Mechanical enhancement of UHMWPE fibers by coating with carbon nanoparticles

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Abstract

Fiber-reinforced plastic (FRP) is composed of reinforced fibers and matrix resin, and has high specific strength and low-density materials. Because of the orientation of the fibers within them, FRPs are prone to buckling damage when under compression along the axial direction of the fiber, especially flexible organic ones. The compressive performance of FRP is largely dependent on fiber properties. the buckling load of FRP will increase with the increasing of fiber's. In this study, we developed a way to improve the compressive and bending strength of ultra-high molecular weight polyethylene (UHMWPE) fibers. Carbon nanotubes (CNTs) and vapor-grown carbon fibers (VGCFs) were coated on the surface of UHMWPE fibers by pyrrole vapor deposition. The transverse compressive strength and bending strength of single UHMWPE fibers were determined by microcompression and single fiber bending measurements, respectively. The experiment result showed that coating UHMWPE fibers with CNTs and VGCFs increased both their transverse compressive strength and bending strength. It is excepted that the improved fiber would applied in FRP for better compressive performance.

Keywords: UHMWPE fiber, surface coating, compression strength, bending strength, carbon nanotube

1 Introduction

1 Introduction

Ultra-high molecular weight polyethylene (UHMWPE) fibers are a type of high-performance organic fibers made by the gel-spinning method that have excellent tensile modulus and low density. Compared with carbon fibers, which are widely used in advanced composites, the advantages of UHMWPE fibers are low density (0.97 g/cm^3), excellent ductility and superior resistance to impact, wear, moisture and chemical agents [1]. However, the axial and transverse compressive performance of UHMWPE fibers is very poor; the compressive yield strength of UHMWPE fibers is around 1% of its tensile strength [2,3].

UHMWPE fibers possess a hierarchical fibrillar structure. A single UHMWPE fiber is composed of highly oriented fibrils approximately 100 nm in diameter. The fibrils are assembled into microfibrils, which are blocks of crystalline UHMWPE connected by oriented amorphous tie molecules[4,5]. This structure causes UHMWPE fibers to have high tensile strength because of the huge number of covalent bonds between carbon atoms of the longitudinal chains, but gives a low transverse bending force. UHMWPE fibers also have very low flexural modulus.

We attempted to improve the compressive and bending moduli of UHMWPE fibers by coating them. If the modulus of a coating is higher than that of a fiber, the compressive and bend modulus of the fiber should be improved upon coating. Consequently, the buckling load of the fiber would increase. McGarry and Moalli [6] coated poly(p-phenylenebenzobisoxazole) fibers with ceramic materials and obtained

promising results for the compressive strength of the coated fibers using the tensile recoil method. Recently, reinforcement with carbon nanomaterials including carbon nanotubes (CNTs), vapor-grown carbon fibers (VGCFs), and graphene has become a topic of considerable interest. The excellent mechanical properties of these materials are well known [7-9]. The nanocarbon particles coating maybe a promising methods for improve the compressive and bending moduli of UHMWPE fibers. A variety of methods have been used to coat the surfaces of fibers with carbon nanoparticles to improve their properties. Kepple *et al*. [10] used a CNT-coated carbon fiber fabric that was functionalized *in situ* to enhance the fracture toughness properties of polymeric carbon composites. Zhang *et al*. [11] directly introduced graphene oxide sheets onto the surface of individual carbon fibers, improving their tensile properties and interfacial shear strength. However, investigations of fiber surfaces coated with carbon nanomaterials have focused on tensile properties, and the binding properties between the fibers and resin in the composite material. Few studies of the transversal compressive and bending properties of carbon nanomaterial-coated fibers have been reported.

In this paper, we used pyrrole vapor deposition to coat the surface of UHMWPE fibers with carbon nanomaterials. Pyrrole is a volatile organic compound that is readily oxidized to form polypyrrole (PPy) [12]. We developed a process to coat UHMWPE fibers with VGCFs and CNTs by pyrrole vapor deposition. The resulting materials have the combined advantages of excellent mechanical strength from VGCF and the cladding ability of PPy.

