

**Doctoral Dissertation (Shinshu University)**

**Improvement of compression performance  
of fiber reinforced polymer**

March 2016

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## **Abstract**

FRP (Fiber Reinforced Plastic) is a composite material made of a polymer matrix reinforced with fibers. The combination of continuous fibers with plastic resulted in composite materials with mechanical properties and durability better than either of the constituents alone. These kinds of materials have obvious benefits with lightweight, high specific strength and chemical corrosion resistance etc. Fiber-reinforced plastic is best suited for any design program that demands weight savings, precision engineering, finite tolerances, and the simplification of parts in both production and operation. FRP are commonly used in the aerospace, automobile, wind turbine blade, sports accessories and so on.

However, because the oriented structure of fiber, FRP are strongest and most resistance to deforming forces when the reinforced fibers are parallel to the force being exerted, but the weakness is that when the compressive force are exerted or fiber are perpendicular to the force, due to fiber buckle or kink bands, the resistance ability are weak. The compressive strength of composites is generally lower than tensile strength, which significantly reduces the advantageous position of FRP materials in structures in which compressive strength is the primary design requirement.

It is desirable to research the compressive failure modes of FRP to improve the compressive property for enhancing the potential of structural applications. Fiber compressive failure is a complex failure mode in FRP composites. Depending on the material and fiber assemble modes, different of compressive failure modes, including micro buckling, kinking and longitudinal fiber splitting fiber failures are possible. For unidirectional glass fiber and carbon fiber composites, micro buckling or kinking of fibers are now understood to be the compressive failure mechanisms. In summary, micro buckling is the main failure modes in FRP under comprehensive state. Kinking, on the other hand, is a highly localized fiber buckling. Kink bands are formed after attainment of the peak compressive load when the region between the fiber breaks is

deformed plastic.

The UHMWPE fiber, which has excellent tensile modulus and strength and low density gives it the highest specific modulus and strength of all commercial reinforcing fibers, is very flexibly, the knot strength is as high as tensile strength, and the UHMWPE fiber reinforced plastic composite has well impact resistance. But the compressive behavior of this kinds of fibers reinforced plastic composite have few studied.

The purpose of this study is to improve the compressive performance of UHMWPE fiber reinforced epoxy resin based on micro-buckling failure theory. The buckling of the fibers throughout a unidirectional composite is initiated by the buckling of the weakest fibers. The surrounding matrix and composite provide appreciable support for a single fiber, so the strain field in the matrix is expected to be localized around the fiber. The critical buckling loads  $P_{cr}$  is related with the mechanical properties of reinforced fibers, plastic matrix and critical wavelength  $l$ , in general, compared to the strength and modulus of the fibers, those properties are relatively low. In this study, the influencing factors of resin are not considered. We improved the  $P_{cr}$  from changing mechanical properties of the fibers and critical wavelength.

Firstly, the compressive and bending module of UHMWPE fibers was improved by surface coating. 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. In this paper, we used pyrrole vapor deposition to coat the surface of UHMWPE fibers with carbon VGCFs and CNTs. Pyrrole is a volatile organic compound that is readily oxidized to form polypyrrole (PPy). A new process to coat UHMWPE fibers with VGCFs and CNTs by pyrrole vapor deposition was developed. The PPy have the combined advantages of excellent mechanical strength from VGCF and the cladding ability of PPy. 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. The transverse

compressive strength and bending moment of single UHMWPE fibers were measured by micro-compression 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. However, the coating method must be conducted with one by one of the UHMWPE fibers, the efficiency was very low, at the same time, the cost of the coating materials is high, so this method was proved has no feasibility. Therefore, the coated fiber reinforced plastic was not prepared.

Next, a filament covering is proposed to improve the longitudinal compressive properties of unidirectional fiber reinforced plastic. Based on compressive buckling theory, fiber buckling can be prevented by shortening the buckling critical wavelength by covering the filament. A UHMWPE fiber bundle and a PBO filament were selected as the reinforcing fiber and the covering filament, respectively, to verify this statement. The effect of a covering PBO filament on a UHMWPE fiber reinforced epoxy resin on compressive performance was investigated by a compressive test and morphology observations. Results show that the filament covering has positive effect on the compressive strength of the FRP, and the tension-exerted filament covering increased the compressive strength and increased the longitudinal compressive modulus of the UFRP. Four kinds of filament were used as the covered yards, including polyester fibers, basalt fibers, PBO fibers and UHMWPE fibers. The effect of different filament and covered spacing on compressive strength and modulus were studied. Results showed that compression strength and modulus of the unidirectional composites reinforced with filament-covered bundles depended strongly on the compressive failure mechanism, which was decided by the type and spacing of the covering filament. With shortening the covered spacing, the compressive strength was increased, that can be explained by the critical wavelength theory. While the compressive modulus was decreased, that can be explained by the wind angle was become small, resulting the resistance of compressive force provided by covered filament fiber became decreasing.

In this dissertation, in order to improve compressive performance of unidirectional fiber reinforced composite, the compressive behavior of single UHMWPE fiber and unidirectional UHMWPE fiber reinforced FRP were investigated. Two novel methods were proposed, the coating nano-particles with pyrrole vapor deposition method was proved can be improve the compressive and bend strength and modulus for single fibers, it has the potential to improve the compressive performance of unidirectional FRP, but this method has the high coat and low Effectiveness. The other method was filament covering fiber bundle, filament-covered fiber bundles can improve the compressive properties of the unidirectional composites. The tension-exerted covering filament could improve the compressive modulus. Compression properties and mechanism of compressive failure of the composites change with the increase of the spacing. By varying the components of composites, we can tailor their mechanical properties according to our target applications.

## CHAPTER ONE

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### **General introduction**

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# Chapter 1: General introduction

## 1.1 High Performance fibers

Starting from agricultural era periods, a variety of fibers have been used by human for daily supplies, for instance, clothing, upholstery and carpets. Among them, mostly are natural fibers, including cotton, wool, silk and so on. With the rise of industrial revolution, in the late nineteenth century, the first synthetic fiber, tradename is Nylon, was developed by DuPont company based on petrochemicals monomers. Ever since, developments continued rapidly. In the meantime, a variety of new applications for fiber have also been developed, from traditional textile applications to new engineering materials, filter materials, battery materials, fibers are plays an important role <sup>[1-3]</sup>.

High performance fibers are those that has high specific strength, stiffness, chemical resistance or other high added value. Their required spinning technology and final mechanical properties can be adjusted by spinning dope own particular crystallographic and molecular structure <sup>[4]</sup>. Based on the spinning dope materials, high performance fibers can be divided into inorganic fiber and organic fiber.

Glass fiber is the oldest inorganic high performance fiber, which has been prepared via a melt spinning process since the 1930s, their structure is usually amorphous. Similarly, the basalt fiber as well as. These fibers can be found using in insulation, fire resistant fabrics materials, and as the reinforced fiber in composite materials. Because these fibers from the minerals, the intrinsic high density results in a relatively low specific strength and stiffness when compared to other fibers <sup>[5-7]</sup>.

Carbon fiber is one of the most important high performance fibers, composed by long strings of molecules bound together by carbon atoms. Although the raw spun materials are organic polymers, mostly is polyacrylonitrile (PAN) as well as petroleum pitch, after carbonizing process at carbon fiber manufacturing, the non-carbon atoms are expelled. the carbon atoms are bonded in microscopic crystals

that roughly aligned parallel to the axis of fiber, the structure of crystal makes the fibers have magical strength. Carbon fibers can therefore be considered as an inorganic fiber. The diameter of those fibers is about 5-10 micrometers. Carbon fibers has some unique properties, such as low electrical resistivity and high thermal conductivity. Nowadays, carbon fiber plays an important part in many products, carbon fiber reinforced composite materials have been widely applied to make aircraft and spacecraft parts, automobile bodies, bicycle frames, fishing rods, and many other parts where high strength and light weight are needed [8-10].

Commercial high-performance organic fibers first became available with the introduction of a meta-aramid (m-aramid) fiber, in the second half of the 1960s. Since that time, several classes of fibers have been commercialized. Solvent based spinning technologies enabled the development of high performance organic fibers. Two classes of such fibers can be distinguished at commercial organic fibers. One type is based on rigid rod molecules, well-known products are Kevlar<sup>TM</sup>, Twaron<sup>TM</sup> or Zylon<sup>TM</sup>, a new fiber M5 has entered late development stages. The molecular chains of these fibers exhibit some bending stiffness, which makes the fibers has high tensile strength and relatively high bending strength. The other type is made of the very flexible polyethylene molecules based gel spinning technology, the most representative production is ultrahigh molecular weight polyethylene (UHMWPE) fiber, as well know trade name is Dyneema<sup>TM</sup>.

Kevlar and Twaron are the commercial products made from aramids, derived from aromatic acids and amines, the aromatic rings and amide linkages added strength make the fibers have high tensile strength, the rigid molecules structure tend to form mostly planar sheet-like structures, which translates into better thermal properties and impact resistance due to their dimensional stability. They are used in thermal-resistant clothing, protective vests and helmets, composites, and sporting goods [11-13,16].

As for other rigid organic polymers fibers, PBO fiber is derivate with a range of thermoset liquid-crystalline polyoxazole, which has higher rigidity than aramids. The tensile strength of PBO fiber is 1.6 times that of Kevlar. It also has better thermal resistance properties and lightweight properties compared with aramid fibers. But the

expensive ingredients and highly aggressive solvent combined with high viscosities of these solutions result in notable higher cost and prices compared with aramid fibers [14], in the meantime, poor resistance to ultraviolet and visible radiation limit its use in some applications [15].

M5 fiber is based a rigid polymer [diimidazo pyridinylene (dihydroxy) phenylene] spun from an anisotropic solution [17]. The tensile properties realized are similar to those of PBO, while crystal structure of M5 is different from aramid fibers and PBO, it characterizes a hydrogen bonded network in the lateral dimensions. The existence of higher level of hydrogen bonding, which improves its structural integrity, results M5 fiber offers potential for significant improvement of compressive properties. M5 fibers also has the high damage tolerance, good temperature resistance, low specific weight, good adhesion to matrix materials. The new fiber M5 offers a potential for a unique combination of properties that promises a unique set of applications due to its advanced properties in one molecular structure [17-19].

Ultrahigh molecular weight polyethylene fiber (UHMWPE) offers another thinking for manufacturing high-performance fibers by ultra-drawing the flexible polymers to from the fully extended chain configuration [20]. The UHMWPE fiber has best illustrated the significance of high molecular orientation related to crystallization. Gel spinning technology is a common approach, the flexible polymers are dissolved in a suitable solvent, and molecular alignment perfection can be improved by redesigning the spinning process. The key element in the formation of UHMWPE fibers is ultra-drawing for molecular chains orientation and removal of the entanglements. Compared the molecular structure of regular and high orientation polyethylene in Fig. 1-1, the process of ultra-drawing resulting in fibers with a nearly perfect orientation and a very high degree of shish-kebab structure crystallinity. This is the reason for very high strength and modulus to polyethylene. Chain-folded lamellar crystals were described by Prof. A. Keller [24]. Who recognized that in flexible macro-molecules the thermos-dynamically most favorable confirmation is a chain-folded lamellar crystal.

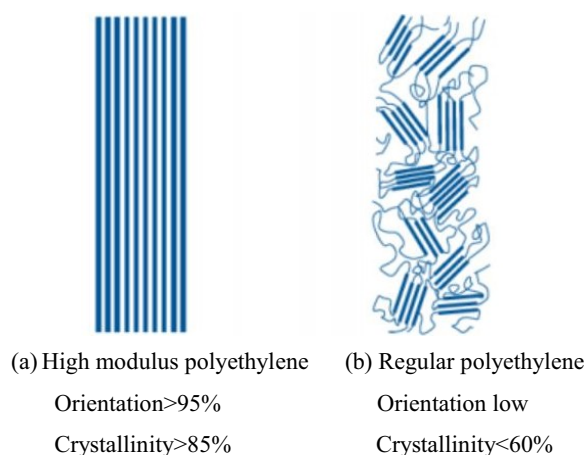


Fig. 1-1. The molecular structure of regular and high modulus polyethylene

UHMWPE fibers has exceptional strength-to-weight ratios, due to its high strength and stiffness and low density. Besides, the good abrasion resistance and low moisture absorption makes this fiber are widely commercially available. A growing need for this fiber in marine rope manufacture and fishing net production [25]. One added advantage of this fiber is its excellent impact properties in composites, in particular, the impact properties of carbon and glass based composites can be improved substantially by adding UHMWPE fiber. UHMWPE fiber can produce composites with extremely with extremely high impact and penetration resistance and with a high capacity of energy absorption [26-27].

However, the high degree of crystallization and regular non-polar molecular chain result in the poor adhesion, the poor adhesion UHMWPE fibers to polymer matrices has been a limiting factor in their use for composite material applications. Recently, many research works of fiber surface treatments, such as ultraviolet, chemical etching, plasma treatment etc., have been carried out to overcome this shortcoming of UHMWPE fiber [28-30]. The ordering or lateral packing phenomenon is caused by lateral interaction which can be non-bonded as in UHMWPE, hydrogen bonded as in Kevlar, or covalently bonded as graphite molecular sheets [22-23]. So, these gel-spun fibers are based on polymers with weak lateral bonds, modest thermal stability and poor compressive properties [21].

## 1.2 Compression properties of single fiber

Owing to the highly oriented molecules chain or crystals along the fiber axis, high performance fibers have strong anisotropy in their mechanical properties. When comparing the various types fibers, it becomes clear that organic polymer fibers can excellent than glass and carbon fiber based on specific tensile properties, while the major concern is the behavior under compressive loading for polymer fiber <sup>[31-32]</sup>. Form the longitudinal direction, the compressive strength of rigid-rod polymers such as PBO is in the 200-300 MPa range, for Kevlar it is about 400 MPa, and for most flexible polymeric fibers including UHMWPE fiber, the compressive strength values are below 200 MPa, the newly developed experimental fiber, PIPD, with a value of over 1 GPa, exhibits the highest compressive strength of any polymer <sup>[33]</sup>. Compared with 5.6 and 4.2 GPa of maximum values found for the compressive strength carbon fibers and E-glass fibers <sup>[34]</sup>, the low compressive strength of polymer fiber is an important disadvantage.

Many efforts have been made to understand the origin of the longitudinal compressive mechanism in polymeric fibers. Deterasa <sup>[35]</sup> stated that the compressive stress of fibers initiates local buckling instabilities, which subsequently lead to kink band formation. Greenwood <sup>[36]</sup> reported on the compressive failure in aramid fibers attributing the plastic kink band formation to micro-fibril separation. Further research by Dobb and Takahashi <sup>[37]</sup> believed the low compressive strengths of polymer fiber were principally the result of weak lateral interactions between polymer chains.

