Doctoral Dissertation(Shinshu University)

Development of flexible carbon fiber reinforced composite fabrics with knitting structure

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Abstract

This dissertation aims to develop the processing and manufacturing technology of composite carbon fibers and improve their elastic modulus, as well as the processing diversification of continuous carbon fibers in carbon fiber composite materials. The experimental method combines the processing technology of long fiber reinforced thermoplastic polymer and uses the co-extrusion processing method and the hot pressing processing method to prepare the composite fabric. The continuous carbon fiber and the thermoplastic polyurethane blend are co-extruded to form a double-layer structure. The processing method of composite carbon fibers formed by coating continuous carbon fiber with thermoplastic resin is studied and evaluated, and the parameters of the thermoplastic polyurethane (TPU) blend in the outer layer and the carbon fiber tow content in the inner layer are discussed. In addition, continuous carbon fibers are processed into composite fabrics, woven and knitted composite fabrics are manufactured, and laminated composite fabrics through the hot pressing process are studied.

Scanning electron microscopy results confirmed the physical bond between TPU and carbon fiber, that is, TPU has a reinforcing effect on the tensile properties of carbon fiber tow. Compared with the original carbon fiber tow, the tensile strength of the TPU-coated carbon fiber tow is increased by 35.87% to 19.62 MPa; the strain of the carbon fiber tow is also increased during the stretching process. The co-extrusion method in the LFT process can produce continuous carbon fiber tows for industrial production; it also provides higher possibilities for the subsequent processing of carbon fiber tows. The adhesion between TPU and carbon fiber is increased by adding polyester hot melt adhesive (MPTU). TPU/MPTU blends have good miscibility. When the ratio is 85

wt%/15 wt%, carbon fiber tow has a good clustering effect and nodule performance, and the tensile strength reaches 349.27 MPa/g/cm^3. In addition, the failure mode of the carbon fiber tow is improved during processing, the axial slip replaces the direct fracture, and the cross-sectional shape is changed from the original flat bundle to an ellipse. Woven and knitted composites made of composite carbon fibers still have the softness, elasticity of fabrics and failure modes similar to composite carbon fibers. Moreover, TPU can reduce the friction generated during knitting, and the prepared carbon fiber knitted composite material has flexibility and resilience. The tensile test results of the composite knitted fabric after lamination show that with the increase in the number of layers, the tensile strength of the composite material also increases. The strength can reach 43.72 MPa when six layers are laminated, but the four-layer laminate has the best elongation.

In addition to the development of composite carbon fibers and fabrics, the electromagnetic interference shielding efficiency has been studied, showing that composite materials have good EMI attenuation effects. The application of LFT technology to the subsequent processing and weaving of continuous carbon fiber is investigated for the first time. It provides a novel method for the development of carbon fiber reinforced thermoplastic, and large-size composite materials can also be manufactured. This breakthrough is a current limitation of carbon fiber processing technology.

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Chapter 1 – General Introduction

1.1. Background of carbon fiber composite materials

In general, a combination of carbon fiber composite material and a reinforcement material from the polymer substrate. The reinforcing carbon fibers are the main materials, and the polymer substrate is generally used as a binder. Coating the substrate using a composite material to provide mechanical support of the carbon fibers can help foreign load to the composite efficient transfer and further enhance the mechanical performance of the composite material [1]. In addition, carbon fiber as a reinforcing material can be divided into various forms, including long fibers, short fibers, ribbons, nonwoven fabrics, and different fabric structures. The use and processing methods of carbon fibers are the same as those of general fabrics. During processing, carbon fibers are first collected into bundles, made into carbon fabrics through weaving, and then combined with resin to prepare various prepreg materials, and finally processed into products [2]. For products made of general carbon fiber composite materials, suitable materials, including epoxy resins and organic polymers, are selected as substrates according to the application requirements of the composite materials. In the preparation process of carbon fiber composite materials, nonpolar fiber surface characteristics are always a problem that needs to be solved. This shortcoming usually results in poor bonding strength between the carbon fiber and the substrate, hindering the ideal mechanical performance reinforcement effect [3]. Therefore, a large number of studies have carried out surface treatment of carbon fiber, and then combined with thermosetting resin to cause irreversible chemical changes between the molecular chains of the polymer to achieve curing and strengthening. At present, the development trend of thermoplastic materials combined with carbon fiber products gradually increases. In addition to environmental protection factors, the heat and pressure generated during the application can synthesize the composite material into a nonreactive solid, and it can be heavy with the support of the heat source. The shape of a plastic composite material has a high degree of flexibility [1].

With the development of science and technology, composite materials made of carbon fiber become increasingly diverse. Carbon fiber composite materials are widely used in various fields due to the excellent properties of carbon fiber. In the aviation industry, carbon fibers have high advantages in light weight and high specific strength. In the fields of automobiles, ships, and sports goods, carbon fibers have also become the preferred material. In addition, carbon fibers have high electrical conductivity, which helps carbon fiber composite materials to obtain good electromagnetic shielding performance. These additional functions expand the application range of carbon fibers, including breakthroughs in the fields of construction, medical treatment, and clothing [3].

The research on new technologies for the production of carbon fiber composite materials has also received remarkable attention due to their diversified market. In recent years, the application of carbon fiber composite materials has gradually developed toward large-scale components. Therefore, the ease of composite material processing has become an important consideration. In addition to the selection of using thermoplastic resin as a substrate, carbon fiber is prepared through mixing and reprocessing between composite materials. Table 1-1 shows the statistics of Taiwan Industrial Technology Research Institute in 2017. Industry and scholars have been committed to studying low-cost carbon fiber raw materials in recent years, reducing production and using labor, customized adjustment design requirements, and recycling of waste carbon fiber composite materials. Reuse, automation combination, digitization, and 3D simulation of weaving, processing, and other processes are performed [4]. In summary, the future of carbon fiber composite materials will be the main type of application. Carbon fiber composite materials have become the most preferred in the industrial field candidates by lowering the cost of production and recycling of industrial technology development.

Table 1-1. Mass production and application technology development of carbon fiber composite materials

Year	Fiber Application Development
	Aerospace, wind energy, and automotive applications promote the mass production of carbon fiber composite materials
2015	Development of low-cost, low-energy carbon fiber
	Cost reduction, development of construction, high-pressure vessels and sporting goods
	Development of mixed application of glass fiber and carbon fiber
2020	Construction, manufacturing industry and medical device application development
	Recyclability of thermoplastic carbon fiber composite materials and development of biomass carbon fiber precursors
2025	Massive use in the automobile and aerospace industries, development of consumer electronics and consumer applications
	Development of carbon fiber regeneration applications

1.2. Method of forming the carbon fiber composite material

The forming method of carbon fiber composite material is similar to the general composite material method. However, the technology of carbon fiber forming is constantly updated to increase its effectiveness. For example, due to low product quality and poor production efficiency, the traditional wet lay-up type has not been used gradually. In the current process technology, injection molding, winding molding, compression molding, and pultrusion molding are used to produce various carbon fiber composite materials. These forming methods are diverse and provide good quality carbon fiber composite materials. However, they are mostly used to produce large-scale flat or simple curved parts and products. Carbon fibers are difficult to bend because of their rigid structure. When the bending amplitude is large, the structure may be destroyed and the fiber may be damaged. Therefore, different processes are combined to prepare carbon fiber composite materials, different from the general production method of carbon fiber composite prepregs. The purpose is to increase the application level of continuous carbon fibers and reduce the shortcomings caused by the forming method. In the following subsections, the processes used are introduced one by one.

1.2.1. Long fiber reinforced thermoplastic polymer (LFT) processing method

In the traditional processing technology of composite materials, an extruder is used to directly melt and mix the fiber with the resin-base material for granulation. The fiber is chopped under the friction and shear action of the screw and the cylinder; reinforced resin pellets <1 mm. The fiber is broken again after this material undergoes the next molding process. Therefore, in the final product, the retained length of most fibers is actually much lower than the effective critical length; thus, the reinforcing effect of the fiber is not fully utilized. In addition, although the performance of the short fiber reinforced polymer composite material is improved compared with that of the pure plastic, its mechanical performance is far less than that of the continuous fiber reinforced composite material. Continuous fibers have better function and efficiency in transferring and bearing loads between composite materials because they have higher specific stiffness and specific strength than the base material [5].

The LFT processing method is a composite material forming method that has been developed in recent years. This method produces composite materials after fiber and thermoplastic polymer are melted through heat. Figure 1-1 shows a schematic of the LFT pellet processing. Continuous fiber (long fiber) and thermoplastic resin are combined through an extruder, collected, and then cut. The resulting composite material breaks the limitation that continuous fiber composite material can only produce products with specific shapes. To make up for the lack of strength of short fiber composite materials, they are often used in the processing of carbon fiber and glass fiber composite materials [6, 7].

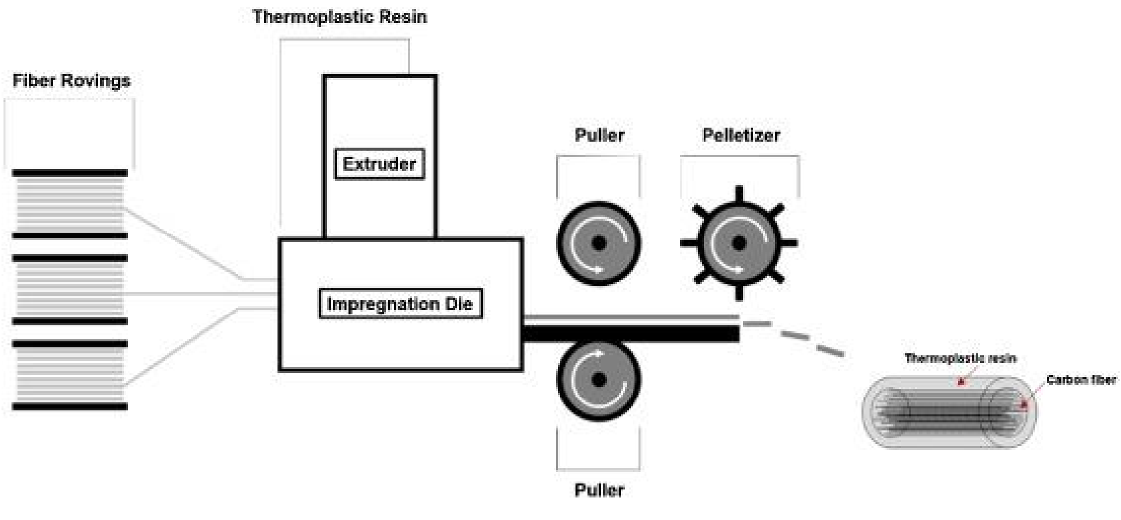

Figure 1-1. Schematic of the LFT pellet processing [6].

The composite material prepared by the LFT processing method can be used for products with special structures or shapes, such as parts with large bending amplitude, jagged structural products, and thin plates. The composite materials usually undergo subsequent processing, such as injection, hot pressing, and extrusion, to prepare various long-fiber composite materials. Therefore, in the LFT processing, evaluating the strength of the reinforcing fiber, the content and proportion of the fiber addition, the compatibility of the interface between the fiber and the polymer, the uniformity of the fiber distribution after extrusion, and the length of the fiber is necessary. Table 1-2 shows the reinforcing trend of fiber length to thermoplastic polymers, indicating that the reinforcing effect on the composite material is better when the fiber has a high aspect ratio, under the same fixed conditions and as the fiber length increases.

Table 1-2. Reinforcement trend of fiber length to thermoplastic polymer [8].

Property	**Fiber length**	
	Short	**Long**
Mechanical strength	poor	well
Impact resistance	poor	well
Durability	poor	well
Product shrinkage	large	few
Appearance	well	poor
Liquidity	well	poor

Some references also proposed the advantages and practical applications of LFT processing methods, comparing the mechanical properties of different fiber lengths and their composites. Figure 1-2 shows the relationship between fiber length and type on the mechanical properties, as well as the mechanical properties. These properties directly affect the fiber length. As the fiber length increases, the mechanical properties of the material are improved [9]. Goel et al. proposed that the composite material prepared by the processing method of LFT has fiber orientation during processing, leading to a better stretching result in the longitudinal direction than that in the transverse direction, and the coating fiber is higher. Molecules can help composite materials conduct heat, leading to better fatigue behavior [8]. Alwekar et al. proposed that this overmolding method can replace the traditional process and improve the impact performance of composite materials without increasing the weight of the product. [10]. Mathijsen proposed that the composite materials prepared by this method have a high degree of design possibilities. As a technical method between short fiber processing and high-performance composite materials, long-fiber thermoplastic products cannot be ignored [11]. We can explain the importance of LFT processing method through literature and information review. The use of LFT as a processing method option for continuous carbon fiber can maintain the integrity of continuous carbon fiber to be processed directly in tow form. The prepared carbon fiber composite material can be pelletized as an intermediate product, and then subjected to subsequent mixing and other manufacturing processes, or it can be directly used to produce composite material products.

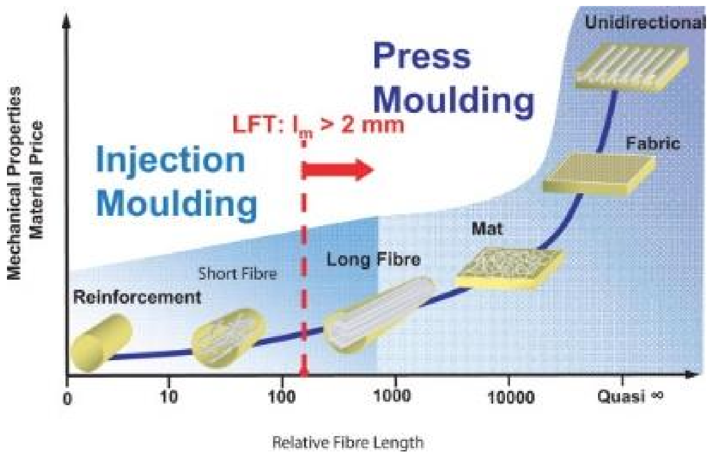

Figure 1-2. Relationship diagram of the influence of fiber length and type on mechanical properties [9].

1.2.2. Co-extrusion processing method

Co-extrusion processing is a widely used method in the thermoplastic plastic processing industry. Its continuous process and low cost have shown the ability of mass production; its manufacturing process is environmentally friendly and requires a short time. It can use materials to the greatest extent and design freely. The structure and size of the components are often used to manufacture light and flexible parts [12]. Figure 1-3 shows a schematic of the co-extrusion processing method. Generally, the machine used for co-extrusion processing has a different die structure according to the needs of the product, and the similar part is an extruder that provides a mixing effect. The products may be fabric/polymer composite products, double/multilayer film laminating, and thermoplastic materials recycling products. Co-extrusion technology reshapes the polymer by melting, and then extrudes it through the die [13, 14]. Table 1-3 shows the difference between the co-extrusion processing method and the traditional coating process. Through this method, complex 3D structures can be prepared, and two or more plastic materials can be combined; the finished product will have different plastic functions. In addition, appropriate materials can be adjusted according to product functions or requirements, and no secondary coating is required to process the adhesive material, through cooling and molding, to achieve the purpose of cost reduction and process simplification.

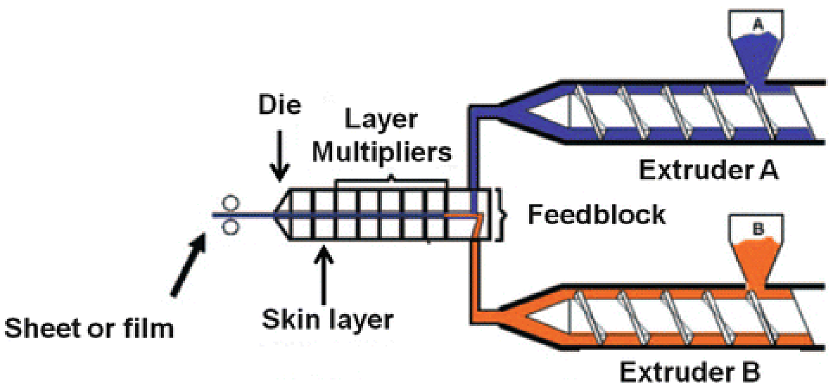

Figure 1-3. Schematic of co-extrusion processing method [15].

Table 1-3. Advantages of co-extrusion processing methods.

Co-extrusion processing method	**Traditional coating process**
High temperature resistance	Not resistant to high temperatures
Solvent-free green process	Use of chemical solvents
No secondary processing required	Adhesive layer for secondary coating
Customize according to manufacturing requirements	Specification limit

Many references propose to use the advantages of co-extrusion processing methods and actual effects. He et al. used the co-extrusion method to prepare composite films, and proposed common composite mold preparation methods, such as lamination, interfacial polymerization, in-situ polymerization, dipping, plasma deposition, and other technologies that require two separate steps, as follows: fabrication of the main structure and subsequent coating. Co-extrusion is the simultaneous extrusion of two or more polymers through a single die to produce a multilayer structure in the form of films, sheets, or fibers [16]. Wang et al. prepared composite tapes with PA6 and PEO fibers through a co-extrusion method. They proposed that this method does not require the use of any organic solvent, which is usually necessary in the traditional solvent-based bonding step. The research results show that the mechanical properties of the composite tape are improved through the orientation process after extrusion [17]. Xu et al. used a co-extrusion method to prepare multilayer alternating conductive composites. Through the addition of conductive fillers in the process, a conductive network was formed along the direction of extrusion [18]. This approach was confirmed through the co-extrusion processing methods that not damage the original properties of the material, and functional composite materials may be further added.

Moreover, the extrusion 3D printing method with high design freedom is becoming popular [19-21] because this method has not only high precision, but also many materials that can be selected. The material in the form of reel is easy to replace and clean. It is mainly used to prepare fine parts with complex shapes. The finished product is smooth and highly flexible; thus, it has become a popular development direction. The extrusion 3D printing method may also achieve the effect of material modification. Zhu et al. used this method to solve the original quasi-brittle behavior of the material, improve the ductility of the composite material, and prove that the geometric structure of the material affects the bending performance of the sample [22]. However, in addition to these advantages, this processing method, through high temperatures, requires similar melting temperatures between materials or additional materials with higher thermal decomposition temperatures to avoid damage to the finished product. [23, 24]. Carbon fiber is used as a reinforcing material, which is an excellent material option and has good heat resistance.

1.2.3. Compression molding processing method

Compression (hot press) molding is a processing method of polymer materials. In the process, the thermoplastic polymer material is initially placed in a flat mold, and the thickness of the sample is set by a metal spacer. Then, the mold is heated to melt the polymer. Subsequently, pressure is applied through the extrusion of the upper mold and the lower mold, or evacuated and extruded at atmospheric pressure, and then solidified in the cooling stage to obtain a hot press molded product. The schematic of the equipment is shown in Figure 1-4. The hot pressing method has many advantages, including rapid and uniform heating of the sample, adjustable temperature and pressure, the thickness of the sample, and the adjustment of the cooling time. In addition, after these thermoplastics are heated, they can be redesigned without raw material loss [25]. Although the processing principle of hot press molding is simple, many parameters still need to be tested in the process, including appropriate temperature. Insufficient temperature may lead to incomplete melting of the material and failure to fill the mold, and excessively high temperature damages the quality of the finished product. Appropriate pressure can also obtain uniform shape of the finished products without excessive deformation. The accuracy of time is related to the speed of melt flow, which is very important in molding the finished product. In addition, the method and material of demolding are critical to the finished product molding. Its roughness and friction may cause material residue or damage to the finished product.

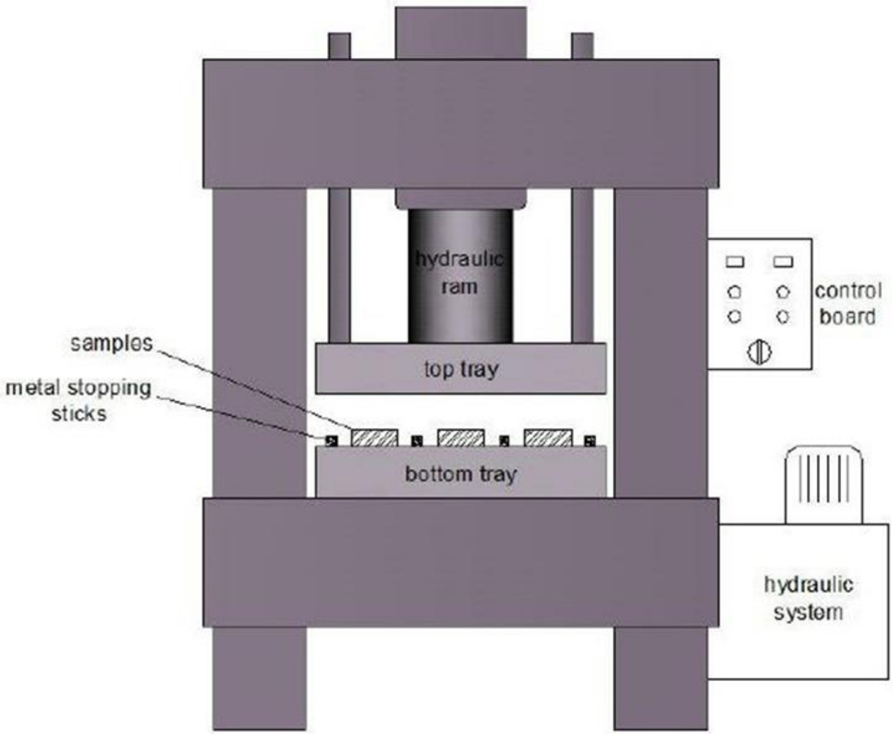

Figure 1-4. Schematic of hot press forming equipment [26]

Processes combined with hot press molding have also been widely used with the development of thermoplastic polymers. Rangaswamy et al. proposed that the use of hot press molding has lower production costs, and the epoxy-based fiber-reinforced polymer composite material has high productivity, complex shape preparation ability, excellent dimensional stability, reproducibility, surface finish, mechanical properties, flame retardancy, and other advantages. Compression molding is also an effective technology. The performance of composite parts can be improved as long as the molding parameters are appropriately selected [27]. Ramakrishnan et al. transformed natural fibers into lightweight composite materials through hot pressing. They suggested that the high-temperature and high-pressure system in the process method can ensure the immersion and consolidation of thermoplastic composite materials [28]. Memon and Nakai proposed that in the process of preparing jute/PLA composites, as the temperature of hot pressing increases, the elastic modulus of the composites improves, and the effect of impregnation and dispersion between fibers is enhanced. However, higher temperatures lead to fiber degradation, and the strength of the composite material is reduced [29]. Peng et al. also proposed the use of polymer melting to bond two thermoplastic bonding materials. Although the materials are different, the use of temperature welding does not require special surface treatment and organic processing procedures, and it requires more time than the cycle. The curing time of the oxy-based adhesive is shorter, and the finished product can be recycled and repaired without adding extra weight to the finished product [30].

The advantages and popularity of the hot press molding method can be verified through combining the literature and information collection. In the manufacturing process, the sensitivity between the polymer and the temperature is used to enhance the crystallinity of the polymer, thereby achieving the purpose of combining. The hot press molding method is used to laminate the composite materials, and the mature processing technology is selected, thereby effectively achieving the interlayer bonding. The bonding between layers can be confirmed by using the properties of thermoplastic polymers, and the controlled temperature cannot be used to damage the reinforced carbon fiber.

1.3. Background of flexible composite materials

Flexible composite materials have soft properties and mechanical and physical and chemical properties. Generally, the composition of flexible composite materials is similar to the structure of composite materials, that is, soft textile materials and flexible substrates, among which textile materials may be woven fabrics and nonwovens. In the current industrial development, many high-performance fibers are made into flexible composite materials, which are widely used in construction, transportation, protective clothing, and other fields. In addition, the flexible base material of the flexible composite material is very important. The base material usually requires greater elasticity to withstand the deformation of the material when the material is subjected to external force. The soft textile material deforms correspondingly with the base material. Thus, the composite material remains under the action of high stress, and the effect of high strength is still maintained. The selection of short fibers can avoid the shortcomings of a single force direction and rotation of the fiber when the composite material is subjected to an external force to achieve this purpose. The use of flat fabrics and high-performance fibers can effectively withstand and transmit external forces [31].

Related studies on flexible composites have confirmed that thermoplastic polyurethane is suitable as a base material for flexible composites given its high flexibility. TPU is a linear block copolymer containing hard and soft segments. Its structure is schematic, as shown in Figure 1-5. TPU can be made into soft material products with any complex structure due to its complexity and flexibility; thereby solving the accuracy and brittleness problems of most traditional products. TPU is used as the substrate, and the pores in its structure are used to provide better deformability of the composite material [32-34].