2 Experimental

2.1. Materials

UHMWPE fibers (Dyneema) were produced by Toray Co. Ltd., Japan. VGCFs (Showa Denko, Japan) had diameter of 150 nm and length of 10–20 μm and were synthesized by the gas-phase method. CNTs were obtained from Wako Pure Chemical Industries, Ltd., Japan. Analytically pure pyrrole and iron(III) chloride (as the oxidant) were purchased from Kanto Chemical Co., Inc., Japan, and were used without any further purification. Concentrated nitric acid was used to disperse VGCF and CNTs. Polyethyleneimine (PEI, Sigma-Aldrich), which is a cationic polymer with amine groups that are able to form covalent and hydrogen bonds, was used to assist adsorption of VGCFs and CNTs on the surface of UHMWPE fibers.

2.2. Preparation of carbon nanoparticle-coated UHMWPE fibers

It is necessary to pre-treat VGCFs and CNTs to improve their dispersion in aqueous solution. To do this, we oxidized VGCFs and CNTs with concentrated nitric acid, as reported in the literature [13,14]. VGCFs and CNTs were added to 60% nitric acid, stirred ultrasonically for 2 h to adequately oxidize their surfaces, filtered and then washed several times with deionized water. Each carbon nanomaterial was added to an aqueous solution of PEI (0.5 wt%) and iron(III) chloride (2 mol/L), and then mixed for 30 min. A single UMWPE fiber was wrapped around a hollow plastic board and soaked in the solution for 4 h. The fiber was removed and dried in a vacuum drier. The VGCF/CNT-adsorbed UHMWPE fibers were then exposed to pyrrole vapor for 10 min in a vapor deposition chamber for polymerization of pyrrole (Figure 1). PPy

layers were directly assembled in the spaces between the CNT networks. The surfaces of fibers were observed by SEM and their transverse compressive performance and bending properties were examined.

2.3 Transverse compression experiments

A microcompression tester (Shimadzu, Japan) was used to investigate the transverse mechanical behavior of single UHMWPE fibers. The equipment consisted of a device to test compressive mechanical properties and an electron microscope. Figure 2 shows a schematic diagram of the measurement of the force and displacement applied to a single fiber transversely. A single fiber was fixed on the glass plate. The diameter of the indenter was 50 μm. After the diameter of the fiber was measured by electron microscopy, the indenter began to exert a transverse compressive force on the fiber. When the indenter touched the surface of the the fiber, the compressive force gradually increased from 0 to 5000 mN at a rate of around 200 mN/s. After 25 s, a compressive force of 5000 mN was maintained for 5 s. The transverse compression tests were concluded ten times for each kind of fibers.

The transverse compression of single fibers has been investigated. As early as the 1960s, Ward *et al*. measured the transverse modulus of polyethylene terephthalate and nylon monofilaments [15,16]. They used two parallel glass plates to compress single fibers, and by measuring the contact width of the fiber during compression, Poisson ratio and extensional modulus, they were able to estimate the transverse modulus of the fiber from a series of equations. Kawabata [17] improved the compressive instrument to make measurement data more accurate. He measured the properties of

many kinds of high-performance fibers, including carbon and Kevlar fibers, and verified the accuracy of equations (1) and (2):

$$U = (4F/\pi)[(1/E_T) - (V_{LT}^2/E_T)][0.19 + \sinh^{-1}(R/b)] \quad (1)$$

$$b^2 = (4FR/\pi)[(1/E_T) - (V_{LT}^2/E_T)] \quad (2)$$

U: change in fiber diameter;

F: compressive force;

E_T= transverse modulus of fiber;

R: radius of fiber;

V_{LT}: longitudinal poisson's ratio of fibre;

b: contact width of the fiber during compression

With the development of fiber synthesis technology, an increasing number of high-performance fibers, like Kevlar KM2, A265and M5, have been synthesized and their compressive properties were examined [18,19]. Most of the methods used to examine the properties of these fibers were derived from that of McEwen. However, in this approach, it is necessary to measure the contact width B to estimate the transverse modulus of a fiber. For some resilient fibers, B is difficult to measure because it may become larger when the fiber is observed by a microscope, as the fiber must be removed using compressive force. In this paper, we made some improvements to the above equations to reflect the structure features of UHMWPE, such as the orientation of the UHMWPE chains, and our experimental method. We developed the formula from the work of Kawabata [17], and the parameters used are given in Figure 3.

