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**Strong and Flexible Carbon Fiber Fabric Reinforced Thermoplastic
Polyurethane Composites for High-Performance EMI Shielding Applications**

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Abstract

Electromagnetic shielding materials play a significant role in solving the increasing environmental problem of electromagnetic pollutions. The commonly used metal-based electromagnetic materials suffer from high density, poor corrosion resistance and high processing cost. Polymer composites exhibit unique combined properties of lightweight, good shock absorption and corrosion resistance. In this study, a novel high angle sensitive composite is fabricated by combining carbon fiber (CF) fabric with thermoplastic polyurethane elastomer (TPU). The effect of stacking angle of CF fabric on EMI shielding performance of composite is studied. When the stacking angle of CF fabric changed, the EMI shielding effectiveness of CF fabric/TPU composite can reach a maximum of 73 dB, and the tensile strength can reach 168 MP. In addition, the composite has anisotropic conductivity, which is conductive along the plane direction and non-conductive along the thickness direction. Moreover, the CF fabric/TPU composite manifests exceptional EMI-SE/Density/Thickness value of 383 dB·cm²/g, which is higher than most of current EMI shielding composites reported in literature. In summary, CF fabric/TPU composite is an excellent EMI shielding material that is lightweight, highly flexible, and mechanically robust, which can be applied to the field of aerospace and some intelligent electronic devices.

1. Introduction

With the rapid development of modern science and technology, wireless communication devices and equipment have aroused serious electromagnetic pollution to environment, and as the electronic equipment develops, in order to meet the development trend of lightweight and miniaturization, the influence of electronic and electrical equipment on external electromagnetic shielding interference is increasing.^[1-3] Nowadays, metal and metal-based composites are the most common EMI shielding materials. Although traditional metal materials have excellent electromagnetic shielding performance, they suffer from many disadvantages, such as high density, poor corrosion resistance and high processing cost.^[4] In this context, it is becoming more and more urgent to develop conductive materials that are low-cost, environmentally friendly, lightweight and widely used for electromagnetic interference shielding.

Conductive polymer composites (CPCs) have many attractive properties, such as low-cost, lightweight, chemical stability, flexibility, easy processing, which make them become promising candidates for EMI shielding applications.^[5-9] Particularly, CFs and their composites have been widely used owing to their excellent electrical properties, high thermal stability, high specific strength and specific modulus.^[10-12] A number of researches have been carried out to study the EMI shielding of CFs. For example, Cao et.al investigated the EMI shielding effectiveness of short carbon fiber/silicon dioxide composite material in the frequency range of 8.2 ~ 12.4 GHz at the temperature of 30 ~ 600°C, which exhibited an EMI SE of 12.4 dB at 12.2 GHz.^[13] Lee SH et al. reported the EMI shielding effectiveness of CF/PP composites, which exhibited an excellent

EMI SE of 48.4 dB at 10 GHz frequency.^[14] Tang et al. studied the influence of carbon fiber concentration on EMI shielding properties of CF/PC film, when the content of CF is 90%, the EMI shielding properties of CF/PC film can reach 38.6 dB.^[15] Im et al. fluorinated carbon black and embedded it into the polyacrylonitrile (PAN) based CF, which showed a decent SE of 50 dB.^[16] Therefore, it is obvious that CFs composites reinforced conducting polymer composites have become perfect potential candidates for EMI shielding materials.

Although there are many studies on CFs composites, most of them are focus on the composites with conductive fillers. Generally, they often require high contents of conductive filler, which will suffer from various drawbacks, such as poor ductility, severe agglomeration, poor flexibility, high cost, high density, poor processing, etc.^[17-19] In order to address these shortcomings of composites with conductive fillers, forming a segregated structure in a composite material has remained the most promising strategy.^[20-24] Zhang et al. prepared polylactic acid/multi-walled carbon nanotubes nanocomposites with conductive isolation network. The multi-walled nanotubes were successfully positioned in continuous L-PLLA phase to form composites with segregated structure. Compared with the composites prepared by random distribution of MWCNT, their EMI shielding performance was improved by 36%.^[25] In Gelves's study, copper nanowire and polystyrene were used to fabricate composites with segregated structures, which achieved a higher EMI shielding effectiveness of more than 20 dB.^[26] Yan et al. fabricated an in situ thermally reduced graphene/polyethylene conductive composite with a segregated structure, which achieved a high

electromagnetic interference shielding effectiveness of up to 28.3–32.4 dB.^[27] In addition, some researchers have found that forming a segregated structure in a composite material can make more conductive fillers contact with the matrix and produce multiple interfaces and microwaves scattered or reflected by multiple interfaces can be well absorbed by the polymer/conductive filler.^[28–30] Therefore, by constructing multiple interfaces in the CPC, multiple scattering /reflection of electromagnetic waves can be enhanced, thereby improving the electromagnetic shielding performance of materials.^[31–33] Li et al. used cotton fiber (CTF) as the carrier to construct a lot of multiple interfaces in PDMS/MWCNT nanocomposites. It was found that in nanocomposites, electromagnetic radiation was effectively attenuated by wave reflections at multiple interfaces and then absorbed by the PDMS/CTF and CTF/MWCNT interfaces. By adding 15% by volume of CTF, the EMI shielding effectiveness (SE) of PDMS/MWCNT nanocomposites with MWMS of 2.0 and 3.0% by volume was increased from about 16 dB to 30 dB, and from 20 dB to 41 dB, respectively.^[34]

Thermoplastic polyurethane elastomer (TPU) is an important material with soft and hard alternating segments and a biocompatible and biodegradable elastomer.^[35–37] The polarity difference between hard and soft sections produces thermodynamic incompatibilities in TPU, which results in excellent mechanical properties and wear resistance. As a result, TPU has been widely used in many fields such as automobile, footwear, building, wire and cable, hose and pipeline owing to the good wear resistance, good processing performance, high chemical stability and mechanical properties.^[38] In

recent years, TPU composite materials have been widely used in electromagnetic interference shielding field. As shown in Jiang's study, the hydrogen bond between TPU and RGO enabled the composite to have good interface adhesion and TPU/RGO foam composite exhibited a good shielding effectiveness of 21.8 dB.^[39] Moreover, Feng et al. investigated the EMI SE of TPU/CNTs composites when the content of CNTs was 5.0 wt%, and it was found that the sample showed an average EMI SE of 35.3 dB.^[40] Therefore, it is a good choice to select TPU as the polymer matrix.

In the present work, we report an environmentally friendly, scalable, facile, and versatile methodology to fabricate carbon fiber fabric/TPU composites with segregated conductive networks for EMI shielding applications. Firstly, CF fabric/TPU composites were prepared by the method of hot compressing, and then, the morphology of composites was observed using a field emission scanning electron microscope (SEM). Afterwards, the functional group changes on the surface of CF fabric were characterized by a Fourier Transform Infrared Spectrometer (FT-IR) and X-ray photoelectron spectroscopy (XPS). Subsequently, it was found that the composite exhibited outstanding flexibility, which can be easily folded into various shapes. Finally, composites with different CF fabric stacking angles were discussed, and the EMI shielding performance and the mechanical properties were also characterized. The results showed that CF fabric/TPU composites possessed an excellent EMI shielding performance and mechanical property. This multifunctional ultralight material provides a promising solution to satisfy high-performance EMI shielding requirements.

2. Results and Discussion

2.1. Composite morphology

The carbon fiber fabrics used in this study are bidirectionally braided, so SEM electron microscopy shows that the bunches in carbon fiber fabrics have horizontal and vertical directions. In order to compare the effect of silane coupling agent on the combination of CF fabric and TPU, **Figure 1a-b** shows the SEM morphologies of untreated-CF fabric/TPU composites. It can be clearly seen that part of the CF bundles are not in close contact with TPU. In addition, there are cracks inside the carbon fiber, indicating that the combination effect of untreated-CF fabric and TPU is poor. **Figure 1c-e** shows the SEM morphologies of one-layer composite prepared by the combination of the treated CF fabric and TPU. The surface of CF fabric is well infiltrated by TPU, which indicates the good combination between CF fabric and TPU. **Figure 1f-g** and **Figure 1h-i** show the SEM morphologies of two-layer and three-layer composites, respectively. It can be observed that a part of the CF fabric is covered by TPU. The TPU can cross the gap between CF fabric, and the TPU on both sides of the CF fabric can be directly connected, which further confirms that CF fabric and TPU has a good combination. Besides, the surface morphology of monofilament carbon fiber was further studied. As shown in **Figure 2a**, the surface of untreated carbon fiber is smooth, with a few narrow and shallow grooves uniformly distributed along the longitudinal direction of the fiber. **Figure 2b** shows the carbon fiber modified by silane coupling agent, it is apparent that some KH-550 molecules are grafted onto the carbon fiber, and the fiber surface becomes rougher, which indicates that it is beneficial for the

combination between CF fabric and TPU. In order to further clarify the modification effect of KH-550 on CF fabric, FT-IR and XPS are discussed.