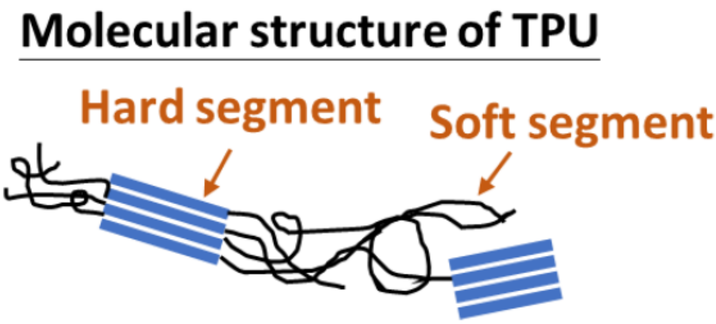

Figure 1-5. Schematic of TPU structure

1.4. Background of the multilayer composite

Multilayer composite materials are composed a high-strength outer layer and a lightweight inner layer, or a high-toughness outer layer material is used to protect the inner layer material for reinforcement to achieve a high ratio of strength and stiffness characteristics. Multilayer composite materials have high performance and light weight, and are often used in various fields. In military applications, many parts of aircraft and ships are designed with sandwich composite structures; in civil applications, bridges, sports equipment, and reinforced concrete, multilayer composite materials are also used to improve seismic performance. Many studies have added high-strength fibers or low-density materials to the structure of multilayer composite materials. Figure 1-6 shows a typical multilayer structure. A thick core layer can increase the thickness of the composite material and effectively improve the mechanical properties of the composite material. In addition, the method of preparing composite materials by stacking is widely used. The laminated composite materials have the advantages of light weight and low cost, and the thinner materials can be laminated to increase their mechanical properties while maintaining softness. In the related research of multilayer composite materials, combining two or more different types or basis weights is proposed, and different composite materials can be prepared by changing lamination. As the number of layers increases, different materials can also be combined. When thickness changes, the laminate of fabrics can provide a high degree of design flexibility and more dimensional reinforcement effects [35-37].

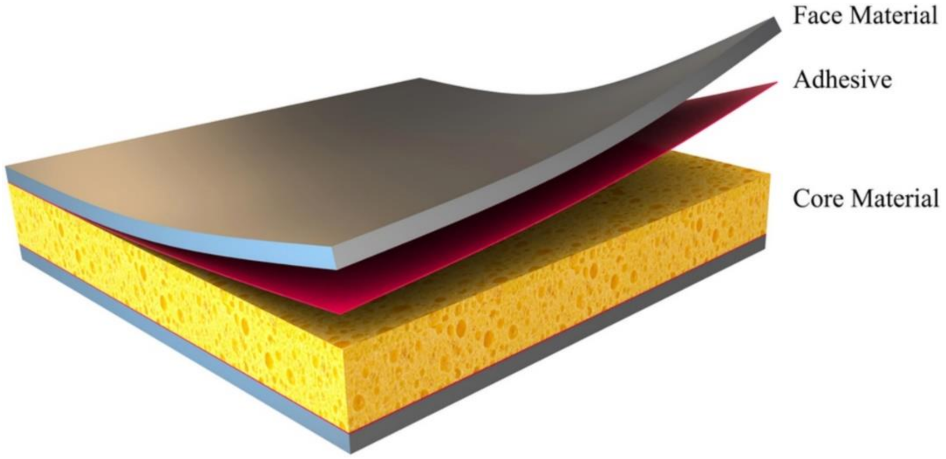

Figure 1-6. Schematic of laminated composite materials [38]

1.5. Fabric structure and composition

In the manufacturing process of composite materials, the processing method and structural composition determine the material characteristics. The parameter change relationship is complex, including the volume content of fibers and fillers, fiber types, number of layers, fabric structure density, processing methods, processing time and pressure, and interface affinity. In addition, these parameters may further affect the static and dynamic mechanical properties, viscoelasticity, toughness, fatigue resistance, and wear resistance of composite materials [39].

The structure and composition of the fabric refer to the most basic fabric geometric structure in the composite material, which directly affects its mechanical properties. Figure 1-7 shows different types of fabric structures, and the difference can be observed from the appearance, such as woven fabrics in interlacing warp and weft directions, knitted fabrics intertwined with loops, and disordered and overlapping nonwoven fabrics. These fabric structures have different characteristics, and the cross and entanglement between fibers are the basic conditions for fabric mechanics [40].

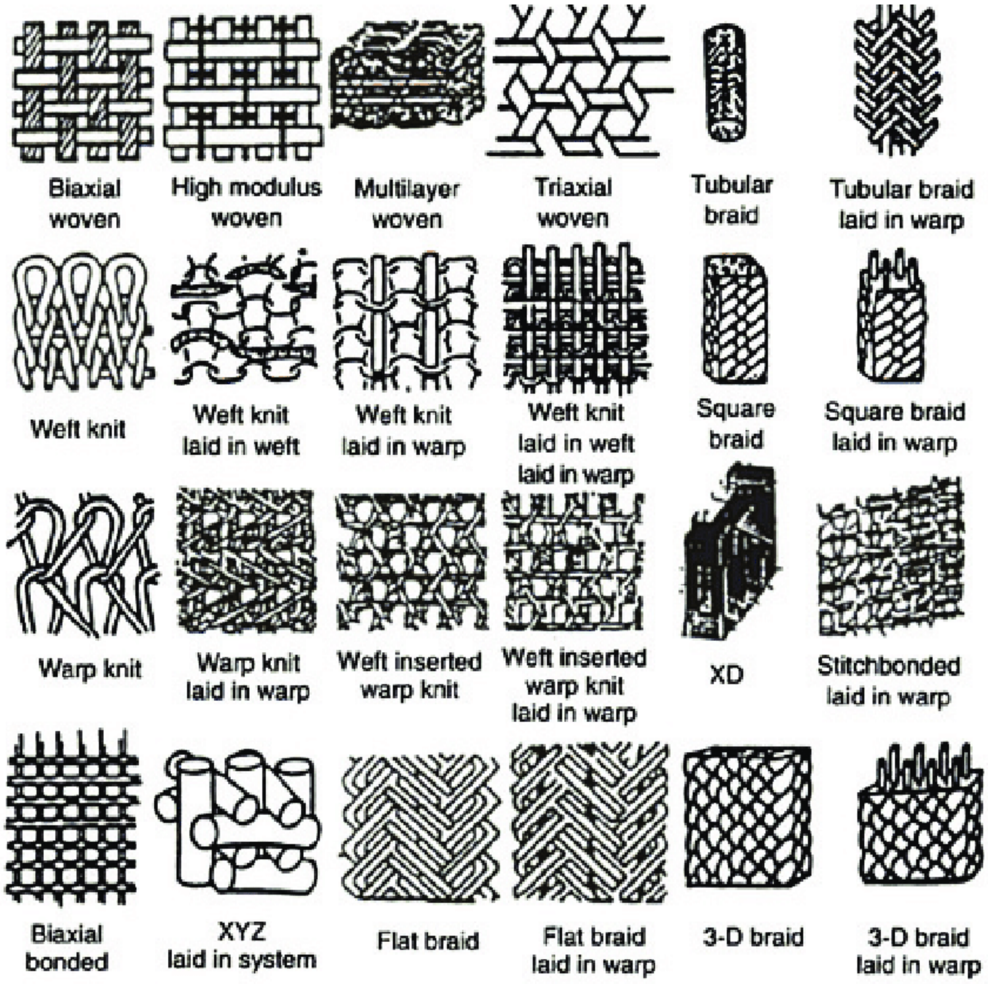

Figure 1-7. Different types of fabric structures [41]

Among them, the nonwoven fabric is not formed by the general yarn weaving process. Its structure is fixed by various physical and chemical methods to form a cotton net-like material. It has the advantages of light weight and easy shaping, as well as low cost due to the lack of yarn. The multiple forming methods for non-woven fabrics can be divided into melt blown method, water jet method, needle rolling method, chemical bonding, and hot melt bonding; they are used in various daily necessities, such as bandages, paper towels, and filters, with good organization and dimensional stability. However, compared with general textiles, nonwoven fabrics have rougher touch, higher thickness, and lower strength and flexibility, thereby limiting their application in apparel and strength-requiring products.

Woven fabrics are made of warp yarns and weft yarns intersecting each other at right angles. The warp yarns are fixed on the loom, parallel to the cloth edge, and the weft yarns are interspersed horizontally between the warp yarns and perpendicular to the cloth edge. The yarn in the woven fabric is fixed in position according to the friction of the interweaving point, and the quality is strong and durable. It can be divided into plain weave, twill weave, and forged weave. Among them, the plain weave structure is the simplest. The two sets of yarns from the warp direction and the weft direction are interlaced with each other. The same structure is presented on both sides of the cloth because they overlap each other continuously. Generally, woven fabrics have a high degree of morphological stability, and their strength and friction are good; thus, they are widely used. However, when subjected to external tension, the woven fabric can overcome the rigidity of the yarn to resist tension. Its extension and contraction in the warp and weft directions are low, and it requires a compact structure to maintain its shape. Therefore, it has low elasticity and is easy to be shaped. Among the clothing materials, they are mostly used for products without elasticity, such as canvas and jeans.

Compared with the two structures, knitted fabrics have different structural characteristics. Knitted fabrics are formed by intertwining yarns with each other. The structure is elastic and easy to deform. According to the drawing direction of the loops, knitted fabrics are divided into warp-knitted and weft-knitted fabrics. Among them, the weft-knitted fabric uses a flat knitting machine to feed the yarn from the weft direction to the working needle of the knitting machine, and only one yarn is used to form a loop at a time. In the weft-knitting structure, each yarn is bent in a course in a certain order to form a loop, the loops that are intertwined with each other have few contact points, and only a small amount of tension can be applied to the fabric to be vertical or horizontal.

The most evident characteristic of knitted fabrics is its stretch ability. When the fabric is stretched by an external force, the loop shape initially changes, and then affects the slippage between the yarns until the final yarn breaks. The elongation of the knitted fabric undergoes three stages, the size of which depends on the loop shape of the knitted fabric, the fineness of the yarn, and its own elongation. The production process of knitted fabrics is short and suitable as a reinforced structure for composite materials of various shapes. Among them, the loop structure of knitted fabrics can produce greater deformation when loaded and can be designed into a more complex structure. The continuous string of fibers is used as the outer layer in the mutual transfer and maintenance of strength and bearing pressure. It can be applied to form special-shaped structures, such as multi-axial, connecting pipes, and 3D structures. Knitted fabrics have elasticity, wrinkle resistance, breathability, and good comfort; they are widely used in underwear and swimwear. After changing the structure and improving the dimensional stability, it can be used in various fields, such as industry, agriculture, and biomedical fields, as a high-pressure tube for filtration, transportation, rubber and plastic liners, artificial blood vessels, and bandages.

1.6. Constitution of the dissertation

We can determine the current popularity of carbon fiber composite materials in accordance with the development and molding methods of carbon fiber composite materials described in the previous section. Carbon fiber composite materials with different characteristics can be obtained through various processes. Among them, continuous carbon fiber tows can be directly processed to enable the fibers to obtain maximum efficiency. However, the processing method and performance requirements should be verified by experiments. In addition, the development of flexible composite materials increasingly diversified the application of carbon fiber composite materials. In addition to the application in the industrial field, the demand for people's livelihood and construction supplies has increased. In the reinforcement of composite materials, the impact of the use of laminates and structural changes on the final performance is also important. The main purpose of the study is to use continuous carbon fiber tow to develop a carbon fiber composite material. In addition, through the structure of the knitted fabric and the coating process, the tensile elongation of the continuous carbon fiber is increased, and its friction performance is improved; thus, it can be used in subsequent processing. The process and development areas are remarkably diversified. The thesis is divided into four parts, and they are introduced in the second to fifth chapters in order. In this section, the abstracts and highlights of each part are mainly described. The detailed experiment content and test results are explained. In the first part of the research content, the difference between the continuous carbon fiber tows before and after being coated with thermoplastic resin is evaluated, and the co-extrusion method of LFT is used to combine the carbon fiber tows and thermoplastic polyurethane plastics. TPU is coated on the outer layer of the carbon fiber tow to prepare a double-layer fiber bundle structure. The study confirms the physical bond between TPU and carbon fiber through scanning electron microscopy (SEM) observation, and TPU has a reinforcing effect on the tensile properties of carbon fiber tow. The research results show that compared with the original carbon fiber tow, the tensile strength of the carbon fiber tow coated with TPU is increased by 35.87% at 19.62 MPa; the strain of the carbon fiber tow during the stretching process is also increased. The co-extrusion method in the LFT process can produce continuous carbon fiber tows for industrial production. It also provides higher possibilities for the subsequent processing of carbon fiber tows, has good flexibility, and can be applied to the preparation of carbon fiber composite materials.

The second section presents the ratio selection of thermoplastic resin and the performance evaluation of composite materials. The outer shell of the continuous carbon fiber tow developed in the previous part is studied. In the LFT process, the continuous carbon fiber is extruded and coated with TPU. The outer layer, through the addition of hot melt adhesive type MTPU in the process, increases the interface adhesion between the TPU and carbon fiber. The influence of TPU blends on the composite carbon fiber and its optimal content ratio are discussed. The results show that TPU/MPTU blends have good miscibility. When the ratio is 85/15 wt%, the carbon fiber tow has a good bundling effect and nodular performance, and the tensile strength reaches 349.27 MPa/g/cm3. In addition, the performance of the composite carbon fabric is evaluated. The results show a tensile curve of toughness, confirming the flexible characteristics of the composite carbon fabric. The results of electromagnetic shielding efficiency show that the average electromagnetic interference (EMI) shielding efficiency (SE) of the laminated composite carbon fabric is 28.35 dB, which indicating a good EMI attenuation effect. The application of LFT technology to the subsequent processing and weaving of carbon fiber is first proposed in this research, providing a novel method for the development of carbon fiber reinforced thermoplastic.

The third section presents the main purpose of the study, that is, to explore the influence of the content of continuous carbon fiber tow on the composite material. The LFT technology combines bundled carbon fiber and thermoplastic polyurethane mixture to prepare continuous composite carbon fibers, in which thermoplastic polyurethane is used. The mixture is the outer layer, which bundles the carbon fiber tows of the core layer. Then, composite carbon fibers are used to make woven composites and knitted composites with electromagnetic shielding benefits. The impact of different contents of carbon fiber tow in composite carbon fibers on two different composite fabrics is evaluated. The research results show that the failure mode of composite carbon fibers is improved, and axial slip replaces direct fracture. The fabric made of composite carbon fibers is soft. The laminated woven composites have an average EMI SE of 27.20 dB at 0–3000 MHz and 44.99 dB at 2450 MHz, indicating good EMI attenuation effect. Applying LFT technology to carbon fiber and making different types of fabric structures are a new concept and breakthrough for the development of carbon fiber composite materials.

The fourth section shows the preparation and initial performance evaluation of knitted composite materials made of continuous carbon fibers. The composite carbon fibers tow and thermoplastic polyurethane blends are processed by extrusion to prepare composite carbon fibers. TPU blends are coated on the outer layer of carbon fiber, followed by knitting, and then laminated by hot pressing to prepare a carbon fiber knitted composite material. The study confirmed the double-layer structure of the composite carbon fibers, the bonding of the interface, and the axial arrangement of the fiber through SEM observation. In addition, TPU can reduce the friction generated during knitting, and the prepared carbon fiber knitted composite material has flexibility and resilience. The mechanical test results show that as the number of layers increases, the tensile strength of the composite material also increases. When six layers are laminated, the strength of the sample can reach 43.72 MPa, and the sample with four layers has the best elongation. Continuous carbon fiber can be woven after extrusion processing, and the composite material with knitted structure can improve the mechanical properties through lamination, resulting in good electromagnetic shielding ability. In addition, large-size composite materials can be manufactured, addressing the current limitations on continuous carbon fiber processing technology.

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Chapter 2 – Combination and Development of Carbon Filament Tows: Application of Coextrusion with Long Fiber-Reinforced Thermoplastics

2.1 Introduction

Carbon fibers have widespread applications in various fields because of high strengths and excellent additional properties, and carbon-fiber-containing composites can provide a light weight [1-3]. Conversely, the use of carbon fibers may render the resulting comosites with brittleness breakage that becomes a disadvantage because carbon fibers possess a low strain and are constrained to absorb the energy of an externally applied force. Therefore, composites made of carbon fibers are required to compensate for this disadvantage. Many studies have used short carbon fibers or carbon nanotubes as reinforcing fillers that are then combined with resin that features high toughness. In this case, composites attain good mechanical properties, high strain, and low brittleness breakage [4-6]. Unlike short carbon fibers, carbon filaments (i.e., long fibers) help reduce stress levels, achieving a high energy absorption level. A longer length of fibers helps transfer an externally exerted force while reducing the weight of the composites, and the composites thus yield a higher production rate [7, 8]. Nonetheless, the incorporation of carbon fibers with composites demands a considerable amount of additives for enhanced lubricity, which reduces friction among fibers but demands more time and money.

Few studies have been performed on the modification of carbon fibers, which in turn restrain the applications of carbon fiber-based composites. According to previous studies on composites, carbon fibers can be characterized with many advantages and a great application potential. Therefore, in this study, carbon fibers are used as a reinforcement to make composites more mechanically robust with a better repetitive fatigue attribute. Bondy et al. combined PA66 and carbon fibers to form composites. The test results indicate that the alignment of carbon filaments has a crucial effect on mechanical properties because the perpendicular combination between carbon filaments and matrices becomes the weakness point [9]. Wollan et al. indicated that carbon filaments possess a greater aspect ratio that creates a larger specific surface area, thereby assisting the stress transmission in the composites and improving the mechanical properties [10-12].

The wrapping provided by the coextrusion machine has been developed and applied to modify long fibers. Moreover, long fiber-reinforced thermoplastics (LFT) has been widely explored and has become commonplace in preparation processing [13-17]. As for the production, LFT technique is beneficial to the successive preparation of long fiber-containing composites. For the starter, polymer plastic pellets are melted at a high temperature and pushed along with the core yarn (i.e. carbon fiber tows) through a bi-layered die, enwrapping the core. Usually, the materials made with LFT technique are collected and trimmed as required This study aims to improve the processing performance of carbon fiber. Therefore, the carbon fiber tows at a filament state are directly used without trimming during the subsequent processing. Thermal treatment allows the thermoplastic TPU to wrap carbon fibers so TPU’s high toughness helps to enhance the carbon fibers’ friction and brittle failure. In the meanwhile, the resulting carbon fiber tows exhibit a cutting section that is transformed from a flat outlook to an elliptical shape. The tows are subsequently fabricated with a knitted structure. The processing, preparation and preliminary tests are presented in this study, and the test results indicate that the processing improves the abrasion resistance of carbon fiber tows and keeps the softness. The proposed materials are suitable for further processing, involves fabrication and composites, and contribute a major breakthrough for processing carbon fibers.

2.2 Experiments

2.2.1 Materials

In this study, carbon fiber tows (Formosa Plastics Co., Taiwan) have a highly aligned molecular arrangement, good mechanical properties, and a fiber quantity of 3K. Figure 2-1 (a) shows the construction of carbon fiber tows used as the core of the wrapped yarns. Figure 2-1 (b) illustrates the configuration of thermoplastic polyurethane (TPU, HE-3285ALE; Headway Polyurethane Company, Taiwan) with a melting point of 140 °C and a melt flow index (MI) of 7.03 g/10 min (175 °C). TPU has a molecular structure composed of hard and soft segments. Hard segments contribute to mechanical properties, whereas soft segments provide good strain and elasticity; as such, TPU is a good sheath for carbon fiber tows [18-21].

2.2.2 Experiment Methods

Carbon fiber tows are used as the core, which is wrapped with a TPU outer layer through LFT and coextrusion. When exposed to the air, TPU easily absorbs moisture, which adversely affect the melt properties and mechanical attributes. Hence, TPU is baked and dried at 70 ℃ in an oven overnight in advance, and then used in the following manufacture. Figure 2-1 (c) illustrates the process of LFT where the extrusion machine is built with a concentration circle structure. Carbon fiber tows are delivered through the pores of inner circle while TPU melt is delivered through the ring of outer circle, enwrapping the fiber tows. First, a single extruder machine is used to melt TPU at high temperatures, enabling TPU to wrap the core evenly during coextrusion. The temperatures of the extrusion machine are set to 155 °C, 160 °C, 165 °C, 170 °C, and 175 °C with a rotary rate of 240 rpm and a discharging rate of 11.88 g/min. The wrapped yarns are then cooled and solidified in a water bath. Afterward, they are trimmed into the desired length. The core should not be rendered with friction and damage.

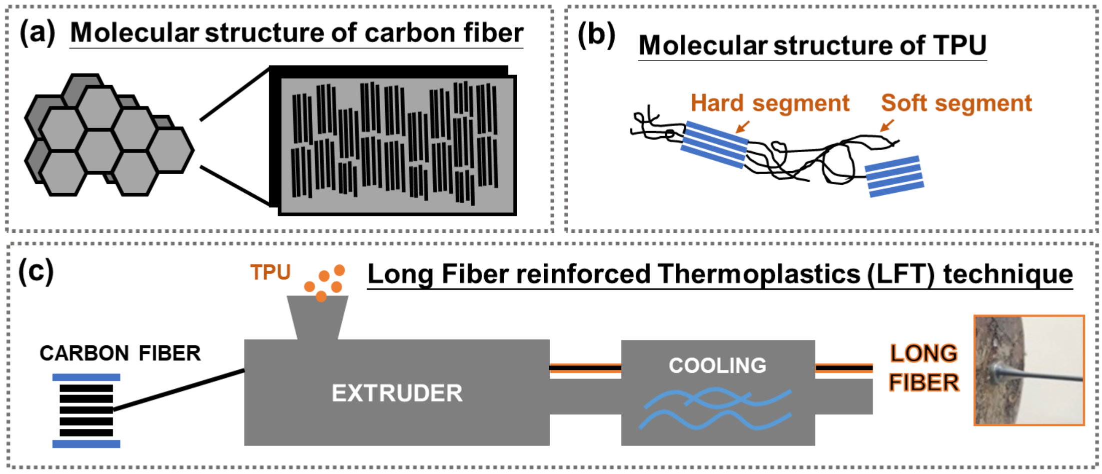

Figure 2-1. Coextrusion with (a) carbon fibers, (b) TPU, and (c) LFT.

2.2.3 Tests

Scanning Electron Microscopy (SEM) Observation

The interface between the core and the TPU sheath is observed under an FE-SEM (S-4800, Hitachi, Japan). Samples are trimmed, fixed to the platform, and coated with a thin gold layer for 60 s by using an ion sputter (E-1010, HITACHI, Japan). Lastly, the morphological characteristics of the interface are observed at an operating voltage of 3 kV.

Tensile Measurement

The tensile measurement is to examine the difference in the failure mode of carbon fiber tows that are coated with TPU via thermal treatment. As specified in ASTM D 2256-02, the tensile properties of the wrapped yarns (i.e., experimental group) and pure carbon fiber tows (i.e., control group) are evaluated using a universal tester (Instron 5566, US). The samples are fixed to the clamps with an infinity shape as Figure 2-2 and then imparted with pre-extension. The distance between clamps is 250 mm, and the crosshead speed is 300 mm/min. Ten samples for each specification are tested for the average.

Figure 2-2. Clamps used in tensile measurements.

2.3 Results

Figures 2-3 (a) and (b) show the image and micromorphological characteristics of carbon fiber tows in relation to the coextruded TPU sheath. Without TPU wrapping, carbon fiber tows demonstrate a loose structure. The tows do not have an even diameter distribution and are prone to deformation because of the different densities among carbon fibers. The average thickness is only 88.87±7.24 μm. Wrapped in a thin transparent TPU sheath, carbon fiber tows are well protected and become compact with a more stabilized structure. Specifically, the carbon fiber tows are processed with a successive method so there is no restriction imposed on the fiber length direction. As a result, the materials can be collected according to test standards and application requirement. Next, the horizontal direction of the materials is observed using an SEM.

Figure 2-3 (c) demonstrates the SEM image showing the microscopic cross-section of the wrapped yarns. When TPU and carbon fiber tows are combined, the interface between the reinforcing fibers and polymer matrices is one factor determining the strength [22]. A fine interfacial face facilitates the transmission of materials as well as blocks the growth of cracks, attenuating the stress concentration. Moreover, the interfacial bonding may induce the change of primary attributes of materials. For example, in this study, the carbon fibers gain better elasticity when bonded with TPU. The core and the TPU sheath comprise the wrapped yarns where carbon fiber tows are more compactly aligned inside a TPU sheath. In addition, carbon fiber tows become elliptical lengthwise as a result of TPU coating, and there are small voids among the aggregated carbon fibers. The original carbon fiber tows are flat lengthwise and are easily flipped and twisted, which is addressed by the presence of TPU coating. The SEM image in Figure 2-3 (d) reveals the interface where carbon fiber tows are in the interior of the TPU sheath. Despite the coextrusion method, TPU forms a hollow tubular shape along the interior tows and does not penetrate the tows. Although carbon fiber tows are aggregated, voids form among them, as presented Figure 2-3 (d), the flat shape of carbon fiber tows are responsible for the embedded TPU during coextrusion as illustrated in Figure 2-3 (e). As a result, a low physical combination retains the unsaturated core well inside the TPU sheath. The experimental group keeps the original softness without the presence of splitting fibers. In summary, coextrusion is a good method to improve carbon fiber tows. With the meticulous control of the screw extruder at a specified feed ratio, the wrapped yarns made of carbon fiber tows and TPU can be easily used to reproduce the desired yarn length and an even TPU thickness [23, 24].

