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The influence of MXenes on the mechanical, antistatic, and heat-resistant properties of CF/PI composites

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Carbon fiber (CF) and MXene were filled in polyimide (PI) to prepare the CF/MXene/PI composite by compression molding. High-resistance meter, thermal conductivity tester, and scanning electron microscope were used to study the antistatic performance, thermal performance, and mechanical performance of the CF/MXene/PI composite, and the effect of heat treatment on the composite's mechanical properties is discussed. The results show that when the mass fractions of CF and MXene increase, the tensile strength and impact strength of CF/PI and CF/MXene/PI composites all show a trend of first increasing and then decreasing. And when the mass fractions of CF and MXene are 15% and 3%, respectively, the performance of the CF/MXene/PI composite is better. The thermal conductivity of the CF/MXene/PI composite shows an increase with increase in the mass fraction of MXene. Heat treatment affects the mechanical properties of the CF/MXene/PI composite. When the treatment temperature is >240°C, the tensile strength and impact strength of the composite do not change much.

Keywords: *carbon fiber, MXene, SEM, PI, mechanical properties*

1. Introduction

At present, carbon fiber (CF)-reinforced polymer (CFRP) composites are widely used in various structural parts [1]. CFRP composites are anisotropic and have good mechanical properties in terms of fiber-reinforcing features, compared with metallic materials; however, the matrix material is susceptible to environmental aging factors. In the period of service, the CFRP composite structure is affected by high-temperature aging. Thermal stress is easily generated in the temperature-affected environment, affecting the mechanical properties of the CFRP composite [2, 3]. The resin matrix in the CFRP composite has strong temperature sensitivity, in particular when the temperature exceeds the glass transition temperature (T_g), resulting in a large change in the mechanical properties [4]. Skourlis and McCullough [5] found that the fiber–matrix interface is more prone to aging when the T_g of the fiber–matrix interface is lower than the T_g of the surrounding matrix. Lowe et al. [6] studied the aging behavior of CFRP composites at high temperatures and found that the mechanical properties were affected by the aging time. Adil et al. [7] tested the compression destruction strength and the stretching modulus of CFRP composites at different temperatures and found that the stress brought on by temperature causes the softening decomposition of the resin. Mamalis et al. [8] studied the evolution of mechanical properties after high-temperature aging and found that high-temperature aging reduces the mechanical properties of CFRP composites. Bullions et al. [9] studied the change of mechanical properties under high-temperature conditions; the tensile strength changed little, but the compression and bending properties increased as the aging time increased.

CFs have high specific strength, high specific modulus, large fatigue strength, and excellent resistance to high temperature and corrosion. They also have low density, low thermal expansion coefficient, excellent creep resistance, good integrity, apt delamination resistance, superior impact resistance, and so on [10]. There are many varieties of CF-reinforced composite materials; the technology for their processing and molding is constantly updated, and their application fields are wide. It has gradually attracted the attention of the ma-

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jority of scholars. Huang et al. [11] studied the effect of the amount of hollow glass beads used for filling on the fluidity and mechanical properties of CF-reinforced polypropylene composites and found that hollow glass beads have the effect of strengthening and toughening the composites. Wang et al. [12, 13] studied the damping properties of hollow glass beads and chopped CF-filled polyurethane/epoxy composites and found that their tensile strength, thermal decomposition temperature, and damping properties were improved, but their impact resistance performance was reduced. CF and graphite filled along with polyimide (PI) alone can improve the antifriction and antiwear performance of the composite, but the use of nano-Si_3N_4 alone has a negative impact on its antiwear performance, and the tribological performance is optimal when PI is filled along with it. Ai et al. [14] prepared CF-reinforced polycarbonate (PC) composite material and found that its mechanical properties are significantly improved compared to glass fiber-reinforced composite materials. When the CF content is 6%, its elongation and impact strength reach the maximum value; CF can also improve the fluidity and conductivity of the material. Yi et al. [15] used deionized water ultrasound, concentrated nitric acid soaking, concentrated nitric acid ultrasound, and so on for the surface treatment of CF, which increased the bonding strength of the interface between the CF and the resin and significantly improved the mechanical properties of composite materials. Han et al. [16] prepared a composite of CF-warp-knitted fabrics with different knitting methods and studied the influence of fabric-knitting methods on the mechanical properties of noncrimp fabric composite materials and found that the bending performance of unidirectional warp-knitted materials is the best. Among warp-knitted materials, the bending performance of chain-stitched fabrics is higher than that of warp-knitted fabrics. Huang et al. [17] studied the mechanical properties of long CF-reinforced amino resin composite foam materials and investigated the mechanical properties of the material when the loading direction is parallel and perpendicular to the direction of the CF. The results show that when the loading direction is parallel to the fiber direction, the fiber can significantly improve the mechanical properties of the composite. Wouterson et al. [18] studied the effect of changes in CF mass fraction and length on the mechanical properties of composite materials. The results show that the ultimate tensile strength and elastic modulus of the composite material are improved; moreover, the material's fracture toughness and energy release rate are greatly improved. In this paper, a series of bending and compression experiments are carried out to further study the mechanical properties of epoxy resin composite foam with high content of hollow glass beads reinforced with CF.

