Excellent tribological properties of epoxy–Ti₃C₂ with three-dimensional nanosheets composites

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Abstract: As a widely used engineering polymer, epoxy resin has been successfully employed in high-performance components and setups. However, the poor thermal and friction properties of traditional epoxy resin greatly limit its application in many extreme environments. In this work, a new kind of epoxy–Ti₃C₂ with three-dimensional nanosheets (3DNS) composite which was designed by freeze-drying method showed up excellent thermal and friction properties. As a result, the coefficient of thermal expansion (CTE) of epoxy–Ti₃C₂ 3DNS 3.0 composites was 41.9 ppm/K at 40 °C, which was lower than that of the traditional epoxy resin (46.7 ppm/K), and the thermal conductivity (TC) was also improved from 0.176 to 0.262 W/(m·K). Meanwhile, epoxy–Ti₃C₂ 3DNS 1.0 composites showed up the best friction property, with wear rate 76.3% lower than that of epoxy resin. This work is significant for the research of high-performance composite materials.

Keywords: epoxy–Ti₃C₂ 3DNS composite; three-dimensional nanosheets; thermal performances; friction properties

1 Introduction

As high-performance parts and equipment move toward more precision and miniaturization, lightweight, efficient heat dissipation, and wear resistance are critical to enhance the longevity of the devices [1, 2]. Meanwhile, for good mechanical and adhesive properties, and chemical stability, epoxy resin is usually used as grinding wheel adhesive, composite matrix, and engineering plastics, and is widely applied in aerospace, military equipment, medical machinery, mechanical processing, and other fields [3, 4]. However, the heat dissipation and wear resistance of traditional epoxy resin cannot satisfy the requirements of high-performance devices serving in extreme conditions, which limit the further application of epoxy resin

in various fields [5]. In order to improve the heat dissipation and wear resistance of traditional epoxy resin, researchers used fillers or nano-fillers to modify the epoxy resin. The modified epoxy resin not only increases the wear resistance and heat dissipation, but also improves the mechanical properties such as strength and hardness [6, 7].

Nowadays, according to the type of filling material, the single-phase filling and multi-phase filling are the most important methods to modify epoxy resin [8–10]. The single-phase filling method includes one-dimensional, two-dimensional, and three-dimensional filling. Raghavendra et al. [11] studied their thermal, tribological, and mechanical properties of epoxy composites prepared using jute fiber and glass fiber as fillers. The results show that the mechanical

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properties of glass fiber/epoxy resin composites were better than those of jute fiber/epoxy resin composites and epoxy resin, but the jute fiber/epoxy resin composites show up the best tribological properties. Wang et al. [12] prepared carbon fiber reinforced epoxy composites and studied the tribological behavior and corrosion resistance with different orientations (0° , 45° , and 90°). The composites with 45° orientation showed the lowest friction coefficient, while the lowest wear rate was observed at 90° orientation. Bazrgari et al. [13] used Al_2O_3 nanoparticles to modify and to strengthen epoxy resin, and the hardness and the impact strength of the composites were improved. In addition, the tensile, compressive, inter laminar shear stress, and tribological properties of the epoxy resin composites with modified graphene prepared by Amirbeygi et al. [14] were improved. Furthermore, for the self-lubricating property of the modified graphene, the wear resistance of the composites has been greatly improved.

Researchers have found that in epoxy resin composites, the advantages of different materials can be used to weaken each other's shortcomings and produce synergistic effect, so that the performance of the composites can be evidently improved [15]. Vaisakh et al. [16] prepared epoxy resin composite with the mixed nanoparticles (SiO_2 and Al_2O_3), which improved the thermal conductivity, mechanical strength, hardness, and tribological properties of the composites. The nano-modified mixed fillers showed better performance under high load conditions, which was of great theoretical value for practical engineering application. Karthikeyan et al. [17] modified epoxy resin with multiwalled carbon nanotubes (MWCNTs) and Al_2O_3 . Due to the synergistic effects of MWCNTs self-lubricating property and Al_2O_3 on the matrix hardness, the friction coefficient and wear rate of the composites were reduced.