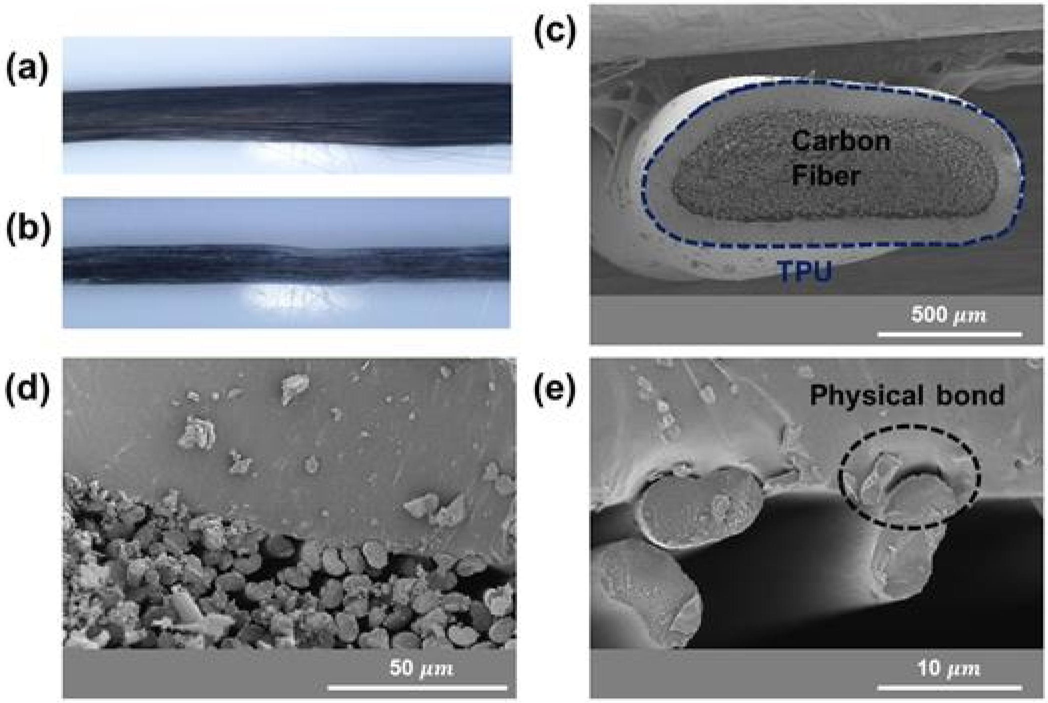

Figure 2-3. Surface morphology and SEM images of (a) original and (b) TPU-wrapped carbon fiber tows, (c) cutting section, (d) interface, and (e) micro perspective interface.

Figures 2-4 (a) and (b) show the friction level of carbon fiber tows in relation to the coextruded TPU sheath. In this study, the wrapped yarns are repeatedly abraded 1, 5, and 10 times with a sand paper, and the damage to the control and experimental groups is separately recorded. The test results indicate that 1-time friction does not interfere the wrapped yarns because of the efficient protection of the TPU sheath. A more significant difference can be observed in the wrapped yarns that undergo 5-time friction as the TPU sheath is damaged. Subsequently, the carbon fiber tows are exposed to air with hairiness, but the cores remain an intact morphology.

By contrast, the control group (i.e., pure carbon fiber tows) immediately shows hairiness (indicated by red arrows) once the friction is rendered. The effects of 5-time friction are demonstrated in two separate parts. A proportion of carbon fiber tows remains as tows but has a smaller amount of residual carbon fibers. The other proportion involves peeled fiber clusters because of multiple frictions. Hence, the majority of the peeled carbon fiber tows are broken.

However, with 10-time friction, the wrapped yarns have the TPU sheath that then bears multiple fractures to expose the carbon fiber tows. This result indicates that the protection against the friction of the TPU sheath is effective because the sheath wraps the carbon fiber tows, generating a lower displacement. Contrarily, the control group shows a total damage, losing the original morphological characteristics and becoming fiber clusters. In summary, the carbon fiber tows present low friction tolerance and should be combined with polymers, but the resulting products usually appear brittle. Therefore, soft carbon fiber composites should be developed. In this study, coextrusion enables the TPU sheath to protect the carbon fiber core, greatly improving the wear resistance.

Figure 2-4. Images of the friction of the (a) original and (b) TPU-wrapped carbon fiber tows.

Figure 2-5 shows the difference in the curvature of the carbon fiber tows in relation to the coextruded TPU sheath. Long fibers are prone to bending in the subsequent process, whereas the matrices of composites may constrain the bending level that causes difficulty in loop fabrication and generates abrasion resistance. A bending force exerts carbon fiber tows with an expanded outer curvature but a compressed internal curvature. As the fiber diameter increases, the curvature shows a larger radius that adversely affects the processing. In addition, the structure of the carbon fiber tows becomes loosened because of multiple bending cycles, which eventually damage and fracture the samples. In Figures 2-5 (a) and (b), the bending curvature of the carbon fiber tows can be compared in terms of the coextruded TPU sheath. Figure 2-5 (a) exhibits that the control and experimental groups can be bent with a great curvature, which is ascribed to the softness of yarns. Nonetheless, the carbon fiber tows are flat, and they easily form twists or cause a splitting phenomenon as indicated by the arrows. Figures 2-5 (c) and (d) present the image of the coiled carbon fiber tows that are wrapped and evenly aligned over a container. As for the subsequent practical processing, the control group without a TPU sheath slides frequently and then piles up in the bottom of the container, which in turn causes failure in the manufacturing. On the contrary, with a TPU sheath, the carbon fiber tows are less forced to go along the horizontal direction and suitable for any type of the yarn feeding device.

Figure 2-6 illustrates the tensile strength of carbon fiber tows in relation to the coextruded TPU sheath. In Figure 2-6 (a), in comparison with the control group, the TPU sheath provides the core with a greater tensile strength. Hence, the tensile strengths of the control and experimental groups are 14.44±5.64 and 19.61±1.88 MPa, respectively. The tensile strength of the control group is lower than that of the experimental group because of the deformation and displacement of a single fiber during the tensile test. The carbon fiber tows are wrapped in the TPU sheath, which restrains the movement of the core. As a result, all the cores are almost broken concurrently, generating a synergistic effect and reinforcing the tensile strength of the wrapped yarns. Figure 2-6 (a) also indicates that the coefficient of variation of the control group is larger than that of the experimental group, and the carbon fiber tows are not broken simultaneously possibly because of the difference in the failure mechanisms regarding tensile damage. Any individual carbon fibers with defects are randomly distributed over the carbon fiber tows, which may jeopardize the whole performance. Therefore, multiple measurements are conducted while the defected fiber distribution is computed, thereby improving the design of products and the reliability of property evaluations. Figure 2-6 (b) illustrates the tensile stress–strain curves where the experimental groups change the brittleness attributes of the carbon fiber tows because of the TPU wrapping; moreover, the tensile stress–strain curves show a smaller slope. The TPU sheath provides the core with a greater strain and simultaneously changes the failure mechanism. This trend is caused by the physical combination between fibers and the polymer melt, indicating that the presence of TPU constrains the displacement of carbon fiber tows during the tensile process, enhancing the strain and improving energy absorption [25-28]. Furthermore, the control group (without the TPU sheath) exhibits one-time breakage followed by brittleness breakage. The TPU sheath ensures the experimental groups undergoing two-stage fractures, which are separately attributed to the carbon fiber tows that provide mechanical support and the TPU sheath that offers ductility. In addition, the toughness of the TPU-wrapped carbon fiber tows is higher. The results of the tensile strength test reveal that the conduction of coextrusion positively influences the carbon fiber tows because the incorporation of TPU concurrently increases the specific surface area, mechanical properties, friction, and bending resistances.

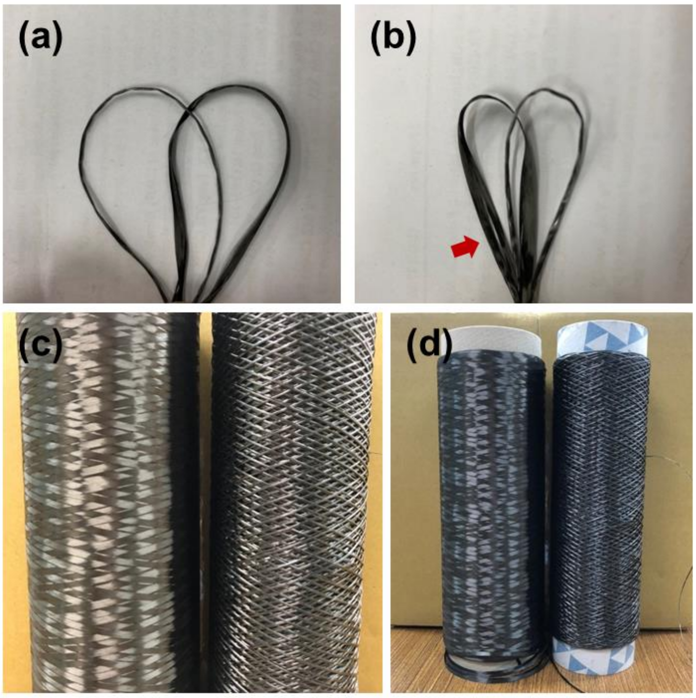

Figure 2-5. Images of the curvature of carbon filament bundles: (a) primary and (b) TPU wrapped carbon filament bundles and (c, d) coiled fiber bundles.

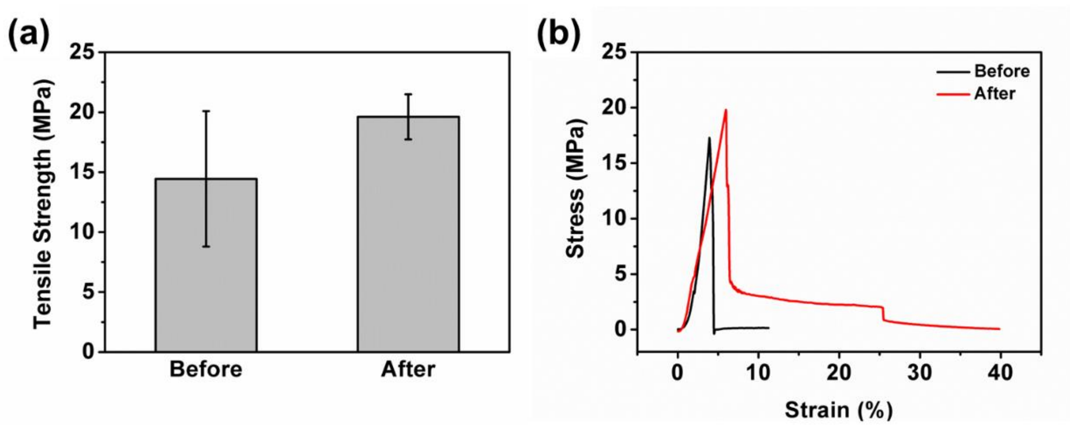

Figure 2-6. (a) Tensile strength and (b) stress–strain curves of carbon fiber tows in relation to the coextruded TPU sheath.

Figure 2-7 shows the knitted composite consisting carbon fiber tows. Usually it is difficult to fabricate carbon fibers, which requires a large-scale manufacturing to reduce the bending curve or lubrication with additives to help reduce friction among carbon fibers. The morphology of the carbon fiber tows is changed, which in turn improves the friction performance and mechanical reinforcement successfully. Unlike the raw carbon fiber tows, the processing materials can be knitted with a knitting machine as Figure 2-7 (a). Moreover, Figure 2-7 (b, c) separately shows the expanded composites that are vertically and horizontally expanded, fully expressing the flexible knitting structure that considerable improves the primary properties of knits. As far as carbon fiber-based composites are concerned, they can broaden the design, properties, and final area, and hence the resulting composites can be used in the mechanical structure of vehicles and aircrafts.

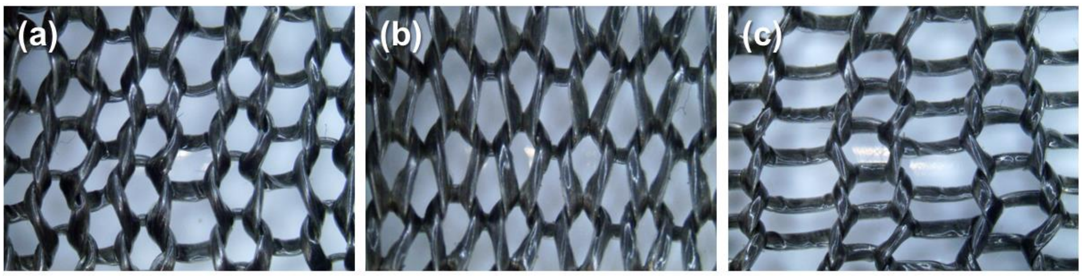

Figure 2-7. Images of (a) original, (b) expanded vertically, and c) expanded horizontally composites consisting of carbon fiber tows.

2.4 Discussion

Figure 2-8 shows the physical combination of the carbon fiber tows and the TPU sheath. In Figure 2-3, during coextrusion, TPU wraps the carbon fiber tows and then shapes the wrapped yarns. A small amount of carbon fibers is embedded in the TPU sheath. In this case, the core–sheath structure is formed due to the physical combination that effectively improves the mechanical properties and provides the core with softness.

Three embedding levels, namely, non-embedding, surface adhesion, and partial embedding, correspondingly demonstrate different levels of influences on the stress–strain curves. At the initial tensile stage, the experimental groups exhibit the maximal tensile strength, which is ascribed to physical combination demonstrated at stage III in Figure 2-8. Carbon fibers are well protected by the TPU sheath and the wrapped yarns, demonstrating greater mechanical properties. With the ongoing tensile test, smaller characteristic peaks are shown at stage II when the TPU-adhered carbon fiber tows are successfully confined and gathered. Consequently, the mechanical properties improve. In addition, at stage I, the TPU sheath is the main source that provides the tensile strength. The TPU sheath that is not physically combined with carbon fibers fastens the core and contributes some of the mechanical properties. The embedded carbon fibers strengthen the tensile strength of TPU composites. In the meanwhile, the tensile stress can be effectively transmitted or dissipated via the aggregation of TPU. Therefore, coextrusion is an effective method to improve the tensile properties of a carbon-based TPU composites, facilitating the subsequent manufacture of carbon fiber tows concurrently. Nevertheless, the strength of the composite material is still insufficient for application, but the expectation of softness has been initially achieved and look forward to the follow-up can be improved through weaving and other processing.

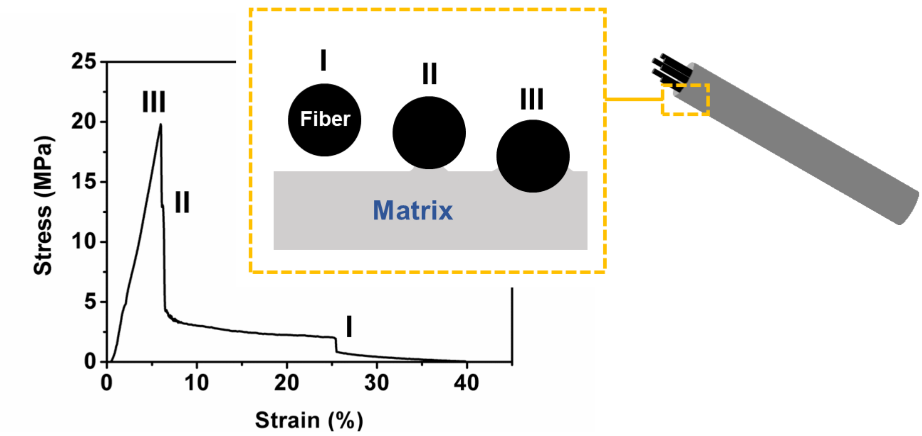

Figure 2-8. Diagram of the physical combination of carbon fibers and TPU.

Figure 2-9 shows the diagram of the failure mechanism of carbon fiber tows in relation to the coextruded TPU sheath. Figure 2-9 (a) illustrates the stereomicroscopic image of the fractured sample. As a general rule, when exerted with an external force, carbon fibers may intersect because of the different displacements of individual fibers. The interlaced fibers generate friction, rendering carbon fiber tows with defects. The defects of carbon fiber tows easily become exposed to a high stress concentration, which in turn causes the failure of the wrapped yarns [29, 30]. As for the control group, the defects may be formed by the TPU-free carbon fibers whose loose structure and sleek surface cause fiber movement. According to physical combination theory in Figure 2-8, the sites where TPU and carbon fiber tows do not physically combine are vulnerable to stress concentration, and this particular area is often found in the center of the carbon fiber tows because TPU simulates the shape of the core through coextrusion. Figures 2-9 (b) and (c) present the failure mechanisms in relation to the coextruded TPU sheath. The TPU sheath transposes and leads the original stress concentration along the axial fibers. Stress concentration is the main factor responsible for the failure of the wrapped yarns, indicating that the samples are no longer useful. On the contrary, the failure mechanism via the movement along the axial direction comparatively extends the service life of the experimental groups. The fastened carbon fibers are imparted with axial displacement because of the tensile force, showing a greater ductility. Therefore, the defect of any single site no longer compromises the properties of the wrapped yarns. In summary, applying coextrusion to combine TPU and carbon fiber tows helps reach physical combination and effectively improves the failure mechanism.

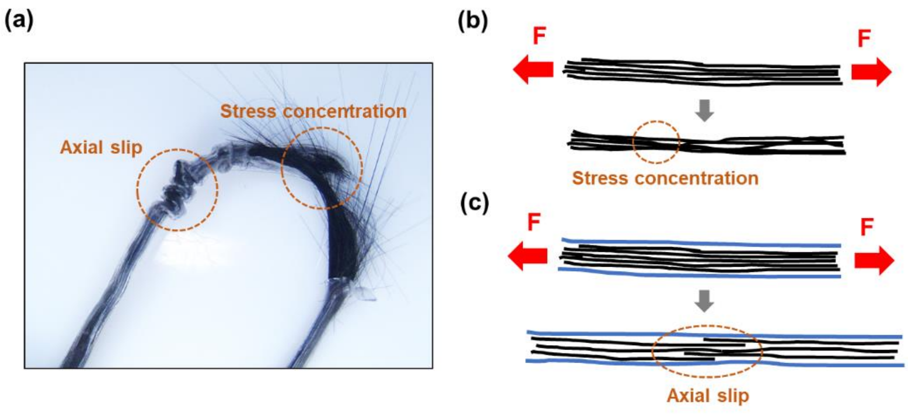

Figure 2-9. Illustrative diagrams of the failure mode of carbon fiber tows: (a) image, (b) stress concentration, and (c) fiber movement.

2.5 Conclusions

In this study, TPU and carbon fiber tows are successfully combined using LFT and coextrusion. TPU melts at high temperatures and becomes the sheath of carbon fiber tows. It adheres to carbon fibers until a shape is formed. Through this process, carbon fiber tows aggregate well because the TPU sheath fastens the core. The results confirm that carbon fiber tows show a sheath core structure while retaining softness with coextrusion. The TPU sheath wraps carbon fiber tows, which mitigate friction that commonly occurs among them. The tensile test results indicate that the physical combination between the sheath and the core effectively enhances the tensile strength and changes the failure mechanism as follows. Friction from the displacement of original yarns transforms the stress concentration phenomenon to axial displacement. The processing of carbon fiber tows helps significantly improve basic properties. The carbon fiber tows can be embedded in the TPU coating and then made into knitted composites. As a result, the composites exhibit the high flexibility of knits and at the same time making co-extrusion method a feasible processing for carbon fiber composites to gain a diversity of subsequent finishing and industrial applications.

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Chapter 3 – Applying TPU Blends and Composite Carbon Fibers to Flexible Electromagnetic-Shielding Fabrics: Long-Fiber-Reinforced Thermoplastics Technique

3.1 Introduction

According to the experimental results in Chapter 2, we can find the importance of covering carbon fiber. In this chapter, the composition parameters of the coating material are discussed and the optimization process of the carbon fiber-reinforced thermoplastics (CFRTP) is evaluated. CFRTP are commonly used in aerospace, military, automobile, construction, and sports fields. Given the good mechanical, thermal, and electrical properties, carbon fibers provide CFRTP with satisfactory reinforcement and functions. Consequently, CFRTP is extensively utilized as an electromagnetic-shielding material [1, 2]. As a result of the increasing demand for CFRTP and their excellent mechanical and functional properties, they are commonly used as a ecofriendly thermoplastic polymers [3, 4], decreasing the interfacial defects between carbon fibers and matrices [5, 6], improving the complex process of producing CFRTPs [7-9], and broadening the application feasibility of CFRTP.

This study proposes a novel technique called long-fiber-reinforced thermoplastic (LFT) technique as a production method for CFRTP. In this method, filaments are made with a core–shell structure through extrusion molding. The extruder is equipped with a double-layer outlet that enables the sheath (i.e. polymer) to enwrap the core (i.e. long fibers). Hence, the extruded polymer melt would be shaped according to the long fiber core and then cooled to stabilize in a water zone. The LFT technique is able to produce filament-contained composites consecutively and thus gains greater dimensional stability than staple fiber-contained composites. The outer polymer layer secures the filament core while makes contribution to stress transmission. LFT provides the fibers with higher strength and flexibility, as well as lighter weight, than staple fibers, thereby preventing the defects caused by multiple processing. Although CFRTP has become prominent in industrial fields, few studies focus on incorporating the LFT technique with the carbon fiber process, especially with the process that treats thermoplastic polymer as matrices [3, 10, 11]. Carbon fibers have low fracture toughness, which restricts the three-dimensional (3D) multi-curvature structure design. Many studies have investigated carbon-based composites with flexible feature [12-15]. Zhu et al. produced 3D graphene/carbon nanotube membranes through filtration and sintering. The resulting products maintained good electromagnetic-shielding effectiveness even after multiple bending [16]. Lu et al. applied the chemical vapor deposition to produce soft and flexible carbon nanotube-contained sponges. The thickness or density of sponges was changed to adjust the electromagnetic-shielding effectiveness. The test results indicated that the sponges exhibited flexibility and electromagnetic-shielding effectiveness [17].

The composites produced using the aforementioned methods are either restricted in terms of the formation or require a complex process, which implies the existence of many areas for improvement. Therefore, this study aims to produce soft and flexible composite carbon fibers to improve the conformity through a convenient process. They can be applied for EMI SE without restricting the shape of the products and thus express the soft feature. The LFT technique is designed for continuous long fibers, which possess a good dimensional stability because of the combination with polymer, and thus have a smaller number of stress concentration points than staple fibers [18]. The blends composed of thermoplastic polyurethane (TPU) and polyester hot-melt adhesive (MTPU) are used to enwrap the carbon fiber tow. First, MTPU is added to increase the viscosity of the blends, and therefore decrease the size of the interface with the fiber tows while improving the enwrapping level. Second, TPU is aligned with the direction of the carbon fibers; the forming axial flow exerts a positive influence on the mechanical properties. Third, the continuous carbon fiber tows are combined with the

TPU blends via the LFT technique to create composite carbon fibers. Fourth, the tensile and rheological properties of the composite carbon fibers are evaluated to determine the optimal parameters. Lastly, the optimal composite carbon fibers are fabricated into the composite carbon fabrics, and the mechanical and electromagnetic-interference shielding effectiveness (EMI SE) of these fibers are examined.

3.2 Experimental

3.2.1 Materials

In this study, two types of TPU are used, which are purchased from Headway Polyurethane Company, Taiwan. One of the TPUs (HE-3285ALE) has a melting point of 140 °C and a melt index (MI) of 7.03 g/10 min. The other is an eco-friendly MTPU (HM-3580AU) with a melting point of 110 °C and an MI of 7.25 g/10 min. The carbon fiber tows (TC-33, Formosa Plastics Corporation, Taiwan) are composed of 3000 counts of filaments with a single fiber strength of 500 ksi and a modulus of 33 Msi. The high-strength polyester filament (PET, Universal Textile Corporation, Taiwan) has a fineness of 500D/96f.

3.2.2 Manufacturing Processes

Preparation of the Composite Carbon Fibers and Fabrics

Figure 3-1 shows the process diagram of the composite carbon fibers and fabrics enwrapped in TPU/MTPU blends using the LFT technique. The machine used in the LFT technique was assembled by our laboratory and Sun Ying Machinery Company, Taiwan. The outer layer of the composite carbon fibers has varying TPU/MTPU ratios (100/0, 95/5, 90/10, 85/15, and 80/20 wt%), which were adjusted using an extruder at a rotary screw rate of 240 rpm. The temperature of the extruder from the barrel to the die is 155, 160, 165, 170, and 175 °C, respectively. Long fibers are fed into the die of the extruder that is equipped with a double-layer outlet designed for the core (i.e. long fibers) and the sheath (i.e. polymer). The carbon fiber tows are first enwrapped in the TPU blend and then collected in clusters. The composite carbon fibers are then yielded after cooling the TPU blend. Moreover, the length of the resulting composite carbon fibers is not restricted and massive products can be collected to facilitate the subsequently fabrication. To study the feasibility of the subsequent fabrication of composite carbon fibers, a shuttle loom is used to fabricate the composite carbon fabrics. The warp yarn is made of polyester fibers, whereas the weft yarn is made of composite carbon fibers with an optimal TPU/MTPU ratio of 85/15 wt%.

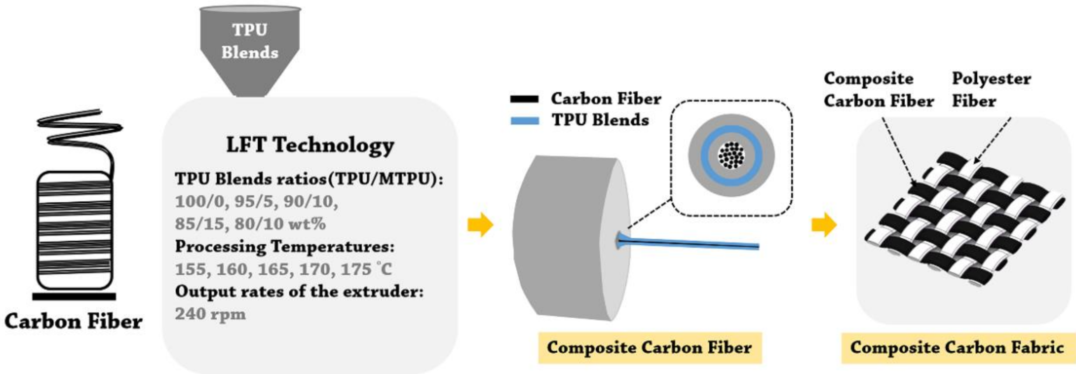

Figure 3-1. Schematic of the production process of composite carbon fibers and fabrics.