At present, the research on PI composite materials mainly focuses on the mechanical properties, and there are few studies on the electrical and thermal properties of composite materials. Based on this, the author proposed the idea of adding CF and MXene to PI, aiming to improve the electrical and thermal properties of PI composites. The factors affecting the electrical and thermal properties of the CF/MXene/PI composites were studied, and the optimal ratio was determined. At the same time, the influence of the heat treatment process conditions on the mechanical properties of the composites was analyzed.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN)-based CF was provided by Shanghai Xinxing Carbon Factory, with

Table 1. Main properties of PI (GCTP^{TM})

Density (kg/m^3)	1,350
Impact strength (kJ/m^2)	25
Tensile Strength (MPa)	95
Thermal expansion coefficient ($^\circ C^{-1}$)	4.8×10^{-5}
Elongation at break (%)	7
T_g ($^\circ$C)	260
Flexural strength (MPa)	150
Thermal decomposition temperature ($^\circ$C)	240

T_g, glass transition temperature; PI, polyimide.

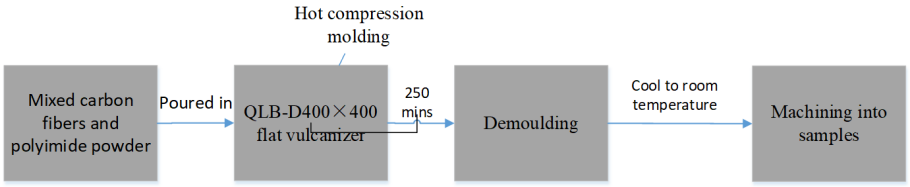


Fig. 1. Preparation process of CF/PI composites by heat treatment. CF, carbon fiber; PI, polyimide

average diameter of 7 μm, length of 75 μm, tensile strength of 2,500 MPa, modulus of elasticity of 200 GPa, and density of 1,760 kg/m^3. GCPI^{TM} PI, produced by Guangcheng Plastic Co., Ltd., is a thermoplastic PI. Its properties are shown in Table 1.

2.2. Composite preparation

In the ozone treatment, the thermally desized CF is put into a tube furnace (Shenghuan ozone generator, model SH-801-5G/H), and ozone is introduced into the tube furnace by an ozone generator at a flow rate of 200 mL/min, and the chamber is ventilated at 140°C for 20 min.

After the PI powder and CF (0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt% are mechanically mixed, they are molded by a QLB-D400×400 flat vulcanizer (Shanghai Changyuan Rubber Machinery Equipment Co., Ltd.); the molding temperature is 340°C, the pressure is 12 MPa, and heat preservation is maintained. The pressure is maintained for 250 min, the sample is cooled down to 200°C for demoulding, and it is machined into a sample of the required size. The preparation process of the composite material is shown in Figure 1, and the temperature and pressure changes with time during the hot compression molding process are shown in Figure 2.