Since the experimental synthesis of graphene in 2004, more and more two-dimensional graphene like materials (such as BN and MoS_2) have been used as reinforcing fillers to improve the thermal, mechanical, and tribological properties of polymer matrix [18, 19]. The methods for these fillers are relatively mature. MXenes was firstly prepared using hydrofluoric acid etching method in Refs. [20–22]. Following this more

and more different kinds of MXene have been studied. Even though Ti_3C_2 MXene can be successfully prepared and stripped by many research groups [23], the price and quality are still different due to the different quality of Ti_3AlC_2 and preparation parameters. Therefore, the preparation methods are not mature enough. In order to prepare high-quality Ti_3C_2 MXene, some of the preparation parameters still need to be explored. Furthermore, for two-dimensional material Ti_3C_2 MXene, most of the research is focused on energy storage, electromagnetic shielding, catalysis, and other fields, but the research on its application in the fields of thermal performance and tribology is rare [24]. Because of the brittleness brought by the network cross-linking structure of epoxy resin, its wear and thermal performance are poor. The traditional epoxy resin and its composite materials cannot meet the requirements of high-performance devices.

In this work, the preparation and stripping parameters of high-quality Ti_3C_2 MXene were studied and epoxy- Ti_3C_2 3DNS composites were prepared by liquid phase blending and three-dimensional structure construction method. The results showed that the composites have the better CTE, TC, and higher microhardness than those of epoxy resin. Furthermore, epoxy- Ti_3C_2 3DNS with 3.0 g nanosheets showed the best thermal properties (TC and CTE) and epoxy- Ti_3C_2 3DNS with 1.0 g nanosheets showed the best friction properties (friction coefficient), which were of great significance for practical application in high-performance devices.

2 Experimental

2.1 Materials

Ti_3AlC_2 powders were purchased from Forsman Scientific Co., Ltd. (Beijing, China). Hydrogen fluoride (HF, 40%) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cycloaliphatic epoxy resin (6105, DOW Chemicals) and methyl hexahydrophthalic anhydride (MHHPA) which was used as curing agent, were purchased from Shanghai Liyi Science and Technology Development Co., Ltd. (Shanghai, China), respectively. Neodymium(III)2,4-pentanedionate (Nd(III)acac) was

provided by Aldrich Chemicals (Milwaukee, USA). Modified carbon nanofiber (CNF) was provided by Guilin Qihong Technology Co., Ltd. (Guilin, China). All the chemicals were of analytical reagent grade.

2.2 Preparation of few-layer Ti_3C_2 MXene

To obtain Ti_3C_2 MXene, Ti_3AlC_2 was treated with HF to etch Al atomic layer. The method was detailed as follows [25, 26], 1 g Ti_3AlC_2 was slowly added into 10 mL HF which was kept in polytetrafluoroethylene containers. The mixture was stirred for 48 h at 40 °C. Then, 200 mL deionized water was added into the mixture and a diluted suspension was obtained. The suspension was centrifuged to collect the sediment. The sediment was washed with deionized water until the pH was close to 7. Finally, the cleaned sediment was filtered onto polypropylene membrane with 0.22 mm pore size and dried in vacuum for 6 h at 80 °C to obtain multi-layer Ti_3C_2 MXene. The dried multi-layer Ti_3C_2 MXene was mixed with deionized water in some proportion (power:deionized water = 1 g:1 L) to obtain the solution. The solution was circulated 100 times under 180 MPa using a cryogenic and ultra-high pressure continuous flow cell crusher (JN 10C, JNBIO, UK), and then dried in a vacuum oven at 50 °C to obtain few-layer Ti_3C_2 MXene.