3.2.3 Tests

Scanning Electron Microscopy (SEM)

A field emission scanning electron microscope (S-4800, HITACHI, Japan) is used to observe the composition of the composite carbon fibers. The fibers are pasted and fixed on the sample holder using carbon paste, and then coated in a thin layer of gold for 60 s using an ion sputter (E-1010, Hitachi, Japan). The morphology and cutting section of the fibers are observed at an operating voltage of 3 kV.

Rheological Feature of the TPU Blends

The rheological properties of the TPU blend is measured using a rheological instrument (TA Instrument, US). The blends at various ratios are trimmed and mounted on a sample tray with a diameter of 25 mm. The rheological feature is measured at an angular frequency of 0.1–100 (rad/s) under 190 °C in a nitrogen environment.

Tensile Properties

An automatic tensile tester (FPA/M, Statimat-M, Textechno, Western-Germany) is used to measure the tensile properties of the composite carbon fibers. The distance between fixture clamps is 250 mm and the crosshead speed is 50 mm/min. Ten samples for each specification are used for testing. In addition, the linear density (λ) of the composite carbon fibers is computed on the basis of the correlation between the weight and the length, and the specific stress is calculated by the stress and the linear density [19].

$$\lambda = (\text{weight (g)})/(\text{length (km)}) \qquad 3\text{-}(1)$$

where λ is expressed in tex computed based on the denier. The specific stress is expressed in N/g/km, which is equal to 10^3 MPa·g^{-1}·cm^3.

The tensile properties of the composite carbon fiber knots and composite carbon fabrics are measured using an Instron 5566 universal tester (Instron, US). The knots of the fibers are tested according to the test standard ASTM D 2256 with a gauge distance of 250 mm and a crosshead speed of 300 mm/min. Then, the tensile properties of the fabrics are tested according to ASTM D 5034, where the sample size is 152 mm x 25 m, the distance between fixture clamps is 75 mm, and the crosshead speed is 300 mm/min. Ten samples for each specification are used in order to have the average value and the dispersion level (indicated by the dispersion of values). In addition, the tensile direction is precisely the weft direction as composite carbon fibers are used as the weft yarns.

EMI SE

A coaxial transmission fixture and spectrum analyzer (KC901S, TS RF Instruments, Taiwan) is used to measure the EMI SE of the composite carbon fabrics according to ASTM D4935-10. A blank specimen is used to rectify the EMI SE during the testing; the result is recorded as SERef. Then, at a scanning frequency of 100 KHz–3 GHz, a spectrum analyzer is used to examine the samples with a size of 150 mm× 150 mm. Ten samples for each specification are used to calculate the average EMI SE (in dB) using the following equation [20-22].

$$SE = 10\log[P_i/P_o] = 20\log[E_i/E_o] = 20\log[H_i/H_o] \quad 3\text{-}(2)$$

where P_{in} is the incident energy, E_{in} is the incident electric intensity, H_{in} is the incident magnetic intensity, P_{out} is the transmitted energy, E_{out} is the transmitted electric intensity, and H_{out} is the transmitted magnetic intensity.

3.3 Results and Discussion

3.3.1 Morphology of Composite Carbon Fibers

Figure 3-2 shows the scanning electron microscopy (SEM) images of the composite carbon fibers. The test results show that the change in the proportion of the TPUs did not affect the smoothness of the composite carbon fiber surface, and the samples of the five parameters demonstrated similar morphologies. Regardless of the TPU/MTPU ratio, the five composite carbon fiber types exhibited comparable morphologies with varying diameters and thicknesses. Increasing the MTPU content decreases the diameter of the fibers, consequently thinning the outer layer. This phenomenon is attributed to the different intrinsic properties of TPU and MTPU. The latter, which is a thermoplastic type, is relatively sensitive to temperature, and thus exhibits high viscosity when melted. Given the variations in the TPU/MTPU ratios during the production of composite carbon fibers, the presence of MTPU affects the shear thinning of the TPU blends and results in a thinner shell than the presence of a 100 wt% TPU blend.

The rheological properties of TPU and MTPU are then investigated because of the crucial effects on the outer layer of the composite carbon fibers. According to the SEM image of the cutting section of the composite carbon fibers, the cluster of these fibers is associated with the rheological properties of the TPU melt. When the blend is composed of 100 wt% TPU, the resulting composite carbon fibers are relatively flat and resemble the original carbon fiber tows. The cluster efficacy of the composite carbon fibers is continuously improved because of the increase in MTPU content. Eventually, the composite carbon fibers achieves an almost cylindrical morphology, which may be ascribed to the viscosity and mobility of the TPU melts. Basing on the morphology observation, two groups (i.e., TPU/MTPU=100/0 and 95/5 wt%) demonstrate undesirable morphologies because of the presence of voids among fibers and TPU blends. This downside, however, is improved when the MTPU content is increased. At a TPU/MTPU ratio of 85/15 wt%, the composite carbon fibers exhibit an optimal cluster effect and are closely aligned with few voids.

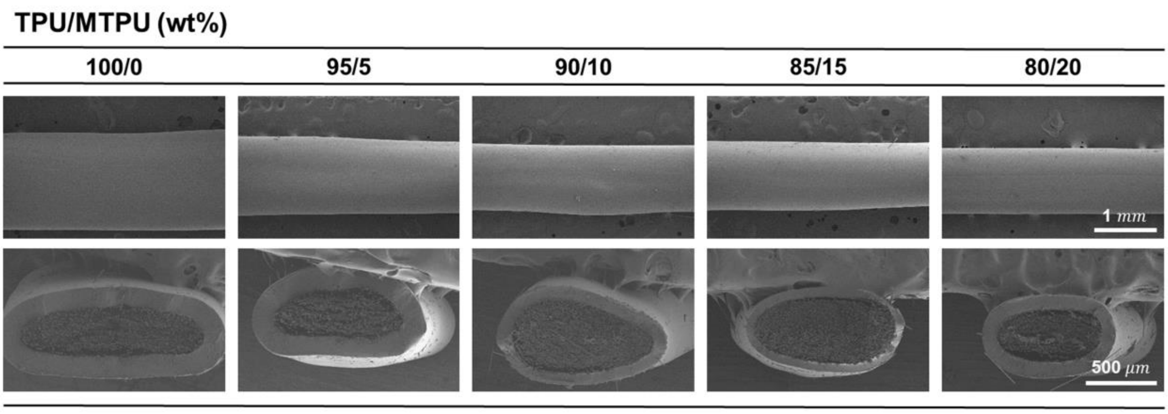

Figure 3-2. SEM images of the composite carbon fibers.

The group with an TPU/MTPU ratio of 85/15 wt% is examined regarding the interface between carbon fibers and TPU blends using SEM. Figure 3-3(a) shows the contact region between two materials synthesized by a concentric die, wherein the TPU blend fails to saturate the fiber tow, leaving voids among the fibers. Thus, the TPU blend adheres only to the outer carbon fibers in the fiber tows. This result indicates that the TPU blend is stuck on the fiber surface and then cools efficiently, resulting in a low adhesion level over the interface. Figure 3-3(b) displays a magnified interface structure. The TPU blend that adhered to the fiber surface is shaped according to the formation of the fibers during the adhesion. In addition, the TPU blend does not interfere with the formation of the outer carbon fibers in the tows. Figure 3-3(c) shows that the sleek TPU blend surface forms a concave spot at the contact point with the carbon fibers, which is attributed to the embedding of the carbon fibers. The TPU blends contact the carbon fiber tows when successively melted, cooled, and solidified. This phenomenon increases the friction between the two materials, as well as helps form a physical bond.

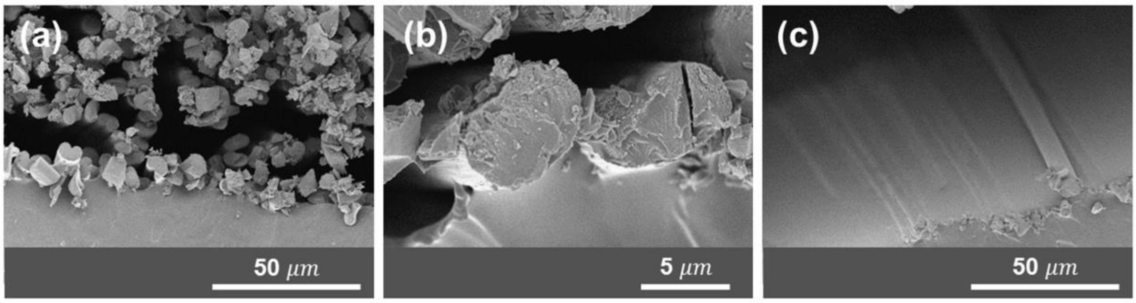

Figure 3-3. (a) Interface between the carbon fibers and the thermoplastic TPU blends interface and (b) its inset with magnification. (c) Physical bonding trace.

Subsequently, the softness of the knotted composite carbon fibers is evaluated in terms of the TPU/MTPU ratio. Figure 3-4(a) presents the knotted carbon fiber tows. Stabilizing the knots is difficult because of the smooth surface of the carbon fibers, hence, the knots are unwrapped easily. The hairiness is attributed to the friction among the loosened fibers. Compared with original carbon fiber tows, composite carbon fibers are easier to knot regardless of the parameters (Figures 3-4[b]–[f]). The TPU blends form the outer layer (i.e., the shell) of the composite carbon fibers, which in turn induces a high friction and protects the internal carbon fiber tows. After being knotted, the carbon fibers remain in the primitive formation without hairiness, and the knots are stabilized and no longer loosened. This result proves that the LFT technique can effectively improve the softness and subsequent processing of composite carbon fibers.

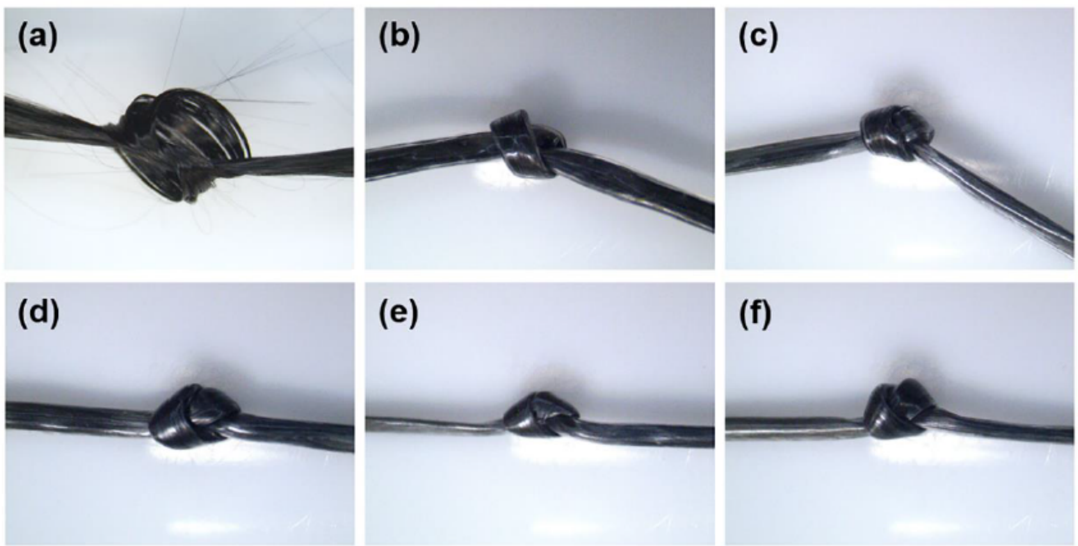

Figure 3-4. Softness of the composite carbon fibers: (a) pure carbon fibers and composite carbon fibers with TPU/MTPU ratios of (b) 100/0, (c) 95/5, (d) 90/10, (e) 85/15, and (f) 80/20 wt%.

3.3.2 Rheological Properties of the TPU blends

The TPU blends serve as the shell of the composite carbon fibers; thus, the corresponding rheological properties are valuable. The processing feasibility of the TPU blends, as well as the microstructure–performance relationship, is evaluated using rheological measurement. Figure 3-5 shows the storage modulus, loss modulus, and complex viscosity of the TPU blends. The complex viscosity depends on many factors, including composition, miscibility, morphology, and interface, which are pertinent to the rheological properties of the blends [23, 24]. Figures 3-5(a) and 3-5(b) indicate that at a low-frequency range, the mild curves of the storage and loss moduli are evident, thereby implying that the TPU and MTPU are effectively synthesized. The curves for the TPU/MTPU blends are as mild as the curves for pure TPU and MTPU melts. In addition, the comparatively low storage and loss moduli of mono materials reflect the reduction in the intermolecular entanglement of the TPU blends, which suggests that the rheological properties of TPU is strongly subjected to the presence of MTPU. A small amount of MTPU decreases the number of entangled nodes in the TPU segments. At a TPU/MTPU ratio of 85/15 wt%, the composite carbon fibers exhibit the optimal storage and loss moduli. Figure 3-5(c) suggests that different ratios provide TPU blends with different levels of miscibility, which makes the viscosity of all mixtures lower than that of a pure TPU melt. This result verifies the good miscibility between TPU and MTPU. The incorporation of MTPU with TPU blends signifies the presence of a material with good fluidity, thereby ensuring that the LFT technique can effectively produce enwrapped carbon fiber tows. However, when the TPU/MTPU ratio exceeds 85/15 wt%, a rheological penetration value might be reached. Consequently, MTPU might render the segments of the TPU blends with a low mobility. In other words, 15 wt% of MTPU can obtain an optimal bonding level with TPU blends, as well as an optimal flow resistance [25]. In conclusion, the high viscosity of the TPU blends worsens the entanglement of the molecular segments, thereby resulting in a small extrusion amount of TPU blends and a thin shell. Moreover, the TPU shell generates additional restrictions because of the presence of nodes, which in turn enhances the cluster effect. Conversely, when the TPU blends have a low viscosity, the shell of the resulting composite carbon fibers is thick, and the nodes hamper structure with minimal restrictions in the TPU blends. As a result, the formed shell is as flat as the original carbon fiber tows.

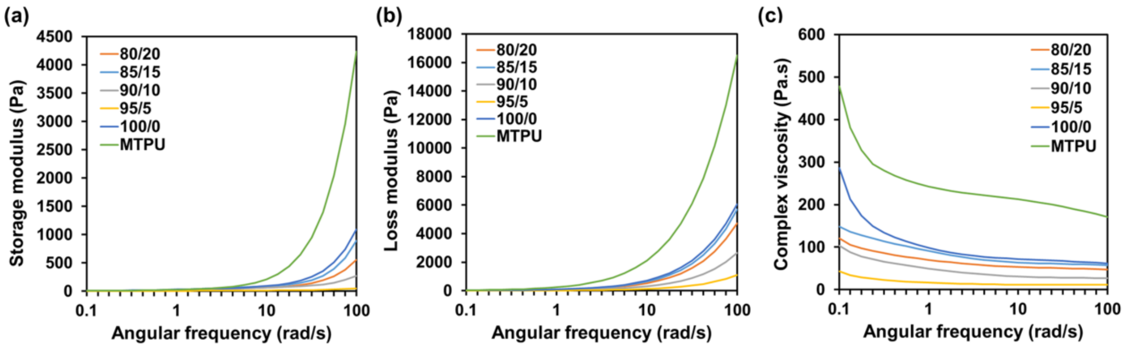

Figure 3-5. Rheological properties of the TPU blends: (a) storage modulus, (b) loss modulus, and (c) complex viscosity.

3.3.3 Tensile Properties of the Composite Carbon Fibers

Table 3-1 and Figure 3-6 show the tensile properties and specific strength of the composite carbon fibers, respectively. An increase in the MTPU content exert a positive influence on the denier of the fibers. Nonetheless, 20 wt% of MTPU slightly reduces the denier of the composite carbon fibers. A similar trend is exhibited by the specific strength (Figure 6). At a TPU/MTPU ratio of 100/0 wt%, the specific strength of the composite carbon fibers is 136.97 MPa·g^{-1}·cm^3. When the MTPU content is changed from 95 wt% to 85.wt%, the specific strength of the composite carbon fibers show an ascending trend with the following values: 205.87, 243.10, and 349.27 MPa·g^{-1}·cm^3

for 95, 90, and 85 wt%. At 80 wt% of MTPU, the specific strength decreases and reaches 330.57 $MPa\cdot g^{-1}\cdot cm^{3}$. These findings are consistent with the findings on the morphology of the fibers and the interface between constitutional materials. As discussed in Figure 3-2, the difference in the cutting-section shape can be ascribed to the TPU/MTPU ratio. When the ratio is 100/0 wt%, the composite carbon fibers appear flat, thereby resembling the original carbon fiber shape. In addition, the space between the carbon fibers and TPU blends is relatively large, and the voids become stress concentration sites. Consequently, the tensile properties of the composite carbon fibers are low. The composite carbon fibers possess an almost circular fiber morphology owing to the high MTPU content. Meanwhile, the voids between the carbon fibers and TPU blends are reduced, which exerts a positive influence on the tensile properties of the composite carbon fibers. Carbon fibers are highly concentrated because of the restriction of the TPU blends, which reduces the bending and slipping levels when conducting the tensile measurement. As a result, the composite carbon fibers exhibit good tensile properties. The knot strengths of the fibers are summarized in Table 3-1. The original carbon fibers are knotted before the tensile test but are then damaged in the knots, which proves that the original carbon fibers do not have any strength along the diameter direction. The composite carbon fibers are also knotted and applied with a tensile force. The reinforcement in the knot strength can be observed because the TPU coating serves as a protective layer that reduces the friction among the composite carbon fibers. Except for a rather standard deviation, no other trend is observed. In summary, the knot strength of the composite carbon fibers depends on the TPU blends rather than on the strength utilization of yarn.

Table 3-1. Tensile properties of the composite carbon fibers.

TPU/MTPU (wt%)	Denier (D)	Tensile		Knotted Stretch	
		Strength (N)	Elongation (%)	Strength (N)	Displacement (mm)
100/0	9592.05	145.98±5.42	1.04±0.11	5.03±0.77	44.13±14.14
95/5	6776.85	155.01±2.26	1.17±0.05	0.34±0.15	61.97±19.98
90/10	6655.65	179.78±4.91	1.12±0.04	0.29±0.17	53.45±14.32
85/15	4995.75	193.87±0.84	1.48±0.05	0.69±0.50	51.16±9.83
80/20	5439.75	199.80±0[*a]	1.12±0.02	0.87±0.63	43.02±9.25

[*a]: The standard deviation is 0 because the tensile strength of the composite carbon fibers exceeds the tolerance of the machine. The maximal tensile strength is 199.80 N with a standard deviation of 0.

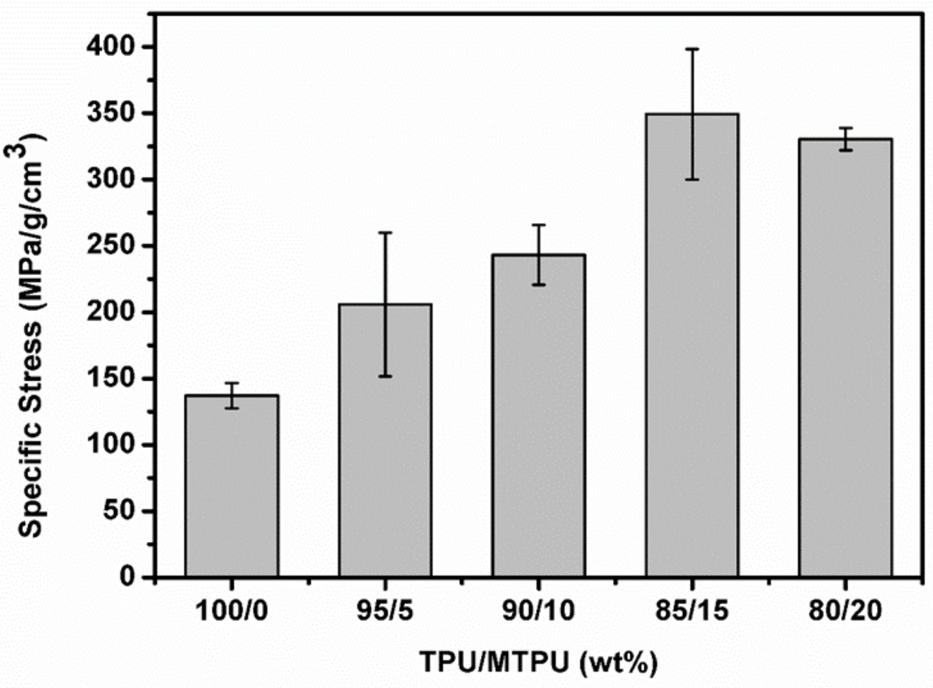

Figure 3-6. Specific strength of the composite carbon fibers.

The elongation at the breakage of the composite carbon fibers (Table 3-1) is similar to the specific strength (Figure 3-6), which proves that the interface between the core and shell has been improved. The composite carbon fibers are exerted with multiple fractures during tensile test from the unwrapping of the carbon fiber tows, friction-then-fracture because of the lessened fiber orientation, and the fracture of the expanded TPU blends. According to the theory in Figure 3-2, the optimal TPU/MTPU ratio is 85/15 wt%. This ratio provides the composite carbon fibers with great elongation at breakage, which is ascribed to the large amount of carbon fibers embedded in the TPU blends that prevents the fibers from slipping. Therefore, the carbon fibers are aligned along the axial direction with a low portion of fiber component force during the tensile test. A TPU/MTPU ratio of 100/0 wt% results in low elongation at breakage. Figure 3-7 shows the morphology of the fractured samples. After the tensile test, the original carbon fibers exhibit a morphology where the fibers become fluffy and exhibit hairiness over the surface (Figure 3-7[a]). This finding confirms that carbon fibers are not tolerant to friction. The TPU blends are then used to protect the carbon fibers and reduce the frictions to enhance the cluster effect. Figure 3-7(b) shows that when the TPU/MTPU ratio is 100/0 wt%, the composite carbon fibers exhibit delamination of the shell, whereas the carbon fiber tows still demonstrate considerable hairiness. The hairiness sheers the TPU shell, which degrades the effectiveness of the samples. With respect to the MTPU content (cf. 5 and 10 wt%), the damaged samples show similar morphologies (Figures 3-7[c] and 3-7[d]). Some parts of the carbon fibers and shell are simultaneously expanded and exhibit wrinkles after the tensile test. Conversely, some parts of the carbon fibers demonstrate delamination and subsequent fracture, which indicates the initial improvement in the interface. At a TPU/MTPU ratio of 85/15 wt%, the tensile force simultaneously expands the shell and the carbon fibers until the carbon fiber tows are broken and all axial fibers at the fractured site are moved (Figure 3-7[e]). The tensile fracture mode of the composite carbon fibers changed when the TPU blends and carbon fibers exhibited no fracture; such behavior features a failure mode different from extension and gliding. Figure 3-7(f) shows that the core and shell have good mutual bonding based on the changes in the failure mode when a tensile force is exerted. At 20 wt% MTPU, the thick TPU blends are not easily extended, which slightly reduces the elongation of the composite carbon fibers at breakage (Table 3-1).

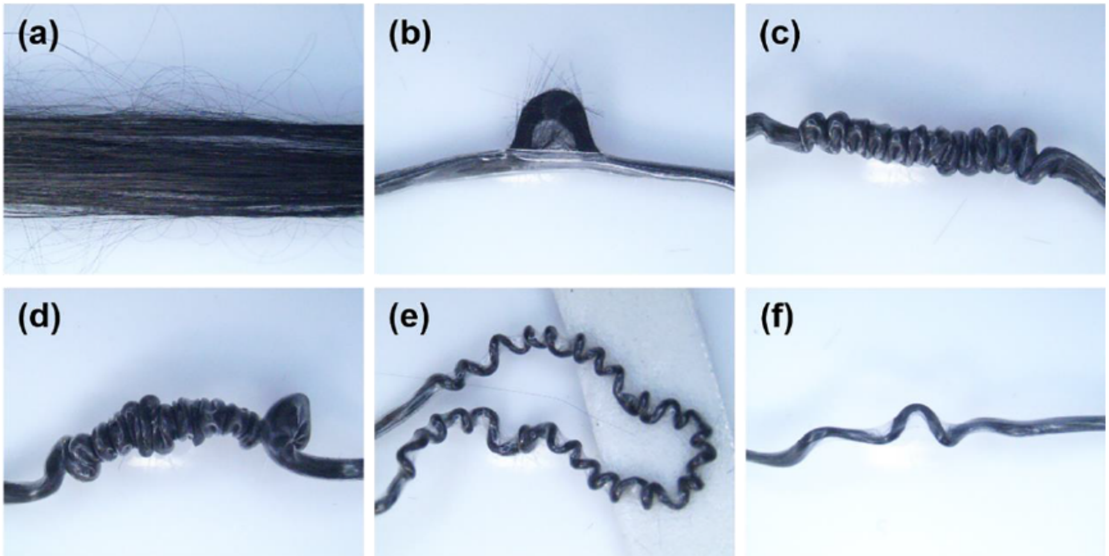

Figure 3-7. Damage morphologies of composite carbon fibers with TPU/MTPU ratios of (a) pure carbon fiber (b) 100/0, (c) 95/5, (d) 90/10, (e) 85/15, and (f) 80/20 wt%.