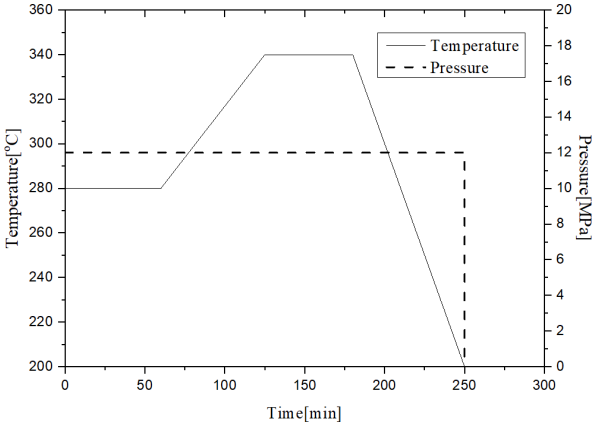


Fig. 2. The variations of temperature and pressure with time

The blast drying box is heated to the set temperature (230°C, 240°C, 250°C, 260°C, and 270°C) and stabilized for 30 min; then, the sample is put into the blast drying box for constant temperature treatment. Subsequently, the sample is cooled at room temperature for 24 h.

2.3. Test and characterization

The surface morphology of CF was observed by atomic force microscopy (AFM) (Solver P47; NT-MDT Company, Russia). The scanning range was 5 μm × 5 μm. The surface resistivity test was done in accordance with GB/T 1410- 2006 using a digital surface resistance tester TM386 (Techman Instruments Holdings Co., Ltd). The tensile properties were tested according to GB/T 1040-2006, and the tensile test speed was 10 mm/min. The impact performance was studied in accordance with GB/T1843-2008, and the test temperature was 25°C.

The thermal conductivity, λ, was measured using the KD2 Pro thermal characteristic analyzer. A field-emission scanning electron microscope was used to observe and test the surface micromorphology of the composite before and after O_3 modification. An appropriate amount of the samples was stuck on the sample stage with double-sided tape, and the sputtering instrument was observed after spraying gold for about 30 s at a voltage of 1.5 kV. The test is carried out at a scanning voltage of 30 kV. Fourier-transform infrared (FTIR) spectroscopy was used to analyze the surface functional

groups before and after the O_3 treatment. The samples were prepared by the potassium bromide tablet method, and the test range was 500–4,000 cm^{-1} at room temperature. The surface resistivity, tensile strength, impact strength, and thermal conductivity tests were repeated at least three times. The error bars represent 5% standard deviation.

3. Results and discussion

3.1. CF/PI composite

3.1.1. Electrical performance

Figure 3 shows the effect of CF mass fraction on the surface resistivity of CF/PI and O_3-treated CF/PI composites. It can be seen that the higher the CF mass fraction, the lower is the surface resistivity of the composite. When the CF content is low, the particle spacing is large. Only a few high-energy electrons cross the gap. Current transmission in the composite is difficult, and the surface resistivity is large. When the amount of CF increases, the distance between the conductive particles becomes smaller, enabling a large number of electrons to cross the gap, and the surface resistivity of the composite material decreases. At the same time, it was found that the surface resistivity of the composite increased after CF was treated by gas phase oxidation. In order to verify the reason for the increase in surface resistivity, relevant tests were carried out. Figure 4 shows the FTIR spectra of CF and O_3-treated CF, and Figure 5 shows the scanning electron microscopy (SEM) photos of CF/PI and O_3-treated CF/PI composites.

As shown in Figure 4, the FTIR spectrum of O_3-treated CF appears at 1,723 cm^{-1}, which is the characteristic peak of –C=O; this indicates that the O_3 oxidation treatment produces polar groups on the CF and increases the surface activity. It can also be seen from the SEM photos that, the surface of O_3-treated CF becomes rougher (see Figure 5B) with obvious grooves and increased specific surface area, compared with the surface of CF (see Figure 5A), which is proved by the surface roughness results, shown in Table 2. These changes are all conducive to the improvement of the interface compatibility between the fiber and the matrix resin. As shown in Figure 5A, there are obvious traces of fiber pullout in the CF/PI composite, and conductive paths are easily formed between the CFs; O_3-treated CF and PI are tightly combined, and fiber pullout is rarely seen. The remaining gully on the fiber surface is covered with a large amount of PI resin; it is difficult to form a conductive path between the resin-coated fibers. Hence, the surface resistivity increases.