Especially to the UHMWPE fiber, when this polymer fiber under the zone drawing during gel-spun process, this becomes a well-aligned structure with needle shaped crystals. Initially the average distance between the lamellar crystals increased by the draw ratio, but the fibril diameter remained constant during the drawing process, at some stages during drawing, lamellar crystals transformed into fibrils. Following the completion of structural transformation, further drawing is still possible, which indicates that inter-fibrillar slippage can occur, which result in weak lateral bonds poor compressive properties <sup>[25]</sup>. The UHMWPE fibers possess a hierarchical

fibrillar structure. A single UHMWPE fiber is composed of highly oriented fibrils approximately 100nm in diameter. The structure of UHMWPE fiber is shown as Fig. 1-2. The fibrils are assembled into micro-fibrils, which are blocks of crystalline UHMWPE connected by oriented amorphous tie molecules [38,39]. 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. Therefore, the use of organic fibers in structural applications has been restricted by their performance under longitudinal and transverse compression.

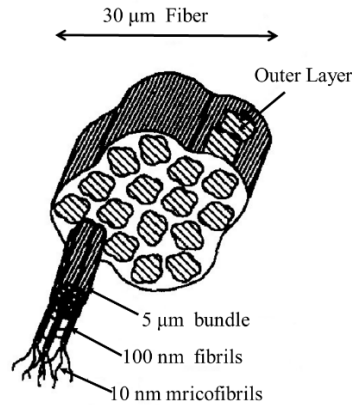


Fig. 1-2. Schematic diagram of UHMWPE fiber fibrillary structure [25]

### 1.3 Fiber reinforced plastic matrix composite (FRP)

Fiber-reinforced plastic, also fiber-reinforced polymer, is a composite material made of a polymer matrix reinforced with fibers. The fibers are usually high strength and modulus fibers, such as glass, carbon, aramid, although other fibers mentioned above, those fibers embedded in or bonded to a plastic matrix, the plastic is usually thermosetting resin including epoxy, unsaturated polyester, phenol formaldehyde resin due to their well infiltration properties, the major short point of fiber reinforced thermosetting resins is hard to be recycled or reused just because of the chemically inert of the cured matrix [44-47]. Recently, there are many thermoplastic plastic, including polyethylene, Nylon, polyether ether ketone, have been applied in FRTP

(fiber reinforced thermoplastic plastic) due to their recyclability and rapid foldability. FRP can be classified in to fiber reinforced thermosetting plastic (FRP) and fiber reinforced thermoplastic (FRTP) by the distinction in the types of matrix resin.

In this form, both fibers and matrix remind their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents acting alone. Many fiber-reinforced composite materials offer a combination of strength and modulus that are either comparable to or better than many traditional metallic materials. In general, fibers are the principal load-carrying members, while the surrounding matrix keeps them in the desired location and orientation, acts as a load transfer medium between them, and protects them from environmental damages due to elevated temperatures and humidity <sup>[40,41]</sup>. There are also some desirable properties including superior corrosion and fatigue resistance for FRP. It has been as a major class of structural material and are considered as substitutions for metal in many weight-critical components in aerospace, automotive, and other industries <sup>[42,43]</sup>.

The manufacturing processes used for FRP are often very different from those used with conventional structural materials, the materials we are considering in this study are the continuous fiber reinforced plastic, based on fine filaments, which are very long with respect to their diameters. There are many aspects of composite manufacture which are common with textile processing. The flexibility of fibers allows them to be woven or wound onto mandrels so that complex forms can be produced which, when impregnated with plastic, and then cured, can lead directly to the final product which requires little or no extra finishing. In this way the total cost of manufacturing a component with a composite material can be reduced, compared with traditional materials. Alternatively, fibers can be chopped and sprayed together with the resin onto an open mold. This technique is useful for large structures including boat hulls but is also used for other smaller low cost structures. The matrix properties determine the resistance of the FRP to most of the degradative processes, for instance impact damage, delamination, water absorption, chemical attack and high-temperature creep, which cause failure of the structure.

In general, the manufacturing process for these composites follows the following flow chart:

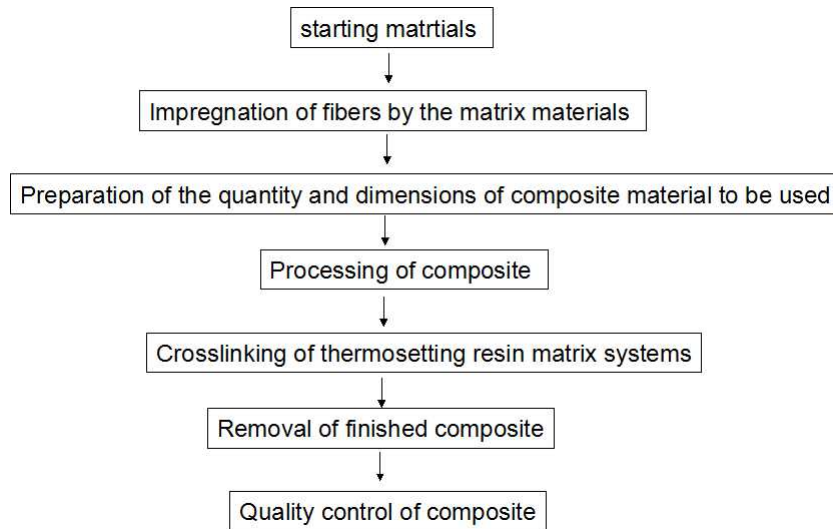


Fig. 1-3. The manufacturing process for a FRP composite

When plastics are reinforced the composite which is formed has properties which depend on both the resin properties and those of the fibers and their arrangements. The fiber arrangement in the matrix influences greatly the final properties of the composite. Unidirectional composites are highly an-isotropic; it has the most efficient reinforcement is provided by continuous fibers aligned in the direction of the applied load. Unfortunately, the favorable properties of this specific direction usually come at the expense of properties in the other directions. In directions perpendicular to the stiff and strong direction, including the transverse and longitudinal compression direction, the FRP is much softer and weaker <sup>[48,49]</sup>.

In general, the FRP which reinforced by inorganic fibers are extremely rigid although somewhat brittle. Moreover, carbon fibers are relatively expensive when compared to glass fibers or plastic fibers. Yet, the organic fibers reinforced plastic composite has the relatively high specific strength because their low density.



## 1.4 Compressive failure in fiber reinforced fibers

Compression failure is a design-limiting feature for the continuous fibers reinforced plastic composite materials. For example, Ishikawa reported a value of 0.71 as being typical for carbon fiber-reinforced plastic (CFRP) composites with a fiber volume fraction of 0.65 <sup>[50]</sup>. The ratios of compressive-to-tensile strength for unidirectional Kevlar49/epoxy and S-2 glass/epoxy composites are approximately 0.15 and 0.49, respectively <sup>[51,52]</sup>. This significantly reduces the advantageous position of these materials in structures in which compressive strength is the primary design requirement. As a result, the causes of this difference have attracted considerable attention over the last several decades' years.

For the continuous fiber reinforced plastic composites, it usually designed to possess a high-axial stiffness and strength. According, the fibers have high strength and modulus, the matrix has a much higher toughness and lower strength than the fibers in order to endow the composite with adequate strength and ductility. The main failure mechanisms of compressive failure are listed as <sup>[53-56]</sup>:

1. Elastic micro buckling. In general, the elastic micro buckling occurs in two possible modes. As shows in Fig.1-4, a transverse buckling mode, whereby the matrix undergoes extensional straining transverse to the direction. The other is shear buckling mode, where the matrix shears parallel to the fibers. In this model, compressive failure is assumed to be triggered by the local instability of fibers embedded in the matrix.
2. Plastic micro buckling. Plastic micro buckling is the dominant mechanism of compressive failure in plastic-matrix composites, especially to these FRP possess a compressive strength of less than 60% of their tensile strength. Plastic micro buckling is also an important failure mechanism in natural composite, the woods. The compressive strength is controlled by fiber misalignment together with plastic shear deformation in the matrix, for the woven reinforced plastic matrix composite, the micro-buckles form at many of the cross-over point of neighboring tow.

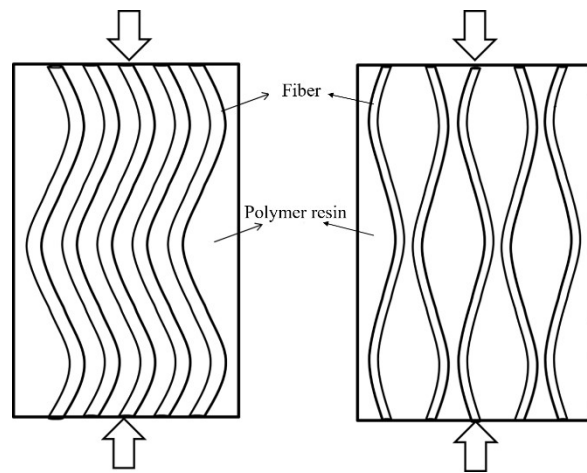


Fig.1-4. Micro-buckling failure modes: (a) Shear mode (b) Extensional mode.

3. Buckle delamination. This occurs by the buckling of a surface layer from a subsurface de-bond. It is observed in both ceramic matrix and plastic matrix composites. Post-impact compressive strength is often a concern in the use of composites, as the impact event leads to a large de-bond. Subsequent compressive loading can induce buckle-delamination growth. Buckle delamination is associated with a low matrix toughness and the presence of a large subsurface flaw<sup>[57-66]</sup>.

Several attempts to improve the compressive performance for FRP, recently, there are three mainstream approaches, being develop novel fibers, resin modification and designing hybrid FRP.

Because the FRP are constitute of fibers and plastic matrix, the properties of matrix and interface of fiber and resin are influence on the mechanical behavior. Subramaniyan proposed enhancing the compressive strength of unidirectional glass fiber reinforced composites using nanoclay<sup>[67]</sup>. The initial elastic modulus of the resin increases with the addition of nanoclay and the improvement is more pronounced with an increase in the nanoclay load. The longitudinal compressive strength of GFRP extracted from off-axis tests shows an increase of 22% and 36% with 3% and 5% nanoclay loadings, respectively. B. Tissington<sup>[68]</sup> found that the plasma treatment for UHMWPE fibers can improve the compressive strength of their composite with minor.

Considering the fine filaments in FRP usually are textile, the two-dimensional (2D) textile plastic composites are vulnerable to delamination failure under compressive loading, this problem has led to the development of FRP reinforced by various three-dimensional (3D) arrangements of fibers, the forms of 3D including structures manufactured by weaving, stitching, knitting and braiding, and there has been considerable success for eliminating delamination failures<sup>[69,70]</sup>. Accordingly, the compressive performance increase.

Moreover, hybridization is a normal method to balance various properties, and it also applied for improving the compressive properties of FRP. Usually, the hybridization classified into interlaminar and interlaminar. Interlaminar, or simply laminate, consists in depositing layers made of different fibers, whereas, in

intralaminates, both fibers are entangled within a single layer <sup>[71]</sup>. Sudarisman found that the hybrid different fiber can alter the failure modes of FRP <sup>[72]</sup>. Compressive failure of unidirectional carbon fiber reinforced epoxy resin was compressive shear and compressive crushing, with the addition of SiC fibers, the fiber kinking and longitudinal splitting being noted.

## 1.5 Improving the compressive properties FRP based on preventing fiber buckling

In this study, we propose a concept for improving compressive properties of FRP based on the buckling failure theory. According to the above explanation about compression failure mechanism of FRP. For the organic fiber reinforced resin, the compressive failure modes usually show interfacial debonding, kink banding, and micro-bulking. The fiber micro-bulking phenomenon occurs in the early stages when FRP under compression, subsequently, the kink banding or interfacial debonding will occurs, which depends on the fiber volume fraction, the interface between fiber and resin, the fibers types and so on. If the fiber micro-bulking is prevented, then the compressive properties will be improved.

Fiber is a long and fine material, which very easy shows bulking under compressive, Fig.1-5 shows a bulking process.

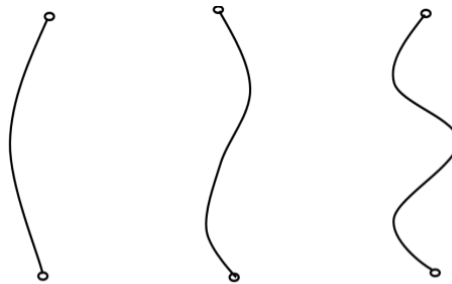


Fig. 1-5. Bulking phenomenon of a long and fine material

The factors affecting the material buckling behavior were investigated by pioneer researchers. And a formula was obtained for buckling load as followed as formula (1).

$$P_{cr} = \frac{\lambda \pi^2 EI}{l^2} \quad (1)$$

In this formula,  $P_{cr}$  is the ultimate buckling load;  $\lambda$  is the fiber's waviness,  $l$  is the critical wavelength,  $E$  is flexural modulus,  $I$  is moment of inertia and  $EI$  is the flexural rigidity. Increasing the ultimate buckling load of fibers by changing various parameters of fibers will increase the buckling load, which play a role to prevent fiber buckling.

In the case of FRP, due to the presence the resin, the critical buckling load  $P_{cr}$  is represented as:

$$P_{cr} = \frac{\pi^2 E_f I_f}{l^2} + \frac{l^2}{\pi^2} \frac{E_m V_f}{r_f (1 - V_f)} \quad (2)$$

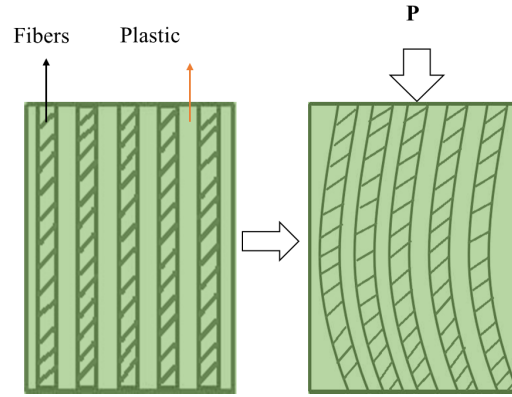


Fig. 1-6. Bulking phenomenon of fibers in FRP

In formula (2), in this formula,  $P_{cr}$  is the ultimate buckling load;  $l$  is the critical wavelength,  $E_f$  is flexural modulus of fiber,  $I_f$  is moment of inertia of fiber,  $E_m$  is the modulus of the polymer resin, the former part is determined by the fiber, while the later part is depended on the resin property. However, in most case, the compressive performance of high performance fiber are much better than common used resin. Therefore, the resin part was omitted in this study, the formula (1) was applicable.

In this work, we want to improve the compressive performance of FRP by means of increasing ultimate buckling load of fiber or fiber bundle. Two kinds of methods were proposed based on above theory and thoughts.

Proposal 1: Because the compressive performance of FRP is largely dependent on fiber properties. the buckling load of FRP will increase with the increasing of fiber's. Therefore, we plan to improve the flexural rigidity of single fiber for better ability of prevent fiber buckling in FRP.