Because $\delta = F/S$, $S = bL$, $E_T = \delta/\varepsilon$, and $\varepsilon = U/D$,

we obtain a transverse compressive modulus of

$$E_T = F\pi / 16RL^2\varepsilon^2 . \quad (3)$$

E_T:transverse modulus of fiber;

F: compressive force;

R: radius of fiber;

L:the length of compressive fiber during compression;

ε: strain of fiber.

2.4 Single fiber bending test

Single fiber bending tests were conducted to evaluate the bending strength and bending modulus of single coated fibers using a single yarn bending tester (S type, Kato Tech Co., Ltd.).

As illustrated in Figure 4, one end of each fiber sample was secured by a fixed chuck, which was connected to a very sensitive torque sensor. The other end was fixed to a mobile chuck and moved along the dotted line. Because UHMWPE fibers are very narrow, we used 20 fibers stuck parallel on a paper frame (Figure 5), and the paper frame was fixed by a chuck and clipped from the middle.

The bending moment M will vary with the curvature of the fiber, and the curve of instantaneous curvature and bending moment would be recorded. The curvature of the sample was measured from 0 to 2 cm^{-1}, and the bending moment was obtained when the curvature of the fiber was 1–1.5 cm^{-1} to calculate its bending modulus.

Bending modulus was calculated by

$$E_b = \frac{4M}{Kr^4\pi} . \quad (4)$$

Bending rigidity is E_bI, where E_b is bending modulus, and I is the second moment of area. K is the curvature of the fiber, and r is its diameter.

3 Results and Discussion

3.1 Transverse compressive behavior of UHMWPE fibers

Figure 6 is a typical load-deformation curve obtained from a microcompressive test. The abscissa is the compressive strain, which is defined as the displacement value of radial length divided by the diameter of the fiber. The ordinate is compressive force determined by the tester. The overall behavior over a large deformation range is obviously nonlinear and nonelastic. However, the UHMWPE fiber could be approximately considered linear elastic at low and high compressive force. The stress-strain curves of the coated fibers were steeper than that of the untreated UHMWPE fiber, especially for the VGCF/PPy- and CNT/PPy-coated fibers. This means that the compressive modulus of the UHMWPE fiber was improved.

During compression, the transverse deformation of the UHMWPE fiber occurred very slowly at first and then became fast after a certain strain. Finally, the single fiber became that as shown in Figure 7. On the part of compressed fiber, the fiber was crushed.

Figure 8 depicts the nominal compressive transverse modulus of different UHMWPE fibers, which was obtained from their compressive force-strain curves and equation (3). The modulus of the VGCF/PPy-coated fiber was higher compared with those of the as-received and PPy-coated fibers. The CNT/PPy-coated fiber exhibited the best compression performance of the fibers because of the excellent mechanical strength of CNTs.

3.2 Bending properties of coated UHMWPE fibers

The compressive strength of a composite depends on the buckling of the fibers, which is controlled by fiber stiffness and bending rigidity. Bending rigidity reflects the capacity of a fiber to resist flexural deformation. Therefore, a fiber with high bending rigidity is less likely to buckle when it is compressed than one with low bending rigidity. The bending rigidity of each fiber was determined from the slope of the curves presented in Figure 9.

In accordance with the position of the slopes, the fibers exhibited both initial and normal bending rigidities. The initial bending rigidity is most important for resisting fiber buckling. From Fig 10, the initial bending rigidities of the coated fibers were improved considerably compared with that of the uncoated fiber. The initial bending rigidity of the CNT/PPy-coated fiber was more than 515%, while that of the VGCF/PPy-coated fiber was improved 276.3%, compared with that of the UHMWPE fiber. However, it is difficult to prove that the coated fibers will have better buckling resistance in FRPs with their increased bending rigidity, because their diameter increases after coating with VGCFs and CNTs. As a result, it is necessary to obtain the bending modulus of the coated fibers. The bending moduli of the fibers were obtained from equation 4, and the bending curvature/bending modulus curves of the four types of fibers are shown in Figure 10. The bending modulus of the coated fibers was indeed improved compared with that of the uncoated fiber, although the range of improvement was small. When the bend curvature was 1.2, the bending modulus of the PPy-, VGCF/PPy- and CNT/PPy-coated fibers increased by 15.3%, 28.8% and

47.0%, respectively, compared with that of the UHMWPE fiber.