Figure 3 presents the FT-IR spectra of untreated and treated CF fabric. After treated with KH-550, the new stretching vibration peak presented at 1030 cm^{-1} belongs to the band of Si-O-Si, and the stretching vibration peak in Si-CH₃ appears at 850 cm^{-1} , they both indicate that the surface of CF fabric is successfully introduced with the element of Si. Besides, the peak at 2930 cm^{-1} can be assigned to the stretching vibration of C-H. The strong absorption peak appears at 1569 cm^{-1} that should be attributed to the stretching vibration of C=O, and the stretching vibration of C-N bonds appears at 1331 cm^{-1} . Similar results were also observed in other literature.^[41-43]

The mechanism of interactions between functional groups of CF fabric surface can be explored on the basis of the XPS spectra, which were collected before and after treatment. As shown in **Figure 4a-b**, the peaks corresponding to O 1s, N 1s, C 1s, Si 2s and Si 2p were clearly identified in the survey scan spectrum. The new appearance of the Si 2s and Si 2p in the XPS spectrum after treated with KH-550 demonstrates that the element of Si is successfully captured, which confirms that the element of Si is successfully grafted on the surface of CF fabric. Besides, the peak height of O 1s, C 1s and N 1s spectrum peaks have changed, which indicates the content of C, N, O on the surface of CF fabric is also changed. The content of O and N are increased, but the content of C is decreased. As can be seen in **Figure 4c-d**, the new functional group C-Si has been captured, which further confirms the element of Si is successfully introduced on the surface of CF fabric. Apparently, according to the analysis of XPS

and FT-IR, the surface of CF fabric has been modified, which is conducive to the combination of CF fabric and TPU.

2.2. Conductivity analysis

The conductivity of composites is closely related to the EMI shielding property of composites, high conductivity can produce significant dielectric loss in the material, which is conducive to the EMI shielding ability of the material.^[44-46] Sample conductivities are presented in **Figure 5**. The average conductivity of one-layer, two-layer and three-layer composite with the stacking layer of 0° was 1.7 S/cm, 4.8 S/cm and 13.3 S/cm, respectively. It is obvious that the CF component renders the composites the electrical conductivity ability because of the electrically insulating nature of TPU. Thanks to the unique structure, the composite is conductive along the plane direction and non-conductive along the thickness direction. As the number of stacking layers increased, the electrical conductivities of samples have improved. This difference might arise from the complexity of conductivity networks. Since TPU is tightly attached on the surface of CF fabric, and two adjacent layers of CF fabric are connected by TPU, just like a bridge. The conductive networks promoted the movement of charge carriers and improved the tunneling effect and field emission mechanism.^[47-49] Besides, as we can see, with the increase of stacking angle, the conductivity of the composite also increases, but the range of this change is very small. Considering that the conductivity of the composite itself changes within a certain range, the conductivity of the composite shows insignificant angular anisotropy.

2.3 EMI shielding property

2.3.1 EMI shielding mechanisms

The EMI SE (SE_T) is the logarithm of the ratio of incident power (P_i) to transmitted power (P_t) of radiation, which is also the sum of reflection shielding effectiveness (SE_R), absorption shielding effectiveness (SE_A), and multiple reflections (SE_M). SE is calculated according to the following equation (1).^[50]

$$SE = 10 \log (P_i/P_t) = SE_A + SE_R + SE_M \quad (1)$$

When SE_T is greater than 15 dB, SE_M is usually neglected.^[51] Therefore, the EMI SE (SE_T) can be expressed as shown in equation (2).

$$SE_T = SE_A + SE_R \quad (2)$$

2.3.2. EMI SE of the composites

Figure 6a-b shows the EMI-SE values of different stacking layers measured in the frequency range of 8.2~12.4 GHz. The maximum SE_T for one-layer sample is 20.9 dB, and this value is found to be substantially improved with increased stacking layers, reaching 35.3 dB for two-layer sample and even higher value of 59 dB for three-layer sample. The EMI-SE values of different stacking layers indicate that the CF fabric/TPU composites prepared in our study possesses excellent EMI shielding properties, which can satisfy the requirements of commercial EMI shielding value of 20 dB.^[43] Besides, It is obvious that the SE_T of pure TPU maintains at 0.8~0.9 dB. The low value of SE_T means that TPU can be regarded as an electromagnetic wave transparent material.^[52,53] The shielding property of CF fabric/TPU is mainly attributed to CF fabric.

To clarify the underlying mechanism, the SE absorption and SE reflection are also investigated, as shown in **Figure 6c-d**. It is apparent that the value of SE_A is higher than

SE_R . With the increase of the stacking layers, the increase of SE_A is quite apparent, but the SE_R increases slowly. Besides, **Figure 7** illustrates the power coefficients A, R and T measured in the range of 8.2~12.4 GHz for CF fabric/TPU composite with different layers at the same angle. The value of R is remarkably higher than that of A, and the value of T can be negligible, which indicates that the actual shielding mechanism for CF fabric/TPU composite in the frequency range of 8.2~12.4 GHz is dominated by reflection.^[54] Since reflection occurs before absorption, most of the incident waves (as absolute values) are reflected. Electromagnetic reflection usually occurs at the corresponding interface, and the enhancement effect of electromagnetic reflection becomes obvious with the increase of interface area.^[55,56] At the beginning, when electromagnetic waves striking the surface of the CF fabric/TPU composites, due to impedance mismatch between the CF fabric/TPU composites and the surrounding environment, some electromagnetic waves were reflected at the interface, resulting in reflection energy loss. With the increase of the number of layers of CF fabric/TPU, the electromagnetic wave continuously rushes to the CF fabric layer and TPU resin layer, which will also cause some reflection. However, because the interface conditions are all electromagnetic waves directly from the air to TPU resin, which has a certain degree of similarity, so the increase of SE_R value of samples with different stacking layers and angles is not obvious.^[57]

The content of carbon fiber also affects the EMI shielding performance of the CF fabric/TPU composite. **Table 1** shows the content of CF fabric in composite with

different stacking layers and angles. For one-layer composite, the thickness of each resin layer is about 0.66 mm. For two-layer composite, the thickness of each resin layer is about 0.38 mm. For three-layer composite, the thickness of each resin layer is about 0.24 mm. When the stacking layers of CF fabric are the same but the angles are different, the content of the CF in composite changes in a very small range, which can be regarded as the same content of CF in composite. However, when the stacking angles are the same and with the increase of the number of CF fabric layers, the content of the CF fabric increases obviously. The content of the CF fabric in the one-layer, two-layer and three-layer of the composite is about 16.3%, 31.1% and 44.6%, respectively. The increase of CFs can form more effectively conductive networks which provides sufficient conductive paths, thereby increasing ohmic loss, and the increasing CFs amplify the energy dissipated of electric dipoles by polarization.^[58,59] Vast mobile charge carriers (electrons or holes) had great mobility to interact with external electromagnetic fields. The network composed of CF establishes the bridge of mobile charge carriers, which can move freely along the bridge. In addition, reciprocating reflection of electromagnetic waves in multilayer composites can increase the absorption and reflection properties of composites. Moreover, carriers in composites can absorb incident electromagnetic waves and give positive feedback. At the same time, they can generate magnetic field energy and the movement of energy produces heat loss in the form of a weak current, which further strengthens the ability to absorb electromagnetic waves.

Furthermore, to study the effect of CF fabric stacking angles on EMI performance, the CF fabric/TPU samples with different stacking layers and stacking angles (0° , 15° , 30° and 45°) were prepared and their corresponding EMI SE was investigated in X-band for an example. As shown in **Figure 8**, it is clear that the shielding performance of composite increases with increasing the sample stacking angles. Among them, the three-layer sample with 45° stacking angle exhibits a maximum EMI performance of 73 dB. **Figure 9a-c** shows the EMI SE of composites with different stacking layers and angles in detail. It shows that the SE_A of composites with different angles is larger than SE_R , and the increase of SE_T is mainly attributed to the increase of SE_A , especially the three-layer composites with an angle of 45° , which the SE_A accounts for nearly 90% of the SE_T . This phenomenon indicates that CF fabric/TPU composites exhibit high angular anisotropy. The reasons are further discussed. When the electromagnetic wave passes through the CF fabric, once the stacking angle of the CF fabric changes, the path of the electromagnetic wave will also change, which will affect the feedback of the moving charge carrier to the electromagnetic wave and increase the absorption of the electromagnetic wave. Due to the stacking angle is different, when a large number of moving charge carriers (electrons or holes) move along the network composed of CF fabric, there will be stronger eddy current, which may enhance the transmission of electromagnetic energy dissipated in the form of micro current, leading to the enhancement in SE_A . In addition, when the carriers move along the conductive network, they can generate a magnetic field to resist the external electromagnetic field, and if the stacking angle of CF fabric changes, the magnetic field generated by the carriers may

also change its angle, and the magnetic fields from different angles may also generate more absorption losses. Moreover, the change of the stacking angle of the CF fabric will lead to the complexity of the internal structure of the composite, which will lead to more electromagnetic wave absorption and reflection inside the composite, and the complex structure makes it difficult for electromagnetic waves to directly penetrate the composite, so the electromagnetic shielding performance of the composite is apparently improved.