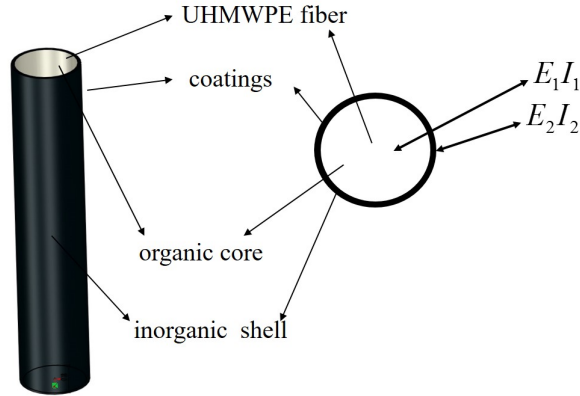


Fig. 1-7. Preventing fiber buckling by increasing flexural rigidity (EI)

As Fig.1-6 shows, when a hard inorganic shell is coated on surface of fibers, the value of inorganic coating flexural rigidity ( $E_2 I_2$ ) is higher than those of fibers. Certainly, the whole coated fibers flexural will be increased. As the formula above, the ultimate buckling load will be increased, correspondingly.

The coating method and experimental results are stated on chapter two.

#### Proposal 2:

When the fiber bundle is considered, we got a more convenient means to increase ultimate buckling load for better compressive properties of fiber in FRP. As the formula (1) shows, the critical wavelength  $l$  influences the ultimate buckling load.

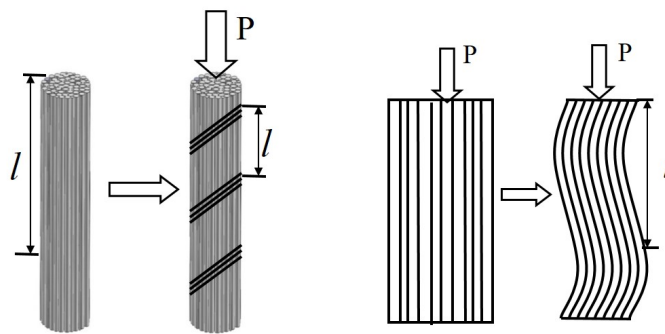


Fig. 1-8. Preventing fiber buckling by shorten critical wavelength

A filament covering is proposed to shorten critical wavelength  $l$  of fiber bundle when FRP under compression. The filament covering method and experimental results are stated on chapter three and four.

## 1.6 Constitution of this dissertation

The fiber reinforced plastic composite materials (FRP) attracted many attentions, for their properties of light-weight, high specific strength and specific modulus, good corrosion resistance and other advantages. is generally lower than the tensile strength, this relative weakness in compression is often the limiting factor in the application of composite materials.

The work presented in this thesis describes two novel approach to improve the compression performance of fiber reinforced plastic.

In the chapter two, 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 micro compression 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 expected that the improved fiber would be applied in FRP for better compressive performance.

In the chapter three, a filament covering is proposed to improve the longitudinal compressive properties of unidirectional fiber reinforced plastic. Based on compressive buckling theory, fiber buckling can be prevented by shortening the buckling critical wavelength by covering the filament. In this paper, a UHMWPE fiber bundle and a PBO filament were selected as the reinforcing fiber and the covering filament, respectively, to verify this statement. The effect of a covering PBO filament on a UHMWPE fiber reinforced epoxy resin on compressive performance was investigated by a compressive test and morphology observations. Results show that the filament covering has positive effect on the compressive strength of the FRP, and the tension-exerted filament covering increased the compressive strength and increased the longitudinal compressive modulus of the UFRP.

In the chapter four, the effects of covering ultra-high molecular weight polyethylene (UHMWPE) fibers with different types and spacing of filaments on the



longitudinal compression properties of unidirectional UHMWPE fiber-reinforced epoxy resin samples were investigated. UHMWPE fiber bundles covered with fiber filaments were prepared using a custom winding machine, and composites were subsequently fabricated by vacuum-assisted resin transfer molding. Covering filament spacing was controlled by the warp speed. Compression testing of the resulting samples was performed and the fracture surfaces were examined by an optical microscope. The results showed that the compression strength and modulus of the unidirectional composites reinforced with filament-covered bundles depended strongly on the compressive failure mechanism, which was decided by the type and spacing of the covering filament.

In chapter 6, A brief conclusion of this dissertation was made.

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## CHAPTER TWO

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### **Mechanical enhancement of UHMWPE fibers by coating with carbon-based particles**

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## **Chapter 2: Mechanical enhancement of fibers by coating with carbon-based particles**

### **2.1 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 ( $0.97 \text{ g/cm}^3$ ), excellent ductility and superior resistance to impact, wear, moisture and chemical agents<sup>[1]</sup>. 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<sup>[2,3]</sup>.

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 micro fibrils, which are blocks of crystalline UHMWPE connected by oriented amorphous tie molecules<sup>[4,5]</sup>. 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<sup>[6]</sup> 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 <sup>[7-9]</sup>. The nano carbon 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.* <sup>[10]</sup> 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.* <sup>[11]</sup> 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) <sup>[12]</sup>. 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.

## **2.2 Experimental**

### **2.2.1. 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  $\mu$ m 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. Polyethylene mine (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.

### 2.2.2. 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 <sup>[13,14]</sup>. 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 (2mol/L), and then mixed for 30 min. A single UHMWPE 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 (Fig. 2-1). 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.

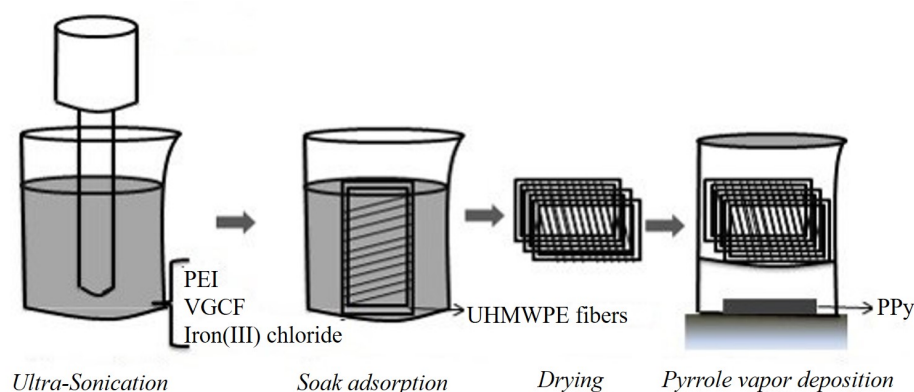


Fig. 2-1. Preparation of VGCF-coated UHMWPE fibers

### 2.2.3 Transverse compression experiments

A micro compression 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. Fig.2-2 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  $50\ \mu\text{m}$ . 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 fiber, the compressive force gradually increased from 0 to  $5000\ \text{mN}$  at a rate of around  $200\ \text{mN/s}$ . After 25s, a compressive force of  $5000\ \text{mN}$  was maintained for 5s. The transverse compression tests were concluded ten times for each kind of fibers.

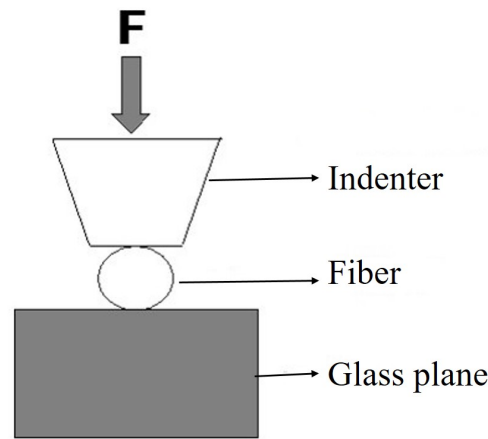


Fig. 2-2. Schematic diagram of the transverse tester

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 <sup>[15,16]</sup>. 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 <sup>[17]</sup> 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 fiber;

$b$ : contact width of the fiber during compression

With the development of fiber synthesis technology, an increasing number of high-performance fibers, like Kevlar KM2, A265 and 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 Fig. 2-3.

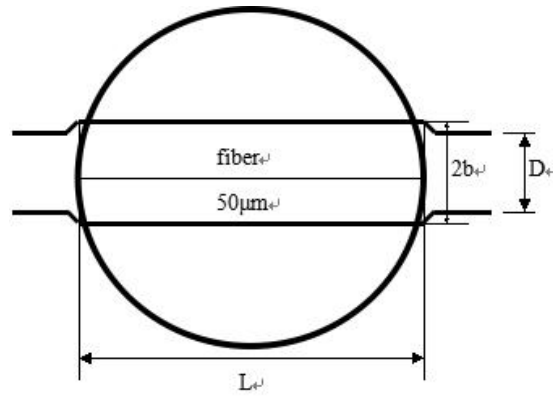


Fig. 2-3. Schematic diagram of the transverse compressive fiber

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;

$L$ : length of compressive fiber during compression;

$\varepsilon$ : strain of fiber.

#### 2.2.4 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 Fig.2-4, 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 (Fig.2-5), and the paper frame was fixed by a chuck and clipped from the middle.

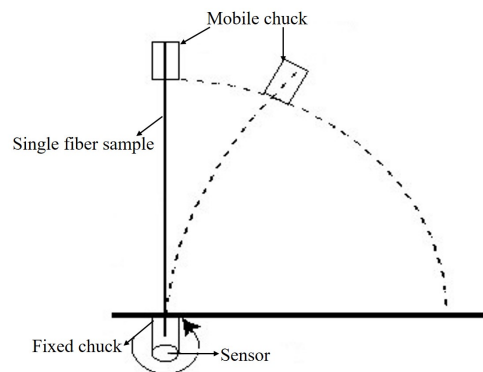


Fig. 2-4. Schematic diagram of the bending tester

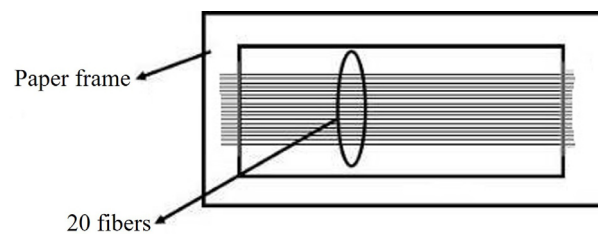


Fig. 2-5. Diagram of a sample used in bending tests

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  $2\text{ m}^{-3}$ , and the bending moment was obtained when the curvature of the fiber was  $1\text{--}1.5\text{ m}^{-3}$  to calculate its bending modulus.

Bending modulus was calculated by

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

Bending rigidity is  $E_b I$ , 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.

## 2.3 Results and Discussion

### 2.3.1 Transverse compressive behavior of UHMWPE fibers

Fig.2-6 is a typical load-deformation curve obtained from a micro-compressive 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 non-elastic. 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 Fig. 2-7. On the part of compressed fiber, the fiber was crushed.

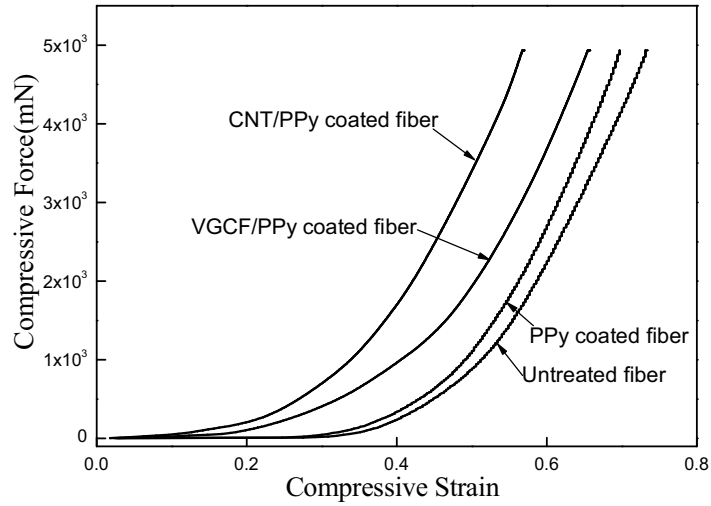


Fig. 2-6. Transverse compressive curve of a single UHMWPE fiber

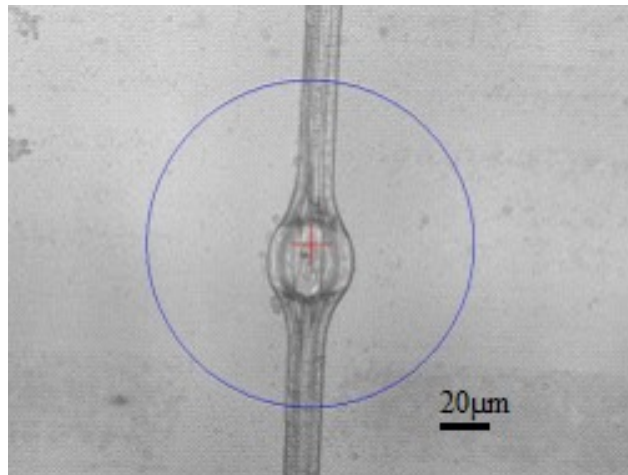


Fig. 2-7. Picture of a single UHMWPE fiber after compression

Fig. 2-8 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.