3.3 The role of polypyrrole during coating process

The surface morphologies of a UHMWPE fiber and VGCF/PPy-coated fiber are shown in Figure 11. The surface of the untreated UHMWPE fiber was comparatively smooth. After pyrrole vapor deposition, the fiber surface had a coating (Figure 11(b)). Interfacial interactions of the molecular motions among the fiber and PPy ensured adhesion between PPy and the surface of the UHMWPE fiber [12]. During fiber coating with VGCFs by the pyrrole vapor deposition method, gaseous pyrrole diffused into the voids between VGCFs and the UHMWPE fiber surface, and was immediately polymerized to form PPy, which can be observed in Fig. 12(C). PPy enables the dispersed VGCFs to form a homogeneous coating on the UHMWPE fiber. PPy also acts as a load carrier and transfers the stress.

4 Conclusions

UHMWPE fibers were coated with carbon nanoparticles by pyrrole vapor deposition to improve their compression and bending modulus. The coating combined the excellent mechanical strength of carbon nanomaterials with the cladding ability of PPy.

The transverse compressive strength and bending moment of single UHMWPE fibers were measured by microcompression and single fiber bending testing. The experimental results indicated that the nanoparticle coating improved the transverse compressive modulus of the fibers, particularly for the CNT/PPy-coated one. The bending modulus of the fibers was also improved by a nanoparticle coating. Because

the coating was homogeneous and composed of isotropic materials, the coated fiber has better axial compressive strength than the uncoated equivalent, which makes it attractive for use in anti-compressive fiber-reinforced composites.