The thickness of composite material also affects the electromagnetic shielding efficiency of the material. **Figure 10a** shows the electromagnetic shielding efficiency of one-layer CF fabric/TPU composite with different thickness at the same angle. It can be observed that the thicker composites exhibit obviously better EMI SE compared with thinner ones. The energy absorption of electromagnetic wave in penetrating the shielding body is mainly caused by eddy current. The eddy current has two functions, one is to generate an anti-magnetic field to counteract the original magnetic field, and the other is to generate heat loss. Therefore, the thicker the composite material is, the longer time it takes for electromagnetic wave to penetrate the material, resulting in the increase of eddy current loss. More interestingly, as shown in **Figure 10b**, the one-layer composite with stacking angle of 0° , suffering 1000 times bending, also has high EMI shielding performance. As we can see, the EMI SE_T has a slight increase, up to 23.2 dB at 12.4 GHz. Because after 1000 times bending, the thickness of composite has increased by nearly 0.04 mm, so the value of SE_T has a slight increase. The result

indicates that the composite shows incredible potential in the application of flexible EMI shielding materials.

Nowadays, electromagnetic shielding materials have been developed towards ultra-thin and lightweight due to the urgent demand of aerospace and some intelligent electronic devices. In order to compare EMI shielding performance with other typical materials in lightweight applications, specific shielding effectiveness ($SSE=SE/D/T$) is derived to compare the effectiveness of shielding materials taking into account of composite thickness (T) and density (D).^[60,61] **Table 2** shows the comparison between $SE/D/T$ of materials prepared in this paper and other shielding materials in literature. As listed in **Table 2**, the $SE/D/T$ value of CF fabric/TPU composite is $383 \text{ dB}\cdot\text{cm}^2/\text{g}$, which is much higher than that of other shielding materials, indicating that it holds great promises in EMI shielding applications. This excellent electromagnetic shielding performance is attributed to the multi-layer structure formed by CF fabric, which leading to more carriers directly contacting with TPU matrix to induce multiple interfaces. The approach is simple, low cost and environment-friendly, which can be widely used in other conductive composites.

2.4. Mechanical properties

Figure 11a shows the tensile strength of composites with different stacking layers and angles. When the stacking angle is the same, the tensile strength of composite with different stacking layers increases with the number of stacking layers. Take 0° as an example, the tensile strength for one-layer sample is 62.4 MPa, and this value is found to be substantially improved with increased stacking layers, reaching 83.2 MPa for two-

layer sample and even higher value of 108.3 MPa for three-layer sample. This is due to the high specific strength and modulus of CFs, the added CFs can form interfacial interaction with TPU matrix to ensure that the stress can be transferred between CFs and TPU matrix. Besides, the surface of the treated CF becomes rough, and the rough surface can improve the wettability of the composite which is conducive to the combination of carbon fiber and TPU.^[68] Moreover, the hydroxyl and carboxyl groups on the surface of CF and ester groups in TPU formed strong hydrogen bonds at a high temperature, which will improve the bonding properties between CF fabric and TPU.

Furthermore, we can also see the effect of different stacking angles on the tensile properties of CF fabric/TPU composite. The tensile strength of the composite will also change obviously when the CF fabric stacking angle increases. Similarly, different stacking layer composites show the same phenomenon. On the one hand, this is due to the different microstructure of composites with different stacking angles. On the other hand, when the CF fabric has a stacked angle, the load applied to the composite is a tangential component along the direction of the force applied by the device, and the load along the texture direction of the CF fabric also varies with the angle, which also causes the difference of tensile strength.

As shown in **Figure 11b**, the flat and rectangular CF fabric/TPU composite can curl several loops and rotate at large angles, which it is difficult for traditional metallic material to achieve this property in the same situation. **Figure 11c** demonstrates what will happen after a CF fabric/TPU sample is folded and released. The sample can be folded easily, and when the sample is released after two folds in half, it can be restored

to its previous shape easily. Moreover, there is almost no crease on the sample surface, which indicates that the composite possesses high flexibility and foldability. **Figure 11d** shows the flexibility of a sample at a given weight. First, a sample is placed on two support blocks and the distance between the two blocks is 60 mm. Then, five iron blocks (each 40g) with a total weight of 200 g are slowly placed on the upper surface of the sample. The bending angle of the specimen caused by the weight is measured and recorded. The results show that the bending angle of CF fabric/TPU composite is about 36° . This test reveals that the CF fabric/TPU composite possesses excellent flexibility, holding great promise for flexible electronic equipment and mobile phones.

3. Conclusions

In this study, we have reported a general, facile, eco-friendly, and lightweight CF fabric/TPU composites with segregated conductive networks for EMI shielding applications. The simple and economical preparation process can be well suited the business applications. The EMI shielding effectiveness of high angle sensitive CF fabric/TPU composites can reach a maximum of 73 dB. In addition, the composites show an excellent tensile strength, which can achieve 168 MPa. In addition, the composite exhibits excellent flexibility, and after having been folded many times, the composites continue to maintain high flexibility. In addition, the composites have anisotropic conductivity, which is conductive along the plane direction and non-conductive along the thickness direction. Moreover, the CF fabric/TPU composite possesses remarkable comprehensive properties, and it can be quantitatively estimated

by an SE/D/T evaluation index as high as $383 \text{ dB}\cdot\text{cm}^2/\text{g}$, which is much higher than that of other shielding materials in literature. The composite prepared in this study not only well meets the requirements of high EMI shielding performance and mechanical strength for aerospace and other intelligent electronic devices, but also opens up a broad road for the lightweight, high flexibility and mechanical strength of high-performance EMI materials.

4. Experimental Section

4.1 Materials

Polyacrylonitrile (PAN)-based CFs (TR30s 3L) were supplied by Mitsubishi Rayon, Japan. The density of CF fabric is 1.79 g/cm^3 , the thickness is 0.18 mm, and the diameter of carbon fiber is 7 microns. Thermoplastic polyurethane elastomer (Texin285) was purchased from Bayer, Germany. The density is 1.2 g/cm^3 . The Shore hardness is 85A and elongation at break is 500%. The silane coupling agent KH-550 ($\geq 98\%$) was obtained from Changzhou Runxiang Electronic Materials Co., Ltd. Deionized water was purchased from Guangzhou Hongwei water treatment Co., Ltd.

4.2 Fabrication of CF fabric/TPU composite

The CF fabric reinforced TPU composites (CF fabric/TPU) were fabricated by stacking TPU plates and CF fabrics layer-by-layer through hot compression (**Figure 12**). Firstly, the granular TPU was dried in an oven, then melted and cooled to form TPU plates. Secondly, the surface of CF fabric was treated with the mixture of silane coupling agent KH-550 and anhydrous ethanol. After surface treatment, the CF fabric

was washed by deionized water. Thirdly, one-layer composite was prepared by hot pressing after a CF fabric was embedded between two TPU plates, and the structure looked like a sandwich. And then, along the texture direction of the CF fabric, we can cut and obtain different angles (0° , 15° , 30° , 45°) of one-layer CF fabric/TPU composite. Finally, in the preparation of two-layer composite, the structure was also like a sandwich, but the texture direction of the CF fabric of the second layer was set at an angle with the texture direction of the first CF fabric, meaning that the texture direction of the first layer of CF fabric is parallel to the horizontal direction, but the texture direction of the second layer of CF fabric has a certain angle (0° , 15° , 30° , 45°) with the horizontal direction. By stacking the CF fabric at different angles, two-layer composites were prepared. Similar to the preparation of two-layer composites, by stacking the CF fabric at different angles (0° , 15° , 30° , 45°), three-layer composites were also prepared.

4.3 Characterization

The EMI shielding of samples was measured by the waveguide method using a vector network analyzer (VNA, N5234A, Agilent, USA), and all samples were cut into a rectangle shape with a size of $22.9\text{ mm} \times 10.2\text{ mm} \times 1.5\text{ mm}$. The tensile strength test was conducted on a microcomputer-controlled electronic universal testing machine WDW-50E. The test temperature is at room temperature and the size of the test sample is $80\text{ mm} \times 10\text{ mm} \times 1.5\text{ mm}$. The tensile speed is 10 mm/min . Morphologies of the samples were investigated using a field emission scanning electron microscope (JSM-6610LV, JEOL, Japan) at an accelerating voltage of 15 kV . Conductivity was

measured on a standard four-probe meter (ST2253, Suzhou Jingge Electronics Co., Ltd., China). And the average conductivity for each sample was determined by five measurements to reduce errors. CF surface elements and functional groups were detected by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

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Conflict of Interest

The authors declare no conflict of interest.