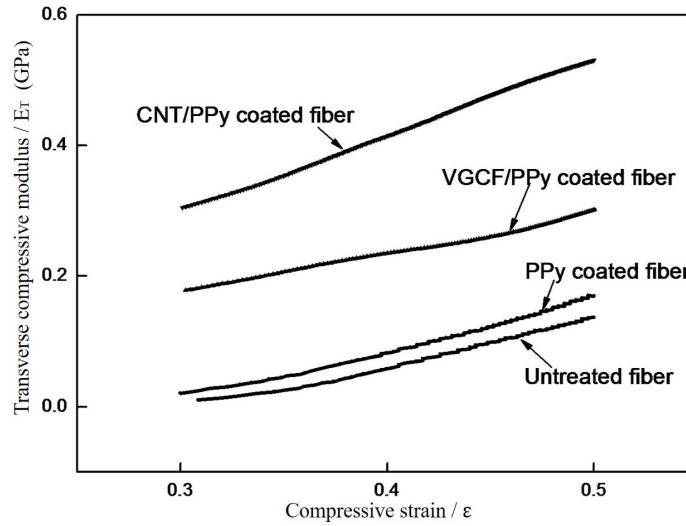


Fig. 2-8. Nominal transverse modulus of coated and uncoated UHMWPE fibers

### 2.3.2 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 Fig. 2-9.

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. 2-10, the initial bending rigidities of the coated fibers were improved considerably compared with that of the uncoated fiber. The initial bending

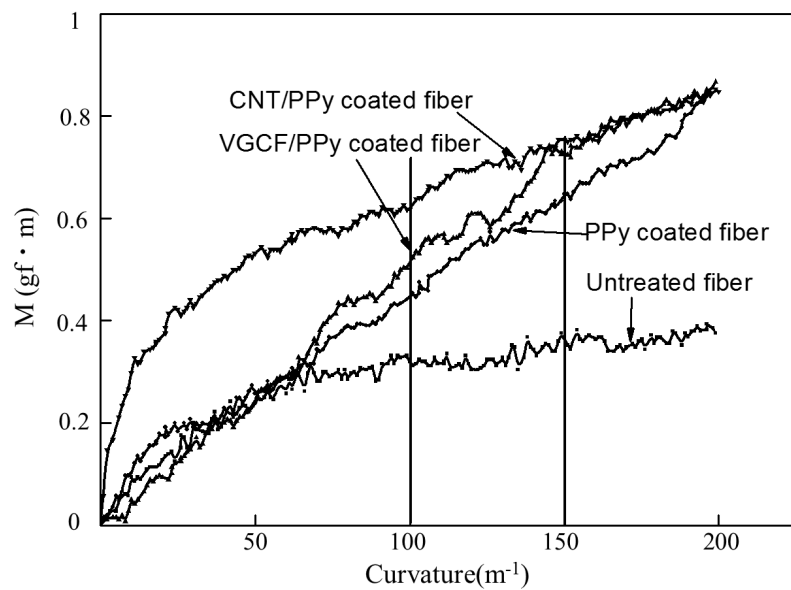


Fig. 2-9. Typical bending curves for single coated and uncoated fibers

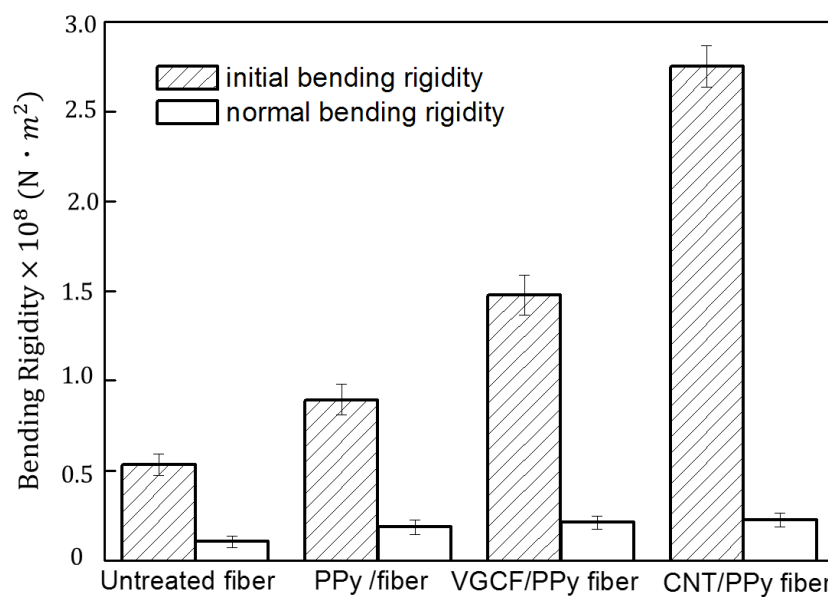


Fig.2-10. Bending rigidity of coated and uncoated UHMWPE fibers

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 Fig. 2-10. 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.

### **2.3.3 The role of polypyrrole during coating process**

The surface morphologies of a UHMWPE fiber and VGCF/PPy-coated fiber are shown in Fig. 2-11. The surface of the untreated UHMWPE fiber was comparatively smooth. After pyrrole vapor deposition, the fiber surface had a coating (Fig. 2-11(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. 2-12(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.

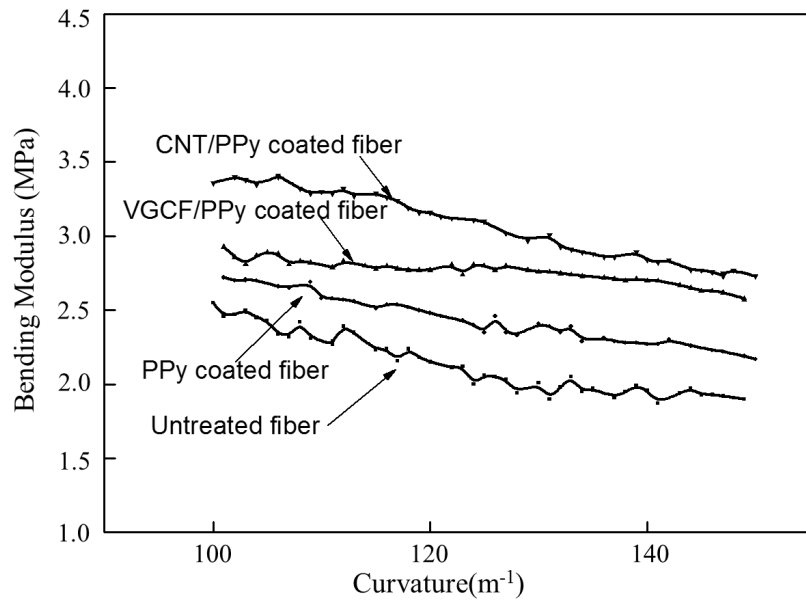


Fig.2-11. Bending modulus of coated and uncoated UHMWPE fibers

## 2.4 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 micro compression 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.

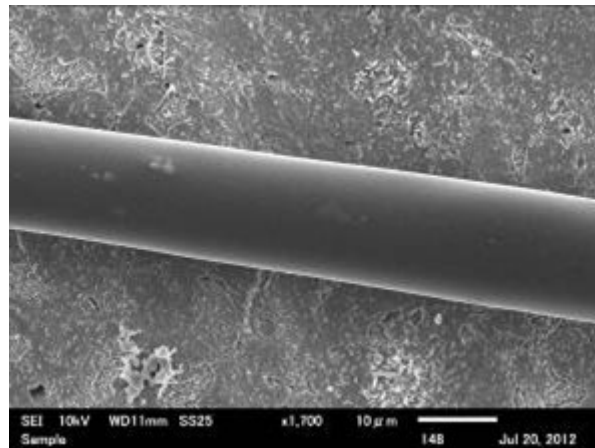


Fig.2-12. (a) SEM images of untreated UHMWPE fiber

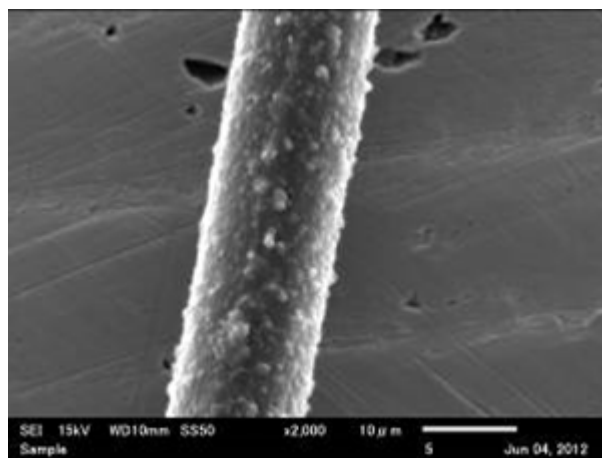


Fig.2-12. (b) SEM images of PPy-coated fiber

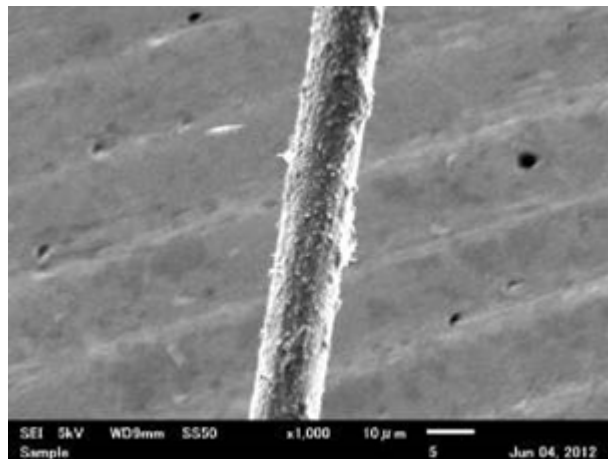


Fig.2-12. (c) VGCF/PPy-coated fiber

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## CHAPTER THREE

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### **Improving the longitudinal compression performance of by a filament covering method**

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## **Chapter 3: Improving longitudinal compression performance of by a filament covering method**

### **3.1. Introduction**

Fiber reinforced composite materials consist of high strength and high modulus fibers embedded in or bonded to a matrix with distinct interfaces between them. In general, fibers are the principal load-carrying members while the surrounding matrix keeps them in the desired location and orientation, and acts as a load transfer medium between them. The principal fibers in commercial use are various types of glass fiber, carbon fiber, basalt fiber, Kevlar 49 and ultra-high molecular weight polyethylene <sup>[1-4]</sup> etc. FRP is a strong, stiff, lightweight material for application in diverse structures from aircraft, spacecraft and submarines to prosthetic devices, civil structures, and transport vehicles etc. <sup>[5-7]</sup>

Unidirectional fiber reinforced plastic has outstanding specific stiffness and strength along the fiber direction and this has led to a wide range of applications as structural materials <sup>[8]</sup>. To varying degrees, FRP materials have directional dependent properties with the directional dependence coming from the strength and stiffness of the reinforced fiber. It is very stiff and exhibits considerable strength along the fiber direction. Unfortunately, the favorable properties of this specific direction usually come at the expense of properties in the other directions.

Over the past several decades much effort has been devoted to understanding. In directions perpendicular to the stiff and strong direction, including the transverse and longitudinal compression direction, the FRP is much softer and weaker <sup>[9-11]</sup>.

The failure mechanisms of unidirectional FRP and their loading in compression. Compressive failure depends on the type of fiber, the fiber volume fraction, the thickness, fiber misalignment, the configuration of the fiber's waviness and other factors. For unidirectional FRP, fiber micro-buckling failure is recognized as the

dominant compressive failure mechanism, and it is more important than the potential micro-buckling instability transition to kink band failure upon compression by small volumes of a composite near defects, free edges or voids. A classic fiber micro-buckling compressive failure analysis of fiber reinforced composites was proposed by Rosen<sup>[4]</sup>. Rosen assumed two possible buckling modes: an extensional mode and a shear mode. In composites of a significant fiber volume fraction  $V_f > 0.3$ , the shear mode governs the compressive strength<sup>[12]</sup>.

They found that micro-buckling occurs as a sinusoidal deformation of the fiber. The critical wavelength of fiber micro-buckling was shown to be linearly dependent on the modulus ratio of the matrix and fibers. Subramaniyan proposed enhancing the compressive strength of unidirectional glass fiber reinforced composites using nanoclay<sup>[13]</sup>. The initial elastic modulus of the resin increases with the addition of nanoclay and the improvement is more pronounced with an increase in the nanoclay load. The longitudinal compressive strength of GFRP extracted from off-axis tests shows an increase of 22% and 36% with 3% and 5% nanoclay loading, respectively. The critical buckling stress for a unidirectional FRP largely depends on the buckling stress of the reinforced fibers<sup>[14,15]</sup>. From a composite material mechanics perspective, a column material undergoes buckling when under compression and the ultimate buckling load  $P_{cr}$  is obtained by the following formula:

$$P_{cr} = \frac{\lambda \pi^2 EI}{l^2} \quad (1)$$

In this equation,  $P_{cr}$  is the ultimate buckling load;  $\lambda$  is the fiber's waviness,  $l$  is the critical wavelength,  $E$  is flexural modulus,  $I$  is moment of inertia and  $EI$  is the flexural rigidity. we attempted to increase the ultimate buckling load of fibers by changing various parameters in formula (1). They tried to improve the flexural modulus of the reinforced fiber by coating with carbon nanoparticles such as VGCF (vapor-grown carbon fiber) and carbon nanotubes onto the surface of a single fiber to improve its bending strength and its stiffness to increase the ultimate buckling loading  $P_{cr}$  of a single fiber. However, this method proved to be inefficient<sup>[16]</sup>. In this paper, a new method is proposed to improve the compressive performance of unidirectional FRP

by preventing fiber buckling with a shortening of the buckling critical wavelength  $l$ .

### 3.2. Proposed filament cover

The impetus for this study comes from the above-mentioned buckling failure theory and the ultimate buckling load formula. From equation (1), the fiber buckling critical wavelength  $l$  has a significant influence on the ultimate buckling loading,  $P_{cr}$ , and the shorter fiber wavelength  $l$  may improve the  $P_{cr}$  when the fibers are under compression. The critical buckling stress of the longitudinal compressive unidirectional FRP may thus be improved. The initial idea was the restriction of the buckling of a single fiber but in practice this is very difficult to achieve. Therefore, it was proposed that a fine filament (a small single fiber in a fiber bundle) be used to cover a bundle of fibers. The covered fiber bundles can then be used to fabricate a unidirectional FRP. A schematic diagram is shown in Fig. 3-2. It was expected that winding in the hoop direction enables the fiber wavelength to shorten and this improves the buckling load,  $P_{cr}$ .

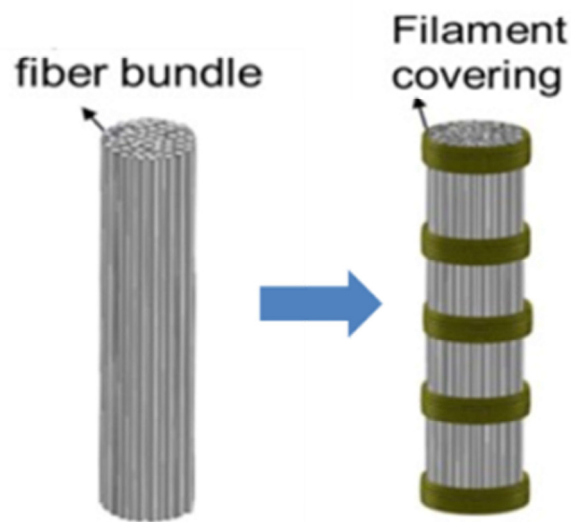


Fig. 3-1. Schematic diagram of a fiber bundle.

This prevents or restricts micro-buckling generation, and propagation will thus result in an increase in the critical buckling stress. The composite compressive performance may thus be improved. For the experiment covered bundles were

prepared, as shown in Fig. 3-2. Covered fiber bundles were then used to fabricate a unidirectional FRP.

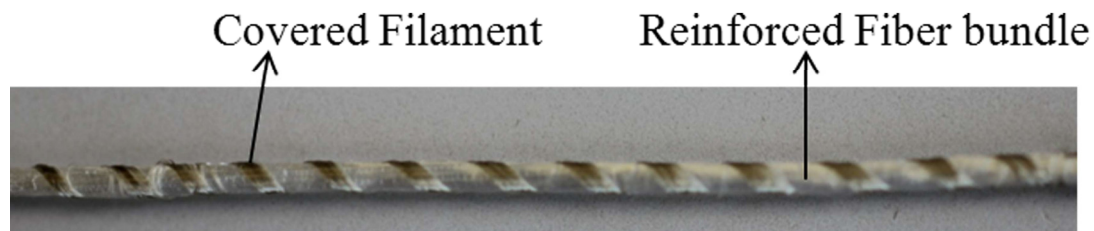


Fig. 3-2. An example of a covered fiber bundle.