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Fig. 1

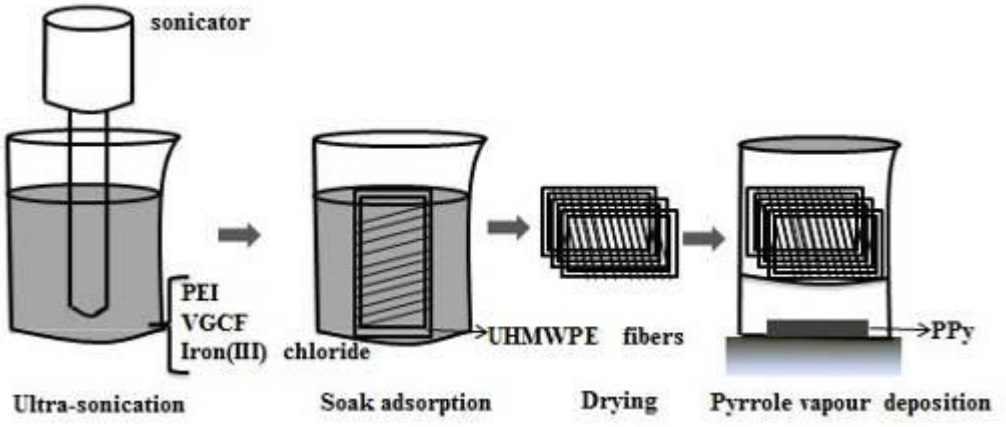


Fig. 2

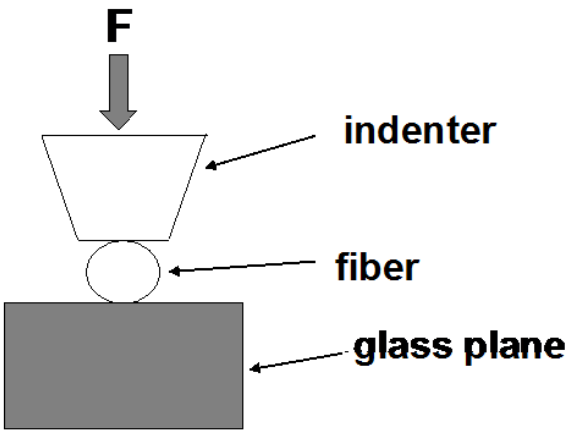


Fig. 3

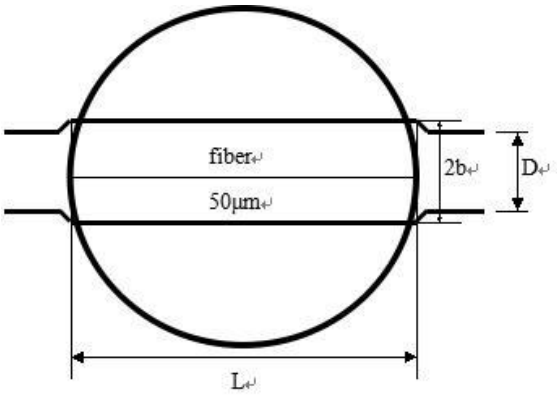


Fig. 4

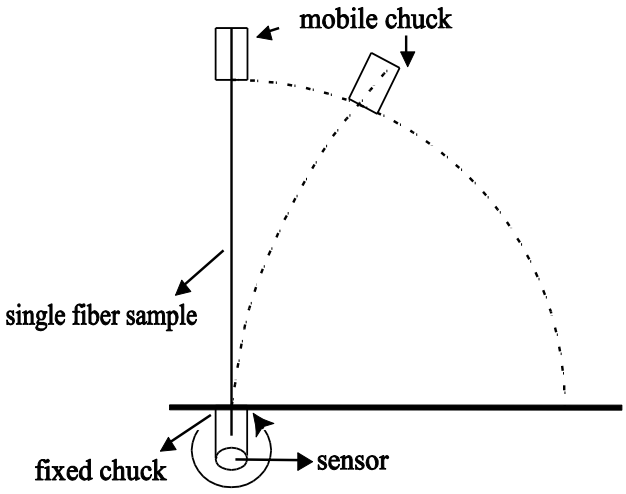


Fig. 5

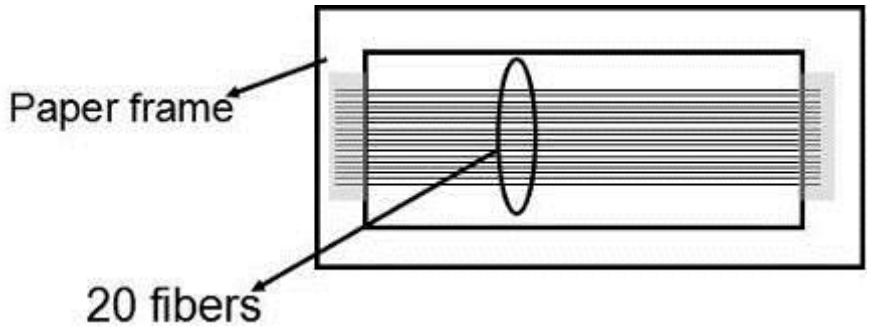

Paper frame
20 fibers

Fig. 6

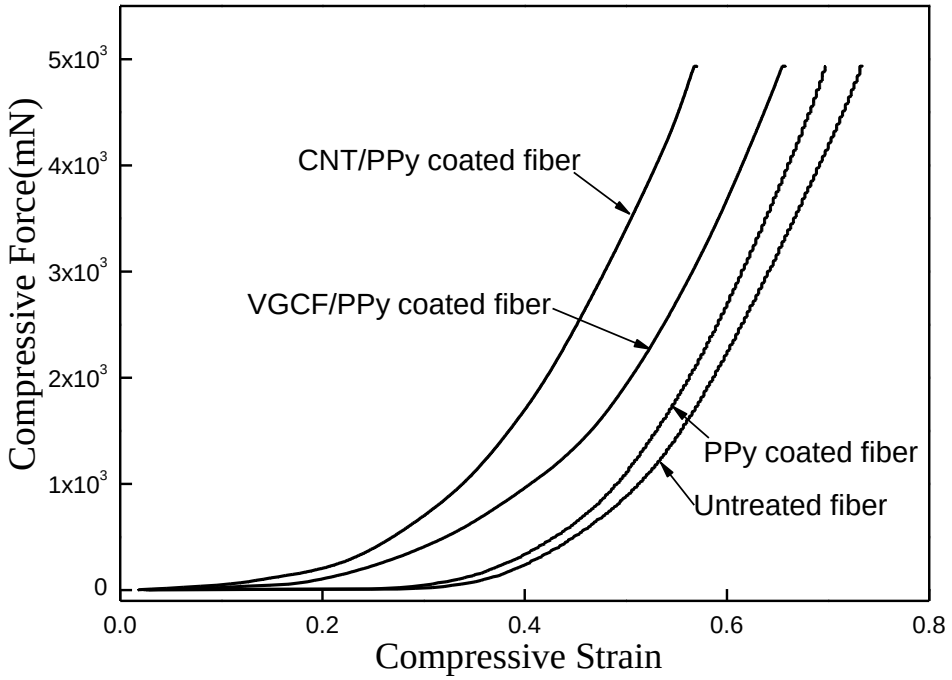

Compressive Force(mN)
5x10^3
4x10^3
3x10^3
2x10^3
1x10^3
0
0.0
0.2
0.4
0.6
0.8
Compressive Strain
CNT/PPy coated fiber
VGCF/PPy coated fiber
PPy coated fiber
Untreated fiber