Reference

- [1] X. Feng, X. Qin, D. Liu, Z. Huang, Y. Zhou, W. Lan, F. Lu, H. Qi, *Macromol. Mater. Eng.* **2018**, *303*, 1.
- [2] Z. Chen, D. Yi, B. Shen, L. Zhang, X. Ma, Y. Pang, L. Liu, X. Wei, W. Zheng, *Carbon*. **2018**, *139*, 271.
- [3] H. Li, M. Jensen, N. Wang, Y. Chen, Y. Gao, X. Chen, X. Li, *Macromol. Mater. Eng.* **2019**, *304*, 1.

- [4] P. R. Agrawal, R. Kumar, S. Teotia, S. Kumari, D. P. Mondal, S. R. Dhakate, *Compos. Part B Eng.* **2019**, *160*, 131.
- [5] J. H. Lin, Z. I. Lin, Y. J. Pan, C. K. Chen, C. L. Huang, C. H. Huang, C. W. Lou, *Macromol. Mater. Eng.* **2016**, *301*, 199.
- [6] L. C. Jia, D. X. Yan, C. H. Cui, X. Ji, Z. M. Li, *Macromol. Mater. Eng.* **2016**, *301*, 1232.
- [7] Y. Liu, D. Song, C. Wu, J. Leng, *Compos. Part B Eng.* **2014**, *63*, 34.
- [8] M. T. Byrne, Y. K. Guin'Ko, *Adv. Mater.* **2010**, *22*, 1672.
- [9] M. Arjmand, K. Chizari, B. Krause, P. Pötschke, U. Sundararaj, *Carbon.* **2016**, *98*, 358.
- [10] J. M. F. De Paiva, A. De Nadai Dos Santos, M. C. Rezende, *Mater. Res.* **2009**, *12*, 367.
- [11] D. I. Chukov, A. A. Stepashkin, A. V. Maksimkin, V. V. Tcherdyntsev, S. D. Kaloshkin, K. V. Kuskov, V. I. Bugakov, *Compos. Part B Eng.* **2015**, *76*, 79.
- [12] K. W. Kim, W. Han, B. S. Kim, B. J. Kim, K. H. An, *Appl. Surf. Sci.* **2017**, *415*, 55.
- [13] M. S. Cao, W. L. Song, Z. L. Hou, B. Wen, J. Yuan, *Carbon.* **2010**, *48*, 788.
- [14] S. H. Lee, J. Y. Kim, C. M. Koo, W. N. Kim, *Macromol. Res.* **2017**, *25*, 936.
- [15] W. Tang, L. Lu, D. Xing, H. Fang, Q. Liu, K. S. Teh, *Compos. Part B Eng.* **2018**, *152*, 8.
- [16] J. S. Im, J. G. Kim, Y. S. Lee, *Carbon.* **2009**, *47*, 2640.
- [17] G. Wang, L. Wang, L. H. Mark, V. Shaayegan, G. Wang, H. Li, G. Zhao, C. B.

- Park, *ACS Appl. Mater. Interfaces* **2018**, *10*, 1195.
- [18] A. Gödel, G. Kasaliwal, P. Pötschke, *Macromol. Rapid Commun.* **2009**, *30*, 423.
- [19] B. P. Grady, *Macromol. Rapid Commun.* **2010**, *31*, 247.
- [20] J. C. Grunlan, W. W. Gerberich, L. F. Francis, *J. Appl. Polym. Sci.* **2001**, *80*, 692.
- [21] J. C. Grunlan, W. W. Gerberich, L. F. Francis, *Polym. Eng. Sci.* **2001**, *41*, 1947.
- [22] H. Pang, C. Chen, Y. Bao, J. Chen, X. Ji, J. Lei, Z. M. Li, *Mater. Lett.* **2012**, *79*, 96.
- [23] M. H. Al-Saleh, U. Sundararaj, *Compos. Part A Appl. Sci. Manuf.* **2008**, *39*, 284.
- [24] H. Pang, L. Xu, D. X. Yan, Z. M. Li, *Prog. Polym. Sci.* **2014**, *39*, 1908.
- [25] K. Zhang, G. H. Li, L. M. Feng, N. Wang, J. Guo, K. Sun, K. X. Yu, J. B. Zeng, T. Li, Z. Guo, M. Wang, *J. Mater. Chem. C* **2017**, *5*, 9359.
- [26] G. A. Gelves, M. H. Al-Saleh, U. Sundararaj, *J. Mater. Chem.* **2011**, *21*, 829.
- [27] D. X. Yan, H. Pang, L. Xu, Y. Bao, P. G. Ren, J. Lei, Z. M. Li, *Nanotechnology* **2014**, *25*, 145705.
- [28] X. H. Tang, J. Li, Y. J. Tan, J. H. Cai, J. H. Liu, M. Wang, *Appl. Surf. Sci.* **2020**, *508*, 145178.
- [29] J. Li, W. J. Peng, Z. J. Fu, X. H. Tang, H. Wu, S. Guo, M. Wang, *Compos. Part B Eng.* **2019**, *171*, 204.
- [30] B. Zhao, C. Zhao, M. Hamidinejad, C. Wang, R. Li, S. Wang, K. Yasamin, C. B. Park, *J. Mater. Chem. C* **2018**, *6*, 10292.
- [31] J. Li, J. L. Chen, X. H. Tang, J. H. Cai, J. H. Liu, M. Wang, *J. Colloid Interface Sci.* **2020**, *565*, 536.

- [32] W. C. Yu, T. Wang, G. Q. Zhang, Z. G. Wang, H. M. Yin, D. X. Yan, J. Z. Xu, Z. M. Li, *Compos. Sci. Technol.* **2018**, *167*, 260.
- [33] Y. J. Tan, J. Li, J. H. Cai, X. H. Tang, J. H. Liu, Z. qian Hu, M. Wang, *Compos. Part B Eng.* **2019**, *177*, 107378.
- [34] J. Li, Y. J. Tan, Y. F. Chen, H. Wu, S. Guo, M. Wang, *Appl. Surf. Sci.* **2019**, *466*, 657.
- [35] W. Xian, L. Song, B. Liu, H. Ding, Z. Li, M. Cheng, L. Ma, *J. Appl. Polym. Sci.* **2018**, *135*, 1.
- [36] H. Y. Mi, X. Jing, M. R. Salick, T. M. Cordie, L. S. Turng, *J. Mech. Behav. Biomed. Mater.* **2016**, *62*, 417.
- [37] M. Dong, Q. Li, H. Liu, C. Liu, E. K. Wujcik, Q. Shao, T. Ding, X. Mai, C. Shen, Z. Guo, *Polymer.* **2018**, *158*, 381.
- [38] D. Rosu, L. Rosu, C. N. Cascaval, *Polym. Degrad. Stab.* **2009**, *94*, 591.
- [39] Q. Jiang, X. Liao, J. Li, J. Chen, G. Wang, J. Yi, Q. Yang, G. Li, *Compos. Part A Appl. Sci. Manuf.* **2019**, *123*, 310.
- [40] D. Feng, D. Xu, Q. Wang, P. Liu, *J. Mater. Chem. C* **2019**, *7*, 7938.
- [41] X. Min, X. Wu, P. Shao, Z. Ren, L. Ding, X. Luo, *Chem. Eng. J.* **2019**, *358*, 321.
- [42] T. Siva, K. Kamaraj, V. Karpakam, S. Sathiyarayanan, *Prog. Org. Coatings* **2013**, *76*, 581.
- [43] M. Sharma, M. Joshi, S. Nigam, S. Shree, D. K. Avasthi, R. Adelung, S. K. Srivastava, Y. Kumar Mishra, *Chem. Eng. J.* **2019**, *358*, 540.
- [44] Z. Yang, Y. Zhang, B. Wen, *Compos. Sci. Technol.* **2019**, *178*, 41.

