MWCNT in epoxy, only 0.1 wt%, results in 20% increase in the elastic modulus of composite thin films. The positive effect of MWCNT in improving the glass transition temperature of thermosetting polyimide as a two-phase composite was reported by others [5]. The carbon nanotube (CNT) reinforced polymers have also been applied for filament wound CFRP rings using 1 wt% CNT in the polymer matrix [6]. It was however concluded that CNT did not noticeably affect the compressive modulus and strength of the filament wound CFRP rings. Alternatively, Iwahori and Ishikawa [7] reported that the compressive strength was improved by CFRP laminates using cup-stacked type carbon nanofiber (CSCNF) dispersed epoxy as three-phase composites.

In the present research, the nanofibers are synthesized via electrospinning process. In this method the solution of MWCNT dissolved in ethanol is used as the precursor. After the addition of Polyvinyl Pyrrolidone (PVP), the solution is

ultrasonicated to obtain homogeneous MWCNT-PVP Nanofibers using electrospinning as a high voltage electric field process. The scanning electron microscopy (SEM) images show that fine MWCNT-PVP nanofibers are clearly synthesized and carbon nanofibers are covered obviously with PVP particles. The produced nanofibers are used to reinforce epoxy resin and to form a composite layer. This layer is combined with some other layers reinforced by woven carbon and Kevlar fabrics to obtain hybrid laminates. Tension tests are performed to characterize the laminates.

3 Synthesis of Nanofibers

3.1 Polymer Solution

A direct method of mixing is used to prepare the suspension mixture of MWCNTs and polymer solution. This solution is used in an electrospinning process to generate the carbon nanofibers. This mixture is prepared in the following steps:

- An amount of 0.03 g of MWCNT is dissolved in 6.73 g of ethanol (C₂H₅OH) as the precursor.
- The solution is placed over a hot plate magnet-stirring machine shown in Figure 1. The mixture is loosely covered and kept stirring until a homogenous solution is formed.
- 10 g of deionized H₂O and 7 g Polyvinyl Pyrolidone (PVP) is added to this solution to provide MWCNT-PVP solution.
- The final solution is ultrasonicated under 50°C to obtain homogeneous MWCNT-PVP solution, see Figure 2. In the next phase of this research, carbon nanofibers will be produced from this polymer Solution.

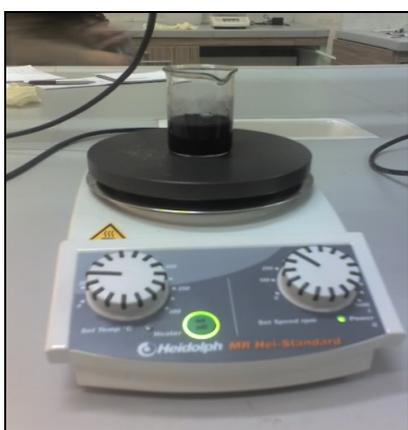


Fig. 1. MWCNT-ethanol solution in stirring machine



Fig. 2. Ultrasonication machine

3.2 Electrospinning Process

Electrospinning process is a simple and effective method capable of generating nanofibers from various polymers or inorganic/organic hybrid nanocomposites or inorganic precursors by the application of an electrostatic force. Electrospinning process can be considered as a variation of the well-known electro-spray process. The final solution prepared in the previous section is inserted in the electrospinning machine as a high voltage electric field processor to produce carbon nanofibers as detailed below.

Some of the final solution is inserted into a syringe with a needle of 0.1 mm diameter. The diameter of the needle is important for the fine diameter of the final nanofiber. A high voltage electric field is prepared between the needle and the fiber collector by a high voltage machine. This high voltage electric field provides the transmission of the solution towards the cylindrical collector. The distance of the needle and the cylindrical collector is about 15 cm as shown in Figure 3. It is here observed that by increasing the distance of the needle and the collector, the diameter of the nanofiber increases, and by decreasing this distance the diameter of the nanofiber decreases. Also, by increasing the pressure of the syringe pump, the diameter of the nanofiber increases, and vice versa.