Fig. 7

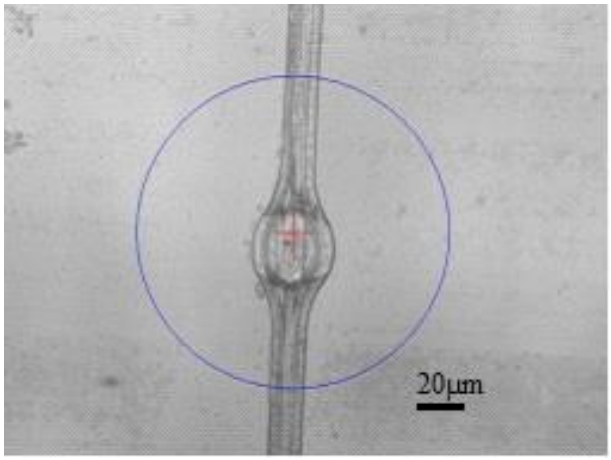

20μm

Fig. 8

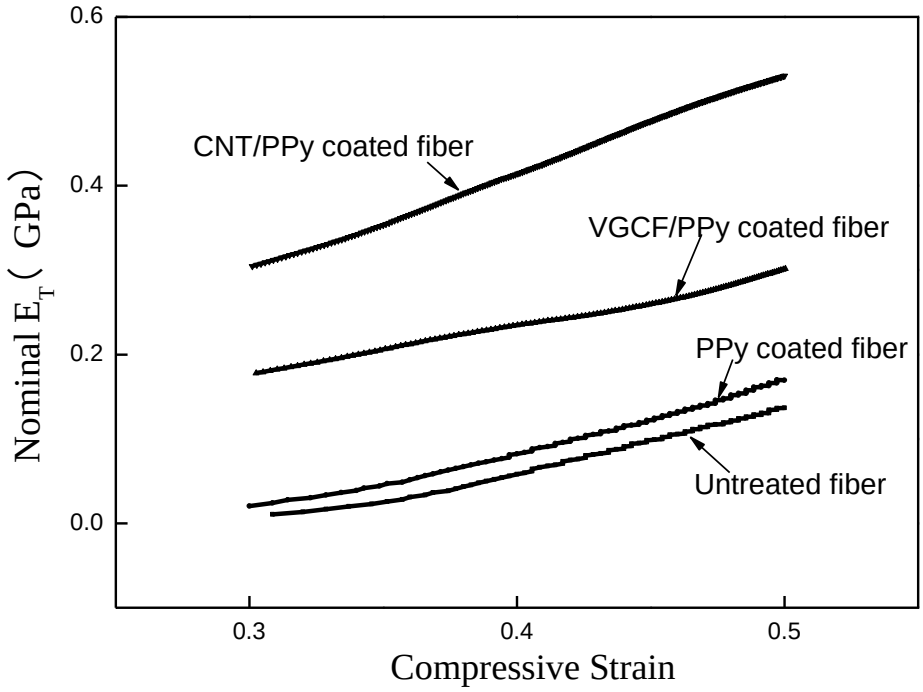

0.6
0.4
0.2
0.0
Nominal E_T (GPa)
CNT/PPy coated fiber
VGCF/PPy coated fiber
PPy coated fiber
Untreated fiber
0.3
0.4
0.5
Compressive Strain