- [45] L. Q. Cortes, S. Racagel, A. Lonjon, E. Dantras, C. Lacabanne, *Compos. Sci. Technol.* **2016**, *137*, 159.
- [46] H. Bin Zhang, W. G. Zheng, Q. Yan, Y. Yang, J. W. Wang, Z. H. Lu, G. Y. Ji, Z. Z. Yu, *Polymer.* **2010**, *51*, 1191.
- [47] K. Krushnamurthy, M. Rini, I. Srikanth, P. Ghosal, A. P. Das, M. Deepa, C. Subrahmanyam, *Compos. Part A Appl. Sci. Manuf.* **2016**, *80*, 237.
- [48] X. Lin, X. Liu, J. Jia, X. Shen, J. K. Kim, *Compos. Sci. Technol.* **2014**, *100*, 166.
- [49] J. Chen, J. Wu, H. Ge, D. Zhao, C. Liu, X. Hong, *Compos. Part A Appl. Sci. Manuf.* **2016**, *82*, 141.
- [50] Y. Li, B. Shen, X. Pei, Y. Zhang, D. Yi, W. Zhai, L. Zhang, X. Wei, W. Zheng, *Carbon.* **2016**, *100*, 375.
- [51] S. Maiti, N. K. Shrivastava, S. Suin, B. B. Khatua, *ACS Appl. Mater. Interfaces* **2013**, *5*, 4712.
- [52] T. K. Gupta, B. P. Singh, S. R. Dhakate, V. N. Singh, R. B. Mathur, *J. Mater. Chem. A* **2013**, *1*, 9138.
- [53] P. Li, D. Du, L. Guo, Y. Guo, J. Ouyang, *J. Mater. Chem. C* **2016**, *4*, 6525.
- [54] X. Mei, L. Lu, Y. Xie, W. Wang, Y. Tang, K. S. Teh, *Nanoscale* **2019**, *11*, 13587.
- [55] Z. Wang, L. Wu, J. Zhou, Z. Jiang, B. Shen, *Nanoscale* **2014**, *6*, 12298.
- [56] L. Kong, X. Yin, X. Yuan, Y. Zhang, X. Liu, L. Cheng, L. Zhang, *Carbon.* **2014**, *73*, 185.
- [57] B. Shen, Y. Li, D. Yi, W. Zhai, X. Wei, W. Zheng, *Carbon.* **2016**, *102*, 154.
- [58] S. Naeem, V. Baheti, V. Tunakova, J. Militky, D. Karthik, B. Tomkova, *Carbon.*

- 2017**, *111*, 439.
- [59] L. Lu, D. Xing, K. S. Teh, H. Liu, Y. Xie, X. Liu, Y. Tang, *Mater. Des.* **2017**, *120*, 354.
- [60] H. Li, D. Yuan, P. Li, C. He, *Compos. Part A Appl. Sci. Manuf.* **2019**, *121*, 411.
- [61] H. Wei, M. Wang, W. Zheng, Z. Jiang, Y. Huang, *Ceram. Int.* **2020**, *46*, 6199.
- [62] H. Bin Zhang, Q. Yan, W. G. Zheng, Z. He, Z. Z. Yu, *ACS Appl. Mater. Interfaces* **2011**, *3*, 918.
- [63] S. Pande, A. Chaudhary, D. Patel, B. P. Singh, R. B. Mathur, *RSC Adv.* **2014**, *4*, 13839.
- [64] J. Ling, W. Zhai, W. Feng, B. Shen, J. Zhang, W. G. Zheng, *ACS Appl. Mater. Interfaces* **2013**, *5*, 2677.
- [65] C. Li, G. Yang, H. Deng, K. Wang, Q. Zhang, F. Chen, Q. Fu, *Polym. Int.* **2013**, *62*, 1077.
- [66] F. Shahzad, M. Alhabeb, C. B. Hatter, B. Anasori, S. M. Hong, C. M. Koo, Y. Gogotsi, *Science.* **2016**, *353*, 1137.
- [67] S. Das Ramôa, G. M. Barra, R. V. Oliveira, M. G. De Oliveira, M. Cossa, B. G. Soares, *Polym. Int.* **2013**, *62*, 1477.
- [68] F. Zhao, Y. Huang, *J. Mater. Chem.* **2011**, *21*, 2867.

Figure 1. a-b) SEM morphology of untreated-CF fabric/TPU composite; SEM morphology of CF fabric/TPU Composites (0°) with different stacking layers: c-e) One-layer; f-g) Two-layer; h-i) Three-layer.

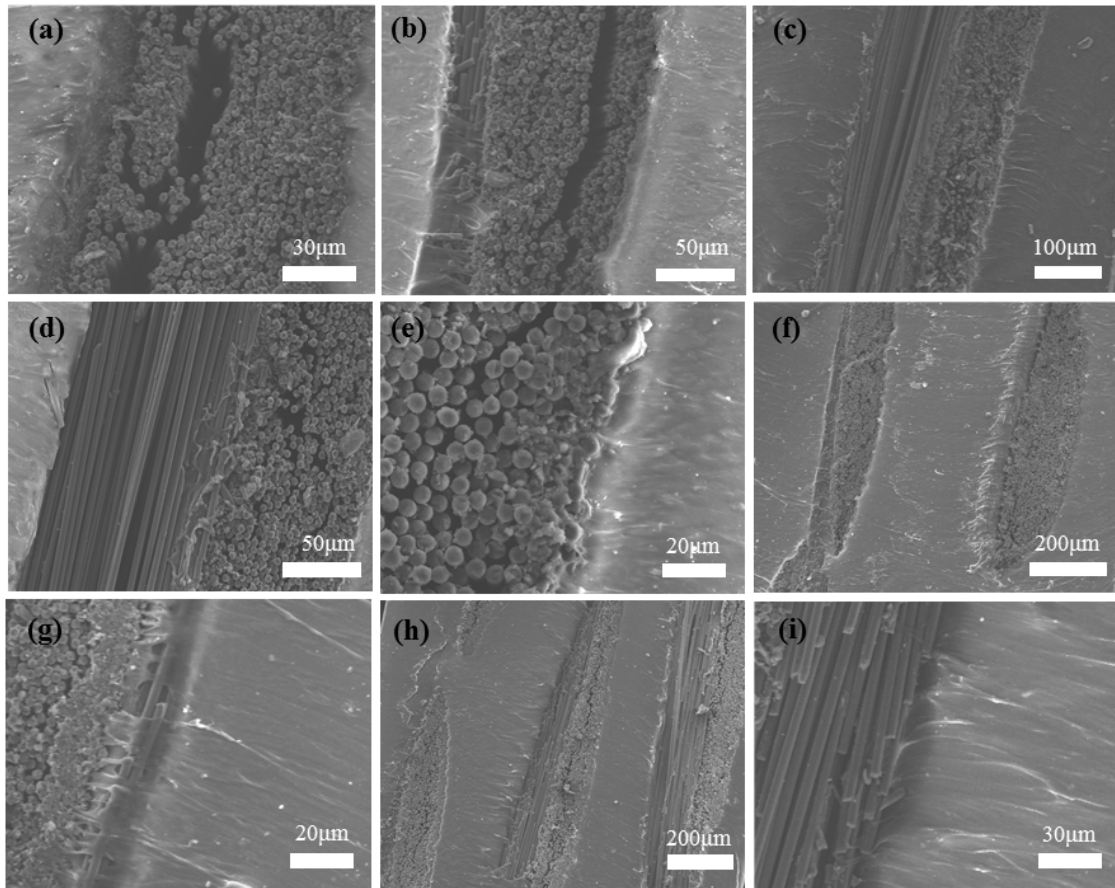


Figure 2. a) Untreated CF Surface; b) Treated CF Surface.

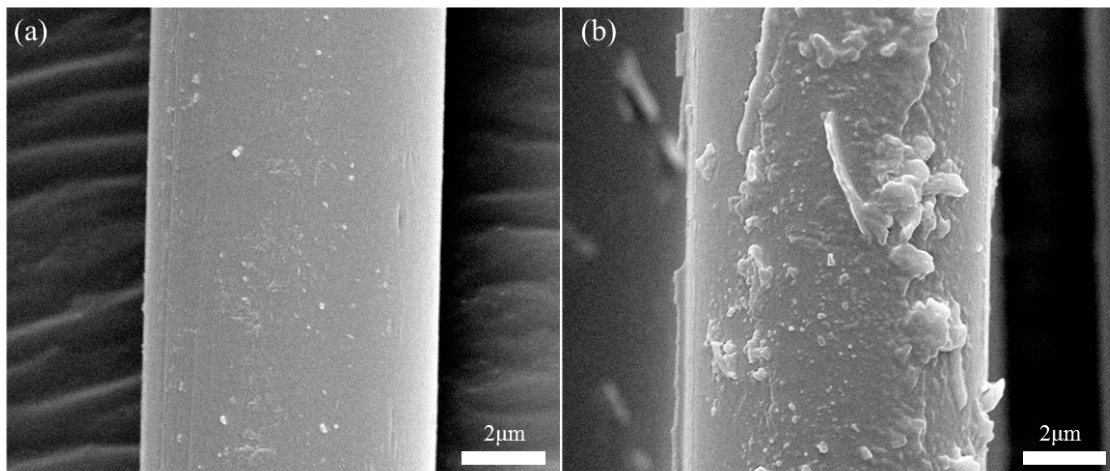


Figure 3. FT-IR of the surface functional groups of carbon fiber fabric.