2.3 Preparation of epoxy- Ti_3C_2 3DNS composites

Epoxy- Ti_3C_2 3DNS composites were prepared by the following procedures, as shown in Fig. 1. In the first step, 0.5, 1.0, 2.0, and 3.0 g few-layer Ti_3C_2 MXene was

mixed with 20 g CNF aqueous solution (the content of CNF is 1 wt%). The mixed solution was stirred for 5 h at 120 rpm in ice bath to obtain uniform Ti_3C_2 MXene/CNF solution. The obtained solution was poured into a polypropylene container which was replaced the bottom by a copper block, and the container was surrounded by insulating cotton. Subsequently, the copper block was immersed in liquid nitrogen for directional freezing until the solution turned block solid completely. Then, the block was freeze-dried for 3 days at -60 °C and 5 Pa in avacuum freeze dryer (LGJ-10E, Beijing, China), and the few-layer Ti_3C_2 MXene with three-dimensional nanosheets could be obtained.

Nd(III)acac was mixed with epoxy resin in a mass ratio of 1:1,000 (Nd(III)acac: epoxy resin), and the mixture was stirred for 3 h at 80 °C. Then, MHHPA was added into the mixture in a mass ratio of 95: 100 (MHHPA: mixture) and stirred for 15 min to obtain epoxy resin with curing agent.

Few-layer Ti_3C_2 MXene with three-dimensional nanosheets blocks were put into a container made of tin foil, and a certain amount of epoxy resin was added into the container. The container was put into vacuum and degassed at 50 °C for 24 h, so that the epoxy resin was fully immersed in the three-dimensional nanosheets blocks. Finally, the samples were pre-cured in an oven at 135 °C for 2 h and cured at 165 °C for 14 h to achieve sample curing. After the samples were cooled to room temperature, the composites were polished to desired shape with sandpaper. For comparison, pure CNF/epoxy resin composites

Fig. 1 Schematic diagram of preparation of epoxy- Ti_3C_2 3DNS composites.

were prepared according to the above method. Epoxy–Ti₃C₂ 3DNS x composites are used to label the composites with x g added Ti₃C₂ MXene.

2.4 Friction and wear tests

The friction and wear tests were carried out using a ball-on-plate high-temperature reciprocating wear test equipment (UMT-3, Instruments, USA). Before tests, the surfaces of friction of pure epoxy and composites samples were polished by sandpaper (#1200) to obtain the roughness of about 0.18–0.20 μm . The samples were cleaned by ultrasonic treatment with alcohol to ensure that the friction surface was not interfered by foreign impurities. The friction pair was GCr15 steel ball with diameter of 3 mm and the hardness was HRC60–65. The type of friction was dry sliding friction, and the test parameters were shown in Table 1. After the friction and wear test, the cross-sectional area of scratches (S , mm^2) was measured by integral method, and the scratch volume was obtained by multiplying the scratch length. Each scratch was measured at three different positions, and the average value was taken as the final experimental data. The wear rate was the change of wear volume in unit length and unit load. The wear rate was calculated by Eq. (1).

$$W = \frac{V}{F \cdot L} \quad (1)$$

where W ($\text{mm}^3/(\text{m} \cdot \text{N})$) is wear rate, V (mm^3) is the volume of scratches, F (N) is the load applied during friction, and L (m) is total friction distance. The friction coefficient curve can be given by the software of the test equipment.

2.5 Characterization

Field emission scanning electron microscope (FE-SEM,

Quanta 250, USA) was used to characterize the cross-section and the micromorphology of friction and wear surfaces. Before the test, a thin layer of gold was plated on the surface of the samples to avoid the accumulation of electric charge. Transmission electron microscope (TEM, TECNAI F20, USA) was used to observe the microstructure of ultra-thin few-layer Ti₃C₂ MXene with an accelerating voltage of 200 kV. The scratches were measured using the laser confocal microscope (LSM700, Zeiss, Germany). CTE was measured by thermomechanical analyzer (TMA 402 F1/F3, Netzsch, Germany). The thermogravimetric analysis (TGA) was performed on a TGA 209 F3 (NETZSCH, Germany) in nitrogen atmosphere. Vickers hardness of the samples was measured by microhardness tester (HV-1000, China). During the measurement, the load was 0.5 N and the loading time was 15 s.