The electrostatic forces can overcome the surface tension of the polymer solution with a suitable viscosity and thus can cause the ejection of a thin jet from the capillary needle tip. This thin jet breaks into droplets as a result of the surface tension in the case of low viscosity liquids. This situation is known

as electro-spray. On the other hand, for high viscosity solutions, the thin jet does not break into droplets, but travels as a jet to reach the collector. During its travel from the tip of the plastic capillary to the collector, the charged thin jet undergoes a stretching and disintegration process, resulting in the formation of many continuous fibers. As the charged thin jet is stretched and the solvent is evaporated, the diameter of the fiber is greatly reduced. Under the action of the electrostatic field, the fibers are forced to travel towards a ground cylindrical collector, and deposited as randomly oriented fiber mats. Two samples of the fiber mats produced in this work are shown in Figure 4.



Fig. 3. Electrospinning machine with a cylindrical collector and a high voltage creator



Fig. 4. Two samples of the thin mats of nanofibers produced by electrospinning process in this work

4 Fabrication of Laminates

Several different laminates are considered to be made using different fibers, in order to be tested and compared. Two types of woven fabrics are used in the laminates, carbon plain fabric 180 g/m² and Kevlar plain fabric 181 g/m². Furthermore, a type of an epoxy resin is here used as the matrix for the laminates. Some of the mechanical and physical properties of the fibers and the resin obtained from their providers are presented in Table 1. The laminates are fabricated through hand lay-up method on a flat glass sheet treated with a release agent wax, shown in Figure 5. After the impregnation of the layers on each other by the epoxy resin, the laminate is covered by another glass sheet and is set under a pressure to decrease air inclusions. Figures 6(a) and 6(b) show the Kevlar fabric/epoxy and nanofiber-carbon fabric/epoxy laminates, respectively. In this research, two types of hybrid laminates are fabricated. One of the hybrid laminates consists of the thin nanofiber layer and the traditional carbon fabrics, and the other hybrid laminate consists of the Kevlar and carbon fabrics. It is intended to observe the effect of the nanofiber layer on the mechanical properties of the carbon fabric/epoxy laminates.

Table 1. Mechanical properties of fibers and resin

Property	Fiber		Epoxy Resin
	Carbon	Kevlar	Epolam 2015
Tensile strength (GPa)	3.9	3.6 – 4.1	0.070
Tensile modulus (GPa)	235	131	3.1
Tensile elongation (%)	1.7	2.8	5
Filament diameter (μm)	7.0	8.5	–
Density (g/cm ³)	1.76	1.44	1.10

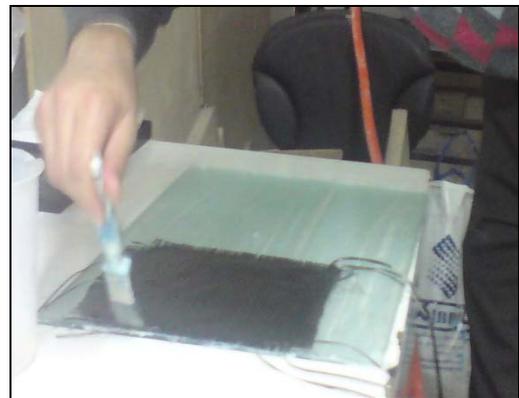


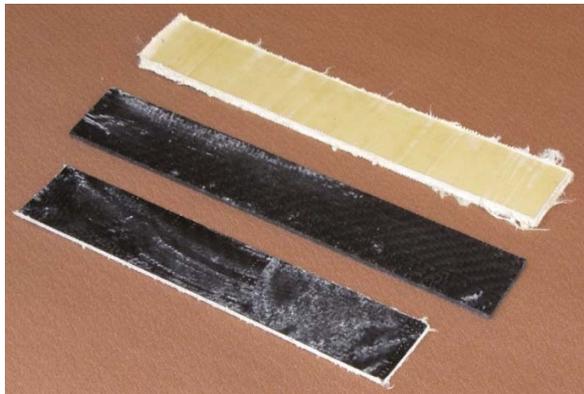
Fig. 5. Hand lay-up of the laminates on a glass sheet



(a)



(b)



(c)

Fig. 6. (a) Kevlar fabric/epoxy laminate, (b) Nanofiber-carbon fabric/epoxy laminate, (c) Test specimens cut from the laminates

These laminates are cut along the warp of the fabrics to obtain standard test specimens with a width of 4 cm and a length of more than 20 cm as shown in Figure 6(c). Table 2 summarizes the structure of the laminates made in this work.