3.3.4 Tensile Properties of the Composite Carbon Fabrics

In this section, composite carbon fibers with a TPU/MTPU ration of 85/15 wt% are fabricated into composite carbon fabrics along with high-strength polyester fibers. Fabrics that are made of carbon fibers are usually afflicted by the damage caused by the repetitively friction happening among fibers and between fibers and the machine. As carbon fibers have long elongation and low anti-shear properties, monofilaments are prone to breakage when ben fabricated. Subsequently, the resulting composites have low mechanical properties. The proposed method in this study takes advantage of TPU blends that has high abrasion resistance, thereby protects carbon fiber tows without being abraded while improving the evenness of the fabrics. With this method, the tensile strength of fabrics is improved significantly. Regarding the improvement in the failure mode, the friction among carbon fibers is attenuated and they can bear an axial external force concurrently. When an external force is applied, the interface in core-shell structure is first exposed. Following the expansion of the sheath, uniformity of carbon fibers is compromised, which eventually leads to the occurring of subsequent failure.

Figure 3-8(a) shows the morphology and tensile properties of the composite carbon fabrics, which possess high resilience. The presence of the TPU blends strengthens the twist resistance of the composite carbon fibers, which enables the fibers to withstand high frictions without generating hairiness. The fabrication indicates that the LFT technique improves the application range of the composite carbon fibers. The composite carbon fabrics are fabricated with equal amounts of warp and weft yarns, and the TPU blends are utilized to protect the composite carbon fibers and provide a good cluster effect.

Figure 3-8(b) shows the tensile properties of the composite carbon fabrics. The optimal tensile strength is 50.79 MPa and the stress–strain curves signify the ductility feature of the resulting fabrics. Moreover, the curves display an increase in the initial modulus, in which the carbon fibers demonstrate high rigidity and the slope is steep. The TPU shell is continuously extended, and the fabrics showed the elongation, during which the strain of the curves increases but the slope decreases. Only one peak value is observed in the stress–strain curves of the fabrics, which suggests that the synthesis of the two polymers protected the fabrics from multiple fractures owing to delamination. The primary reason for the failure is the voids in the core caused by the tensile force, which allow fibers to move easily. An increase in the voids adversely affects the cluster effect of the composite carbon fibers, followed by the slip, deformation, twist, and eventual failure of the non-axial fibers.

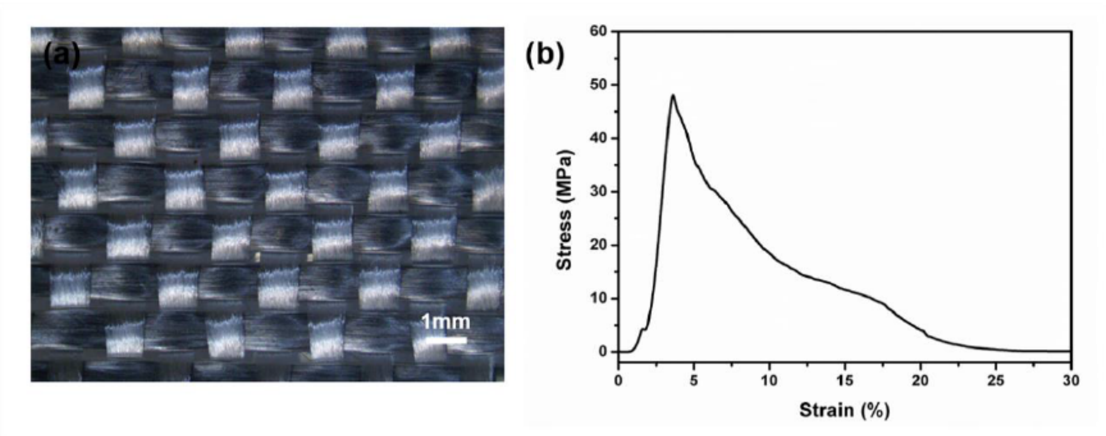

Figure 3-8. (a) Surface morphology and (b) tensile properties of composite carbon fabrics.

The fractured composite carbon fabrics in the tensile test are observed to investigate the damage mechanism. Figure 3-9(a) shows the slipping phenomenon of the fabrics during the test. The fabric structure first deforms (indicated by the arrows), followed by the abrasion of the interlaced warp/weft yarns. At this point, however, no damage is occurred. Figure 3-9(b) shows the failure morphology of the composite carbon fabrics. The results indicate that the fabrics may suffer from two or more fracture modes during the test because of the previously mentioned fabric deformation. The outer layer of the composite carbon fibers is almost peeled off, leaving carbon fibers exposed and fluffy (white rectangle). By contrast, the red rectangle represents a similar result to Figure 3-7. The TPU shell and carbon fiber core are simultaneously expanded, and the carbon fibers are protected by the shell without delamination before slipping.

The fracture mechanism shows the slipping of the carbon fibers (Figure 3-9[c]). The TPU shell elongates as a result of the applied tensile force and even exceeds the thermoplastic deformation. The shell also fails to regain a smooth surface, and then exhibits relaxation because of elastic fatigue. The black rectangle indicates that the carbon fibers are arranged in a random manner instead of a parallel one. Consequently, the fibers are entangled and not fractured directly. Figure 3-9(d) displays the failure morphology of the carbon fibers. The composite carbon fibers and fabrics exhibit the same damage mode. The slip and deformation of the fibers are indicated by the red arrows. The fiber twisting leads to entanglement, and the samples eventually show friction-to-failure behavior. In the specified damaged site, the carbon fibers and TPU shell display deformation, followed by accumulation because of the elastic recovery when the test is completed. The tensile property test confirms that the combination of two materials with TPU blends fortifies the internal carbon fibers, thereby improving the damage mode after the tensile test. In addition, composite carbon fibers that are enwrapped in TPU blends do not collapse when they fail. Because the carbon fibers only demonstrate axial slippage without being broken, it helps retain the intact fabric structure and prolong the service life. Conversely, without the protection of TPU sheath, carbon fibers would be directly broken, which adversely affects the interlaced fibers and generates unnecessary friction to damage the fabric structure.

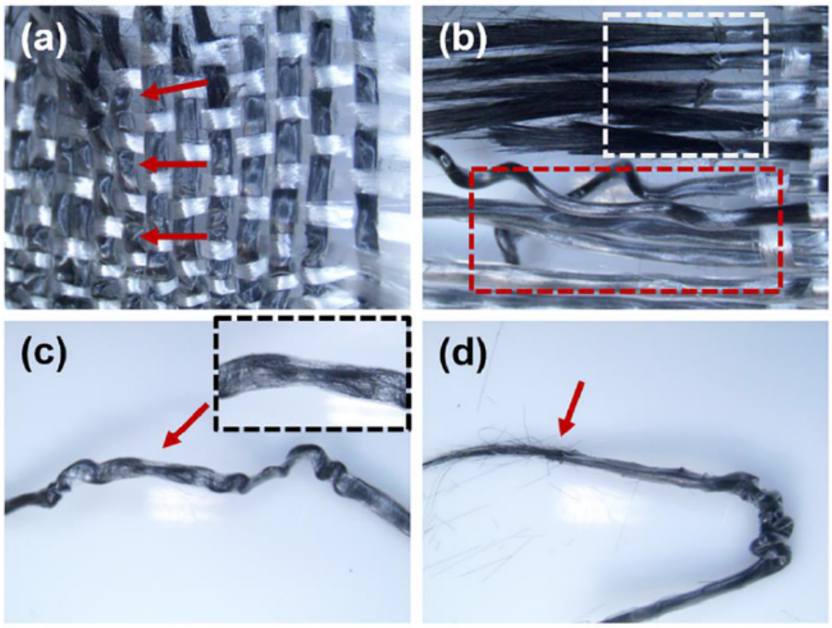

Figure 3-9. Failure morphology of composite carbon fabrics after the tensile test: (a) gliding and (b) failure, (c) slippage of fibers, and (d) failure of fibers.

3.3.5 Functions of Composite Carbon Fabrics

The previous results substantiate that the use of the LFT technique is helpful to the combination of carbon fibers and TPU blends as well as the subsequent fabrication. The modified polymer-coated carbon filaments are malleable and the resulting composite fabrics are soft. The resilient composites can insulate the high frequent electromagnetic interference and protects components and equipment that are vulnerable to EMI. The composites debilitate EMI without any restriction on the shape of products and improve the EMI SE of final products.

Figure 3-10 shows the EMI SE of the composite carbon fabrics within a frequency range of 30–3000 MHz. The composite carbon fabrics demonstrate better EMI SE than polyethylene terephthalate (PET) fabrics. The average EMI SE of the former increases from 1.36 dB to 8.83 dB, exhibiting an increment of over 84.59 %. Nonetheless, the fabrics are composed of composite carbon yarns (weft yarns), which allows the formed strip areas to perform EMI SE exclusively. By contrast, the warp direction is a carbon-free fiber, and is therefore not involved in the EMI SE.

The composite carbon fabrics are laminated at 90° and reached an average EMI SE of 8.83–28.35 dB, which can attenuate 99% of the EMI [26]. The EMI SE of the fabrics can be attributed to the constituent composite carbon fibers composed of a core–shell structure, which allows the fabrics to achieve an acceptable EMI SE by absorbing the electromagnetic waves. The carbon fiber core is composed of a conjugate structure that will demonstrate resonance when affected by the electromagnetic energy. Therefore, the core can attenuate the electromagnetic energy via absorption loss [27]. In addition, the composite carbon fabrics are fabricated with warp (i.e., PET fibers) and weft yarns (i.e., composite carbon fibers), both of which have different fineness. Warp-floating points where two types of fibers cross are present, and this phenomenon becomes increasingly distinct when the fabrics are laminated. In addition to the large surface of the carbon-contained areas, the interior interfaces among the different materials continue to resist the electromagnetic waves, thereby generating multiple reflection losses. This mechanism is identical to that proposed by Kumar et al. Given that carbon-based composite hollow balls consist of voids, triggering the conductive dissipation and multiple reflection against electromagnetic waves will allow the final products to attain an acceptable EMI SE [28, 29].

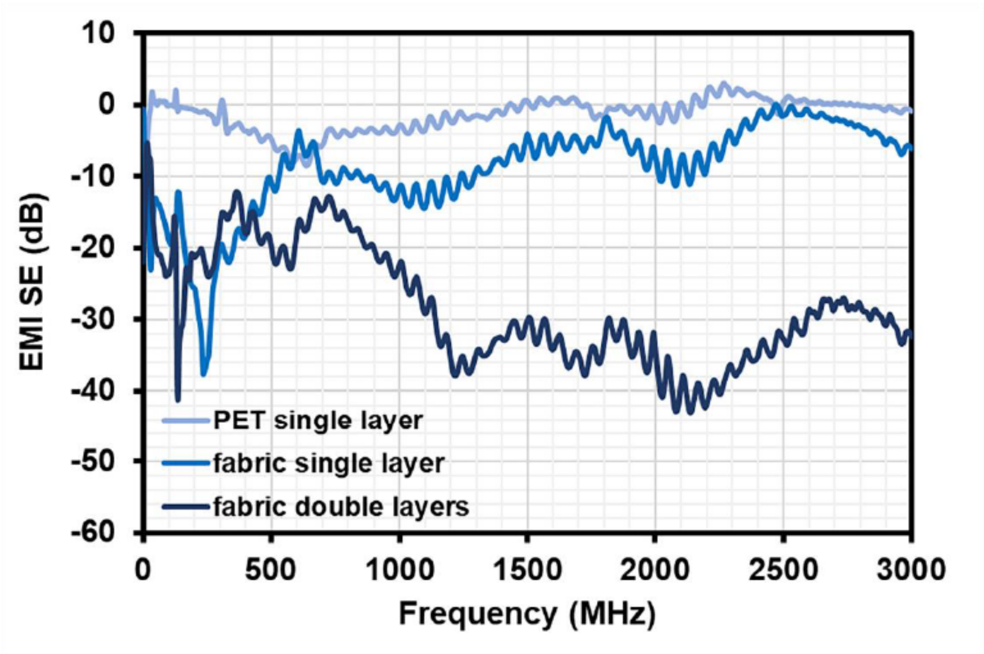

Figure 3-10. EMI SE of the composite carbon fabrics. The legend for the colors in this figure is provided in the web version of the article.

3.4 Conclusions

This study improves the softness feature of composite carbon fibers and fabrics. The LFT technique is used to produce continuous carbon fiber tows, and thermoplastic TPU blends are extruded to coat the carbon fibers. The TPU/MTPU ratio exert a considerable influence on the morphology of composite carbon fibers. The SEM images and rheological properties indicated that the melt viscosity of the TPU blends can be improved, which is beneficial to the cluster effect of the carbon fiber tows. The resulting composite carbon fibers exhibited good knot formation. The optimal specific strength of the composite carbon fibers (349.27 $MPa \cdot g^{-1} \cdot cm^3$) is observed when the MTPU content is 85 wt%. The combination of carbon fibers and TPU blends improved the failure mechanism of the composite carbon fibers, which also improved and changed the friction-to-fracture behavior into axial slipping. This study proves that the LFT technique can help in the efficient fabrication of composite carbon fibers without hairiness during the manufacturing process. Moreover, composite carbon fabrics demonstrated high ductility and a comparable failure mode to composite carbon fibers. The EMI SE of the laminated composite carbon fabrics reached 28.35 dB. The preliminary results suggested that the LFT technique can effectively improve the application feasibility of carbon fibers and realize the fabrication requirement of continuous carbon fiber tows. In conclusion, this novel manufacturing technique can substantially contribute to the development of CFRTPs.

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Chapter 4 – Thermoplastic Polyurethane Reinforced with Continuous Carbon Fiber Tows: Manufacturing Technique and Fabric Property Evaluation

4.1 Introduction

According to the experimental results in Chapter 2 and Chapter 3, it is known that TPU blends are the most suitable processing conditions when the composition ratio is 85/15 wt%. Therefore, in the fourth chapter, the composition of the inner carbon fiber tow is changed as a parameter, and its influence on the composite material is evaluated. As mentioned in the previous section, carbon fibers have excellent mechanical and thermoelectric properties and play an important role in development of novel materials. Carbon fibers are one of the prior materials and are used in the military, industrial, aerospace, and construction fields [1-3]. The frequent utilization of carbon fibers naturally increases the relative waste products that damage the environment. Thus, using carbon fibers while ensuring environmental protection remains a challenge, and all countries advocate the environmental policy of recycling as an alternative to burying. The crucial point of recycling carbon fibers is to reduce chemical finishing in the manufacturing process, which enables the easy recycling of materials [4-7].

The combination of thermoplastic polymer and carbon fibers can generate more eco-friendly composites than the combination of epoxy resin and carbon fibers. Moreover, there is also a greater diversity of manufacturing methods. Based on our previous study, the well-developed technology of thermoplastic polymer wrapped yarns help the polypropylene coated polyester yarns to form composite fabrics with good functions, a lightweight, and flexibility [8,9]. Prorokova et al. found that coating PTFE over polypropylene yarns provided the core yarns with lower coefficient of friction, chemical resistance, and a significantly reduced processing cost [10]. The coextrusion method is used to extrude the polymer melt in order to wrap the filaments, after which the wrapped filaments are cooled for shaping. The resulting filament composites have flexibility, efficient process, and environmental protection, and are suitable to construct multi-dimensional structures. As for common carbon-based composites, they are mostly reinforced by using carbon staple fibers, carbon-based fillers, or prepreg materials [11]. Hence, traditional carbon-based composites have complex preparation procedure, demanding more process time, but the constituent carbon fibers are not successive [12]. By contrast, continuous carbon fiber composites show greater production efficiency and the use of coextrusion method mitigates to wear the fibers when carbon filament composites are at the stage of granulation. Moreover, this method also reduces production time and contributes good mechanical properties to the composites [13,14]. Besides, coextrusion method allows to produce composite materials with a longer length, thereby improves the constraint set by carbon fibers during the manufacturing. However, there are more difficulties regarding techniques when fabricating carbon fibers. For example, when woven fabrics are fabricated, a specified heald frame should be selected and the formation of loops should be designed. Carbon fibers have high elastic modulus, friction, and friction coefficient; however, carbon fibers are difficult to curve, made into loops, and fabricate because they are prone to fracture. As a result, the protection provided by a polymer shell is necessary during fabrication because it provides reinforcement to the core of the filaments.

In this study, carbon fiber tows and thermoplastic polyurethane (TPU) are made into composite carbon fibers (CCFs) by co-extrusion. TPU has good abrasion resistance and elasticity, and its use TPU as the shell of CCFs can enhance the toughness of CCFs and realize their fabrication. In addition, the tensile strength of CCFs is measured in relation to the content of carbon fiber tows. The interface between fibers and matrices and the morphology of CCF are also observed. Next, CCF is made with woven and knitted structures, and the effect of co-extrusion is studied. Given the high conductivity of carbon fibers, woven fabrics and knitted fabrics are tested for electromagnetic shielding effectiveness. The proposed fabrics are expected to provide users with electromagnetic radiation resistance and high flexibility. The use of carbon fiber composites is an innovative concept and has a broad range of application prospects.

4.2 Materials and Methods

4.2.1 Materials

The materials and specifications used in the study are shown in Table 4-1.

Table 4-1. Specifications of materials.

	Materials	Model	Specification	Supplier	Abbreviation
Shell layer	Thermoplastic polyurethane, TPU	HE-3285ALE	Melting point: 140 °C MI: 7.03 g/10 min	Headway Polyurethane Co., Taiwan	TPU
	TPU-based hot melt adhesives, MTPU	HM-3580AU	Melting point: 110 °C MI: 7.25 g/10 min		MTPU
Core layer	Carbon fiber tows	TC-33	Number of fibers per tow: 1500 Single Fiber Strength: 500 KSI Modulus: 33 MSI	Formosa Plastics Co., Taiwan	1.5K
	Carbon fiber tows	TC-33	Number of fibers per tow:3000 Single Fiber Strength: 500 KSI Modulus: 33 MSI		3K
	Carbon fiber tows	TC-33	Number of fibers per tow: 6000 Single Fiber Strength: 500 KSI Modulus: 33 MSI		6K
Woven composites (Warp Yarn)	High Modulus Low Shrinkage (HMLS) PET Industrial Yarn		1000D/192F	Nan Ya Plastics, Taiwan	HMLS Polyester

4.2.2 Preparation

Preparation of Composite Carbon Fibers, Woven Composites, and Knitted Composites

Three types of carbon fibers are used in this study, and they are separately made into CCFs. TPU that is exposed to the air is very susceptible to moisture, which in turn compromises the performances of TPU melts and then mechanical properties of resulting materials. Therefore, TPU needs to receive pretreatment beforehand, which means that TPU is required to be dried at 70 °C at an oven for overnight before the subsequent process. TPU and MTPU are blended at a ratio of 85/15 wt% beforehand. TPU blends are processed using an extruder to enwrap the carbon fiber tow and serve as the shell. With the co-extrusion technique, carbon fiber tows are combined with the TPU blend as the extruder (Sun Ying Machinery Company, Taiwan) enwraps the tows with a specified amount of the TPU blend being 11.88 g/min (Figure 4-1). In addition, a vent hole is made in the middle section of the screw in advance, which protects the materials from the damage during the extrusion process. Furthermore, carbon fiber tows and TPU blends are bonded with the co-extrusion technique with TPU blends being extruded from the die and then coating the carbon fiber tows. The take-up speed of the rewinder is set as 25 rpm. The temperatures from the barrel to the die are 155 °C, 160 °C, 165 °C, 170 °C, and 175 °C, while the rotary rate of the screw is 240 rpm. Based on the fiber counts per tow, the CCFs are divided into 1.5K-CCF, 3K-CCF, and 6K-CCF. Different CCFs are made into woven and knitted composites. Woven composites are composed of HMLS polyester yarns as the warp yarns and 1.5K-CCF, 3K-CCF, or 6K-CCF as the weft yarns. The woven fabrics are denoted as 1.5K-CCF-Woven, 3K-CCF-Woven, and 6K-CCF-Woven, while the knitted composites are denoted as 1.5K-CCF-Knitted, 3K-CCF-Knitted, and 6K-CCF-Knitted.

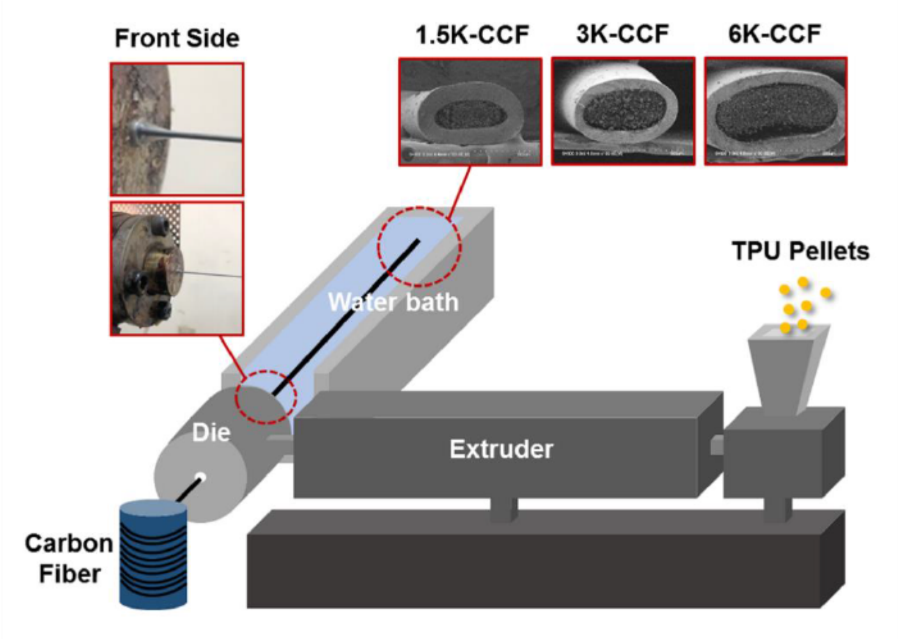

Figure 4-1. Diagram of co-extrusion process.

4.2.3 Tests

Morphological Observation

The structure and interface of CCFs are observed via field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). Samples are trimmed and then fixed onto the platform for 60 s gilding by using ion sputtering (E-1010, Hitachi, Japan), after which the sample morphology is observed at the voltage of 3 kV.

Tensile Properties

The tensile properties of CCF, woven composites, and knitted composites are measured using an Instron 5566 universal tester (Instron, US) as specified in ASTM D 2256-02 for CCFs, ASTM D 5035 for woven fabrics, and ASTM D 5034 for knitted fabrics. As for the CCF, the sample is tangled in an “8” shape as Figure 4-2 (a), the clamps impart CCF with a pre-extension force, which in turn ensures that CCF will be evenly rendered with a load so damaged right in the middle point of samples as Figure 4-2 (b). Because CCF is affixed to the clamps, its outer and inner layers are stretched concurrently so CCF demonstrates different damage mechanisms as a result of the difference in the elongation as well as slippery and broken filaments. Ten samples for each specification are used for measurement. The distance for the fixture is 250 mm, and the crosshead speed is 300 mm/min. As for the woven composites, the sample size is 150 mm × 25 mm, the fixture distance is 75 mm, and the crosshead speed is 300 mm/min. As for knitted composites, the sample size is 200 mm × 25 mm, the fixture distance is 100 mm, and the crosshead speed is 300 mm/min.

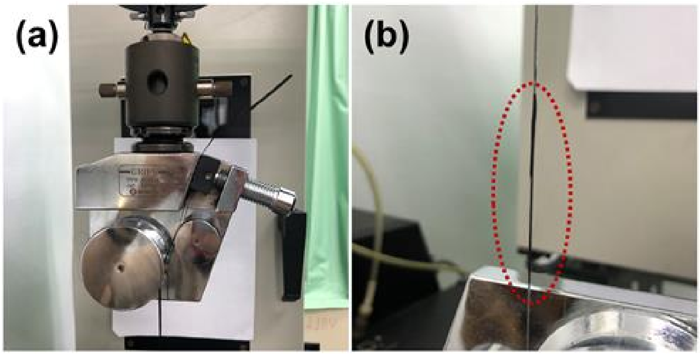

Figure 4-2. Image of tensile test process: (a) tensile clamps and (b) fractured sample.

Electromagnetic Interference Shielding Effectiveness (EMI SE)

Single-(0°) and double-layered (0°/90°) woven composites and knitted composites are tested for EMI SE by using a coaxial transmission fixture and a spectrum analyzer (KC901S, TS RF Instruments, Taiwan) as specified in ASTM D4935. The EMI SE (SERef) of a blank specimen is tested for rectification. The scanning frequency is between 100 kHz and 3 GHz. The sample size is 150 mm × 150 mm. Ten samples for each specification are used to determine the average. EMI SE is presented in decibel (dB) and computed using Equation 4-(1) as follows [15,16]:

$$SE = 10 \log[P_i/P_o] = 20 \log[E_i/E_o] = 20 \log[H_i/H_o] \quad 4\text{-}(1)$$

where P_{in} is the incident energy, E_{in} is the incident electric intensity, H_{in} is the incident magnetic intensity, P_{out} is the transmitted energy, E_{out} is the transmitted electric intensity, and H_{out} is the transmitted magnetic intensity.