3 Results and discussion

3.1 Microstructure characterization

In order to study the etching effect of HF on Ti₃AlC₂, SEM images of etched Ti₃C₂ MXene were taken and displayed in Fig. 2(a). It can be seen from Fig. 2(a) that the etched Ti₃C₂ MXene has a layer by layer accordion-like morphology, and the distance between layers is different. Figure 2(b) is a SEM image of few-layer Ti₃C₂ MXene after peeling. It can be found that the peeling effect is obvious and very thin few-layer nanosheets. Figure 2(c) is a TEM image of few-layer Ti₃C₂ MXene which shows that the peeled sample is very thin and transparent. Figure 2(d) shows the high-resolution TEM images of few-layer Ti₃C₂ MXene. The inset of Fig. 2(d) is the corresponding fast Fourier transform (FFT) of the thin Ti₃C₂ MXene nanosheets, and the lattice structure of the samples is hexagonal,

Table 1 Friction and wear test parameters of different content of few-layer Ti₃C₂ MXene.

No.	Material	Content (g)	Frequency (Hz)	Time (min)	Load (N)	Scratch (mm)
1	Epoxy	0	2	30	5	5
2	Ti ₃ C ₂ MXene	0	2	30	5	5
3	Ti ₃ C ₂ MXene	0.5	2	30	5	5
4	Ti ₃ C ₂ MXene	1.0	2	30	5	5
5	Ti ₃ C ₂ MXene	2.0	2	30	5	5
6	Ti ₃ C ₂ MXene	3.0	2	30	5	5

Note: Room temperature is 25 °C; relative humidity is 60%.

Fig. 2 SEM images of (a) mult-layer Ti_3C_2 MXene after etching and (b) few-layer Ti_3C_2 MXene after peeling, (c) TEM and (d) high-resolution TEM images of few-layer Ti_3C_2 MXene, the inset of (d) is the corresponding FFT of the thin Ti_3C_2 MXene nanosheets.

which is the same as the structure of Ti_3AlC_2 .

Figures 3(a)–3(e) describe the fracture surfaces morphology of the samples which contains 0, 0.5, 1.0,

2.0, and 3.0 g few-layer Ti_3C_2 MXene nanosheets, respectively. In addition, the insets are the corresponding high-resolution SEM images. Figure 3(a) shows that CNF forms three-dimensional nanosheets with a certain direction. It can be clearly seen from Figs. 3(b)–3(e) that more and more few-layer Ti_3C_2 MXene nanosheets appear on the frame surface of CNF, and their arrangement is also directional. The reason for this phenomenon is that in the preparation of the few-layer Ti_3C_2 MXene nanosheets, the ice crystal growth direction of the aqueous solution is along the temperature gradient direction with the single direction. In this process, the CNF in the aqueous solution and the few-layer Ti_3C_2 MXene nanosheets will be aligned with the ice crystal growth direction. During the process of freeze-drying, the ice crystal sublimed, and the directional few-layer Ti_3C_2 MXene nanosheets with three-dimensional nanosheets were retained. Furthermore, the CNF increased the strength of the structure which makes it difficult to collapse. The CNF used in this experiment is surface modified, and the surface has $-\text{COOH}$ and $-\text{OH}$ groups, which are conducive to the distribution and combination of few-layer Ti_3C_2 MXene nanosheets on the surface. Moreover, it can be seen from Fig. 3 that the distance

Fig. 3 SEM images of the fracture surfaces of the block with (a) 0 g, (b) 0.5 g, (c) 1.0 g, (d) 2.0 g, and (e) 3.0 g few-layer Ti_3C_2 MXene three-dimensional nanosheets.

between adjacent wall layers is 20–30 μm along the arrangement direction.