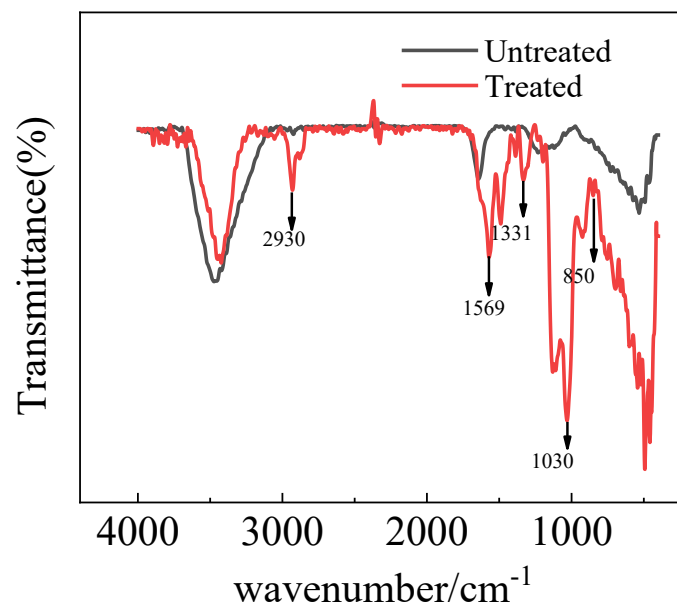


Figure 4. a) Scan spectrum of untreated CF; b) Scan spectrum of treated CF; c) C1s spectrum of untreated CF; d) C1s spectrum of treated CF.

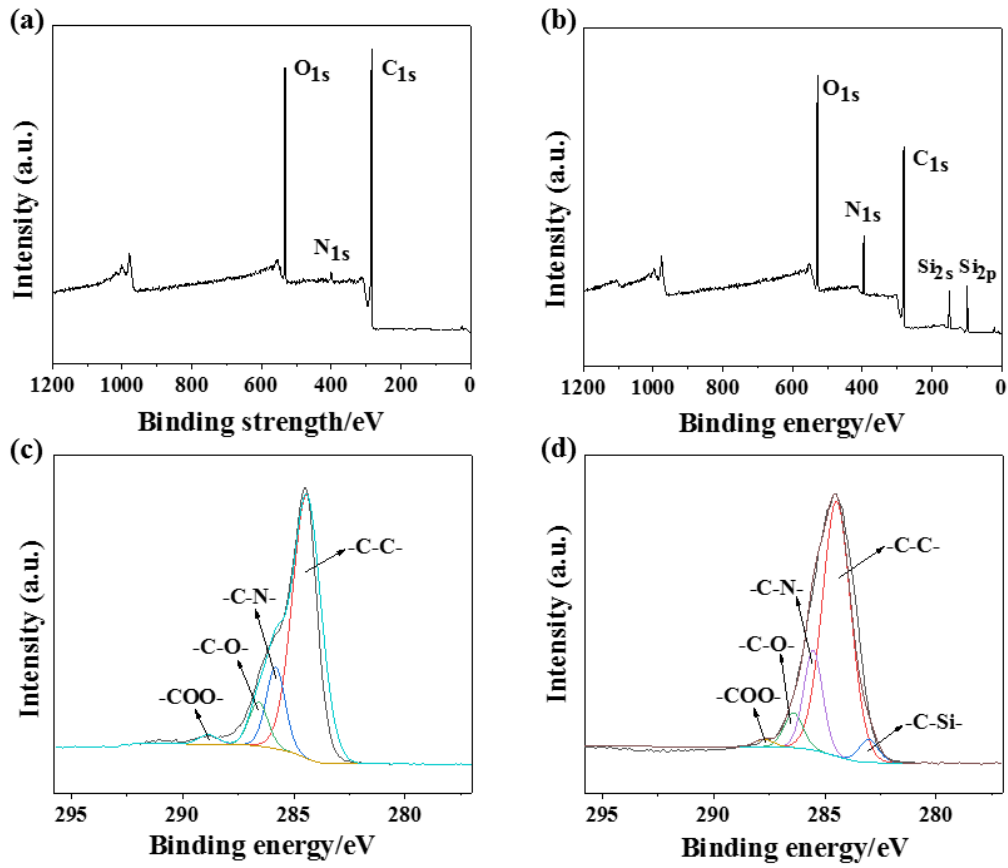


Figure 5. Conductivity of composites with different stacking layers and angles.

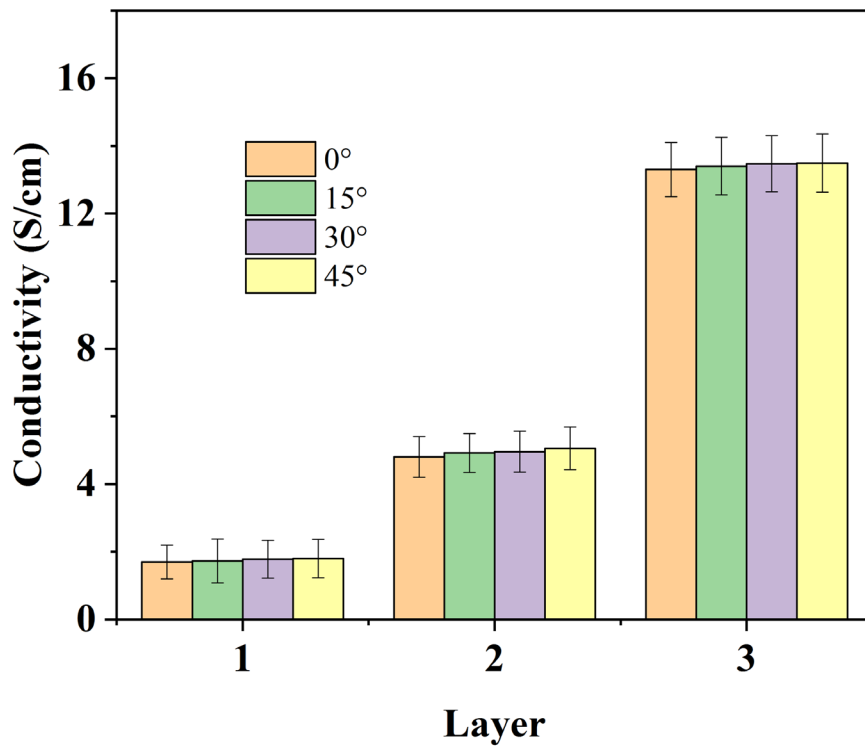


Figure 6. a) The maximum EMI-SE of composites with different stacking layers; b) Total shielding effectiveness (SE_T); c) Absorption shielding effectiveness (SE_A); d) Reflection shielding effectiveness (SE_R).

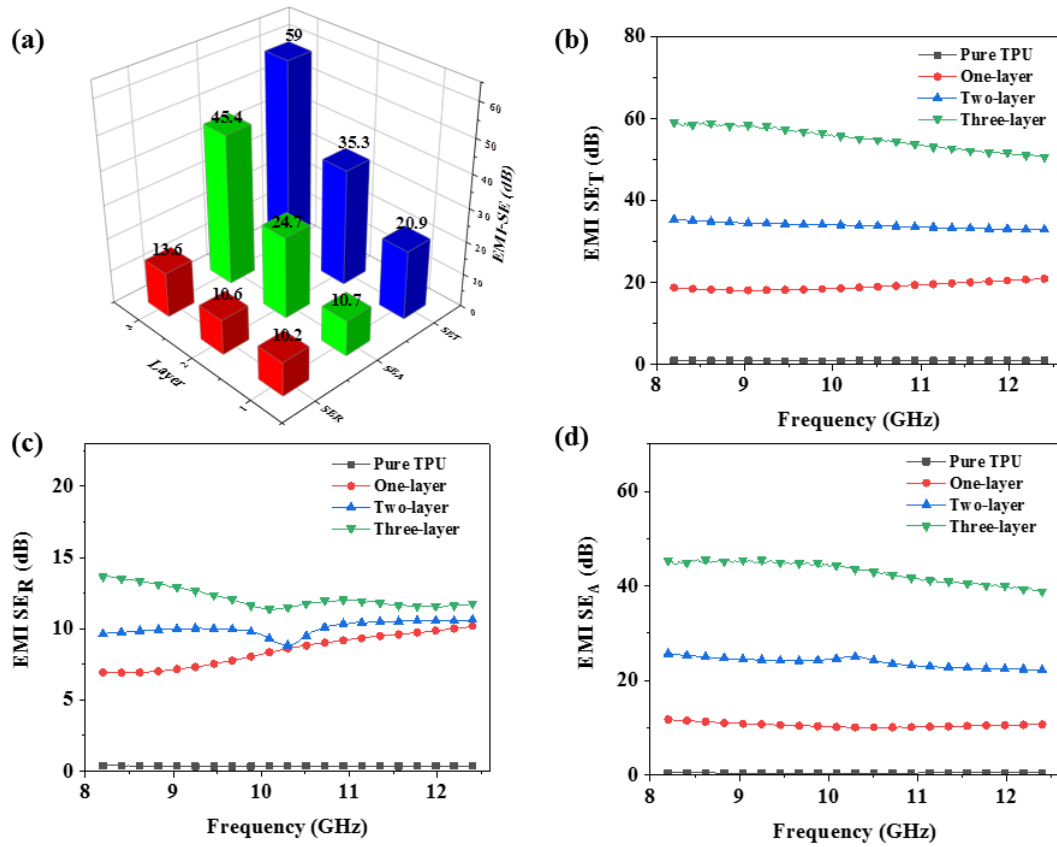


Figure 7. The power coefficients A, R and T for different layers of CF fabric/TPU composite with the stacking angle of 0° .