### 3.3. Experimental

#### 3.3.1 Materials and fabrication

In this work, it was intended to verify the effect of the covering filament on the compressive property of a unidirectional FRP. UHMWPE fiber bundles were selected as the primary bundles and these were converted into a unidirectional FRP. The advantages of a covered filament are high modulus, low elongation at break, and the low number of single fibers in a bundle. The UHMWPE fiber material used in this study was Dyneema SK60, which is produced by Toyobo Co., Ltd. Japan. It is also excellent at absorbing impact energy, has good abrasion resistance and good fatigue resistance. Dyneema fiber reinforced FRP has poor compressive performance. The cover filament used in this study was a kind of PBO fiber, ZYLON, which is also manufactured by Toyobo Co., Ltd., and it consists of rigid rod chain molecules of poly (p-phenylene-2, 6-benzobisoxazole). It has high tensile strength and a high modulus. This kind of fiber bundle has the lowest number of single fibers among the relevant fiber bundles available in Japan. The properties of these two fiber materials are listed in Table. 3-1.

Table. 3-1. Properties of the fibers used in this paper

Fiber Types	Decitex /dtex	Density g/cm <sup>3</sup>	Tensile Strength /GPa	Tensile Modulus /GPa	Fracture Elongation/%
Dyneema SK60	1320	0.97	More than 2.6	More than 79	3~5
ZYLON HM	273	1.56	5.8	270	2.5

The covered UHMWPE fiber bundles with a PBO fiber filament were prepared using a custom winding machine and a schematic diagram is shown in Fig.3-3. The PBO filament was warped on the spool rather than having a sleeve on the hollow shaft. With the Dyneema bundle throughout the center of the shaft the PBO filament covered the Dyneema bundle upon spool rotation. The exerted tension of the PBO filament can be changed by adjusting the friction between the spool and the shaft. In the actual operation, it was found that when a tensile force was exerted on the cover filament during the cover process, the covered UHMWPE fiber bundle had higher stiffness. Therefore, an additional experiment was designed to investigate the effect of exerted tensile force on the compressive strength and modulus of the unidirectional FRP.

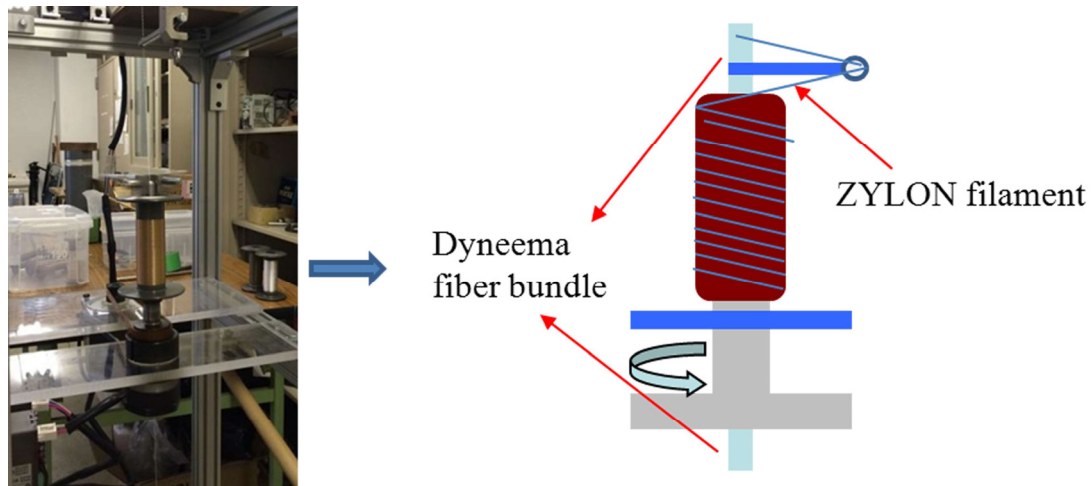


Fig. 3-3. The covered UHMWPE fiber bundle with a PBO filament.

A thermosetting epoxy resin (XNR6815) was obtained from Nagase ChemteX Corporation and was used as the matrix for the CFRP. A hardener (XNH6815) was also purchased from Nagase ChemteX Corporation. The epoxy resin and the hardener

were 100 and 27 parts by weight. The covered UHMWPE bundle was converted into a fiber sheet using the winding method. The FRP specimens used for the tests were fabricated by the VARTM (vacuum assisted resin transfer molding) process. A unidirectional UHMWPE FRP (UFRP) and a PBO covered UHMWPE FRP (PBO/UFRP) were thus prepared. The FRP specimen preparation process is shown in Fig.3-4. The covered UHMWPE fiber bundle with a PBO filament is shown in Fig.3-5.

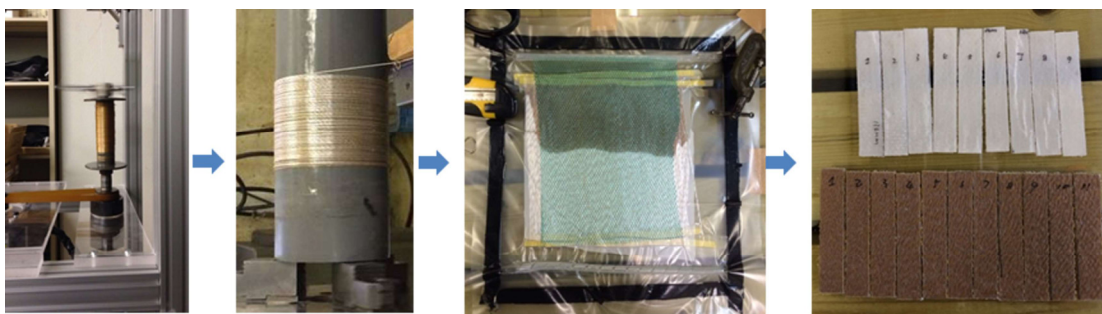


Fig. 3-4. Preparation of the specimens: filament wrap → unidirectional fiber sheet  
→ FRP by the VARTM method → test specimen.

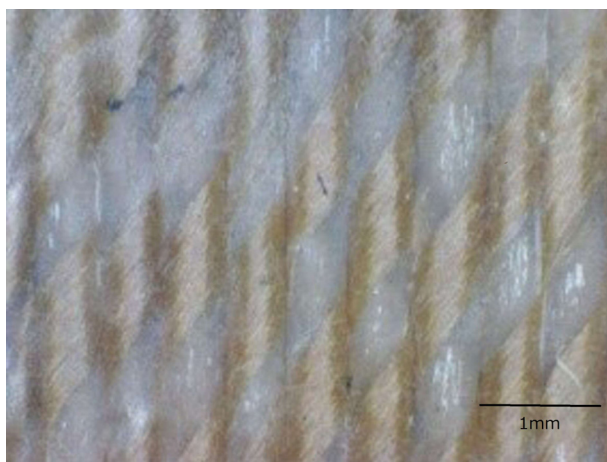


Fig. 3-5. Covered UWMWPE fiber bundle with a PBO filament.

The PBO/UFRP specimens were divided into two types and these depended on whether tension was applied to the filament winding process. With tension applied we obtained (PBO/UFRP1) and without tension we obtained (PBO/UFRP2). The UHMWPE fiber volume fractions were 49.4% (UFRP) and 43% (PBO/UFRP), respectively.

### 3.3.2 Compression Tests

During the compression test, a flat surface normal to the load axis ensured a proper load introduction. The top and bottom ends were polished to ensure that the specimen was parallel to the load axis to diminish stress concentration effects on the specimen ends and to avoid resin cracking near the loaded ends. The specimens were then clamped in a custom holding device and the compression test was performed on an autograph test machine (Shimadzu). Two groups of specimens consisting of unidirectional UHMWPE FRP (UFRP) and PBO covered UHMWPE FRP(PBO/UFRP) were compressed at a constant displacement rate of 1 mm/min according to JIS K7076. Specimens of length ( $L_o=78$  mm) were used as with end tabs on both ends and these were 35 mm in length ( $L_T$ ). The gauge length of the specimen was 8 mm ( $L$ ). The width of the compressive specimens was 12.5 mm ( $b$ ) with a thickness ( $h$ ) of  $2.3\pm0.2$  mm. As shown in Fig.3-6, a single strain gauges were attached to the center of the specimen in the longitudinal direction to measure the compressive strain. Additionally, the lateral constraint provided by the grips led to the failure observed in the gauge section for all the specimens. Four specimens for each batch, the compressive test dates are listed on table2.

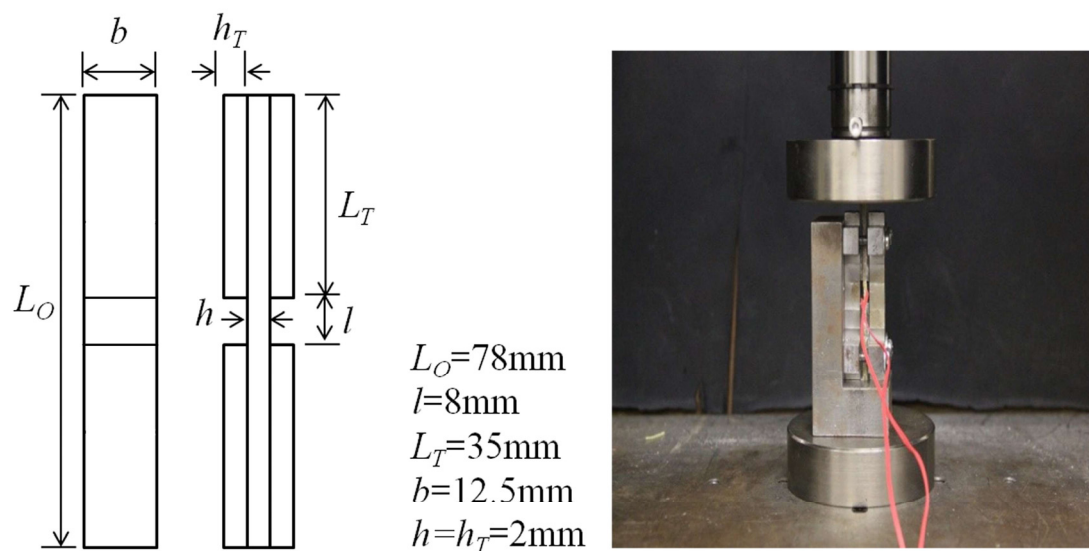


Fig. 3-6. Diagram showing the dimensions of the compression test specimens.



Table.2 The compressive strength and modulus of UFRP and PBO/UFRP

	UFRP		PBO/UFRP1		PBO/UFRP2	
	Compressive strength/MPa	Compressive modulus/GPa	Compressive strength/MPa	Compressive modulus/GPa	Compressive strength/MPa	Compressive modulus/GPa
Specimen 1	67.80	10.58	74.24	12.00	74.08	15.15
Specimen 2	65.38	9.08	73.34	11.04	76.98	17.53
Specimen 3	64.26	10.86	73.93	11.56	74.02	16.34
Specimen 4	66.73	10.58	75.83	11.87	74.45	16.85
Average value	66.04	10.28	74.34	11.62	74.13	16.47
CV	1.34	0.7	0.93	0.37	0.19	0.87

### 3.3.3 Morphology observations

Fibrous impregnation with a resin is an important technology in FRP fabrication. Although epoxy resin is a low viscosity thermosetting plastic it can easily infiltrate fibers when using the VARTM method. However, after covering the fiber bundle with a filament by tension, the impregnation situation may not be the same. Therefore, PBO/UFRP1 sections were observed by scanning electron microscopy to confirm the FRP internal impregnation status. The observed specimens were prepared using an ion milling apparatus (Hitachi). Moreover, the compressed specimen morphology was observed using an electron microscope (KEYENCE).

### 3.3.4 Test results and discussion

Fig. 3-7 shows micrographs of a section of the PBO/UFRP1 wherein tension was exerted during the winding process. As the left photo shows, the Dyneema fiber bundles are closely aligned in a one by one manner and are surrounded by resin. The yellow parts are covered by PBO filaments. The SEM picture on the right indicates that the wound UFRP has a good impregnation property since no voids are apparent between the fibers.

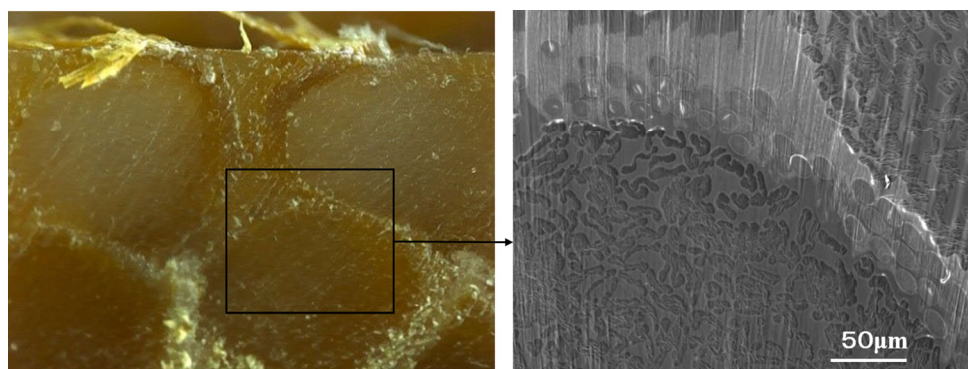


Fig. 3-7. Micrographs of a section of PBO/UFRP1.

The columns in Fig. 3-8 and 3-9 show a comparison of the compressive strength and the modulus of the UFRP and the PBO/UFRP materials, in which the filament covering process was carried out with tension (PBO/UFRP1) and without tension (PBO/UFRP2). Compared with the UFRP, filament covering can improve the compressive strength by about 15% for both the PBO/UFRP1 and the PBO/UFRP2

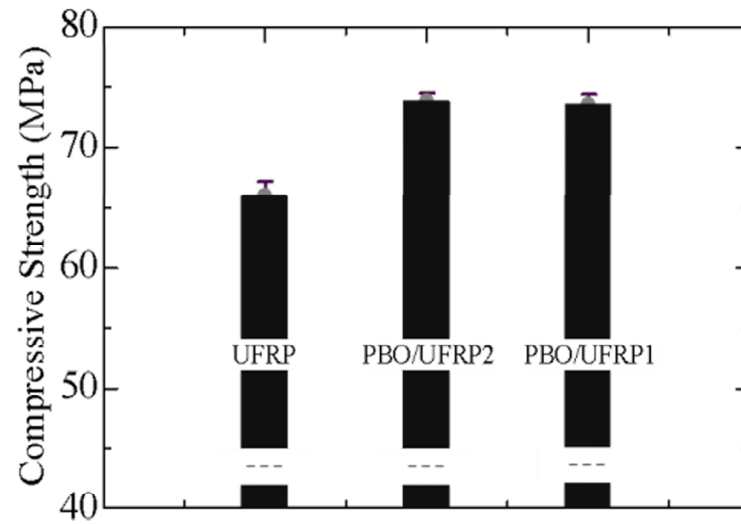


Fig. 3-8. Comparison of the compressive strength of the different specimens.