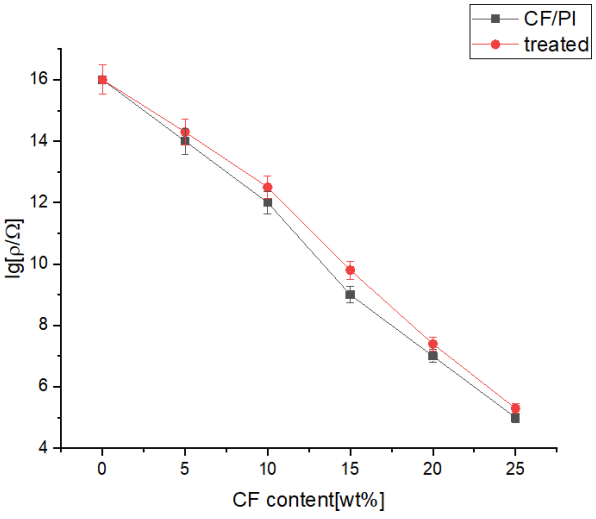


Fig. 3. The effect of CF mass fraction on the surface resistivity of CF/PI and O_3-treated CF/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

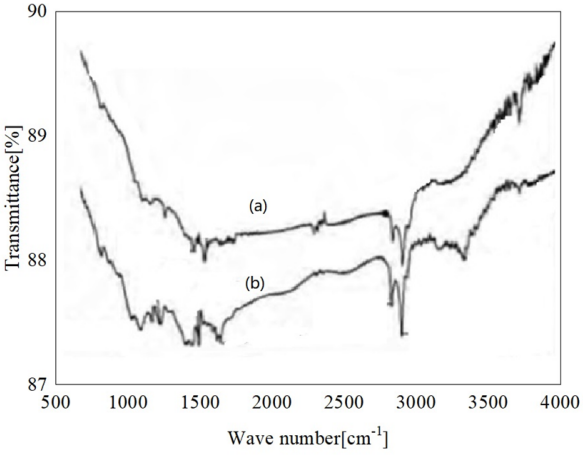
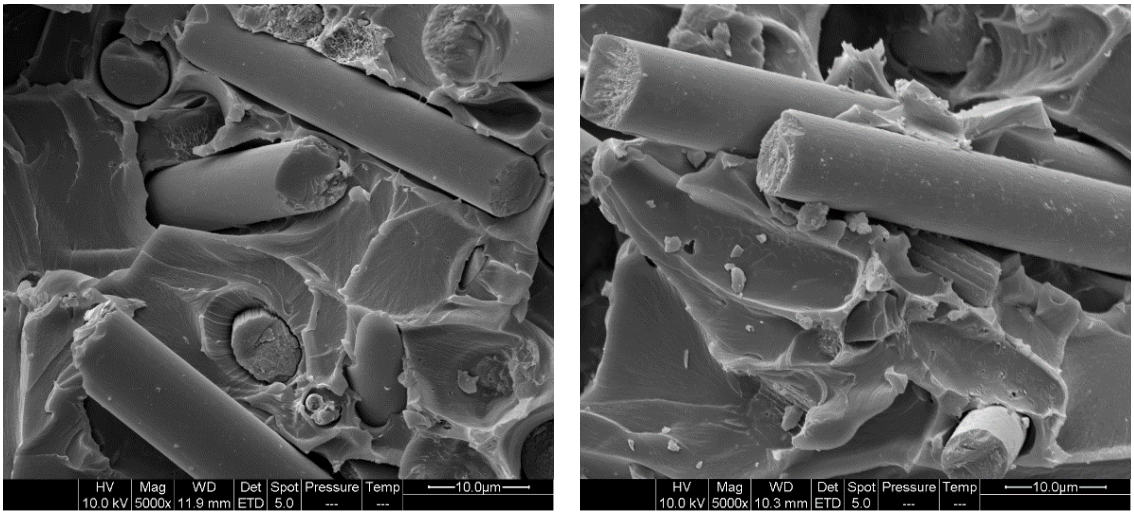


Fig. 4. FTIR spectrum of CF and O_3-treated CF: **(A)** CF; **(B)** O_3-treated CF. CF, carbon fiber; FTIR, Fourier-transform infrared



(A) (B)

Fig. 5. SEM photos of (A) CF/PI and (B) O_3-treated CF/PI composites. CF, carbon fiber; PI, polyimide; SEM, scanning electron microscopy