4.3 Results and Discussion

4.3.1 Morphological Observation of CCFs

Figure 4-3 shows the SEM images of the CCF morphology. Regardless of the core of carbon tows, that is, 1.5K-CCF, 3K-CCF, or 6K-CCF, the morphology is sleek, which is ascribed to the presence of a TPU shell. At the same time, the diameter of CCFs varies due to the core of carbon fiber tows (1.5K, 3K, and 6K); the greater the fiber counts per tow, the greater the CCF diameter. According to the cross-section of CCFs, co-extrusion technique ensures that carbon fiber tows (i.e. the core) are firmly wrapped in the TPU shell. The resulting CCFs are shaped in accordance with the tow formation as the TPU blend restricts the scattering of carbon fibers. A simple core–shell structure is formed as the TPU blend does not infiltrate the fiber tows. Figures 4-3 (a, b) show the oval-shaped cutting section of 1.5K-CCF and 3K-CCF. 1.5K-CCF features a relatively thick TPU shell. Figure 4-3 (c) shows that 6K-CCF and 3K-CCF have a comparable shell thickness (1.42 μm) but in a flat form. The different shapes of cutting sections are due to the effectiveness of the co-extrusion technique. A specified amount of TPU blend is extruded as shown in the bottom row in figure where the various lengths of cone are indicated by red lines. Figure 4-3 (a) shows that 1.5K-CCF has the longest cone length because low fiber counts per tow leads to a thick shell (0.99 μm and 1.09 μm). The occurring of different wall thicknesses is attributed to a specified extrusion amount, a specified pick-up rate, but different fineness of carbon fiber bows, thereby examining the feasibility of a combination of a co-extrusion process and the finishing of carbon fibers. A small amount of TPU blends would be bonded with carbon fibers which make it difficult to attain a specified wall thickness. Despite the difficulty, all of composite carbon fibers (i.e.1.5K to 6K groups) can be produced. By contrast, the cone lengths of 3K-CCF and 6K-CCF are shorter, which allows the immediate adhesion of the TPU blend over the carbon fiber tows, resulting in the small thickness of the shell. The cutting section of 6K-CCF appears flat, which may be due to great fiber counts per tow that hampers the securement of TPU blend. Based on the morphology in the SEM images, the morphology of CCFs is dependent on the fiber counts and the TPU content. When the fiber counts per tow are low (cf. 1.5K-CCF), a rounded cutting section and a thick shell are presented. When the fiber counts per tow are high (cf. 6K-CCF), an oval cutting section and a thin shell are presented.

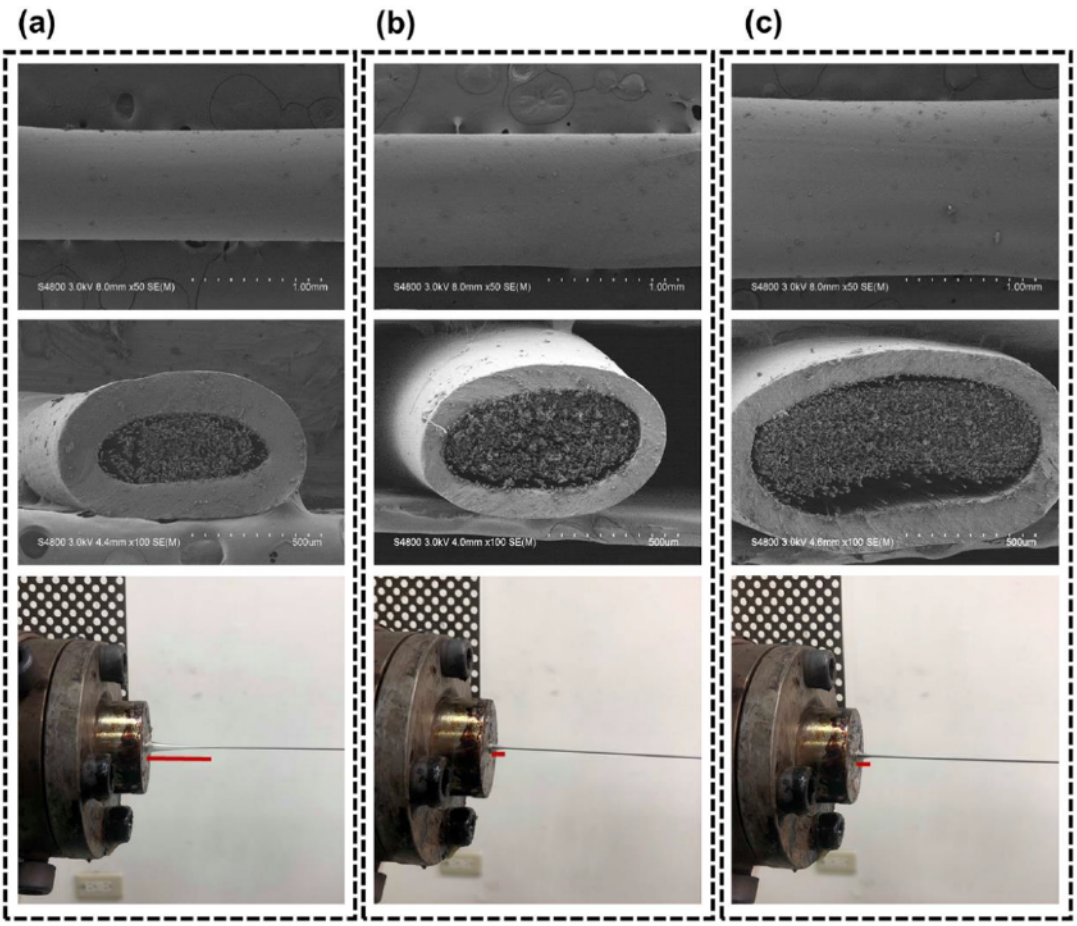

Figure 4-3. SEM images showing the morphology of composite carbon fibers: (a) 1.5K-CCF, (b) 3K-CCF, and (c) 6K-CCF.

Figure 4-4 shows the SEM images of the interface in CCFs. The physical bond between the TPU blend and carbon fibers is illustrated in Figure 4-4 (a). Given that carbon fibers have a high density and the TPU blend cools efficiently, TPU only coats carbon fibers instead of saturating them as indicated by the red rectangle in Figure 4-4 (b). In this case, CCFs obtain a high softness, while carbon fiber tows are protected. Figure 4-4 (c) shows the morphology of the interface between the TPU blend and carbon fibers, indicating that the bond is formed when the TPU blend cools and is adhered to carbon fibers. Thus, the morphology of CCFs is built on the fiber packing and the TPU content. Figure 4-4 (d) shows that some proportions of carbon fibers are embedded in the TPU shell, which in turn improves the mechanical properties of CCFs. Subsequently, it facilitates the propagation of load and reduces the friction caused by carbon fibers when a force is exerted [17].

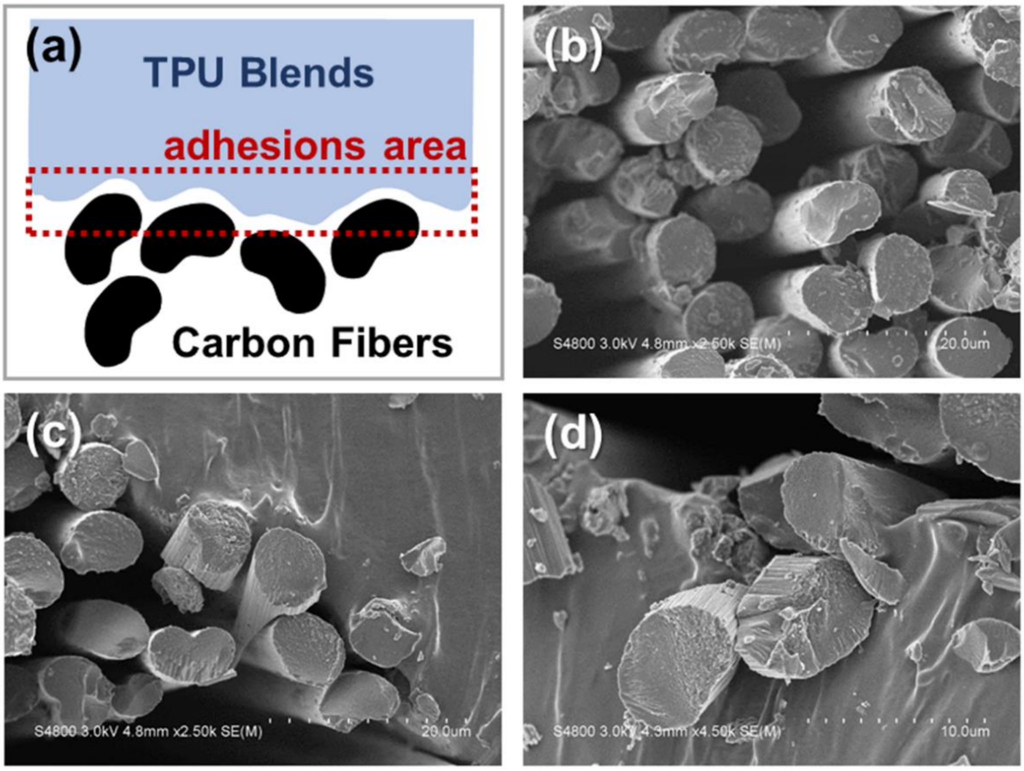

Figure 4-4. (a) TPU/carbon fiber interface: (b) fiber bundle, (c) interface between TPU and carbon fibers, and d) embedded carbon fibers in the TPU shell.

4.3.2 Tensile Properties of CCFs

Figure 4-5 (a) shows the microscopic images of 1.5K-CCF, 3K-CCF, and 6K-CCF with different thicknesses, and they can be bent as shown in Figure 4-5 (b). Carbon fibers have a low strength along the diameter, and they cannot be knotted. By contrast, the proposed CCFs can form knots without being unfastened due to the friction caused by the TPU blend. In addition, the hairiness of carbon fibers is absent in the knots (Figure 4-5(c)). This result is consistent with the ability of the TPU blend to form a shell to protect the carbon fibers. Besides, previous studies also substantiated that original carbon fibers with a sleek surface were susceptible to slippage in response to a bending stress, yet the presence of TPU with a high friction enhanced the knotting performance of carbon fibers [18]. Afterwards, CCF morphology is observed after the tensile strength test. Figure 4-5 (d) shows that when 1.5K-CCF is expanded, the core (carbon fibers) exhibits slippage. The TPU shell recovers and forms a curve in the presence of CCFs' failure. Figure 4-5 (e) shows that 3K-CCF with an oval cutting section changes the initial damage mode in the tensile test. The carbon fibers demonstrate slippage and failure, instead of brittleness fracture. Figure 4-5 (f) shows the morphology of 6K-CCF after the tensile test, and this group exhibits the lowest slippage level compared with that of other groups. Moreover, a thin TPU shell is prone to fracture, which separates the core and the TPU shell. The interfacial contact between two constituent materials in the double-layered CCF is undoubtedly the most crucial position where the mechanical properties can be reinforced. The SEM image in Figure 4-4 shows that there are only a few fibers are embedded in the interface. This phenomenon then causes delamination in the double-layered structure. At the same time, another interesting finding is that this phenomenon also changes the damage pattern of composite fibers and fabrics while generating a soft feature of yarns when a load is externally applied to them. The conduction of co-extrusion provides the fibers with more voids, which is exactly the factor that the composite yarns become softer. In addition, the composite yarns mainly have the load propagated via the spatially restricted carbon fibers. Hence, carbon fibers is the primary source of supporting strength while the TPU shell serves as a protective layer for carbon fibers. Figure 4-5 (g) shows that the tensile strength of CCFs is not correlated with the co-extrusion technique. Despite an improved failure mechanism, the tensile strength of 3K-CCF increased by twofold compared with the 1.5K-CCF, so is the case of 6K-CCF compared with 3K-CCF. This result also further confirms that co-extrusion technique provides carbon fibers with stability and protection without compromising the original good tensile properties.

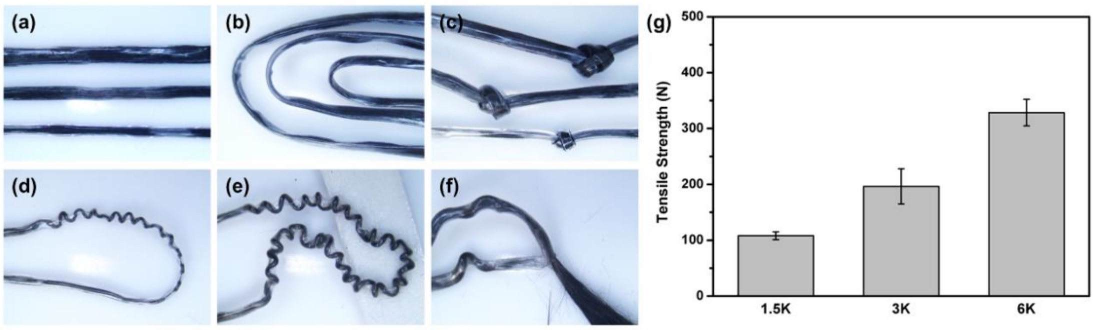

Figure 4-5. Images of the (a) morphology, (b) bending, and (c) knots of CCFs. Images of (d) 1.5K-CCF, (e) 3K-CCF, and (f) 6K-CCF after the tensile test. (g) The tensile strength of CCFs.

4.3.3 Morphology of Composites

Figures 4-6 (a–c) show the morphologies of woven composites with a specified warp yarn of HMLS polyester fibers. During the woven fabrication, a shuttle is used to induce the weft yarns (i.e., 1.5K-CCF, 3K-CCF, or 6K-CCF). Weft insertion requires a great fraction, whereas original carbon fibers require less friction, which makes the fabrication difficult. The TPU blend is used as the shell to compensate for the negative effects of carbon fibers. Figures 4-6 (a–c) show that woven composites are composed of evenly interlaced warp and weft yarns; thus, CCFs counteract the torsion resistance of carbon fibers, thereby maintaining the good morphology of the woven fabrics. With the same fabrication condition, 1.5K-CCF-Woven has the lowest density, while 6K-CCF-Woven has the highest density, which is ascribed to the CCF diameter. Figures 4-6 (d–f) show the morphology of knitted composites. 1.5K-CCF consists of an unstable loop size and a thick TPU shell that lead to a rugged surface. Although loops are interlocked, it is difficult for the elastic TPU shell to secure the loop formation. By contrast, 3K-CCF-Knitted has a more even loop structure than 1.5K-CCF-Knitted (Figure 4-6 (e)), suggesting that the ratio of the core is an important parameter to CCFs. In addition, a great amount of carbon fibers also fixes the loops in place and generates a stabilized structure. Although 6K-CCF has a great amount of carbon fibers, it does not have a good knitting structure (Figure 4-6 (f)). A flat formation and a large diameter make the knit process of 6K-CCF challenging. Its morphology is barely shown in the image, but the manufacturing of 6K-CCF-Knitted still fails to gain good quality. Given that 6K-CCF cannot be interlocked with the new loop after being removed from the old loop, 6K-CCF has a considerable compression and friction. The resulting loops are not formed in a specified size and are prone to fracture. 6K-CCF-Knitted is thus excluded from the following EMI SE test.

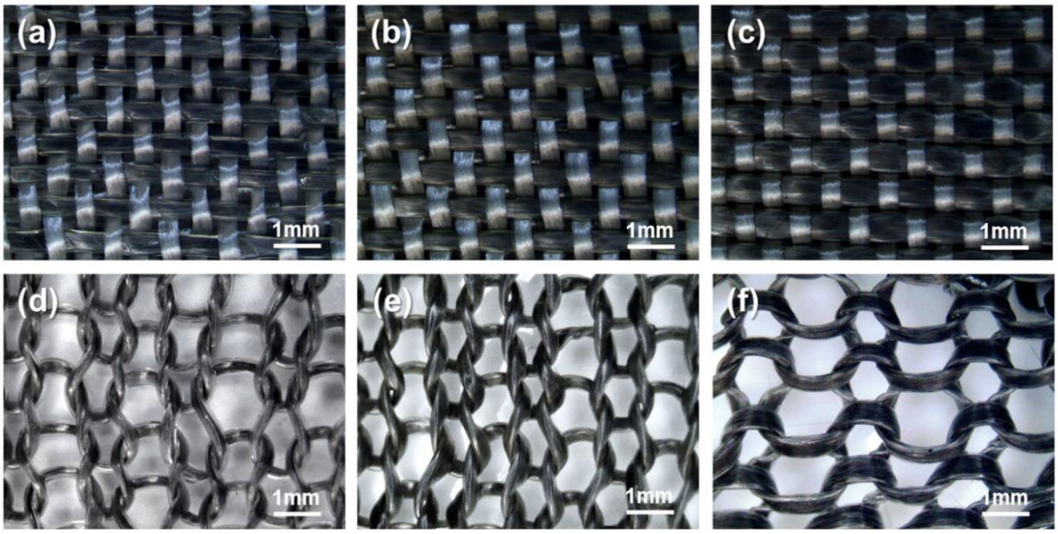

Figure 4-6. Morphologies of woven composites of (a) 1.5K-CCF-Woven, (b) 3K-CCF-Woven, and (c) 6K-CCF-Woven and knitted composites of (d) 1.5K-CCF-Knitted, (e) 3K-CCF-Knitted, and (f) 6K-CCF-Knitted.

4.3.4 Tensile Properties of Woven and Knitted Composites

Figure 4-7 (a) shows the tensile strength of woven composites that are expanded along the weft direction. 1.5K-CCF-Woven and 3K-CCF-Woven have comparable tensile strength values, which are 697.66 and 710.67 N, respectively. The tensile strength of 6K-CCF-Woven is 1193.13 N. Given that 1.5K-CCF-Woven has a thick TPU shell while 3K-CCF-Woven has many fiber counts per tow. This result suggests that two constituent materials have a physical bond that is helpful to the tensile strength of woven composites. Figure 4-7 (c) indicates the load–displacement curves of woven composites. Regardless of whether it is 1.5K-CCF-Woven, 3K-CCF-Woven, or 6K-CCF-Woven, the woven composites exhibit a high rigidity similar to carbon fibers. When the TPU shell of woven composites is expanded, that is, it extends until the sample is fractured. The presence of TPU shell changes the failure mechanism of CCFs, but the residual tensile force of the woven composites is low [19].

Figure 4-7 (b) shows the tensile strength of knitted composites, and the samples are expanded along the loop direction. The test results show that the tensile strength of 3K-CCF-Knitted (77.03 N) is higher than that of 1.5K-CCF-Knitted (18.04 N), which suggests that the knit density is a crucial factor in tensile strength. 3K-CCF-Knitted has a compact structure and an even loop size and can transmit a great load during the tensile test. Conversely, the loose structure of 1.5K-CCF-Knitted is fragile and subjected to fractures. Figure 4-7 (d) shows the load–displacement curves, and the two knitted composites have different trends in the curves. 1.5K-CCF-Knitted has a high displacement and low tensile strength, but the opposite is the case for 3K-CCF-Knitted.

Figures 4-7 (c) and (d) compare the load-displacement curves of the woven and knitted composites. Woven composites exhibit typical brittleness fracture, high tensile strength, and low displacement as samples exhibit displacement for failure. By contrast, the knitted composites exhibit greater strain than woven composites, which is ideal as expected. CCFs made via the co-extrusion technique are as soft as ordinary yarns, thereby facilitating fabrication. The test results prove that knitted composites have the vertical elasticity because of weft-knitting; the greater the density, the higher the tensile strength of knitted composites.

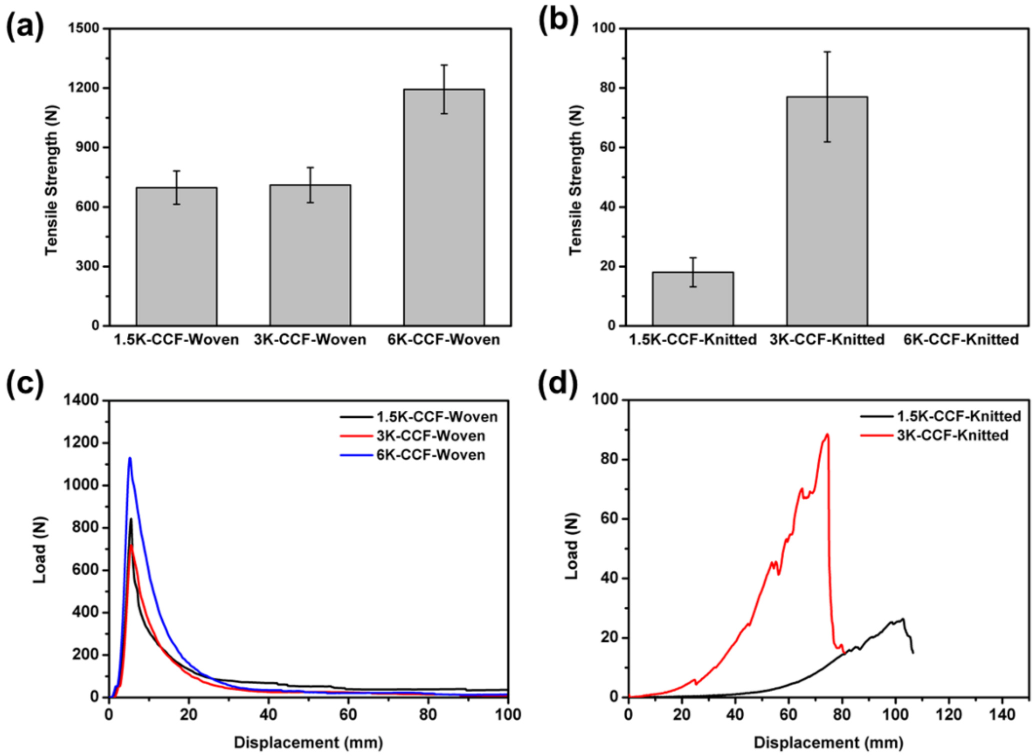

Figure 4-7. Tensile strength of (a) woven composites and (b) knitted composites, and load-displacement curves of (c) woven composites and (d) knitted composites.

The morphology of the fractured loops in the knitted composites is difficult to observe. Woven fabrics are observed for the tensile fracture to determine the failure mechanism (Figure 4-8). Given the different densities, 1.5K-CCF-Woven, 3K-CCF-Woven, and 6K-CCF-Woven show different compact structures. Figure 4-8 (a) shows the fractured morphology of 1.5K-CCF-Woven whose small density allows the slippage and aggregation of the HMLS polyester yarns, resulting in 1.5K-CCF deformation. The deformed CCFs in the woven fabrics exhibit a similar failure mechanism, such as single CCF, and the TPU/carbon fiber delamination is absent, yet both of the two materials are expanded, while the carbon fibers fail because of the slippage along the axial direction. At the same time, TPU shell also becomes curly due to relaxation. Figure 4-8 (b) shows that during the tensile test, woven composites first undergo deformation, after which the friction between the warp and weft yarns rises. Moreover, 6K-CCF-Woven has a failure mechanism that shows an instant fracture. A core–shell structure and a right shell/core ratio are crucial for the failure mechanisms of CCFs, which is in conformity with the expanded morphology of woven composites. Hence, the physical bond between the TPU shell and carbon fibers forces CCFs to glide axially, instead of entangling. Thus, friction gives rise to hairiness and eventually breaks the CCFs. The slipped carbon fibers are first expanded with the TPU shell, followed by being entangled and eventually fractured.

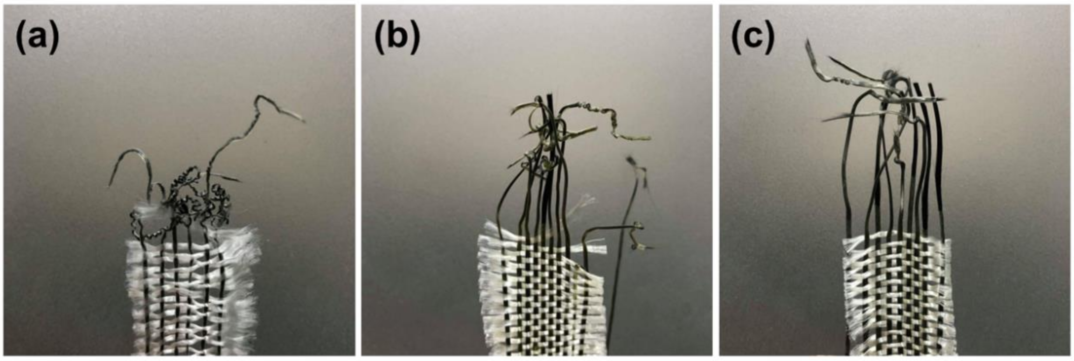

Figure 4-8. Morphologies of the expanded woven composites of (a) 1.5K-CCF-Woven, (b) 3K-CCF-Woven, and (c) 6K-CCF-Woven.

The user ends of carbon fiber composites require good electrical and thermal conductivities. The shielding effectiveness of carbon composite fabrics is a widespread knowledge. A previous study indicated that the EMI shielding effectiveness was dependent on the intrinsic conductivity, aspect ratio, and connection of the fillers. The study explored the difference in the shielding performance between composites that consisted of ABS that was separately made of carbon nanotubes and graphene. The test results indicated that the group containing oxidized graphene and carbon nanotubes showed EMI SE of 49.6 dB while the groups containing multi-walled carbon nanotubes and carbon nanotubes exhibited EMI SE of 38.6 dB and 36.7 dB, respectively [20]. Namely, with carbon-based materials as a polymer filler has a positive influence on strengthening the EMI SE. However, different carbon materials exhibit different reinforcement effects. Successively arranged carbon fibers can enhance and connect the conductive network in an insulating composites, and a rise in the thickness also helps carbon-based materials to attain a synergistic effect in mechanical and functional properties. Furthermore, previous studies also investigated the effects of internal transmission of composites on blocking EMI, and a rise in the thickness attenuated a greater level of EMI [21]. In addition, another study also indicated that carbon fiber composites had SE of 11-29 dB, and the synergistic effect of sample thickness and PU foam structure provided the carbon black PU foam with SE as high as 10-31 dB [22]. Therefore, two parameters, composite types and sample thickness are also used in this study for further investigation.