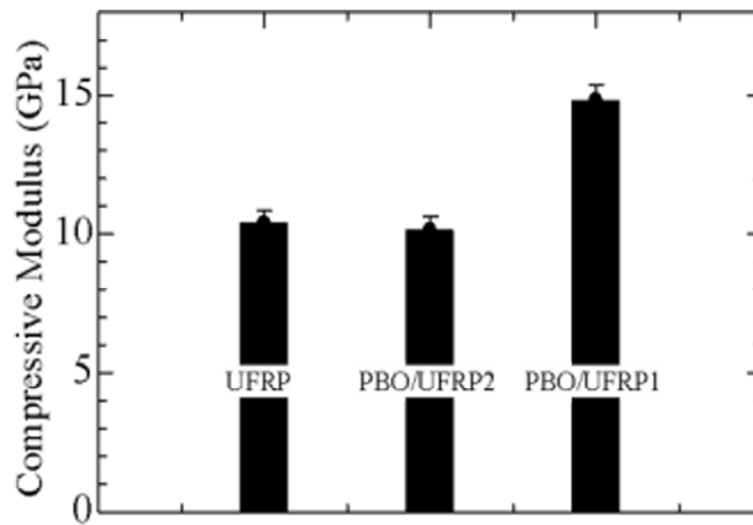


Fig. 3-9. Comparison of the compressive modulus of the different specimens.

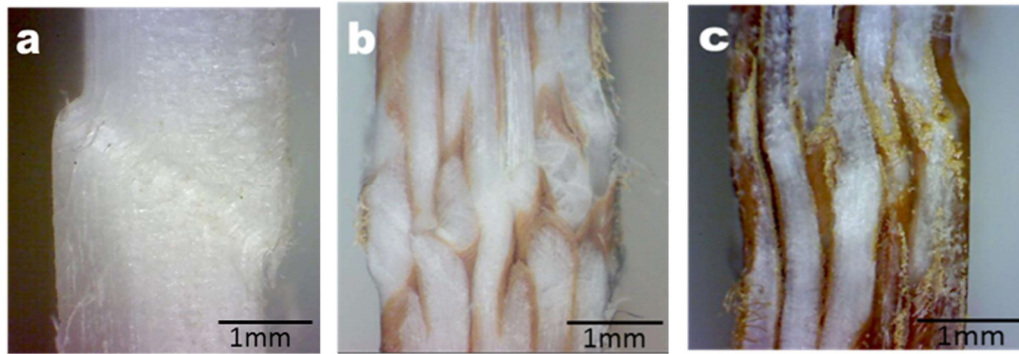


Fig. 3-10. Compression failure specimen of: (a) the UFRP (b) the PBO/UFRP1 and (c) the PBO/UFRP2 materials.

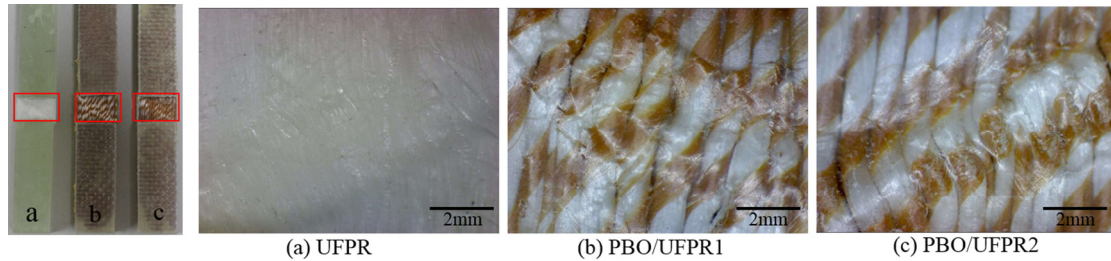


Fig. 3-11. Compressive failure surface of FRP

materials. A compression failure section morphology of UFRP is showed in Fig. 3-10 (a) and Fig. 3-11 (a), it appears fiber buckling on the side of specimen. From Fig. 3-10, Fig 3-11(b) and (c), the failure mode of PBO/UFRP is different, there are fiber bundle buckling, the cover filament make the bundles have a higher buckling load, and it appears some fiber shear failure in internal part bundle of PBO/UFRP. This result confirms our original assertion but the specific reinforcing mechanism requires further study.

It is interesting to note that the compressive modulus of the PBO/UFRP1 specimen increased by approximately 45% by comparison with the UFRP, while that of PBO/UFRP2 provided no advantage. This means that the exerted tension has a significant effect on the compressive modulus. When a specimen of PBO/UFRP2 is under compression, the compression modulus of PBO/UFRP2 is no greater than UFRP because individual fibers within the bundle can buckle as shown in Fig.

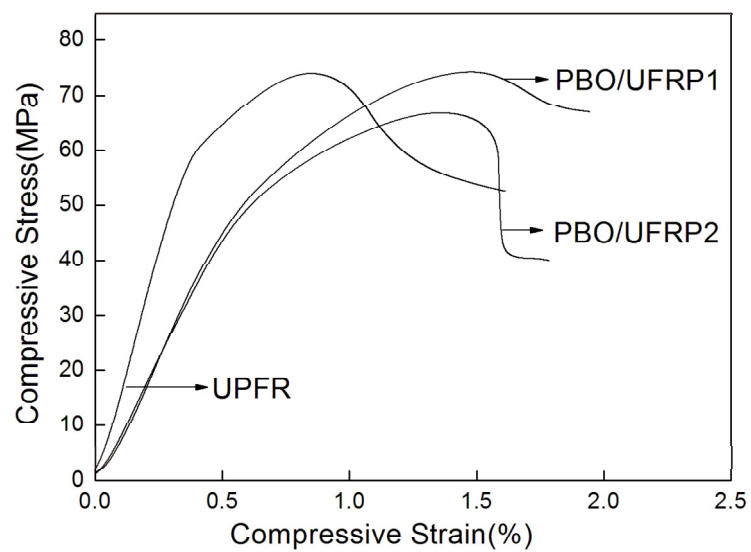


Fig. 3-12. Typical compressive stress–strain curve for UFPR and PBO/UFPR.

3-11(c).

A typical compressive stress–strain response of the UFRP and the PBO/UFRP was determined using the PBO filament covering method with the tension shown in Fig. 3-12 for comparison purposes, it shows that the tensile exerted PBO filament covering improved the compressive stress–strain response of the UFRP, the maximum value of the PBO/UFRP1 is lower than that of the UFRP, in other words, it has higher resistance to deformation, which results in a higher compressive modulus. The tension exerted on the covered filament enhances this effect and the mechanism will be investigated using various tension strengths, winding spacing and angles, and filament fiber types in future studies to determine the specific reinforcing mechanisms.

### **3.4. Conclusion**

In this paper, a tension filament covering is proposed to improve the longitudinal compressive properties of a unidirectional FRP. Dyneema fiber bundles and a PBO fiber filament were employed in this work to verify this idea. A unidirectional Dyneema fiber reinforced epoxy resin (UFRP), a unidirectional Dyneema fiber covered with PBO filament/epoxy (PBO/UFRP1) and a Dyneema fiber covered with PBO filament/epoxy (PBO/UFRP2) were prepared by the VARTM method.

Using JIS K7076 compression testing standards, stress-strain curves for the prepared specimens were obtained. Compared with the compressive strength of UFRP, those of PBO/UFRP increased by approximately 15% because of the shortened buckling wavelength that comes from the restriction imposed by the covering filament. The compressive modulus of the PBO/UFRP1, which was covered by the tension PBO filament improved by about 45% compared to the UFRP and the PBO/UFRP2. The tension-exerted covering filament caused this effect and the mechanism will be investigated in a subsequent study.

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## CHAPTER FOUR

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### **Effect of covering filaments on the compression performance and failure mechanism of FRP**

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## **Chapter 4: Effect of covering filaments on compression performance and failure mechanism of FRP**

### **4.1 Introduction**

Fiber-reinforced plastic (FRP) composite materials have been widely used in various engineering fields because of their superior specific strength and stiffness and lower density compared with those of many traditional materials <sup>[1-3]</sup>. In general, FRP materials have directional dependent properties with the directional dependence coming from the strength of the reinforced fiber. FRP parts can be produced that achieve good performance under tensile loads, but these parts often do not sufficiently resist buckling or kinking during compression <sup>[4]</sup>. For example, the ratios of compressive-to-tensile strength for unidirectional Kevlar-49/epoxy and glass/epoxy composites are approximately 0.15 and 0.49, respectively <sup>[5]</sup>. Meanwhile, Ishikawa <sup>[6]</sup> found that the ratio of compressive-to-tensile strength of carbon fiber-reinforced plastic (CFRP) with a high fiber volume fraction of 65% is 0.71. Li et al. <sup>[7]</sup> suggested that the bend strength of ultra-high molecular weight polyethylene (UHMWPE) fiber-reinforced epoxy resin is only one fifth that of CFRP. The dominant failure mode of bending damage is also the type of compressive failure displayed by some FRPs <sup>[8,9]</sup>. Overall, FRPs are much softer and weaker in directions perpendicular to the rigid, strong direction. However, compressive loads are inherently present in many structural systems either directly or indirectly, and the failure mechanism of such systems is usually controlled by compressive stresses. The poor compression of FRPs limits their structural efficiency, so it is considered a design-limiting parameter <sup>[10]</sup>. However, the compression properties of FRPs are very complex because a large number of factors influence them. Unlike metals, FRPs exhibit a variety of compressive fracture mechanisms including interfacial de-bonding, splitting, fiber breakage, kink banding, and micro-bulking <sup>[11]</sup>. Numerous factors influence the

compressive performance of FRPs. In general, fibers are the principal load-carrying component of FRPs, while the surrounding matrix keeps the fibers in the desired location and orientation and acts as a load transfer medium between them. Therefore, the type of reinforced fibers, and the interface between fiber and resin both affect the compressive performance of a FRP. The performance also depends on fiber misalignment, and the configuration of the fibers <sup>[12]</sup>. To obtain better compressive performance, researchers have optimized the design of FRPs using approaches like hybridization, stitching and resin modification <sup>[8,13,14]</sup>. In particular, hybrid composites have unique features that can be used to meet various design requirements in a more economical way than conventional composites. Usually, hybridization is classified into interlaminar, or laminate, which involves depositing layers composed of different fibers, and intralaminar, where different types of fibers are entangled within a single layer <sup>[15]</sup>. In this study, we propose a novel type of fiber hybridization named filament covering. This approach is used to improve the longitudinal compressive properties of unidirectional FRP.

## 4.2 Filament covering

Based on the buckling failure theory and ultimate buckling load formula, equation (1) below reveals that the fiber buckling critical wavelength  $l$  has a marked influence on the ultimate buckling loading  $P_{cr}$ ,

$$P_{cr} = \frac{\lambda \pi^2 EI}{l^2}. \quad (1)$$

A shorter  $l$  may improve  $P_{cr}$  when the fibers are under compression. The critical buckling stress of the longitudinal compressive unidirectional FRP may thus be improved. A filament-covered bundle is shown in Fig.4-1. It was expected that winding in the hoop direction would shorten  $l$ , thus restricting micro-buckling. This should improve  $P_{cr}$ , and thus the compressive performance of the composite.

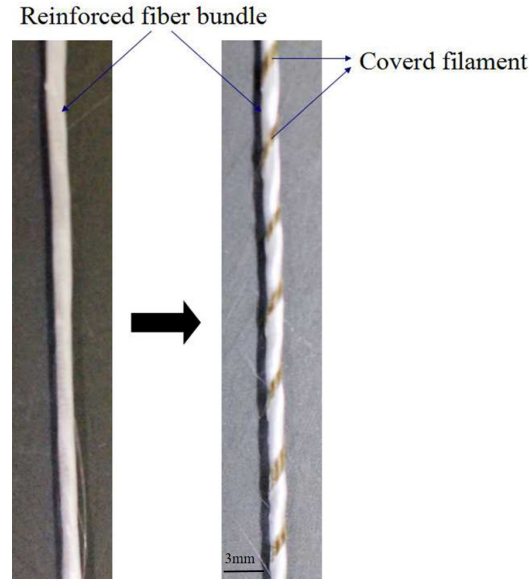


Fig. 4-1. Diagrams of a fiber bundle and covered fiber bundle

The covered fiber bundles were then used to fabricate a unidirectional FRP with epoxy resin. The preparation process is presented in Fig. 4-2. It is found that the tension exerted on the covering filament strongly affected the compressive modulus of unidirectional FRPs. According to equation (1) above, this is because part of  $P_{cr}$  is converted to tensile load of the fiber filament under compression. It is credible that the modulus or elongation at break of a covered filament affects  $P_{cr}$  and the failure strength of the reinforced bundle. At the same time, the space of a covered filament influences  $l$  when a FRP is under compression buckling. In the present work, the effects of the type of filament fiber and winding spacing on the compression properties of unidirectional UHMWPE FRPs are studied.

## 4.3 Experimental procedure

### 4.3.1. Materials

In the present study, we attempted to develop new FRP materials with high compressive performance. To verify the enhancement achieved by filament covering, UHMWPE fibers were chosen as the reinforced fibers because such FRPs have relatively poor compression performance. UHMWPE fibers are also suitable to reinforce composite materials because of their light weight and high strength,

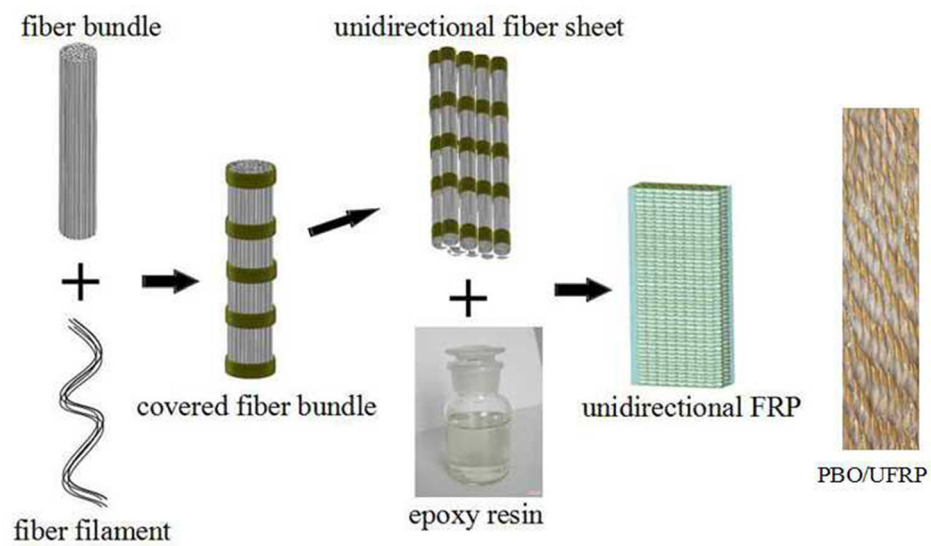


Fig.4-2. Outline of the filament covering method

modulus, impact strength, and abrasion resistance <sup>[17]</sup>. The UHMWPE fiber material used in this study was Dyneema SK60 produced by Toyobo Co., Ltd., Japan. The physical properties of this UHMWPE fiber are listed in Table 1. Four types of fine fiber bundles with different tensile strength, elastic modulus, and elongation at break were used as covering filament fibers, including basalt fibers, poly (p-phenylene benzobisoxazole (PBO) fibers, UHMWPE fibers (named Dyneema) and polyethylene terephthalate (PET) fibers. The physical properties of these fibers are also listed in Table 1. The lower the fiber volume content of a filament fiber, the smaller its effect on the fiber volume fraction of UHMWPE fiber bundles in the FRPs. It is noted that the filament fiber bundles were finer than the UHMWPE fiber bundles used as the reinforcing fibers; in other words, the number of single fibers in a covering filament is smaller than that in a reinforced fiber bundle. For example, the decitex of each Dyneema filament was 55 *dtex* and it contained 48 single fibers, whereas that of the UHMWPE fiber bundle was 1320 *dtex*, and each contained 1170 single fibers.