Table 2. Surface roughness results by AFM

Type	Surface roughness (nm)
CF	30.7
O_3-treated CF	42.9

AFM, atomic force microscopy; CF, carbon fiber

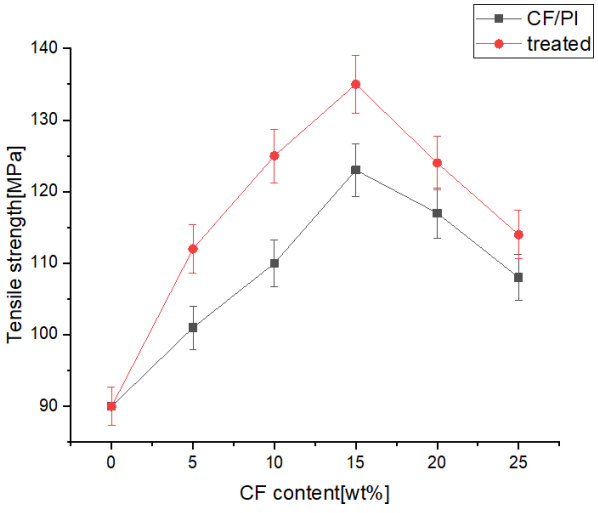


Fig. 6. The effect of CF mass fraction on the tensile strength of CF/PI and O_3-treated CF/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

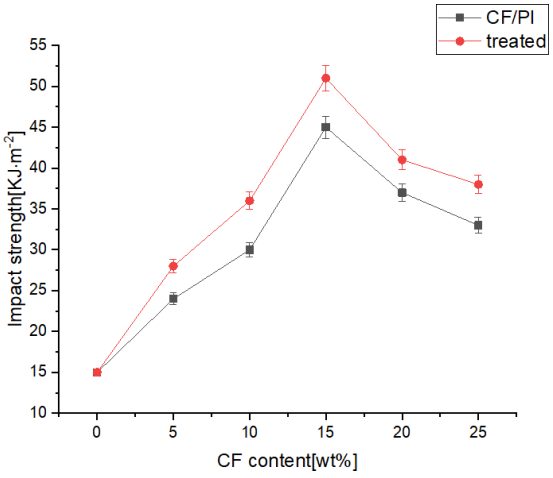
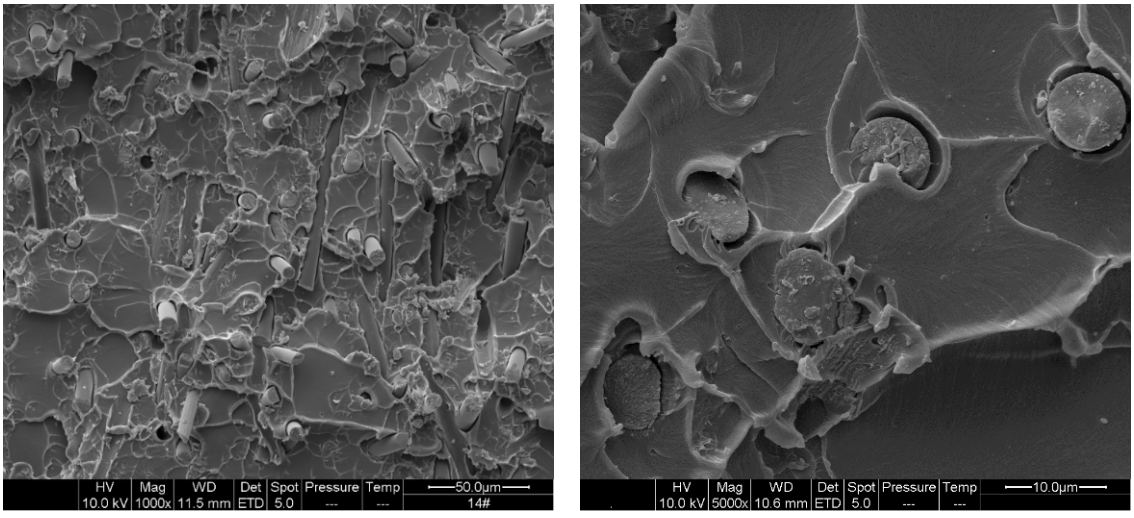


Fig. 7. The effect of CF mass fraction on the impact strength of CF/PI and O_3-treated CF/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