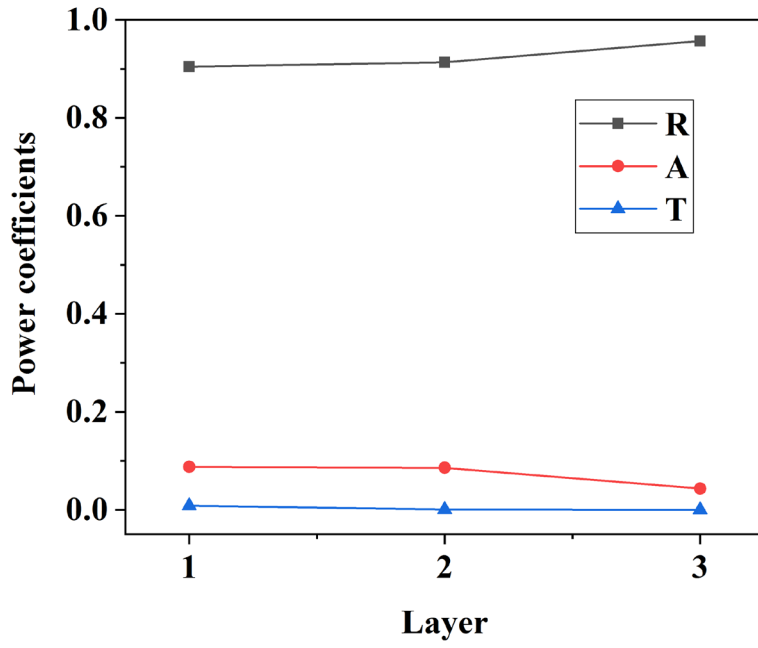


Figure 8. The total EMI SE of composites with different stacking layers and angles.

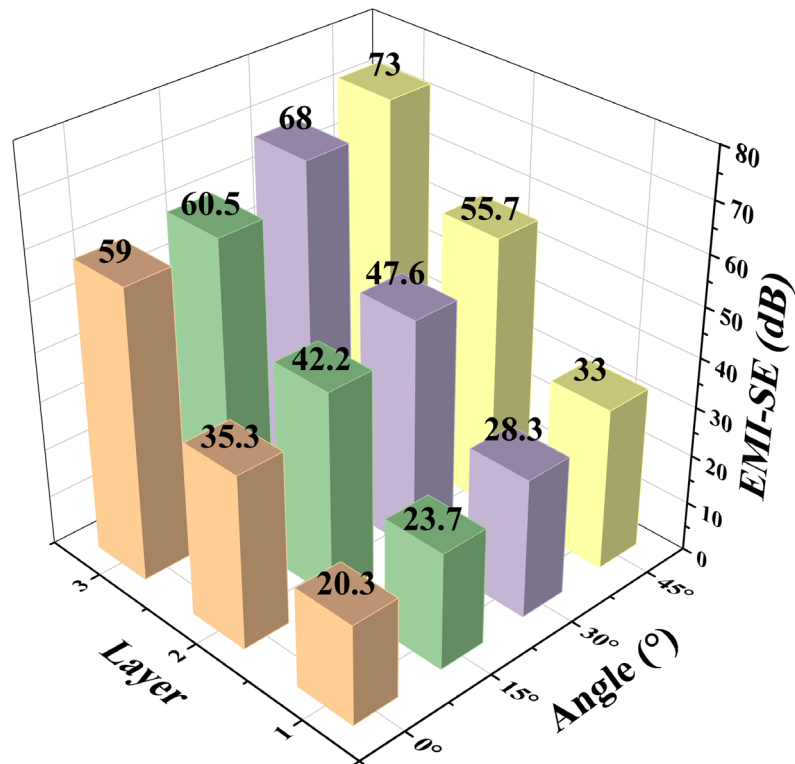


Figure 9. a) SE_T , SE_A and SE_R of one-layer composites material with different angles; b) SE_T , SE_A and SE_R of two-layer composites material with different angles; c) SE_T , SE_A and SE_R of three-layer composites material with different angles.

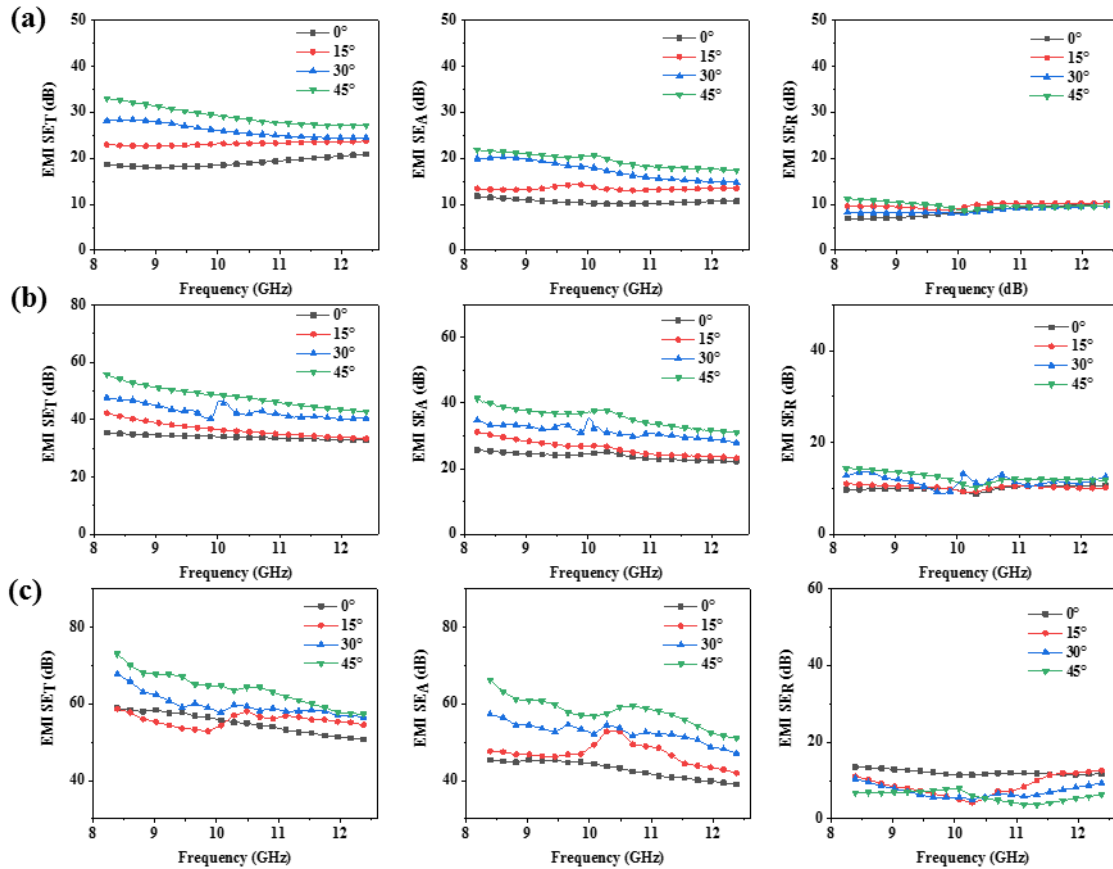


Figure10. a) The EMI shielding efficiency of one-layer CF/TPU composite with different thickness at the same angle (0°); b) EMI shielding performance of one-layer composite with stacking angle of 0° after 1000 times bending.