#### **4.3.2. Fabrication of composite laminates**

FRPs were prepared with unidirectional fiber sheets for reinforcement and epoxy resin (XNR 6815, Nagase ChemteX Co.) as the matrix. The hybrid composite laminates were fabricated using a vacuum-assisted resin transfer molding (VARTM) process. VARTM is a liquid molding technique used to manufacture complicated composite structures. Generally, VARTM involves five steps, which include: (1) mold preparation and fabric lay-up, (2) sealing of the mold and formation of a vacuum, (3) resin preparation and degassing, (4) resin impregnation, and (5) curing of fabricated panels. After VARTM, hot pressing was used to smooth the surface of each composite.

#### **4.3.3. Samples**

Two groups of samples were prepared, one with different filaments, Dyneema/UFRP, PET/UFRP, Basalt/UFRP, and PBO/UFRP, where UFRP represents UHMWPE FRP, and the other with different cover spacing, PBO1/UFRP,

Table. 4-1. Properties of fibers

Property	Unit	UHMWPE	Basalt	PBO	Dyneema	PET
Density	g/cm <sup>3</sup>	0.97	2.75	1.56	0.97	1.35
Tensile strength	MPa	2600	3340	5800	2600	1890
Elastic modulus	GPa	79	89	270	79	33
Elongation at break	%	4	3.15	2.5	4	6
Decitex	dtex	1320	330	273	55	90

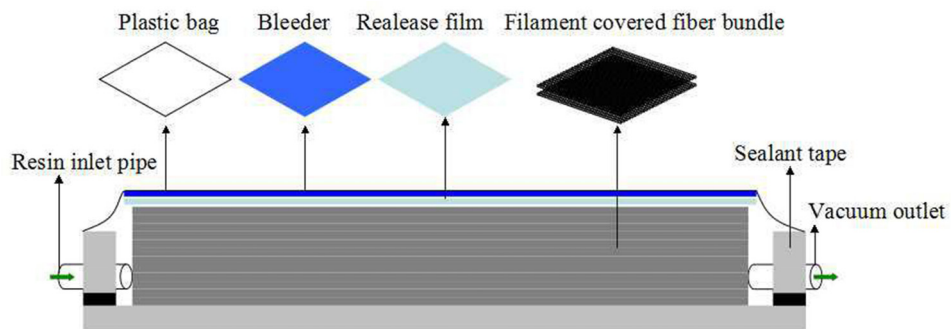


Fig. 4-3. Schematic diagram of the set-up for VARTM

PBO2/UFRP, PBO4/UFRP, and PBO6/UFRP, as listed in Table 2. Fig.4-4 depicts the covering spacing in the sample PBO4/UFRP.

#### 4.3.4. Measurement and characterization

Compressive tests of the FRP composites were conducted using an Auto Graph (AG-20KND) with a load cell manufactured by Shimadzu. A strain gauge was attached to each compression sample. The size of each compression sample conformed to JIS-K 7054 (Japanese Industrial Standards). Each compression sample was mounted on the grips of the testing machine, taking care to align the long axis of the sample and the grips with an imaginary line joining the points of attachment of the grips to the machine. Samples were loaded at a cross-head speed of 1 mm/min. A strain-collecting system digitally recorded load/displacement and stress/strain using wave-logger software. Values of compressive modulus  $E$  were calculated at a loading condition of 0.1% strain. A minimum of five of each sample were tested, and the failure mode of each sample was determined through visual inspection and optical microscopy.

Table. 4-2. Type of covering filament and spacing of UFRP samples

Sample	Dyneema/ UFRP	PET/ UFRP	Basalt/ UFRP	PBO/ UFRP	PBO1/ UFRP	PBO2/ UFRP	PBO4/ UFRP	PBO6/ UFRP
Covering filament	UHMWPE	PET	Basalt	PBO	PBO	PBO	PBO	PBO
Spacing/ mm	2	2	2	2	1	2	4	6

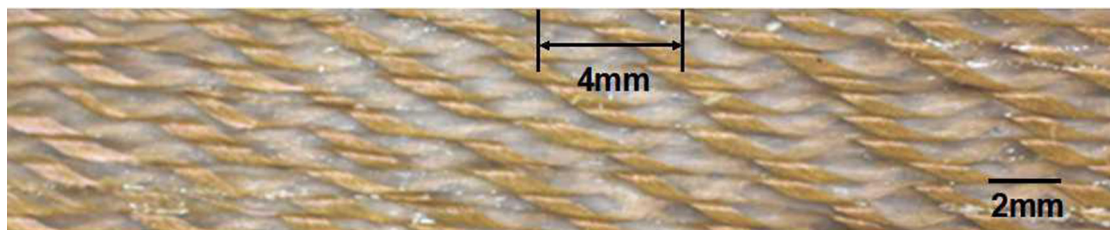


Fig. 4-4. Image of a PBO UFRP sample with a covering filament spacing of 4 mm (PBO4 UFRP)



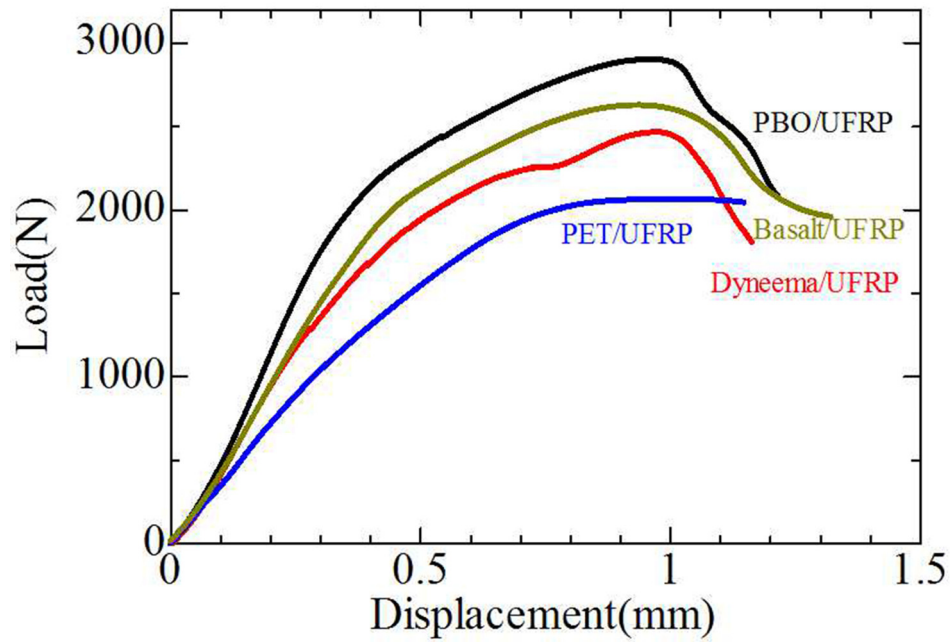


Fig. 4-5. Typical load-displacement curves for different filament-covered UFRP sample

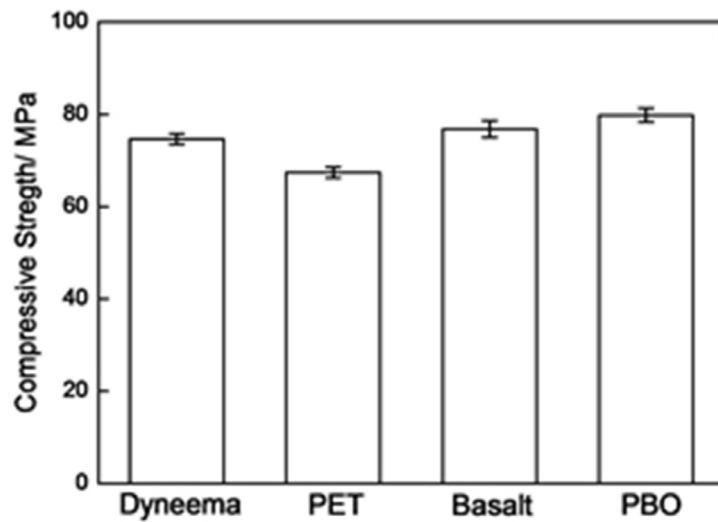


Fig. 4-6. Effect of filament type on the compression strength of UFRP samples

## **4.4 Results and discussion**

### **4.4.1. Effect of filament type on compression performance**

Typical load–displacement curves of the samples with different covering filaments are presented in Fig.4-5. Meanwhile the average compressive strength and modulus of the UFRPs covered with different types of filaments are shown in Figs.4-6 and 4-7, respectively. The mean compressive strength ranged between 67.4 MPa for the PET filament-covered UFRP to 79.8 MPa for the basalt filament-covered UFRP. The higher compressive strength of the samples with covered filaments was attributed to the superior compressive strength of covered filaments compared with that of an UHMWPE FRP (65 MPa). The results show that filament covering increased the compressive strength of the samples compared to that of UHMWPE FRP. This finding is consistent with previous work, which indicated an approximate 15% increase in compressive strength upon covering with PBO filaments. Meanwhile, Fig.4-7 reveals that the compressive modulus of PET and Basalt filament-covered UFRPs increased slightly compared with that of uncovered UFRP (10.2 GPa). In comparison, the UHMWPE (Dyneema) and PBO filament-covered UFRPs displayed considerable increases of compressive modulus, with improvements of about 36% and 45%, respectively. Therefore, the type of covering filament strongly influences the compressive strength of FRP composites. The covering filament causes the UHMWPE bundles to have a higher buckling load, and the compressive force is converted into the tensile force of the filament fiber. The difference in the compression strengths of the hybrid composites was attributed to the varying tensile strength, elastic modulus, and elongation at break of the different filament fibers. PET fibers have low tensile strength and elastic modulus and high elongation at break, which would account for the relatively weak compressive strength of the samples containing this type of covering filament.

To provide insight on the damage mechanism of the present samples after compression testing, optical images of the front and fractured surfaces of the

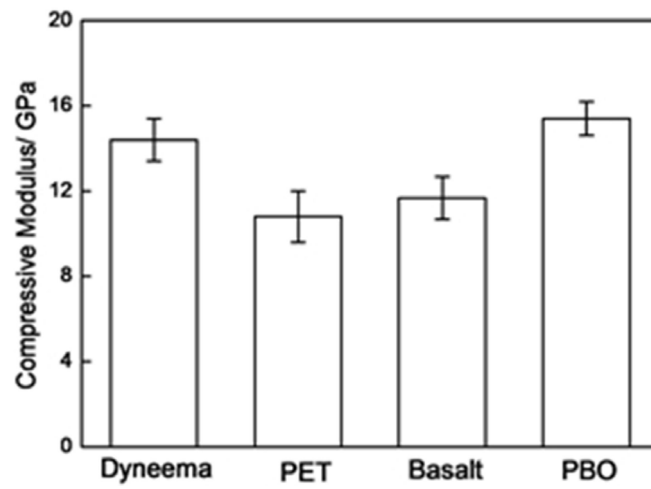


Fig. 4-7. Effect of filament type on the compression modulus of UFRP samples

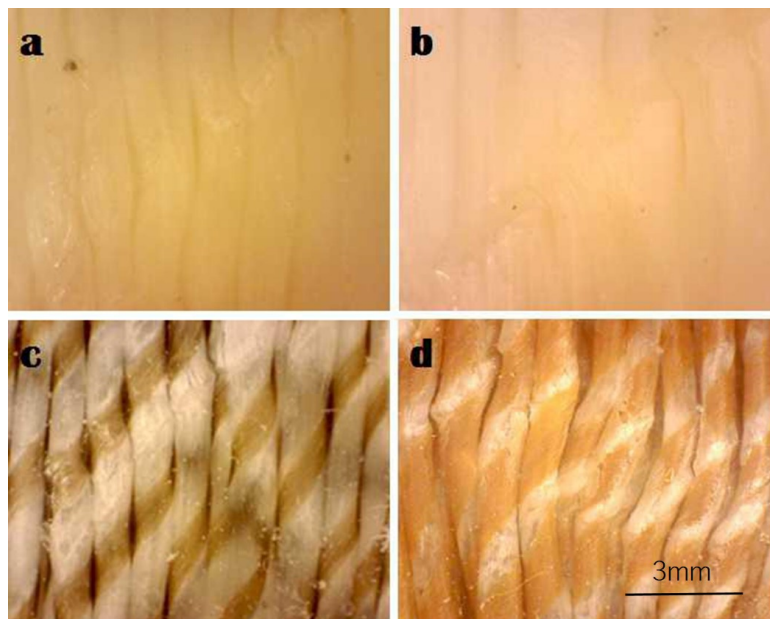


Fig. 4-8. Failure surfaces of UFRP samples after compression testing

composites were taken, as shown in Fig.4-8. The failure mode of all samples was buckling failure. The present results suggest that the incorporation of basalt fiber layers in FRPs could improve their compressive properties. No debonding, splitting, or fiber breakage was observed in the samples.

#### **4.4.2 Effect of covering fiber spacing on compression performance**

Figs.4-9 and 4-10 illustrate the influence of covering filament spacing on the compressive strength of samples. Compressive strength decreased as the covering filament spacing increased, suggesting that the shorter the filament spacing, the higher the resistance force against compressive load. Fig.4-12 reveals that the compression failure mode depends on covering filament spacing. Samples with a spacing of 1 or 2 mm failed through micro-buckling Fig.4-12(a, b), while those with a spacing of 4 or 6 mm exhibited a shear failure mode (Fig.4-12(c, d)). In the micro-buckling failure mode, the termination of a buckling fiber bundle provides an imperfection for the initiation of the next imperfection. It may be inferred that the lower flexural strength and modulus values of the samples with spacing of 4 or 6 mm are mainly caused by shear failure.