Therefore, the EMI SE of woven composites and knitted composites is examined. Figure 4-10 (a) shows that the EMI SE is -8.03 dB for 1.5K-CCF-Woven, -8.15 dB for 3K-CCF-Woven, and -8.33 dB for 6K-CCF-Woven in the frequency range between 30 and 3000 MHz, which suggests that the EMI SE does not depend on the content of carbon fibers. This result is surmised due to the presence of the warp yarns (i.e., HMLS polyester yarns) of woven composites, which is not conductive. Therefore, the three groups have EMI SE along the weft direction showing a smaller difference because they all have CCFs as the weft yarns. Two layers of woven composites are laminated in 0°/90° angle, after which the EMI SE is examined again. A rise in the fiber content leads to the EMI SE of -24.20 dB, -27.85 dB, and then -29.53 dB in order. The average EMI SE of three types of CCF-Woven increases from -8.17 dB to -27.20 dB, indicating that the reinforcement is higher than 233 %. To sum up, the compact structure of laminated double-layered woven fabrics contributes to good EMI SE. The strips of CCF regions are crossed or overlapped to form a good 3D shielding network. Among the studies on carbon-based composites, there are quite few studies regarding single-layered porous EMI fabrics. However, Xing et al. proposed a multi-layered carbon fiber composites, and the yielded EMI SE was improved as a result of the number of lamination layers. The EMI SE was -13.5 dB and -30 dB for the single-layered and five-layered composites, respectively [23]. On the other hand, materials with EMI SE >20 dB are capable of shielding 99.0 %electromagnetic waves in the commercial applications [24].

Figure 4-10 (b) shows the EMI SE of knitted composites. As for 1.5K-CCF-Knitted and 3K-CCF-Knitted, the EMI SE is -8.75 and -8.99 dB, respectively. However, knitted fabrics exhibit good EMI SE in a broader frequency range than the woven composites. Besides, the curves of EMI SE for 1.5K-CCF-Knitted and 3K-CCF-Knitted are not similar. The weft-knitted structure is composed of a single yarn in interlocked loops, which in turn provides knitted composites with even EMI SE. This result also shows the density of weft-knitted composites is pertinent to EMI SE critically [25]. Moreover, when the double-layered 1.5K-CCF-Knitted and 3K-CCF-Knitted composites are laminated in 0°/90°, they exhibit a comparable frequency range. The double layers increase both knitted groups with a high density, so the EMI SE is -16.73 dB for 1.5K-CCF-Knitted and -17.42 dB for 3K-CCF-Knitted. The employment of the coextrusion process enables CCF being wrapped in TPU layer, which facilitates the fabrication of carbon fibers and then the knitted composites. The composites are then laminated in order to increase the density of CCF, thereby strengthens the EMI effectiveness of the materials. Notably, the two groups have similar EMI SE because the space of voids among knitted fabrics is decreased, which also indicates that the distribution of CCFs is crucial to EMI SE.

The presence of CCFs provides woven composites and knitted composites with good EMI SE. The TPU shell of CCFs is not conductive; therefore, the EMI SE mechanism of woven composites and knitted composites could be ascribed to reflection, absorption, and multiple reflection. In addition, the carbon fibers of CCFs have high electrical conductivity, which involves the reflection shielding by moveable charge carrier, as well as the absorption shielding by Ohmic loss by the resonance of six-membered rings in carbon when exerting an electromagnetic energy [16]. However, a lamination configuration further enhances the shielding effectiveness, and CCFs serve as electric dipole, intensifying the energy of polarization dissipation [16]. Besides, the TPU blend is an elastomer, which forms additional voids between two layers of woven composites or knitted composites. An increase in the coverage of CCFs also improves the interface between different materials, which in turn constantly changes the impedance of electromagnetic waves and triggers multiple reflection loss (Figure 4-9 (b)) [26-28]. In summary, CCFs made by co-extrusion technique contain numerous carbon fibers enwrapped in the extruded TPU blend. After CCFs are made into fabrics, the fabrics also feature good matrices and fiber distribution, which has a positive influence on the EMI SE of woven composites and knitted composites. Composed of a multiple-layered lamination, the woven composites attain EMI SE of -32.96 dB at 1800 MHz and -44.99 dB at 2450 MHz. The resulting composites have shielding effects against electromagnetic hazards and with good application prospects [29].

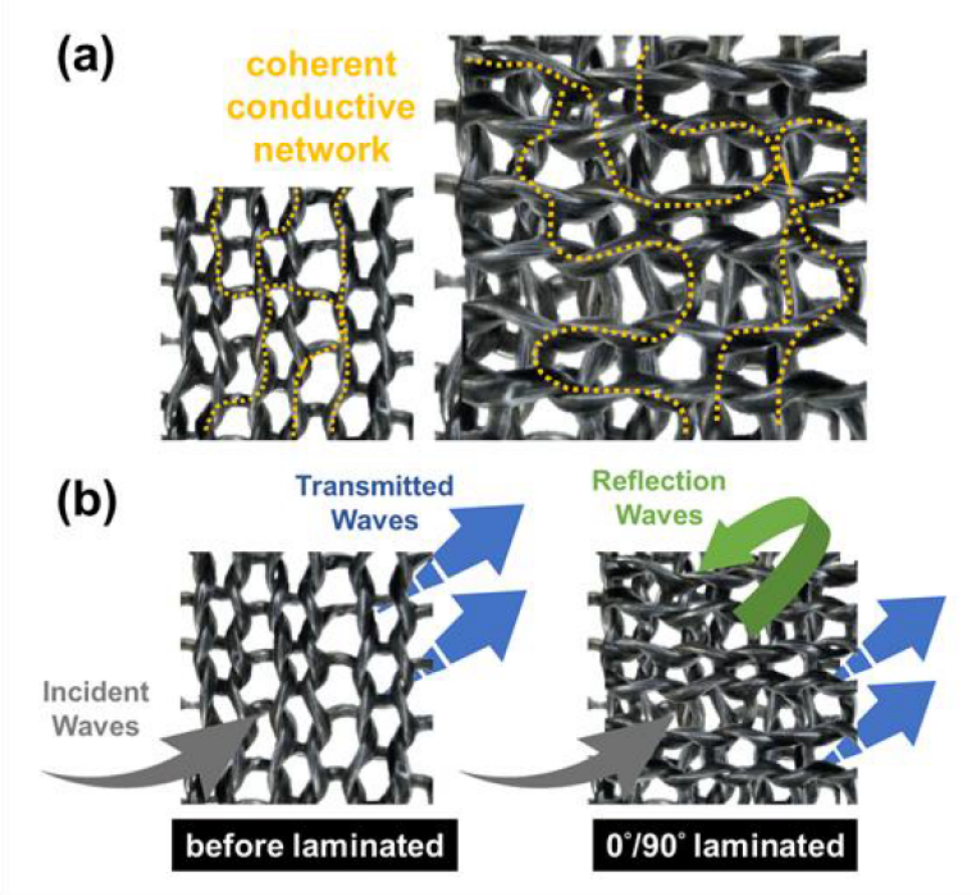

Figure 4-9. Diagrams of (a) a conductive network and (b) shielding mechanism of laminated samples.

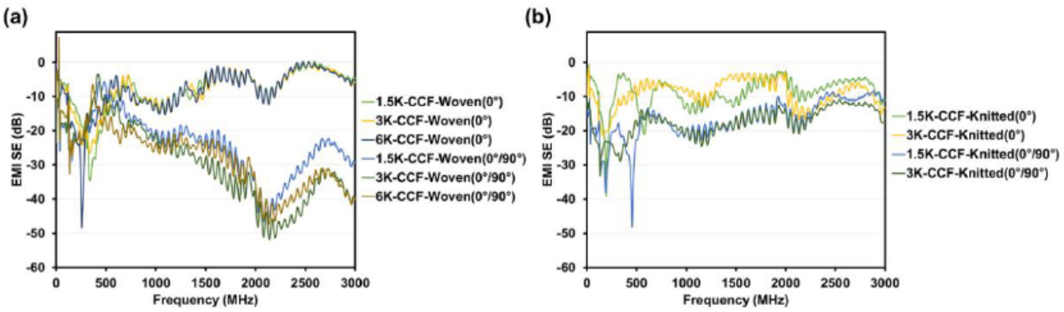

Figure 4-10. EMI SE of (a) woven composites and (b) knitted composites.

4.4 Conclusions

This study successfully combines carbon fiber tows and a TPU blend via the co-extrusion technique. The TPU blend is extruded to wrap carbon fibers and serves as the shell. The resulting CCFs retain good softness. Carbon fibers are aggregated well, and the cutting section of CCFs changes from a flat tow to an oval shape. The effects of the fiber counts per tow on the morphology and tensile strength are examined. For 1.5K-CCF and 3K-CCF, the presence of TPU shell improves the fracture mode of CCFs because carbon fibers slip with the TPU shell along the axial direction, thereby improving the brittleness fracture of carbon fibers caused by friction. Moreover, friction during the manufacturing of CCFs is reduced using co-extrusion technique, and CCFs can be made into woven composites and knitted composites with softness and elasticity similar to those of ordinary fabrics. The resulting woven composites and knitted composites that yield the same failure mechanism as CCFs. Finally, double-layered woven composites and knitted composites in a 0°/90° lamination have EMI SE of -27.20 and -17.08 dB, respectively. The preliminary results of this study suggest that using co-extrusion technique can continuously process carbon fiber tows. The resulting CCFs are suitable for fabrication. As such, the feasibility of carbon fiber composites is advanced, and an innovative approach that facilitates the applications of the proposed composites is provided.

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Chapter 5 – Extrusion/Hot Pressing Processing and Laminated Layers of Continuous Carbon Fiber/Thermoplastic Polyurethane Knitted Composites

5.1 Introduction

Combining fibers and polymer is an effective and commonly used method to form mechanically robust composites. In general, the filling fibers are not continuous and are dispersed in the polymer matrices, which can transmit external forces while mechanically strenghening the composites. Nonetheless, a greater structure can be attained simply by the production of conventional composites and the reinforcement of continuous fibers. These composites are usually in one piece or prepared with specifically custom-made Z-axis fabrics as the stress carrier; therefore, the composites have a high fiber content and structure stability [1, 2]. In particular, composites composed of carbon fibers have a light weight, low density, and high strength and thus are commonly applied to the vehicle, machinery, and aerospace industries [2-6]. Composites composed of thermoplastic polymer and carbon fibers have advantages. In addition to the recycling feasiblity and formability of thermoplastic polymer, the production cost is also low and the production is effective [7, 8]. Other than the selections of fibers and polymers, the number of lamination layers, interfacial adhesion, and fiber orientation also influence the mechanical properties of the resulting composites [4].

As a typical elastic polymer, thermoplastic polyurethane (TPU) possesses ideal properties because it is a block copolymer composed of hard segments and soft segments, the former of which provides strength while the latter of which provides elasticity [9]. Furthermore, the combination of TPU and carbon fibers contributes to a synergistic effect that carbon fibers can strengthen TPU while TPU improves the resilience of composites and the constituent carbon fibers [10-12]. As a result, there are a great number of studies investigating high-malleability thermoplastic composites and the combination of carbon fibers. Qu et al. used thermoplastic polyurethane (TPU) at different molecular weights. TPU and epoxy resin were combined to produce toughening carbon fiber reinforced plastics (CFRP). The test results indicate that TPU with a low viscosity increases the wettability between CFRP and epoxy resin, thereby increasing tensile strength. Furthermore, TPU prevents the crack growth of CFRP [13]. Aravind et al. incorporated 3D printing with continuous carbon fibers, producing CCF/PLA composites. For the starter, continuous carbon fiber tows were processed with twisting; during 3D printing, the voids among the twisting angles facilitate the entry of PLA, subsequently improving the mechanical properties of CCF/PLA composites [14]. Dong et al. combined continuous carbon fibers and carbon nanotubes via extrusion to synthesize TPU and PLA and form shape memory composites. Test results indicated that the presence of carbon fibers positively influences the mechanical properties of composites and provides composites with a light weight [15]. Pascual-González et al. indicated that continuous carbon fibers for direct use could be produced into functional spare parts with a sophicated and custom-made production; however, this process is difficult to realize with regular methods. Therefore, they used 3D printing to peroduce carbon fiber composites and examined the influence of post processing over the composites. The test results indicate that the employment of melt-deposition process is difficult for continuous carbon fibers because of the presence of air. By contrast, the post-processing is substantiated to be beneficial for a rise in the crystallinity, which in turn makes the composites more mechanically robust [16].

In sum, carbon fibers at an original state have been processed and then combined with thermoplastic materials in many recent studies. Also, carbon fibers have been commonly used for obtaining the EMI shielding functions because they have fine electrical conductivity. The mechanism of EMI shielding effectiveness is introduced as follows. The electromagnetic energy is attenuated and blocked between two areas or components based on the reflection and absorption theories, thereby decreasing the negative influence exerted by EMI electromagnetic energy. Moreover, the EMI shielding effectiveness of composites is depednent on the inherent conductivity, aspect ratio, and the combination manner of conductive materials [17]. Hence, it has a positive effect of EMI shielding effectiveness incorporate carbon serial materials as fillers for polymers. Continuous carbon fibers enhance the integration of conductive network of insulating composites, while a rise in the thickness also achieves a synergistic effect, strengthening the mechanical and functional properties of composites. Hence, we could develop a greater diversity of thermoplastic composites while exploring more potential application value.

In our previous study, continuous carbon fiber tows and TPU were processed with the extrusion method to form compound carbon fibers. With the TPU coating, the resulting compound carbon fibers are firmly bonded and thus gain greater tensile properties [18]. Two TPUs at different molecular weights were used to provide compound carbon fibers with an oval cross section other than a flat cross section to facilitate the subsequent fabrication [19]. Meanwhile, the influence of the content of the interior carbon fiber tows was also investigated. An excessively low carbon fiber content requires a thicker TPU sheath, which causes a distinct interface between carbon fiber tow and TPU. Thus, fabrics composed of such carbon fiber composites may have an uneven structure because of the low bending level of the composites. By contrast, TPU may fail to bond an excessively high carbon fiber content. The knitting needles may be restricted to the small voids among compound carbon fibers; thus, high friction forces among fibers could break the carbon fibers [20]. The basic properties, manufacturing process, and fabrication parameters of compound carbon fibers have been discussed, whereas those of carbon fiber knitted composites remain unclear.

Therefore, this study continues to produce TPU-cladded continuous carbon fibers with an attempt to create a three-dimensional structure for carbon fiber knitted composites. In this study, carbon fiber tows are directly processed, after which the bi-layered compound carbon fibers are prepared into carbon fiber knitted composites. Herein, the outer TPU layer enhances the friction resistance of carbon fiber composites while retaining the softness of carbon fiber tows. Next, the knitted composites are laminated and then hot pressed, after which their morphology, softness, elasticity, tensile properties, and electromagnetic interference shielding effectiveness (EMI SE) are characterized. As a result, the proposed TPU-cladded carbon fiber tows can be made into knits with a structural stability and better abrasion resistance of the carbon fibers. The size of soft carbon fiber knitted composites has no limits, suggesting a major breakthrough in the production of continuous carbon fibers that are suitable for automobile spare parts and aerospace applications.

5.2 Experimental

5.2.1 Materials and Fabrication of Carbon Fiber Knitted Composites

Table 5-1. Specifications of materials in the experiment.

Materials	**Specification**	**Suppliers**
Carbon Fibers (TC-33)	PAN Sizing Agent: water-based epoxy resin Unit: 3K Yield Tex (g/ 1000 m): 200 Density (g/cm^2): 1.8 Filament Diameter (μm): 7	Formosa Plastics Corporation, Taiwan
Thermoplastic polyurethane, TPU	Polyester Type (HE-3285ALE) Hardness (SHORE A/D): 87A Melt Viscosity (POISE): 2818 (50Kg/ 200 °C) Melt Point (°C): 140 Melt Flow Index: 7.03 g/10 min (175 °C/ 2.16 Kg) Polyester Type (HM-3580AU) Hardness (SHORE A/D): 83A Melt Viscosity (POISE): 3000 (50Kg/ 200 °C) Melt Point (°C): 110 Melt Flow Index: 7.25 g/10 min (175 °C/ 2.16 Kg)	Headway Polyurethane Company, Taiwan

Table 5-1 shows the specifications and sources of materials. For the starter, the melt-blending method is used to blend two types of TPU at a ratio of 85/15 wt% via an extruder. Two TPU types with different molecular weights and different viscosities significantly improve the bonding between TPU and carbon fiber tows [19]. Two types of TPU, including HE-3285ALE and HM-3580AU (Headway Polyurethane Company, Taiwan), are blended at a ratio of 85:15 wt%. HM-3580AU is an eco-friendly polyadipate hot-melt adhesive. Carbon fiber tows (Formosa Plastics Co., Taiwan) have a count of 3 K.

For the starter, TPU pellets are dried at 70 °C in an oven in advance to remove the moisture from the pellets and reduce the drawbacks of composites. The TPU blends are processed at a rotary speed of 240 rpm in an extruder with single-screw (Sun Ying Machinery Co., Taiwan) equipped with section temperatures of 155°C–160°C–165°C–170°C–175°C. Through a concentric double-ring mold (Figures 5-1 (a, b)), the blend is extruded to coat the carbon fiber tows at an extrusion rate of 11.88 g/min. Next, the TPU-cladded carbon fiber tows are stretched via a roller, cooled in water bath, and finally coiled at a rate of 25 rpm, forming compound carbon fibers. Figure 5-2 shows the fabrication of carbon fiber knitted composites. The compound carbon fibers are fabricated using a flat knitting machine (3.5 gauge needles, Sheng Meei Machine Manufacturing Company, Taiwan), as shown in Figure 5-2 (a). During the knitting process in Figures 5-2 (b, c), compound carbon fibers are very soft and the knitted loops are interlocked well. Additionally, Figure 5-2 (d) are diagrams comparing the carbon fiber tows as related to the TPU coating. The TPU coating layer prevents carbon fiber tows from friction or hairiness, while increasing the flexiblity concurrently. Afterwards, two, four, or six layers of carbon fiber knitted composites are laminated along the same direction and then processed with hot press (Yii Fuu Industrial Company, Taiwan) at

160 °C with a pressure of 5 MPa for 1 min. Samples are then cooled at room temperature and trimmed with a specified size, as shown in Figure 5-1 (c), forming carbon fiber knitted composites. Hot pressing stabilizes the shape of sample to a certain extent, which is ascribed to the TPU outer layer. Figure 5-1 (d) shows the lateral view of the samples. The test results indicate that the carbon fiber knitted composites demonstrate a thickness that is in direct proportion to the number of lamination layers, which is 1.56±0.05 mm for two layers, 2.39±0.08 mm for four layers, and 3.40±0.08 mm for six layers.

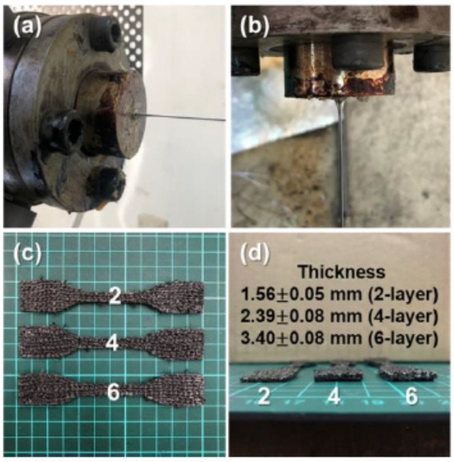

Figure 5-1. Images of (a) extrusion mold, (b) extrusion process, (c) front of the sample, and (d) lateral view of sample.

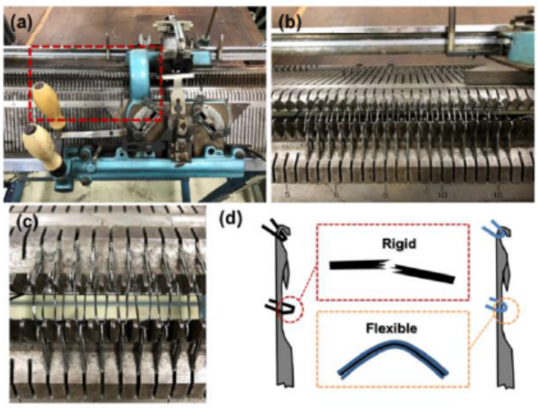

Figure 5-2. Images of (a) overlook of the knitting machine as well as (b) and (c) carbon fibers and knitting needles. (d) Illustrative diagram showing the protection of TPU layer over carbon fiber tows.

5.2.2 Characterizations

Samples undergo gilding for 60 seconds using an Ion Sputter (E-1010, HITACHI, Japan). Next, a field-emission scanning electron microscope with a voltage of 3.0 kV, (FE-SEM, S-4800, HITACHI, Japan) is used to observe the cross section and interfacial morphology of carbon fiber knitted composites.The images are intercepted and processed using the Toup View software (Hangzhou ToupTek Photonics Co., Ltd, China), and then the surface morphology is examined under a stereomicroscope (SMZ-10A, Nikon Instruments Inc., Japan).

The resilience of the samples is measured using a vertical rebound resilience tester. The 2-, 4-, and 6-layered carbon fiber knitted composites are trimmed into 100 mm*100 mm squares. Ten samples for each specificaiton are used. Samples are affixed to the platform, and the drop weight resilience rate is recorded.

The tensile properties of the samples are evaluated at a test rate of 5 mm/min and a static load cell of 10 kN using an Instron 5566 (Instron 5566 Universal Tester, US). The 2-, 4-, and 6-layered carbon fiber knitted composites are trimmed into dumbbell-shaped as specified in ASTM D638-14 Type IV. Ten samples for each specificaiton are used.

A spectrum analyzer (KC901S, TS RF Instruments Co., Ltd., Taiwan) is used to measure the EMI SE of the samples (150 mm x 150 mm) in a frequency range of 100 KHz–3 GHz. The calibration is conducted as specified in ASTM D4935. EMI SE is computed according to Equation 5-(1), where P_{in} is the incident power, P_{in} is the reflection power, SE_R is the surface reflection, SE_A is the electromagnetic absorption, and SE_M is the multiple reflection loss [21, 22].

$$\mathrm{SE} = 10\log(\frac{P_{in}}{P_{out}}) = SE_R + SE_A + SE_M \qquad 5\text{-}(1)$$

5.3 Results and Discussion

Figure 5-3 shows the surface morphology of the carbon fiber knitted composites that are treated with hot pressing. The merits of hot pressing are that the samples can be heated thoroughly and efficiently and that the processing temperture and pressure, the thickness of samples, and the chill time can be adjusted. When being heated, thermoplastic can be melted without loss of mass, which in turn facilitates the bonding among layers effectively [23]. In the meanwhile, the heating temperature does not damage the orientation of carbon fibers as well as the fabric structure, so when the laminated composites are hot pressed once again, the voids among materials are highly reduced via the heat and pressure [24].

Figures 5-3 (a, b) show the control group, the single- and double-layered carbon fiber knitted composites. Test results indicate that single-layered composites have an even structure and high porosity caused by the knitting loop structure. The TPU-cladded carbon fibers are in interconnected loops with the TPU sheath protecting them from friction or squeezing in the curly parts. The double-layered carbon fiber knitted composites demonstrate a greater density, and the laminated knitted composites increase the area that carbon fiber tows cover. Figure 5-3 (c) shows the trimmed edge of the hot pressed carbon fiber knitted composites. Hot pressing melts the TPU sheath, and the carbon fiber knitted composites retain the knit structure as the hot pressing lasts a short time with a lower pressure. This result indicates that hot pressing improves the structural stability of carbon fiber knitted composites without compromising the protection and wrapping of TPU. Without TPU coating, carbon fibers are prone to displacement and hairiness, as indiated by red circles in Figure 5-3 (c).

Figures 5-3 (d–i) show the laminated carbon fiber knitted composites. No signficant difference is found over the surface of knitted composites regardless of the number of laminaton layers. The 2-, 4-, and 6-layered carbon fiber knitted composites demonstrate the knit structure, and the melted TPU further strengthens the lamination effect. These results suggest that hot pressing exerts a positive influence on the bonding between thermoplastic polymer composites, and the adjustment in the hot pressing parameter helps produce carbon fiber knitted composites with different thicknesses.