Table 2: Specifications of the fabricated laminates

Laminate codes	Layers	Thickness (mm)
CT1, CT2, CT3	7 carbon fabric layers	1.91
K1, K2, K3	7 Kevlar fabric layers	2.30
CL1, CL2, CL3	2 carbon fabric layers	0.55
CK1, CK2, CK3	7 layers: car./Kev./car./Kev./car./Kev./car.	1.98
CN1, CN2, CN3	3 layers: carob/nanofiber/carbon	0.75

5 Experimental Procedure

The test machine in this work is a hydraulic one equipped with hydraulic grips so that the gripping pressure can be adjusted. To prevent the composite specimens from slipping in the grips during tensile test, grinding paper is used at the ends of the specimens, see Figure 7. This is a simple and cheap alternative for the aluminum or composite tabs typically recommended in the literature, although its performance is not satisfactorily good. The test machine is also equipped with an extensometer to measure the strain at the middle of the specimen directly and accurately, see Figure 8. The tensile tests are carried out with an elongation rate of 2 mm/min to obtain a quasi-static behavior of the laminates. The sampling frequency is chosen as one per second.



Fig. 7. A test specimen of cut from the laminates and equipped with tabs



Fig. 8. Tension machine equipped with extensometer

6 Results and discussions

The raw results of the tension tests on the thick carbon and Kevlar laminates are presented in Figures 9(a) and 9(b), respectively. It is noted that some of the tests were not successful due to the breakage of the specimen in the grip, and thus are not presented in the graphs. It can be observed that carbon fabric laminates have a linear elastic behavior up to the fracture point, while the Kevlar fabric laminates behave nonlinear with an increasing slope. The increasing slope of the stress-strain curve for the Kevlar laminates is attributed to the presence of the voids in the laminate and thus the gradual load transfer to the fibers. In this work, the Kevlar fabric was not so compatible with the epoxy resin which caused the voids. On the other hand, the carbon laminates show a relatively higher strength, while the Kevlar laminates show a seriously higher breaking strain.

Figures 10(a) and 10(b) show the raw test results on the hybrid Kevlar-carbon and nanofiber-carbon laminates. The stress-strain curve of the carbon fabric laminate is also presented there for the aim of comparison. It can be observed that the hybrid Kevlar-carbon laminate behaves linearly up to the fracture point, Figure 10(a), and its breaking strain is about the same as that of the carbon laminate. However, the Kevlar-carbon laminate shows a lower modulus and strength relative to the carbon laminate. This is attributed to the lower modulus and strength of the Kevlar layers relative to the carbon layers. Furthermore, the lower modulus and strength of the hybrid nanofiber-carbon laminate relative the carbon laminate is observed in Figure 10(b).

It is noted that the test results for the two specimens of the nanofiber-carbon laminate, CN1 and CN2, coincide each other. Further, the breaking strain for the hybrid nanofiber-carbon laminates is about the same as that for the 2-layer carbon laminates but much lower than that of the 7-layer carbon laminates. This is attributed to the fracture of the thin 2-layer laminates in the hydraulic grips of the tension machine. The decreasing effect of the nanofiber layer on the modulus of the carbon laminate leads to the conclusion that our synthesized nanofiber does not reinforce the resin as much as that the carbon fabric does. This is due to the method of the nanofiber synthesis in this work.