Figures 4(a)–4(f) show the SEM images of fracture surfaces of epoxy resin and epoxy– Ti_3C_2 3DNS composites with 0, 0.5, 1.0, 2.0, and 3.0 g few-layer Ti_3C_2 MXene nanosheets, and the insets are the corresponding higher-resolution SEM images. It can be seen from Fig. 4(a) that the fracture surface stripes of epoxy resin are river-like, and the surface between the stripes is very smooth, which are typical characteristics of brittle thermosetting polymer. As shown in Figs. 4(e) and 4(f), the fracture surfaces of epoxy– Ti_3C_2 3DNS composites also have some stripes, indicating that their brittleness is the same as that of epoxy matrix. Furthermore, the longitudinal ordered texture fringes and few-layer Ti_3C_2 MXene nanosheets are obvious, and with the increase of the nanosheets, more and more nanosheets appear on the fracture surfaces. Besides, some groups on the CNF surfaces (such as $-\text{COOH}$ and $-\text{OH}$) and on the Ti_3C_2 MXene surfaces (such as $-\text{OH}$, $-\text{O}$, and $-\text{F}$) can participate in the curing reaction of epoxy, which can strengthen the interface combination of three-dimensional nanosheets and epoxy matrix. Furthermore, the fracture surface of epoxy– Ti_3C_2 3DNS composites has neither bubbles nor cracks.

3.2 Thermal performances

Figure 5(a) shows the thermal diffusivity and TC of epoxy resin and epoxy– Ti_3C_2 3DNS composites with different Ti_3C_2 MXene content. It is clear from Fig. 5(a) that the TC and the thermal diffusivity of these composites increase gradually with the increase of Ti_3C_2 MXene content. The thermal diffusivity and TC values of epoxy resin are 0.110 mm^2/s and 0.176 $\text{W}/(\text{m}\cdot\text{K})$, respectively. The thermal diffusivity values of epoxy– Ti_3C_2 3DNS composites with 0.5, 1.0, 2.0, and 3.0 g fillers are 0.142, 0.161, 0.173, and 0.191 mm^2/s , respectively. TC values of these composites are 0.207, 0.220, 0.236, and 0.262 $\text{W}/(\text{m}\cdot\text{K})$. Compared with epoxy resin, TC value of epoxy– Ti_3C_2 3DNS 1.0 composites increased by 48.9%.

In the longitudinal direction of two-dimensional nanomaterials, with the increase of fillers content, more and more continuous high thermal conduction paths may be formed, which will further improve TC of epoxy– Ti_3C_2 3DNS composites. The surface groups of CNF and Ti_3C_2 MXene are favorable to form good interface compatibility with epoxy matrix, which could reduce the interface thermal resistance and improve TC. According to the percolation threshold theory, when the fillers content increases to a certain

Fig. 4 SEM images of the fracture surfaces of (a) epoxy resin and epoxy– Ti_3C_2 3DNS composites with (b) 0 g, (c) 0.5 g, (d) 1.0 g, (e) 2.0 g, and (f) 3.0 g few-layer Ti_3C_2 MXene nanosheets.

Fig. 5 Thermal performance of epoxy resin and epoxy-Ti₃C₂ 3DNS composites: (a) thermal diffusivity and TC, (b) TC at different temperatures, (c) TC under heating and cooling cycle, (d) CTE curves, (e) TDP curves, and (f) TGA curves.

critical value, TC value will be greatly improved. TC values of epoxy-Ti₃C₂ 3DNS composites increase slowly with the increase of the fillers content, which indicates that the fillers content has not reached the critical value. The continuous heat transfer channels are less or discontinuous, resulting in the slow increase of TC.

To study the effect of temperature on the TC of these composites, TC is measured at 25, 50, 75, 100, and 125 °C, respectively, and the results are shown in Fig. 5(b). TC values of these samples increase with the increase of the fillers content, which is well matched with Fig. 5(a). From Fig. 5(b), the values of TC increase with temperature. Epoxy-Ti₃C₂ 3DNS composites are opaque amorphous polymer. The main heat conduction mechanism is phonon heat conduction. In the test temperature range, the phonon velocity is only related to the density and elastic mechanical

properties of the materials, which can be considered as a constant [27]. With the increase of temperature, the volume of epoxy-Ti₃C₂ 3DNS composites and the segment mobility of the molecular chain increase leading to the decrease of the interaction or entanglement between the molecular chains, which is conducive to the increase of the mean free path of phonon. Therefore, TC of the composites increases with temperature.