Different from compressive strength, the compressive modulus is decided by the initial stage of compression. Therefore, the compressive modulus is decided by the fiber modulus. Because the modulus of PBO is much higher than that of the UHMWPE fibers, the PBO fibers absorb the main compressive force. The covering filament spacing marked influenced the compressive properties of the samples. The compressive modulus increased with the covering filament spacing. The modulus of a PBO fiber is much high than that of an UHMWPE fiber. Compressive failure includes kinking, micro-buckling, shearing or splitting. Incorporation of PBO fibers into a UHMWPE fiber composite altered the failure mode of the sample. Micro-buckling on the compressed side is a predominant feature of shear failure. It should be noted that the presence of shear damage may account for the low compressive modulus

shear stresses in test samples because of additional displacement that in turn yields a

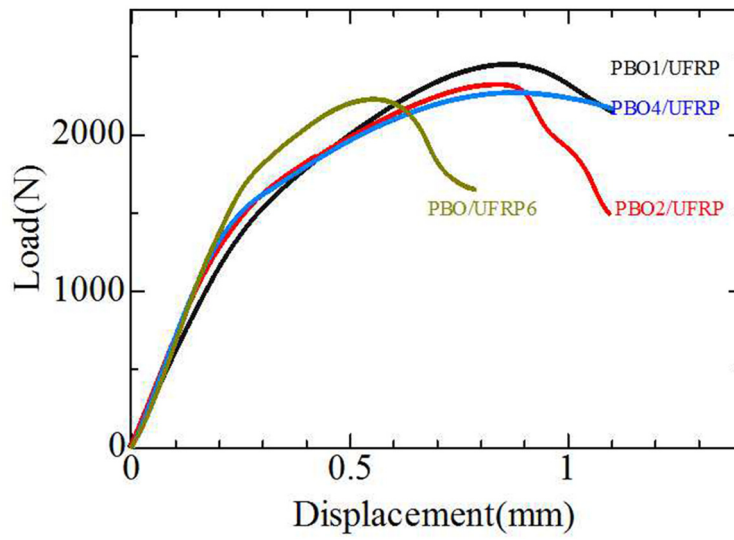


Fig. 4-9. Typical load-displacement curves for UFRPs with different covering filament spacing

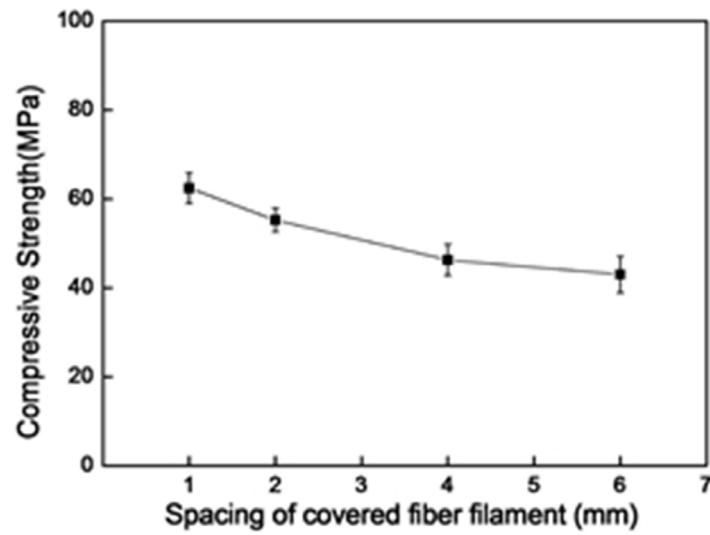


Fig. 4-10. Effect of filament spacing on the compression strength of UFRPs

lower modulus. Fig.4-13 presents a model that explains when the spacing between covering filaments  $\alpha$  is small,  $\delta_y$  will increase. The elastic modulus of the samples decreased as the cover filament spacing increased. This result was attributed to the PBO fibers possessing a much higher compressive elastic modulus than the UHMWPE ones.

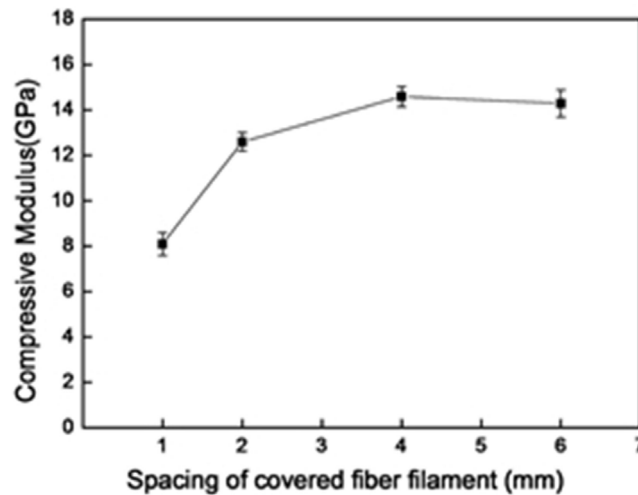


Fig. 4-11. Effect of covering filament spacing on the compression modulus of FRP

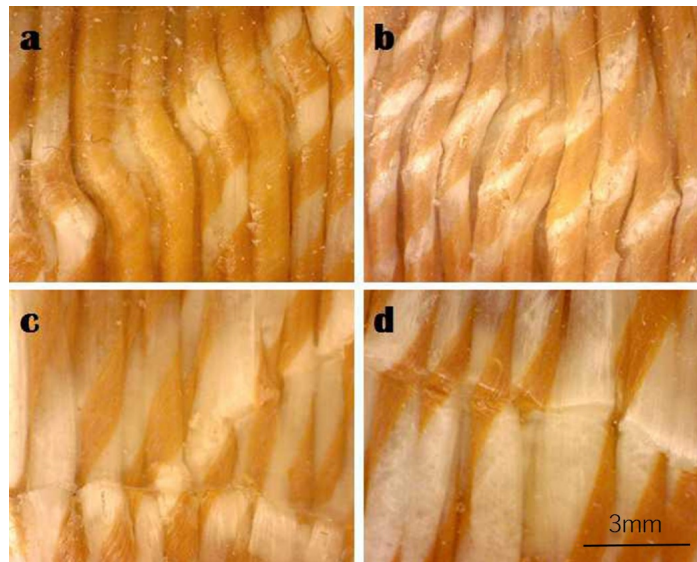


Fig. 4-12. Failure surfaces of FRP samples after compression testing

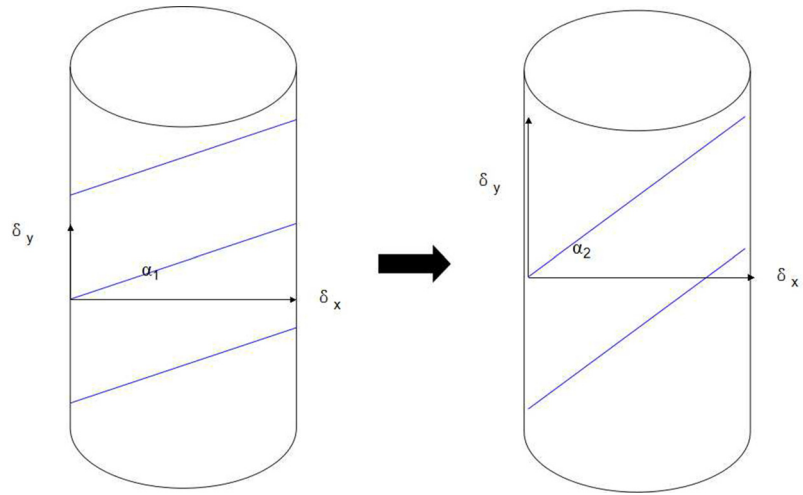


Fig. 4-13. Model of a filament-covered fiber bundle

## **4.5. Conclusion**

Filament-covered UHMWPE bundles with four kinds of filaments and different covering spacing were prepared, and then the covered bundles were made into FRPs. Based on comparisons of the compressive strength and modulus of these hybrid FRP materials, the following conclusions are drawn:

- 1) The covering filaments affected the compressive properties of the composites.
- 2) The dominant failure mode depended on the spacing of the covering filament.

By varying the components of composites, we can tailor their mechanical properties according to our target applications.



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## CHAPTER FIVE

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### **Conclusions**

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## Chapter 5: Conclusion

The objectives of this study is to investigate the compressive behavior and improve methods of ultrahigh-molecular-weight polyethylene fiber and its reinforced epoxy resin composite, both of improve methods are based on the materials buckling failure theory. In general, FRP materials have directional dependent properties with the directional dependence coming from the strength of the reinforced fiber. Compression failure is a design-limiting feature for the continuous fibers reinforced plastic composite 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 chapter one, an introduction on the fiber and fiber reinforced plastic composite, compressive performance of FRP and failure mechanism was made, and the theory foundation of improve methods in this thesis is to prevent buckling of fibers in FRP was indicated.

In chapter two, 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 micro compression 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.

However, the coated fiber cloud not prepared into fiber reinforced plastic

composites because the efficiency of this means, it need large quantity of fibers in fiber reinforced plastic, but the coating fiber is made by one by one, the cost of this method is too high, although the probability of this method was verified.

In chapter three, a tension filament covering is proposed to improve the longitudinal compressive properties of a unidirectional FRP. UHMWPE fiber bundles and a PBO fiber filament were employed in this work to verify this idea. A unidirectional UHMWPE fiber reinforced epoxy resin (UFRP), a unidirectional Dyneema fiber covered with PBO filament/epoxy (PBO/UFRP1) and a UHMWPE fiber covered with PBO filament/epoxy (PBO/UFRP2) were prepared by the VARTM method. Using JIS K7076 compression testing standards, stress-strain curves for the prepared specimens were obtained. Compared with the compressive strength of UFRP, those of PBO/UFRP increased by approximately 15% because of the shortened buckling wavelength that comes from the restriction imposed by the covering filament. The compressive modulus of the PBO/UFRP1, which was covered by the tension PBO filament improved by about 45% compared to the UFRP and the PBO/UFRP2.

In chapter four, the tension-exerted covering filament caused this effect and the mechanism will be investigated. The covering filaments affected the compressive properties of the composites. The dominant failure mode depended on the spacing of the covering filament. By varying the components of composites, we can tailor their mechanical properties according to our target applications.

## **List of publications**

- [1] Fangtao Ruan, Limin Bao. Mechanical enhancement of UHMWPE fibers by coating with carbon nanoparticles. *Fibers and Polymers*, Vol.15, No.4, PP 723-728 (2014).
- [2] Fangtao Ruan, Limin Bao. Improved longitudinal compression performance of a unidirectional fiber reinforced composite with a filament covering. *Polymer Composites*, (Accepted).
- [3] Fangtao Ruan, Limin Bao. Effect of covering filaments on the compression performance and failure mechanism of unidirectional fiber-reinforced plastic. *Polymer Composites*, (Accepted).

## **Scientific presentation**

- 1 Fangtao Ruan, Limin Bao. Nanoparticles coated UHMWPE fiber by pyrrole vapour deposition to improve transversal compressive strength. POLYCHAR 21th world forum on advanced materials. Poster. March11-15th,2013. Gwangju, Republic of Korea.
- 2 Fangtao Ruan, Limin Bao. Surface modification of UHMWPE fiber for improving compressive modulus of UFRP. The 42nd Textile Research Symposium. Poster. Aug28-30th,2013. Shizuoka, Japan.
- 3 Fangtao Ruan, Limin Bao. Nano-carbon particles coated UHMWPE fiber by pyrrole vapor deposition to improve transversal compressive and bend strength. The 12th Asian Textile Conference. Oral. Oct 23-27th,2013. Shanghai, China.
- 4 Fangtao Ruan, Limin Bao and Yukinari Okuyama. Study on improvement of compression performance of UHMWPE fiber reinforced plastic. International Symposium on Fiber Science and Technology 2014. Oral.Sep29th-Oct1th, 2014.Tokyo, Japan.
- 5 Fangtao Ruan, Limin Bao, Yukinari Okuyama. Enhancing compressive performance of fiber reinforced composite by filament covering method. The 89th

Textile Institute World Conference 2014. Nov2th-Nov6th. Wuhan, China.

6 阮 芳涛, 鮑 力民, (東洋紡)山中 淳彦. 超高分子量ポリエチレン繊維の圧縮特性を向上. H25 年度繊維学会年次大会. 口頭発表. June12-14th. 2013 日本東京.

7 阮 芳涛, 鮑 力民, 奥山 幸成. 強化繊維の曲げと圧縮特性及び繊維表コーティングによる特性の改善. 第 5 回日本複合材料会議. 口頭発表. March4-6th. 2014 日本京都.

8 阮 芳涛, 桜田 亮, 奥山 幸成, 鮑 力民. フィラメントカバリング方法によって FRP の圧縮強度を向上する. 第 40 回複合材料シンポジウム. 口頭発表. Sept 18-19th. 2015 日本金沢.

## Acknowledgments

It is my pleasure to write this message and express my gratitude to all those who have directly or indirectly contributed to the creation of this thesis.

First of all, I would like to express my deepest gratitude to my supervisor, **Prof. Limin Bao**, for his continuous instruction with important suggestion, precious advice and large support and encouragement thorough my doctoral course in Shinshu University.

Naturally, these studies have joint efforts with many other researchers. Thanks also would be given to my group-mates, senior members and juniors (*Mr. Jian Shi, Mr. Anchang Xu, Mr. Peng Zhu. Mr. Liang Xu, Mr. Chika Uchijo, Mr. Shinya Soma, Mr. Ryoji Muramatu, Mr. Takuro Fujii, Mr. Kameel, Mr. Yuki Miura, Mr. Bing Liu, Mr. Yuji Nanki, Mr. Shunsuke Sato, Mr. Takuya Okazawa. Ms. Yanling Wang. Mr. Rio Sakurada, Mr. Kouki Horiutu, Mr. Tokusei Saito. Mr. Naoki Okuno. Mr. Kentairo Suzuki. Mr. Keisukei Sukiura. Mr. Jiang Yang.*) for their joining part of experiment work, as well for pleasant and enjoyable work environment that they made.

I am sincerely appreciative of Japanese Government Scholarship program for financial support, Grants for Excellent Graduate Schools, MEXT, Japan from December 2012 to March 2014. I am very grateful to Pro. Bao for providing financial support with research assistant for my remaining Ph. D career.

I would like to say that I am very lucky to meet lots of kind friends during learning career in Ueda. They are always there, to laugh with me in the happy times and to lend a helping hand, when I meet difficulties. We share many experiences and help each other. I am heartily grateful to all my friends at Shinshu University for playing along with me and making the wonderful clips and precious memories.

I dedicate my greatest thanks to my beloved family. Words fail to express my deep gratitude to my parents for their patience, understanding, love, meticulous care and unlimited support over the years. And I also express my gratitude to my sister and little brother, for their always bought me encouragement and optimistic for future.