Fig. 9

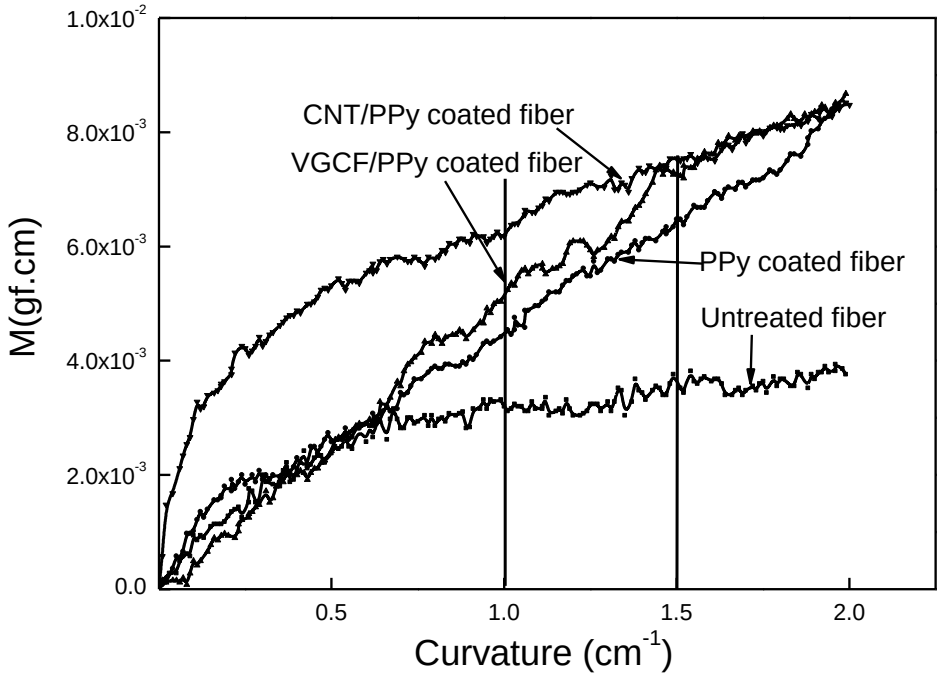

1.0x10-2
8.0x10-3
6.0x10-3
4.0x10-3
2.0x10-3
0.0
M(gf.cm)
CNT/PPy coated fiber
VGCF/PPy coated fiber
PPy coated fiber
Untreated fiber
0.5
1.0
1.5
2.0
Curvature (cm-1)

Fig. 10

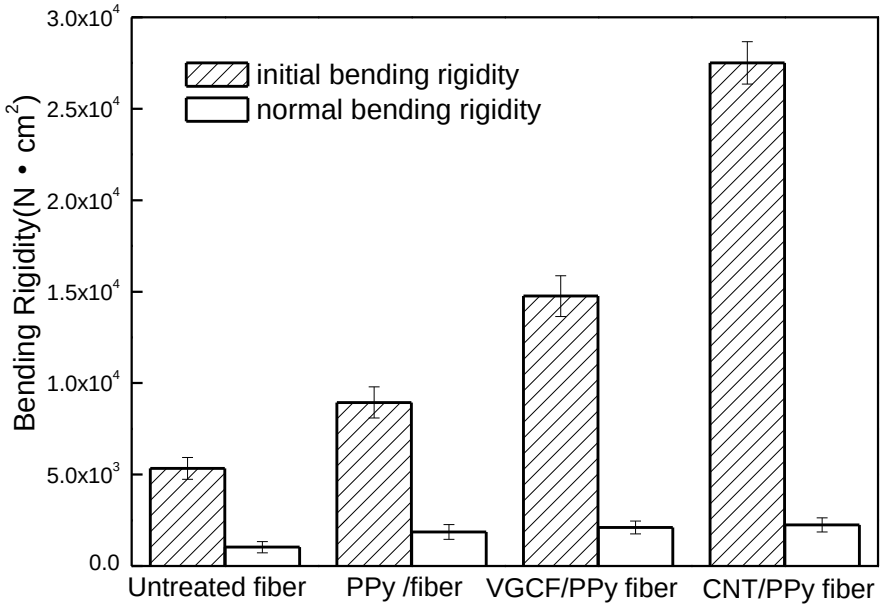

3.0x10^4
2.5x10^4
2.0x10^4
1.5x10^4
1.0x10^4
5.0x10^3
0.0
Bending Rigidity(N • cm^2)
initial bending rigidity
normal bending rigidity
Untreated fiber
PPy /fiber
VGCF/PPy fiber
CNT/PPy fiber