Under heating and cooling cycle, TC curves of epoxy resin and epoxy-Ti₃C₂ 3DNS composites are shown in Fig. 5(c). In the process, the temperature alternates between 25 and 100 °C. TC curves of epoxy resin and epoxy-Ti₃C₂ 3DNS 3.0 composites are relatively stable and slightly fluctuates in 20 cycles, which shows that the sample has stable TC in this temperature range. As shown in Fig. 5 (d), the CTEs of epoxy resin and epoxy-Ti₃C₂ 3DNS 3.0 composites

are measured at 40–160 °C. The trend of the CTE is decreasing with the increase of the fillers content in the studied temperature range. At 40 °C, the CTE of epoxy resin is 46.7 ppm/K, and the CTEs of epoxy–Ti₃C₂ 3DNS composites with 0.5, 1.0, 2.0, and 3.0 g filler are 42.5, 42.4, 44.7, and 41.9 ppm/K, respectively. The thermal movement of epoxy molecular chain and the distance between the molecular chains increase with the temperature increase, which could lead to volume expansion. In epoxy–Ti₃C₂ 3DNS composites, the three-dimensional nanosheets block composed of few-layer Ti₃C₂ MXene nanosheets arranged longitudinally and CNF can effectively inhibit the increase of epoxy molecular chain distance between the wall layers, reduce the extent of epoxy volume expansion, and make the composites have a smaller CTE [28].

In this work, thermal design power (TDP) is introduced to characterize the comprehensive thermal properties of engineering materials. It is defined by Eq. (2) [29, 30].

$$\text{TDP} = \frac{\text{CTE}}{T_c} \quad (2)$$

where T_c is thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

Low TDP value means excellent thermal performance, which indicates that the sample has relatively high TC and low CTE. The calculation results of TDP of epoxy resin and epoxy–Ti₃C₂ 3DNS composites are shown in Fig. 5(e). From the Fig. 5(e), it can be seen that TDP decreases with the increase of the filler content, and the TDP of epoxy–Ti₃C₂ 3DNS 3.0 composite is the lowest. The results show that Ti₃C₂ MXene is ideal filler for improving the thermal properties of epoxy resin matrix.

Figure 5(f) is the TGA curves of Ti₃C₂ MXene, epoxy resin, and epoxy–Ti₃C₂ 3DNS composites, with a temperature range of 45 to 1,000 °C. The degradation curves of the composites are similar, and the initial degradation temperature is near 300 °C, which indicates that the epoxy resin is modified by few-layer Ti₃C₂ MXene with three-dimensional nanosheets. However, the degradation mechanism has not changed significantly, which ensures the similar thermal stability of epoxy matrix. In addition, the calculation results show that the fillers content in epoxy–Ti₃C₂ 3DNS 0.5, epoxy–Ti₃C₂ 3DNS 1.0, epoxy–Ti₃C₂ 3DNS

2.0, and epoxy–Ti₃C₂ 3DNS 3.0 are 3.7, 5.5, 8.8, and 12.2 wt%, respectively.