3.1.2. Mechanical properties

Figure 6 shows the effect of CF mass fraction on the tensile strength of CF/PI and O_3-treated CF/PI composites. It can be seen that with the increase of the CF mass fraction, the tensile strength of the two composite materials showed a trend of first increasing and then decreasing. Moreover, O_3-treated CF/PI composites have a higher tensile strength



(A) (B)

Fig. 8. The SEM image of the CF/PI composite when the CF mass fraction is 15%. CF, carbon fiber; PI, polyimide; SEM, scanning electron microscopy

at the same CF content. This may be due to the fact that more functional groups are attached to the surface. When the CF mass fraction is 15%, the tensile strength of the CF/PI composite reaches the maximum value of 123.5 MPa. This is because CF has greater strength and modulus. The bonding of the interface gradually becomes worse, which inevitably affects the mechanical properties of the composite material; therefore, the mechanical properties show a downward trend. As the stress concentration, it can resist strain in the surrounding part of the matrix. At the same time, load or stress can be transferred from the fiber to the adjacent fiber through the matrix, changing the stress distribution state. When the amount of added fibers exceeds a certain value, agglomeration occurs due to the bonding force between the matrix and the fibers being greater than the force between the fibers, which reduces the tensile strength of the composite.

Figure 7 shows the effect of CF mass fraction on the impact strength of CF/PI and O_3-treated CF/PI composites, which shows the same trend as tensile strength. When the CF mass fraction is 15%, the impact strength is the best. When the matrix is impacted by an external force, the stress is transferred and dispersed by the flexible transition layer between the CF and the matrix. The fibrous structure of the CF can cause crazing and local yield deformation, and the impact can be absorbed; thus, the impact strength is greatly improved. However, when the mass fraction of CF is large, CF will agglomerate, which will cause the rapid development of crazing into cracks and produce defects in the composite, which will reduce the impact performance of the composite.

Figure 8 shows the SEM image of the CF/PI composite when the CF mass fraction is 15%. It can be seen that when the mass fraction is 15%, the CF is uniformly dispersed in the composite material, and there are many broken fibers, indicating that the CF has a reinforcing effect in the composite material, and the strength of the composite is increased. Compared with the CF/PI composite material, the mechanical properties of the O_3-treated CF/PI composite material are obviously better. This is because the O_3 oxidation treatment can improve the interface bonding performance of the composite material, which is consistent with the results of the electrical performance test. O_3 oxidation treatment improves the mechanical properties of the composite material, but at the same time, it increases the surface resistivity of the composite material.

It can be seen from Figure 8A that a CF was broken, and a part of it remained on the resin matrix, leaving a clear dent. During the loading process, the CF effectively blocks the propagation of the crack, and a large amount of energy is consumed as the CF is peeled or broken, thereby enhancing the mechanical properties of the composite material. It can be clearly seen that the resin matrix has stepped fracture morphology and obvious discontinuities in the fiber, indicating that the fiber has played a role in hindering the propagation of the crack surface, as shown in Figure 8B.

3.2. CF/MXene/PI Composite

3.2.1. Electrical performance

Figure 9 shows the effect of MXene content on the surface resistivity of CF/MXene/PI composites. It can be seen that with the increase of the MXene mass fraction, the resistivity of the composite shows an upward trend. Because MXene is an insulating material, as the content of MXene increases, the dispersion of the composite becomes poor, and defects such as bubbles are easily generated. The distance between the conductive particles increases. It is difficult to form a conductive path on the surface of the CF.

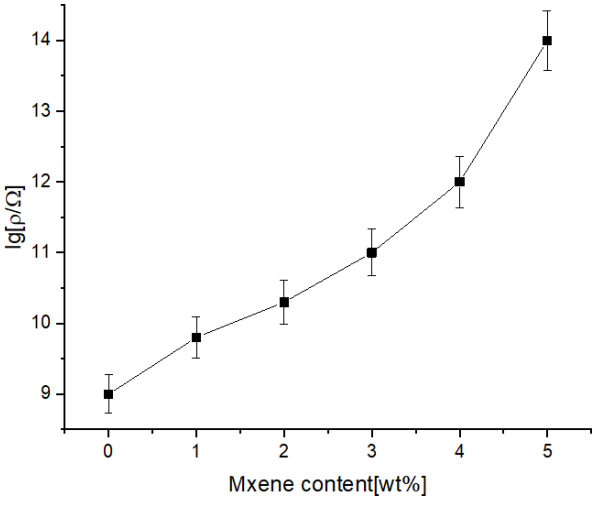


Fig. 9. The effect of MXene content on the surface resistivity of CF/MXene/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