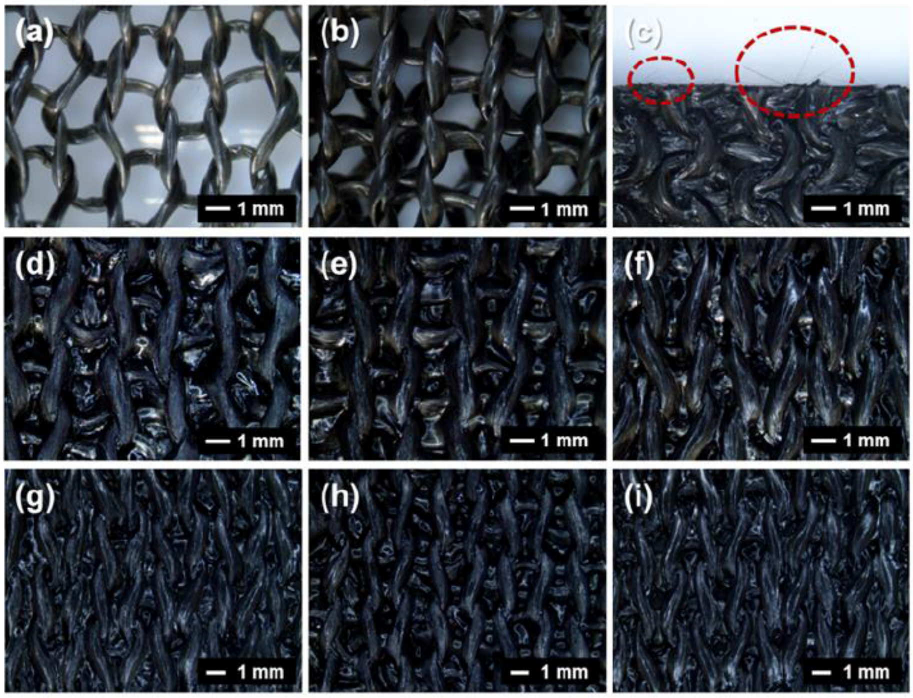

Figure 5-3. Surface morphology of carbon fiber knitted composites: (a) single- and (b) double-layered structure before hot pressing; (c) edge of a trimmed composite; (d/g) 2-, (e/h) 4-, and (f/i) 6-layered hot pressed composites.

Figure 5-4 shows the SEM images of carbon fiber knitted composites in terms of softness and cross section. Regardless of the number of lamination layers, all of the carbon fiber knitted composites are flexible, which can be ascribed to the presence of TPU. TPU is a highly resilient thermoplastic material and commonly used to produce flexible composites [25-27]. In this study, a TPU blend and carbon fiber tows are combined into compound carbon fibers, which are then fabricated into knitted composites. Afterward, the carbon fiber knitted composites are laminated and hot pressed. SEM images indicate that the TPU outer layer is melted to provide the carbon fiber knitted fabrics with a one-piece structure as a result of hot pressing and the subsequent cooling. Hot pressing is only conducted for a short time with a low pressure that is insufficient to enable TPU melt to infiltrate the interlaced carbon fiber knits. Hence, the hot pressing parameters help retain the primary knitted structure and a high flexibility of carbon fiber knitted composites.

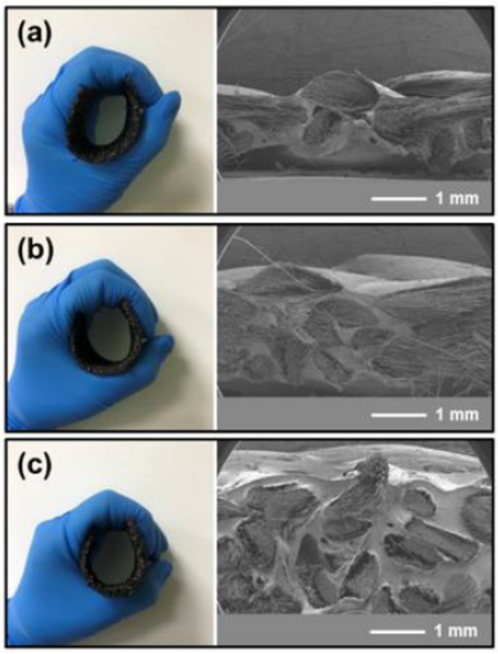

Figure 5-4. Images of (a) 2-, (b) 4-, and (c) 6-layered carbon fiber knitted composites in terms of flexibility with corresponding cross-section.

Figure 5-5 displays the SEM image of the carbon fiber knitted composites, showing the interface between the carbon fibers and the TPU blend. Figure 5-5 (a) shows that carbon fiber tows are wrapped in TPU where the carbon fibers are aligned in a tidy manner and that TPU restricts the position of the carbon fiber tows instead of infiltrating among the fibers. Figures 5-5 (b and c) are insets of the sections indicated in two circles in Figure 5-5 (a). Figure 5-5 (b) shows a loose interfacial structure of the carbon fiber composites. The carbon fibers are not damaged while being produced into knitted composites, and they are aligned parallel and do not curl in a large area. In addition, a small portion of the carbon fibers are embedded in TPU so their displacement is immobilized in the carbon fiber knitted composites, indicating that they serve as stress carriers. In other words, the aggregated carbon fibers improve the mechanical properties of the composites.

According to a previous study, the optimal mechanical performances occur along the fiber axis, which is also the extrusion direction. When polymer is extruded from the single-screw extruder, a considerable amount of fibers is also aligned along the same direction. However, when samples are damaged along the fiber axis, the majority of fibers is very likely being fractured, detached, and pulled out, and fails eventually. Only a small portion of adhered fibers that exist between the fiber/matrix interface may be pulled out and detached [28].

The micro-structure in Figure 5-5 (c) indicates that even without resin infiltration, the carbon fibers still have compact connection because of the restriction offered by the TPU outer layer. In sum, a small amount of voids in the carbon fiber knitted composites are presented during extrusion because of the adhesion and shaping of TPU over carbon fiber tows. The voids contribute to the flexibility of the carbon fiber knitted composites while restricting carbon fibers. Besides, the bending property of carbon fiber tows that have been processed is highly dependent on the wrapping material. Because of the pores in the interface, the composites consume the strength of matrices completely when being bent [29]. With the weaving process, both the properties of matrices and voids among materials make composite flexible while protecting carbon fibers from friction.

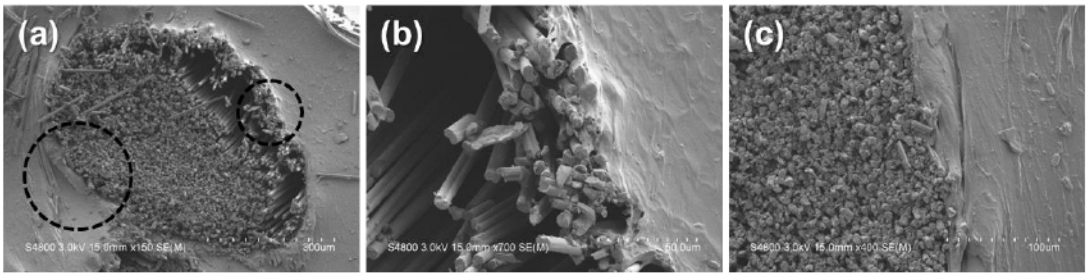

Figure 5-5. SEM images of the interface of carbon fiber knitted fabrics: (a) carbon fiber tows and (b/c) micro views of interface between carbon fibers and TPU.

Figure 5-6 shows that vertical rebound rate of the carbon fiber knitted composites is related to the number of lamination layers. The resilient TPU may exert a positive influence over the impact resistance because the carbon fiber knitted composites are flexible and can store and effectively dissipate an external force. The rebound rate increases when the number of lamination layer increases. The rebound rates of the 2-, 4-, and 6-layered carbon fiber knitted composites are 11.7%, 14.1%, and 17.7%, respectively. The results are attributed to the presence of TPU among layers. Hot pressing melts and compresses TPU, which increase the contact area and interaction between TPU and carbon fibers, thereby enhancing the entanglement of the molecular chains of the two TPU types. In addition, the TPUs re-crystalize in the subsequent cooling process and ensure the success of the intra-layer bonding and the yield of a great elastic energy. The buffering efficacy improves with increasing TPU thickness [30, 31].

Carbon fiber knitted composites are composed of knitting loops that are interlocked and have an evenly composed structure, which allows the continuous carbon fibers to convey stress efficiently [32]. Despite the specified fabric structure and size of carbon fiber knitted composites, the more the lamination layers and the more the laminated loops, the greater the fabric density. The 6-layered carbon fiber knitted composites with a high density can withstand a higher impact energy than the other composites. In conclusion, the proposed carbon fiber knitted composites are mechanically robust along the axial direction, and their vertical mechanical strength can be reinforced proportionally by laminating.

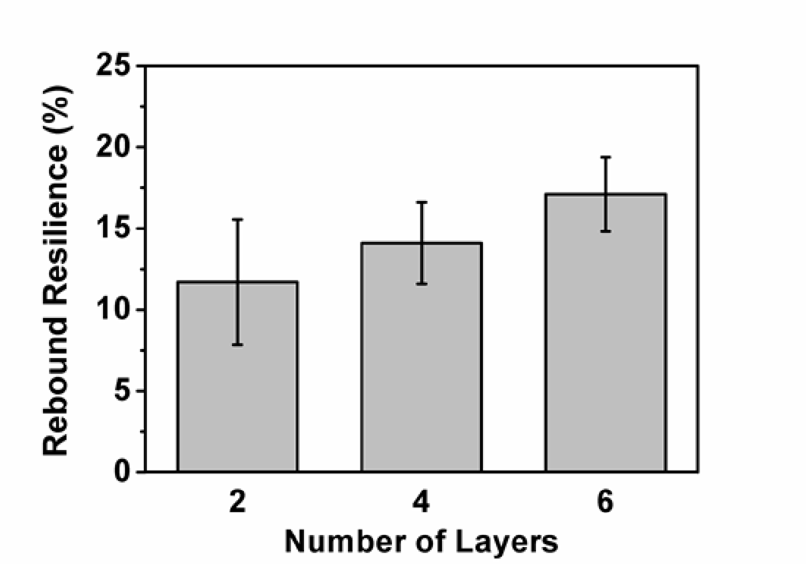

Figure 5-6. Vertical rebound resistivity of carbon fiber knitted composites.

Figure 5-7 shows the tensile properties of the carbon fiber knitted composites. Figure 5-7 (a) shows that the tensile strength is proportional to the number of lamination layers. The tensile stress values of the 2-, 4-, and 6-layerd carbon fiber knitted composites are 12.50, 29.53, and 43.72 MPa, respectively. The stress shows a rising trend because more carbon fibers are present in the knitted composites. Carbon fibers strengthen the tensile stress. The more the lamination layers, the more the carbon fibers, and the greater the tensile stress. In addition ,loops are the main structure of knits, the stability of which has a significant influence on the mechanical properties of composites. The employment of hot pressing stabilizes all the component layers, which means that the number of loops shows a declining trend with the number of lamination layers being increased. Concurrently, hot pressing also reinforce the density of fabrics. The difference in the loop formation causes different unwrapping loops phenomenon. The fractured samples exemplify that a rise in the number of layers leads to more concentrated failure of carbon fibers. The content of undone carbon fiber loops is lower in the 4-layered carbon fiber knitted composites than in the other composites.

The main goal of this study is to improve the elongation of carbon fiber knitted composites. The knitted composites exhibit stress-strain curves that feature non-typical brittleness, as shown in Figure 5-7 (b). The incorporation of TPU provides the carbon fiber knitted composites with a higher tensile strain, and the curves appear more smooth than common carbon fiber composites. Nontheless, the tensile strain and stress of carbon fiber knitted composites show different trends, and the strain initially increases and then decreases when the number of lamination layers increases. In addition, the tensile strength of carbon fiber knitted composites is dependent on the carbon fiber tows aligned along the axis, but the strain is dependent on the TPU outerlayer otherwise. Based on the test results, carbon fiber knitted composites demonstrate a tensile modulus being 0.45, 0.82, and 1.53 Mpa when the number of layers is increased from 2, 4, to 6 layers, respectively. The more the number of lamination layers, the higher the TPU content, and the higher the tensile strain. Notably, the 6-layered carbon fiber knitted composites show a strengthened rigidity. This result may be ascribed to TPU that fastens layers in position. When the laminated knitted composites are hot pressed, TPU is once again melted and thus restricts the expandsion of the knitted composites. Conversely, a greater content of carbon fibers adversely affects the strain of carbon fiber knitted composites [33]. Contrary to the results of previous studies, carbon fiber knitted composites demonstrate a two-stage failure, namely, failure of carbon fibers and failure of TPU [18-20]. Carbon fiber knitted composites are shaped in one piece because of hot pressing. They have no damage in several sections, and tensile failure is simply presented in a specified section. On the basis of the tensile test results, a knitted structure grants carbon fiber knitted composites with a longer elongation at break, and the mechanical properties of carbon fiber knitted composites are highly correlated with the number of lamination layers.

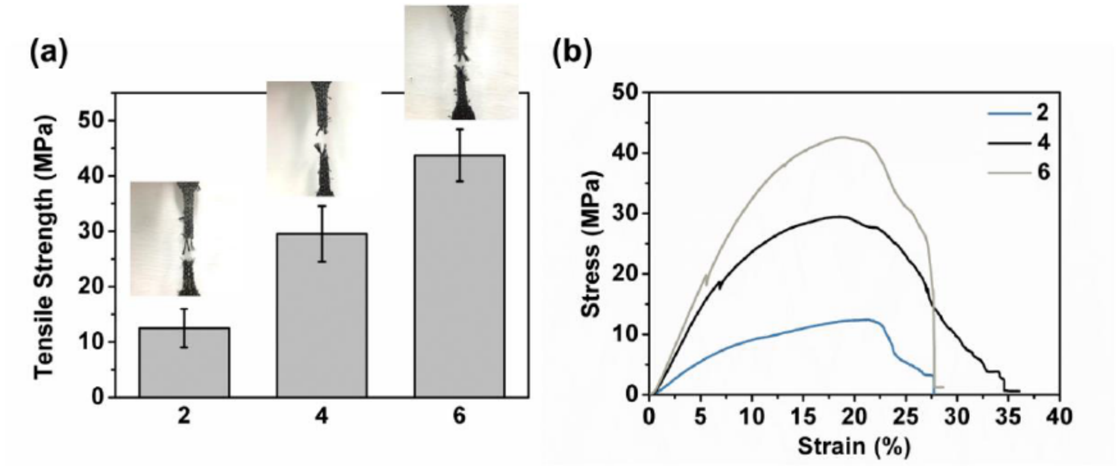

Figure 5-7. Tensile properties of carbon fiber knitted composites.

Figure 5-8 shows the EMI SE results of the carbon fiber knitted composites. When the carbon fiber knitted composites contain a large coverage of carbon fibers, they harvest the corresponding mechanical properties and EMI SE, the latter of which enables the application for electromagnetic compability and increases the added value. Figure 5-8 (a) shows that an increasing number of lamination layers has a positive influence over the EMI SE of carbon fiber knitted composites. Hence, the average EMI SE is -30.04 dB for 2-layered composites, -38.19 dB for 4-layered ones, and -48.91 dB for 6-layered ones. Randonly laminated carbon fiber knitted composites with more lamination layers have a greater coverage area of carbon fibers equivalently, generating a complete electromagnetic wave shielding network. Take 2-layered carbon fiber knitted composites as an example, caron fibers serve as a conductive layer while the TPU outer layer protects carbon fibers while providing the carbon fiber knits with flexibility. As for the 6-layered carbon fiber knitted composites, they exhibit the maximal EMI SE, suggesting that hot pressing does not affect the EMI SE.

A high density also reduces the porosity of the knitted composites, thereby improving the EMI SE mechanism [34]. The EMI shielding mechanism involves reflection by the surface, transmission, absorption by the interior, and dissipation by the multiple reflection, as shown in Figure 5-8 (b). Providing EMI SE, the carbon fibers used as the staple protection are subjected to the mobile charge carrier in the composites, and the reflectin loss in the interior attenuates a great amount of electromagnetic energy [22]. With the accumulation of carbon fiber content along with the lamination process, the six-membered ring of carbon structure triggers resonance due to the electromagnetic energy, causing ohmic loss. Meanwhile, the internal absorption loss becomes more distinct and the increasingly more voids among layers strengthen the reflection loss of electromagnetic waves [21]. In the study by Hong et al., they proved that carbon fiber composites have EMI shielding effectiveness that is associated with fiber alignment, arrangement distance, and lamination angles. In order to obtain better EMI shielding effectiveness, composites are then prepared with more lamination layers. Specifically, the 4-layered composites exhibit an optimal EMI shielding effectiveness of 28.90 dB. Furthermore, the test results also suggest that when the fiber alignment is random, the mechanism for EMI shielding effectiveness is converted from absorption to reflection, which reinforcement is provided as a whole [35]. Zhu et al. also indicated that when composites were composed of a diversity of media, there was impedance matching that further reinfored energy loss of multiple reflection. The 4-layered pure carbon fiber composites achieved 39.77 dB [36]. On top of that, EMI shielding effectiveness has a rise in demand in many appliations. When a material shows a shielding range between 0-10 dB, it is not qualifed for EMI shielding. Materials with EMI shielding effectiveess of 10-30 dB meet the requirement of daily necessities, and those with EMI shielding effectiveess of 30-60 dB for the use in the fields of industry and commerce [37]. Additionally, the lamination process provides carbon fiber knitted composites with a 3D EMI shielding network that blocks electromagnetic waves efficiently. In particular, the 6-layered carbon fiber knitted composites exhibit an EMI SE of -47.83 dB at 1800 MHz and -53.11 dB at 2450 MHz, suggesting that they can block the jeopardy of EMI, adding a new and innovative protection to this field [38].

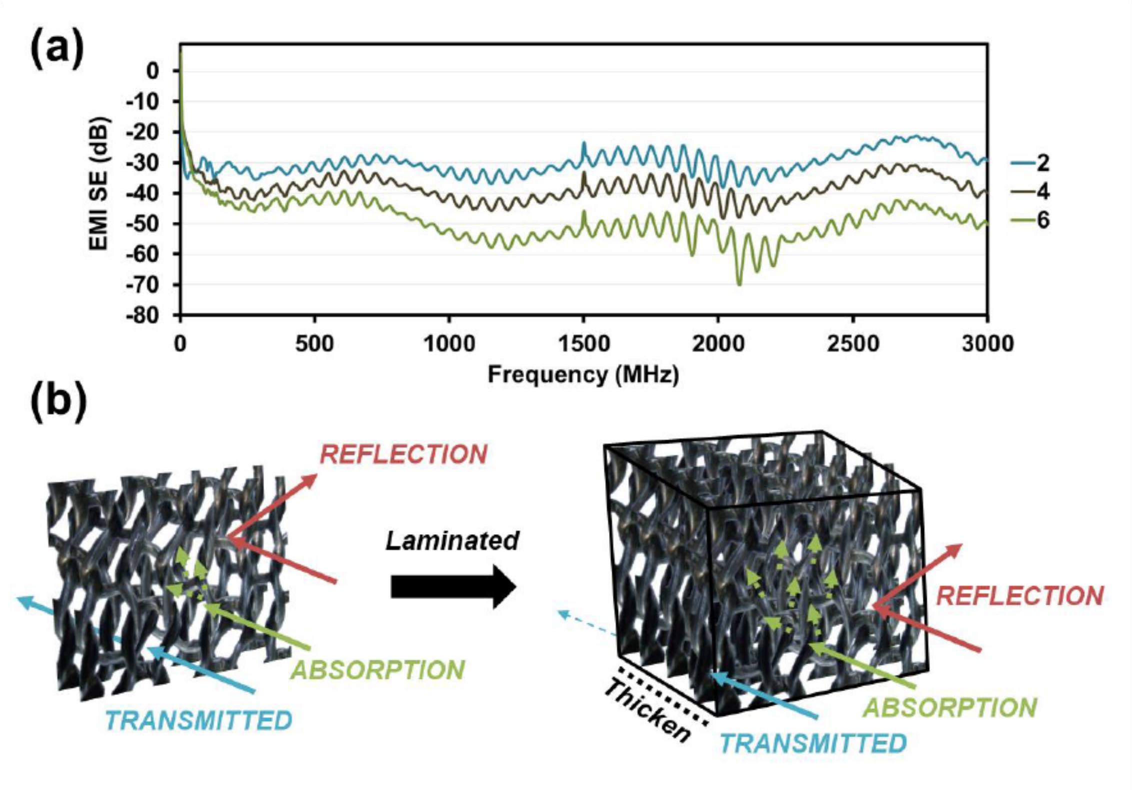

Figure 5-8. (a) EMI SE and (b) shielding mechanism of TPU/carbon fiber knitted composites.

5.4 Conclusions

Continuous carbon fiber tows and a thermoplastic TPU blend are successfully combined to form compound carbon fibers by using the extrusion method. The compound carbon fibers are fabricated into knits and then laminated. The multiple-layered carbon fiber knitted composites are composed of core–sheath fibers where the TPU outer layer can fix and protect the carbon fibers (the core). SEM images show that via hot pressing, the knitted composite layers can be effectively bonded without compromising the flexibility. In particular, 6-layered carbon fiber knitted composites demonstrate good vertical rebound rate (17.7 %), maximal tensile strength (43.72 MPa), high tensile strain, and an average EMI SE of -48.91 dB, qualifying their use as flexible electromagnetic shielding materials. The test results suggest that the production of TPU-cladded carbon fibers qualifies continuous carbon fibers for subsequent processes and applications. Moreover, the resulting carbon fiber knitted composites have high flexibility and functions. They meet no limits in terms of size and brittleness, and their EMI SE expands their applications in various fields.

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Chapter 6 – Conclusions

In this dissertation, the new type of composite carbon fibers with good elongation properties is successfully developed, which increased the development and application fields of carbon fiber composite materials. The research content is mainly about the preparation and processing technology of composite carbon fibers made of continuous carbon fiber, as well as the evaluation of the composition and basic properties of composite materials. The thesis is divided into many subsections for separate explanations.

Chapter 1 presents the introduction section, where the research background of carbon fiber composite materials is discussed. Then, a comprehensive introduction to its processing method and fabric composition structure is presented. The applicability of the method and structure is proposed, as well as the advantages of applying it to composite carbon fibers. The actual development and related testing and discussion are shown in Chapters 2 to 5.

Chapter 2 is the main development experiment of composite carbon fibers. According to the research results, the carbon fiber tow is well assembled after processing. TPU is melted at high temperature, coated on the outer layer of the carbon fiber tow, and attached to the outer layer of the carbon fiber tow to form. Coating TPU on the outer layer of the carbon fiber tow can improve the friction characteristics of carbon fiber, and the tensile test results show that the physical combination between TPU and carbon fiber tow can effectively strengthen the tensile strength of composite carbon fibers. The tensile failure mode is determined by the friction caused by the staggered displacement of the original yarn that causes the phenomenon of stress concentration to change into axial displacement. The carbon fiber tow processing significantly affects the improvement of its basic performance.

Then, Chapter 3 is about the effect of the change of the outer layer composition of the composite carbon fibers. According to the research results, the content ratio of TPU blends significantly affect the shape of the composite carbon fibers. The SEM and rheological properties show that the blends melt and the increase in the body viscosity positively affects the bundling of carbon fibers, and the composite carbon fibers have good nodular properties. Chapter 4 shows the influence of the change in the inner layer composition on the composite carbon fibers. According to the research results, when the carbon fiber content is 1.5 and 3 K, TPU blends improve the failure mode of the composite carbon fibers. The carbon fiber produces axial direction along with the coating layer. Slippage replaces the brittle fracture of the original carbon fiber caused by friction. In addition, the LFT technology enables the composite carbon fibers to reduce friction during the weaving process; thus, it is successfully made into a woven and knitted composite fabric in the research. Despite the use of composite carbon fibers as the material, woven composites and knitted composites still possess the softness and elasticity of fabrics, with a failure mode similar to composite carbon fibers.

Finally, in Chapter 5, the composite carbon fibers are subjected to subsequent weaving and lamination evaluation. According to the research results, in a multilayer composite fabric with a knitted structure, the composite carbon fibers has a double-layer fiber structure, and the TPU wrapped in the outer layer of the carbon fiber tow can provide fixation and protection. SEM observations show that the hot pressing method can effectively promote the interlayer bonding of the multilayer composite fabric, and the softness of the composite material has also been confirmed. The research results suggest that the preparation of composite carbon fibers can effectively improve the subsequent processing and application of composite materials prepared based on continuous carbon fibers, and the high flexibility and functionality of carbon fiber knitted composite materials can break through the limitations on its size and brittleness. In addition, given the good conductivity of carbon fiber, the EMI SE of its composite material has also expanded the field of use.

The conclusions of each chapter show that this dissertation has successfully developed composite carbon fibers and composite carbon fabrics and conducted parameter trials and evaluations of its basic characteristics. Data are expected to be established to provide more diversified developments in the continuous carbon fiber processing. This finding provides a novel method for the application of carbon fiber composite materials.

List of Publications

1. Chapter 2 –

   Mei-Chen Lin, Jia-Horng Lin, Limin Bao*. Combination and Development of Carbon Filament Tows: Application of Coextrusion with Long Fiber-Reinforced Thermoplastics. Polymer Composites. 2021, 42(9): 4199-4206.

2. Chapter 3 –

   Mei-Chen Lin, Jia-Horng Lin, Limin Bao*. Applying TPU blends and composite carbon fibers to flexible electromagnetic-shielding fabrics: Long-fiber-reinforced thermoplastics technique. Composites Part A: Applied Science and Manufacturing. 2020, 138(17): 106022.

3. Chapter 4 –

   Mei-Chen Lin, Jia-Horng Lin, Limin Bao*. Thermoplastic Polyurethane Reinforced with Continuous Carbon Fiber Tows: Manufacturing Technique and Fabric Property Evaluation. Applied Composite Materials. 2021, 28, 1531-1546.

4. Chapter 5 –

   Mei-Chen Lin, Jia-Horng Lin, Limin Bao*. Extrusion/Hot Pressing Processing and Laminated Layers of Continuous Carbon Fiber/Thermoplastic Polyurethane Knitted Composites. Polymer International. 2021, 71(3), 283-291.

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