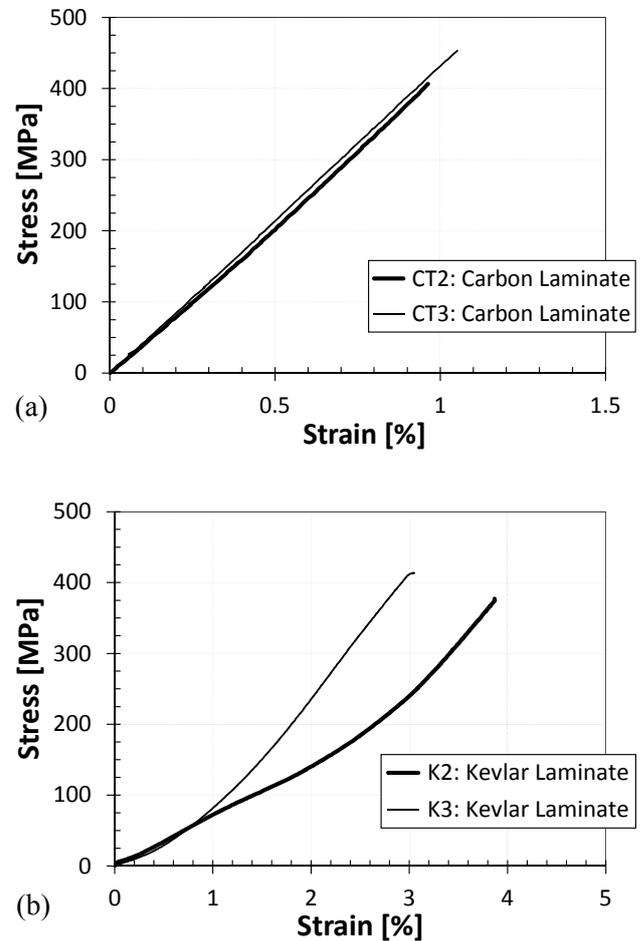


Fig. 9. The results of the tension tests on (a) Carbon fabric laminates, (b) Kevlar fabric laminates

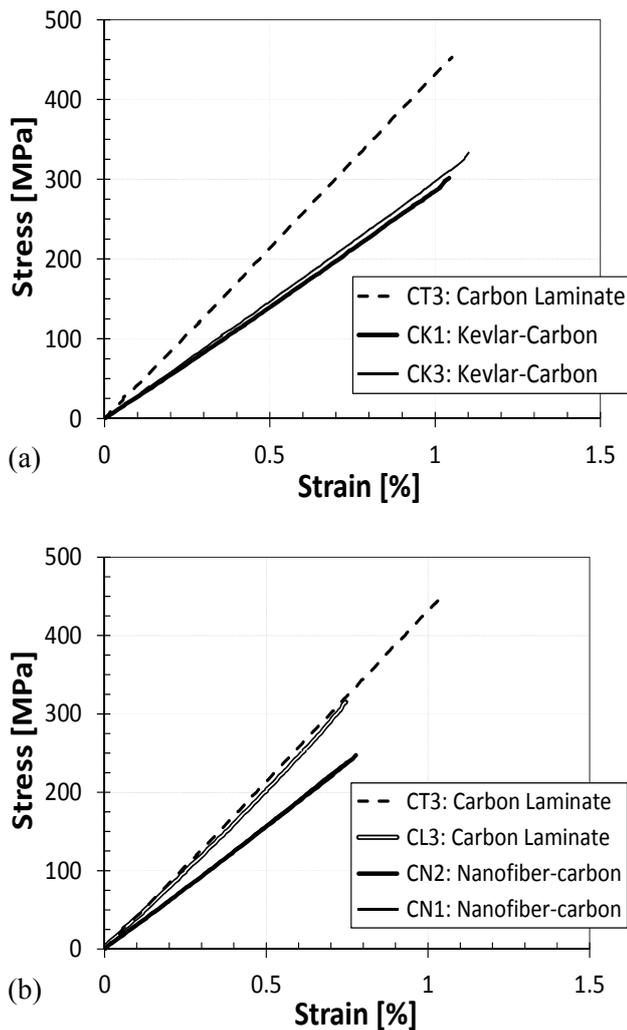


Fig. 10. Test results for (a) Hybrid Kevlar-carbon laminates, (b) Hybrid nanofiber-carbon laminates

7 Conclusions

In this work, the carbon nanofibers are synthesized via electrospinning process where thin sheets of nanofiber are obtained. These sheets are used to reinforce the epoxy resin and to form a composite layer. The layer is combined with some other layers reinforced by woven carbon and Kevlar fabrics to obtain hybrid laminates. The experimental results show that the thin nanofiber layer has low reinforcing effect on the laminate properties, not as much as the effect of the woven carbon layer. This is attributed to the improper method of nanofiber fabrication used in this work. It is here understood that the synthesized nanofibers are discontinuous.

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