3.2.2. Thermal conductivity

Figure 10 shows the effect of MXene mass fraction on the thermal conductivity of CF/MXene/PI composites. It can be seen that the thermal conductivity of the composite increases with the increase of the MXene mass fraction. The most significant property of MXene is its high thermal conductivity. The more the amount used, the better is the dispersion in the matrix resin, and the better it is to form a thermal network chain, thereby increasing the thermal conductivity of the composite.

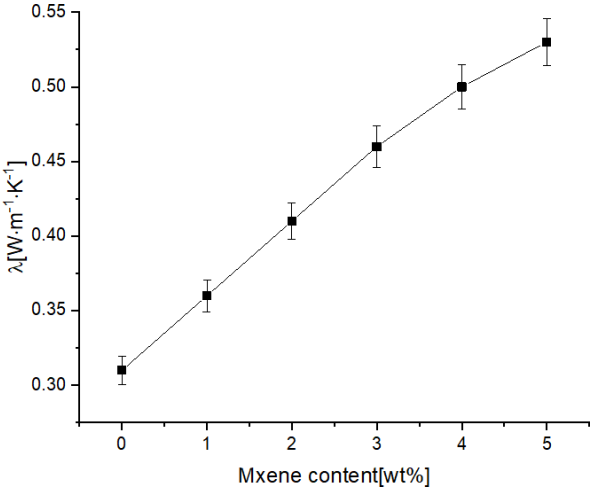


Fig. 10. The effect of MXene mass fraction on the thermal conductivity of CF/MXene/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

3.2.3. Mechanical properties

Figure 11 shows the effect of MXene mass fraction on the tensile strength and impact strength of CF/MXene/PI composites. It can be clearly seen that with the increase of the MXene mass fraction, the tensile strength and impact strength of the composite material increase first and then decrease. When the MXene mass fraction is 3 wt%, the tensile strength and impact strength of the composite material are the best. This is because the addition of an appropriate amount of MXene can effectively transmit stress and hinder the expansion of cracks, improving the mechanical properties. The increase of the MXene mass fraction makes the dispersion of the composite worse, and defects

such as bubbles are easily generated, forming more stress concentration points, destroying the continuous structure of the matrix and lowering the mechanical properties. The electrical properties, thermal properties, and mechanical properties of the CF/MXene/PI composites were compared and analyzed. Finally, it was determined that the optimal mass fraction of MXene in the composites was 3%.

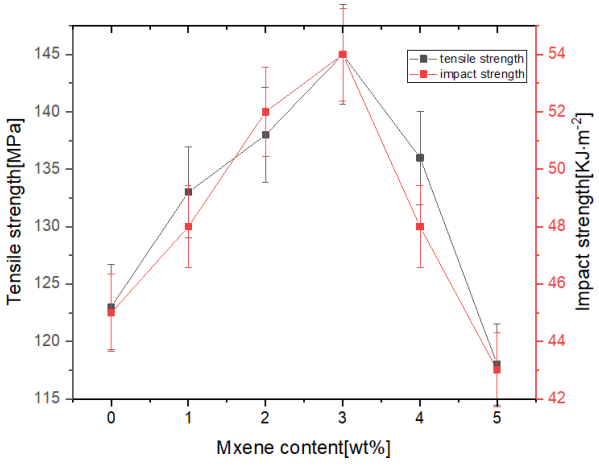


Fig. 11. The effect of MXene mass fraction on the tensile strength and impact strength of CF/MXene/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