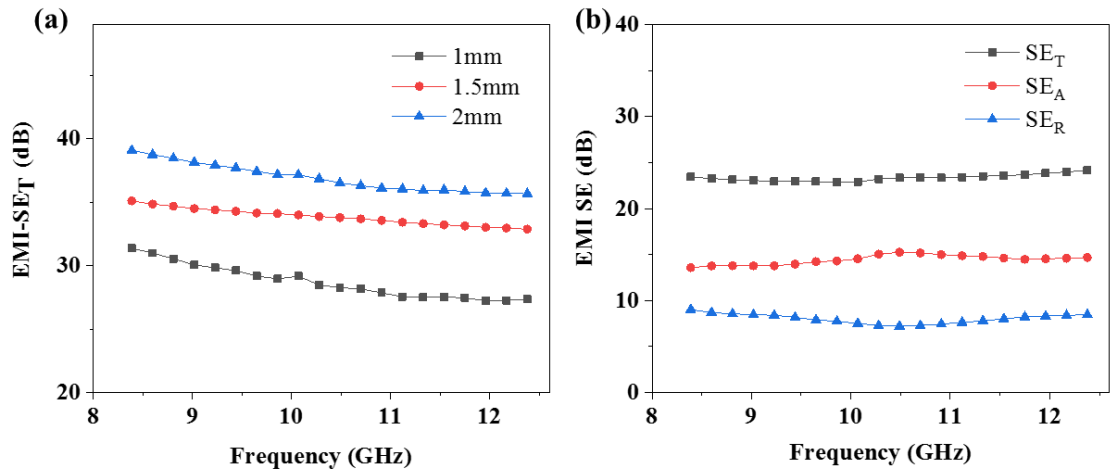


Figure 11. a) Tensile strength of CF fabric/TPU composites; b) The flat, curling and rotating morphologies of CF fabric/TPU composites; c) Folding and releasing processes of CF fabric/TPU composites; d) The flexibility at a given weight.

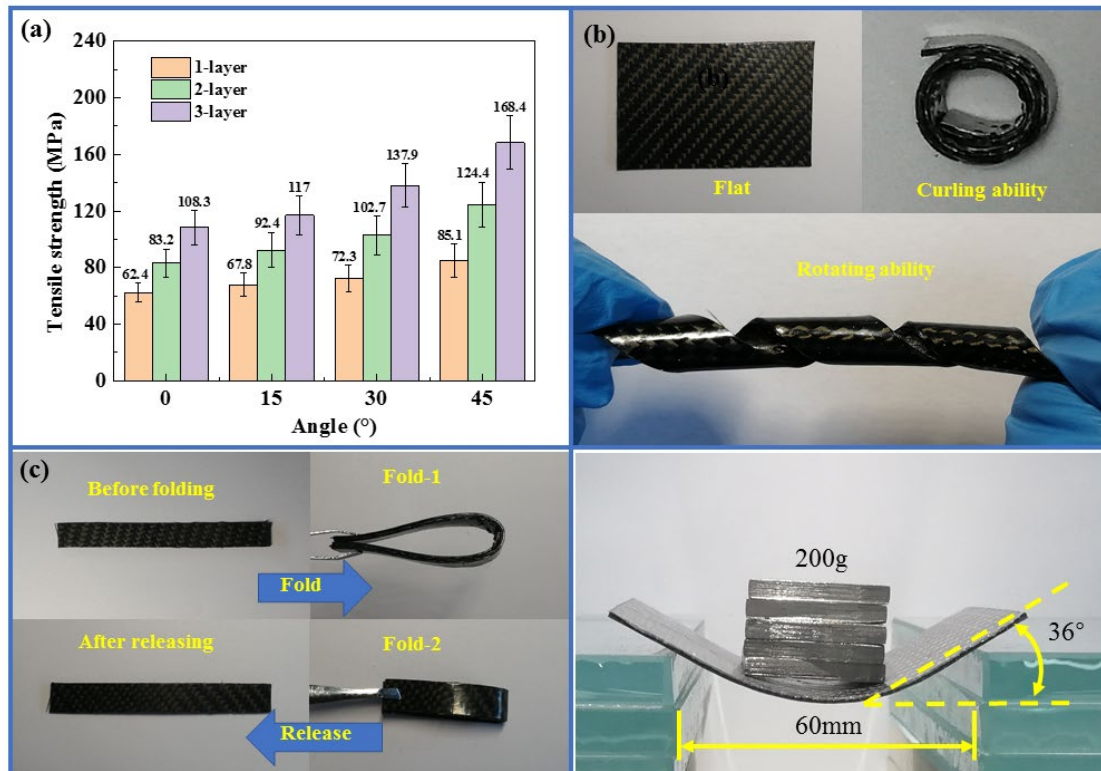


Figure 12. Schematic illustration of the fabrication process for CF fabric/TPU composites.

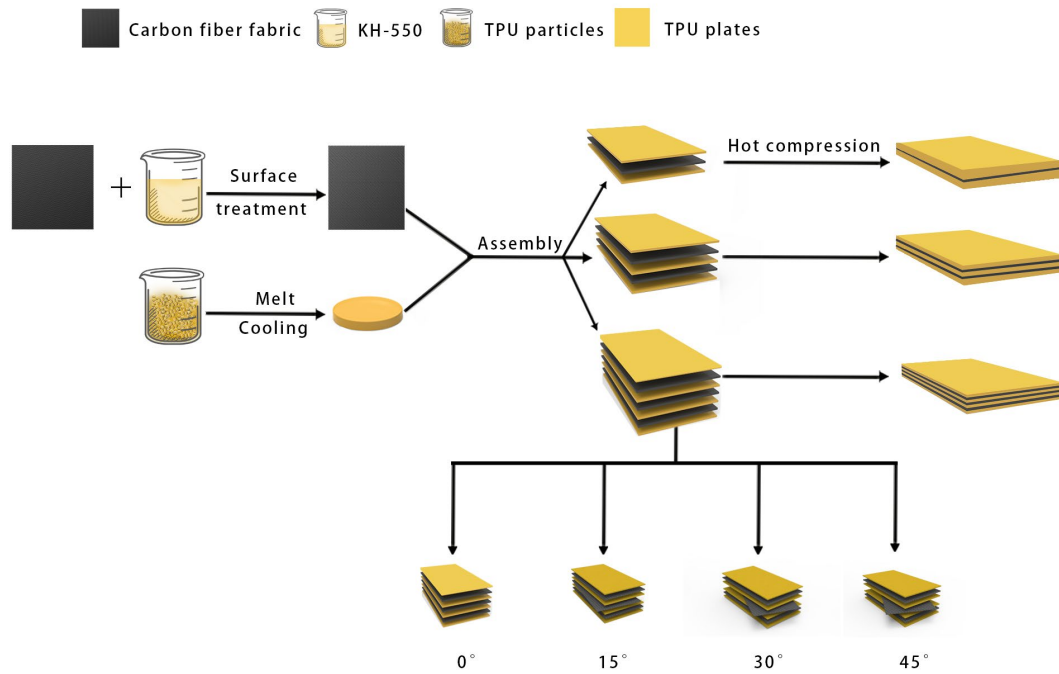


Table 1. The content of CF fabric in composite with different stacking layers and angles. (%)

Layer	0°	15°	30°	45°	Ratio of CF/TPU
One-layer	16.3 ± 0.1	16.1 ± 0.2	16.4 ± 0.2	16.3 ± 0.3	19.4 ± 0.2
Two-layer	31.1 ± 0.2	31.3 ± 0.1	31.2 ± 0.1	31.5 ± 0.2	45.5 ± 0.5
Three-layer	44.6 ± 0.4	44.5 ± 0.3	44.7 ± 0.2	44.8 ± 0.3	80.5 ± 0.5

Table 2. Comparison of CF fabric/TPU composite and other shielding materials.

Sample	EMI-SE (dB)	Density (g/cm ³)	Thickness (mm)	SE/D/T (dB·cm ² /g)	Reference
CF fabric/TPU	73	1.27	1.5	383	This work
PMMA-graphene	19	0.79	2.4	100	[62]
MWCNT/PC	27	1.1	2	123	[63]
PEI/graphene	9.6	0.32	1.8	167	[64]
PEI/graphene nanocomposite foams	20	0.29	2.3	300	[64]
PS/graphene	24	0.63	2.8	136	[65]
Stainless steel	89	8.1	4	27	[66]
Copper	90	9	3.1	32	[66]
MWCNT/TPU	22	1.3	2	85	[67]

Table of contents

This study presents a general, facile and eco-friendly approach to prepare carbon fiber fabric/TPU composites with different stacking layers and angles. The electromagnetic shielding performance of the lightweight CF fabric/TPU composite can be improved with the increase of stacking layers and stacking angles. The CF fabric/TPU composite also possesses excellent mechanical properties.

Keyword: Carbon fiber fabric; lightweight; Electromagnetic interference shielding

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Title: Strong and Flexible Carbon Fiber Fabric Reinforced Thermoplastic Polyurethane Composites for High-Performance EMI Shielding Applications

ToC figure