Fig. 11

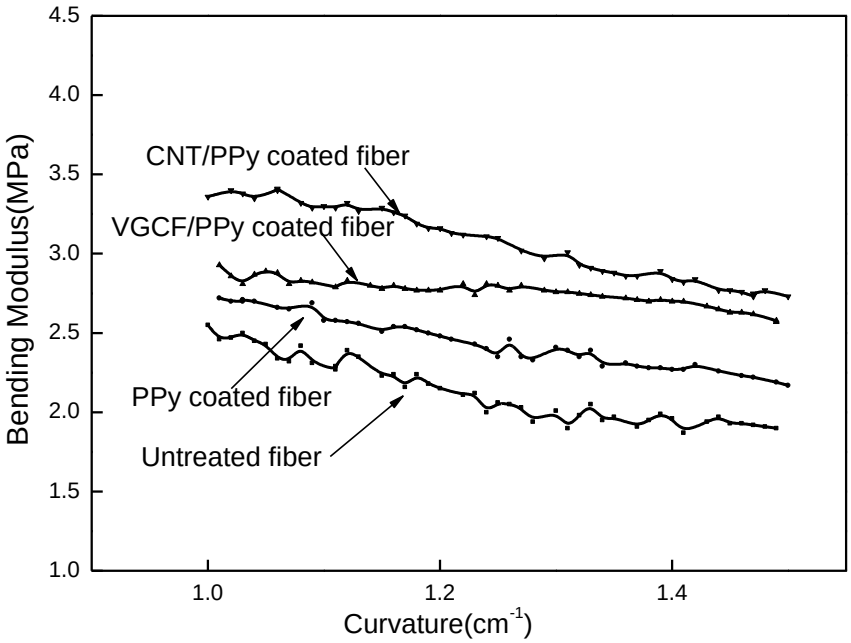
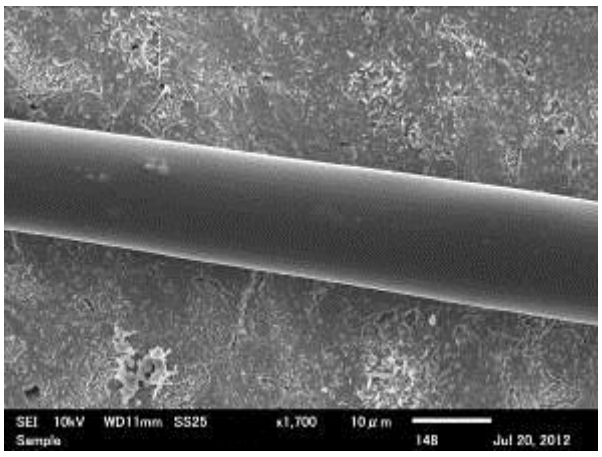
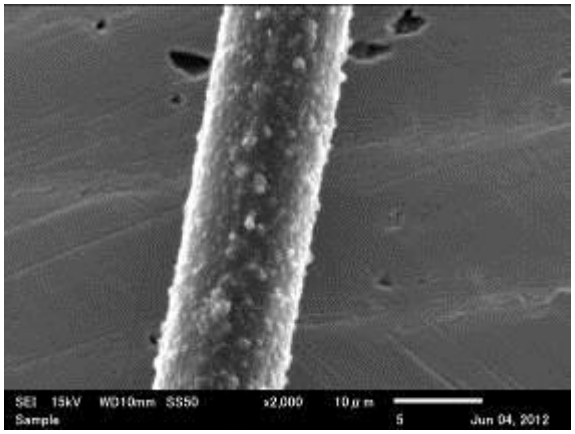


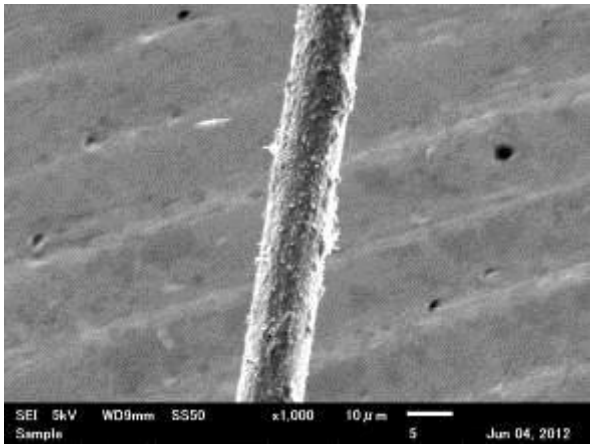
Fig 12



a


SEI 15kV WD10mm SS50 x2,000 10 μ m
Sample
5
Jun 04, 2012

b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Sample
5
Jun 04, 2012

c