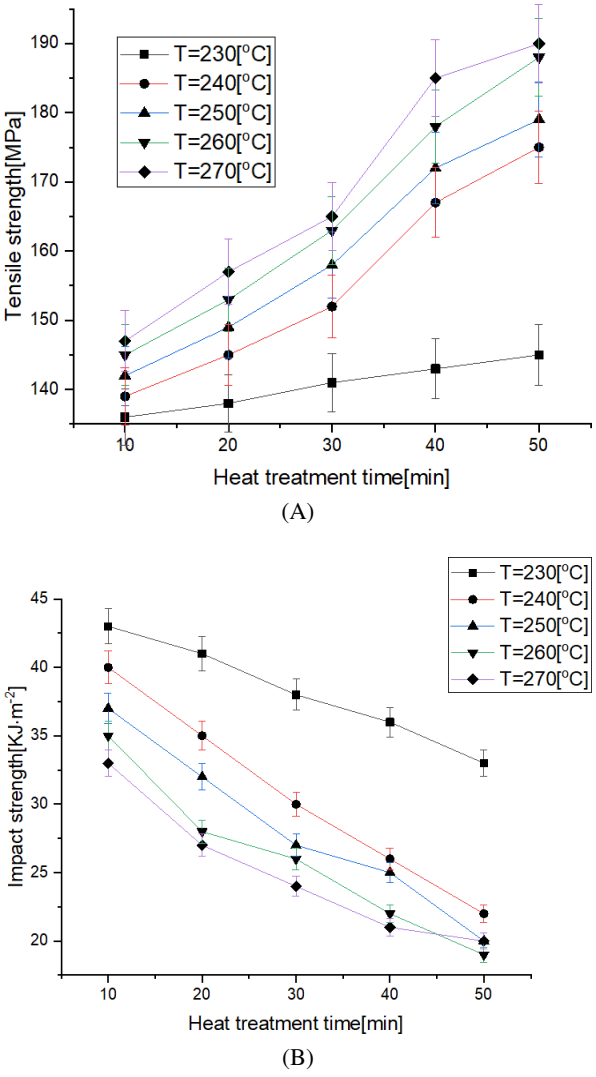


Fig. 12. The effect of heat treatment on the tensile strength and impact strength of CF/MXene/PI composites. CF, carbon fiber; PI, polyimide. The error bars represent 5% standard deviation

3.2.4. The effect of heat treatment on the properties of CF/MXene/PI composites

Figure 12 shows the tensile strength (Panel A) and impact strength (Panel B) of the CF/MXene/PI composite when heat-treated at different temperatures for 10 min, 20 min, 30 min, 40 min, and 50 min. The tensile strength of the composite showed an overall upward trend with increase in the processing time, and the impact strength decreased with the increase of processing time. When the treatment time is >2.0 h and the treatment temperature is >240°C, the tensile strength and impact strength of the composite do not change much, indicating that the crystallization behavior of the composite material tends to be complete, which further confirms the above conclusion.

Both the duration and temperature of heat treatment can affect the crystallinity of the composite material since it takes a certain time for the macromolecular segments to be arranged regularly. When the heat treatment period is short, the crystallization is insufficient. The heat treatment temperature affects the formation of crystal nuclei during cooling. When the temperature is lower, the space for the movement of molecular segments is limited. Therefore, the formation of crystal nuclei is less. The phase nucleates and easily forms

large spherulites, which renders the composite brittle. The tensile strength of the composite depends on the regularity of the molecular chain. With the increase of crystallinity, the orderly arrangement of the molecular chain increases, and the tensile strength of the composite increases. The impact strength of a polymer depends on the number of disorderly arranged and intertwined molecular chains. The more complete the crystallinity of the composite, the more orderly is the arrangement of the molecular chains, and the smaller is the number of disorderly arranged molecular chains. Therefore, during the impact process, the effective segment capable of absorbing the impact energy is reduced, making the propagation of cracks easier and reducing the impact strength of the composite.

4. Conclusion

The addition of CF can reduce the surface resistivity of the composite material, and the CF treated with O_3 oxidation can improve the mechanical properties and surface resistivity of the CF/PI composite material. As the mass fractions of CF and MXene increase, the tensile strength and impact strength of CF/PI and CF/MXene/PI composites all show a trend of first increasing and then decreasing. When the mass fractions of CF and MXene are 15% and 3%, respectively, the tensile strength, surface resistivity, and thermal conductivity of the CF/MXene/PI composite are the best. The addition of CF and MXene affects the thermal performance of the composite. Heat treatment affects the mechanical properties of the CF/MXene/PI composite. When the treatment temperature is $>240^{\circ}$C, the tensile strength and impact strength of the composite do not change much.

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