3.3 Microhardness

The Vickers hardness of epoxy resin, epoxy–Ti₃C₂ 3DNS 0, epoxy–Ti₃C₂ 3DNS 0.5, epoxy–Ti₃C₂ 3DNS 1.0, epoxy–Ti₃C₂ 3DNS 2.0, and epoxy–Ti₃C₂ 3DNS 3.0 composites are 121.5, 118.1, 132.2, 167.3, 186.7, and 212.5 Hv_{0.5}, respectively. When Ti₃C₂ MXene is not added, the hardness of the three-dimensional nanosheets of pure CNF composites is lower than that of epoxy resin, but the difference is very small. When Ti₃C₂ MXene is introduced into the three-dimensional network, the hardness of epoxy–Ti₃C₂ 3DNS composites is higher than that of epoxy resin, and the hardness of these composites increases with the increase of fillers content. The hardness of epoxy–Ti₃C₂ 3DNS 0.5, epoxy–Ti₃C₂ 3DNS 1.0, epoxy–Ti₃C₂ 3DNS 2.0, and epoxy–Ti₃C₂ 3DNS 3.0 composites is 8.8%, 37.7%, 53.7%, and 74.9%, respectively, which are higher than that of the epoxy resin. Ti₃C₂ MXene is a two-dimensional ceramic material with high hardness. The existence of –OH and –O groups on the surfaces allows Ti₃C₂ MXene to have a good interface combination with epoxy matrix and CNF surface. What's more, the groups such as –COOH and –OH on the CNF surfaces can take part in the curing reaction of epoxy resin, which is beneficial to enhance the cross-linking strength of epoxy resin molecular chain, so the hardness of epoxy–Ti₃C₂ 3DNS composites is improved.

3.4 Friction and wear properties

The friction coefficient histogram of epoxy resin and epoxy–Ti₃C₂ 3DNS composites with different content few-layer Ti₃C₂ MXene is shown in Fig. 7. The friction coefficients of epoxy resin, epoxy–Ti₃C₂ 3DNS 0, epoxy–Ti₃C₂ 3DNS 0.5, epoxy–Ti₃C₂ 3DNS 1.0, epoxy–Ti₃C₂ 3DNS 2.0, and epoxy–Ti₃C₂ 3DNS 3.0 composites are 0.716, 0.690, 0.240, 0.170, 0.186, and 0.210, respectively. Figure 8 shows the wear rate and wears volumes of epoxy resin and epoxy–Ti₃C₂ 3DNS composites with different content few-layer Ti₃C₂ MXene. Furthermore, the friction coefficient of neat epoxy resin is 0.46 (under an applied load of 4.0 N) which is higher than the composites in Ref. [31]. The wear rates of epoxy resin, epoxy–Ti₃C₂ 3DNS 0,

Fig. 6 Microhardness of epoxy resin and epoxy-Ti₃C₂ 3DNS composites.

Fig. 7 Friction coefficients of epoxy resin and epoxy-Ti₃C₂ 3DNS composites.

Fig. 8 Wear rate and wear volumes of epoxy resin and epoxy-Ti₃C₂ 3DNS composites.

epoxy-Ti₃C₂ 3DNS 0.5, epoxy-Ti₃C₂ 3DNS 1.0, epoxy-Ti₃C₂ 3DNS 2.0, and epoxy-Ti₃C₂ 3DNS 3.0 composites are 30.4×10^{-5} , 28.9×10^{-5} , 38.1×10^{-5} , 24.1×10^{-5} , 22.0×10^{-5} , and 9.9×10^{-5} mm³/(m·N), and the corresponding wear volumes are 5467.6×10^{-5} , 5198.4×10^{-5} , 6863.1×10^{-5} , 4332.2×10^{-5} , 3952.4×10^{-5} , and 1789.5×10^{-5} mm³, respectively. So, the few-layer Ti₃C₂

MXene with three-dimensional network can effectively improve the friction and wear properties of the epoxy resin matrix. In particular, the epoxy-Ti₃C₂ 3DNS 1.0 composites have the best friction coefficient, which is 76.3% lower than that of epoxy resin, and the epoxy-Ti₃C₂ 3DNS 3.0 composites have the lowest wear rate, which is 67.3% lower than that of epoxy resin.

Figure 9 shows the SEM images of the worn surfaces of epoxy resin, epoxy-Ti₃C₂ 3DNS composites with 0, 0.5, 1.0, 2.0, and 3.0 g few-layer Ti₃C₂ MXene nano-sheets. The scratch surfaces morphology of epoxy-Ti₃C₂ 3DNS composites filled with Ti₃C₂ MXene are different from that of epoxy resin. From Fig. 9(a), it can be seen that there are a large number of brittle fracture traces on epoxy resin worn surface, which indicates a typical wear form of brittle materials. In the process of friction and wear, due to the normal load and shear force, the surface of epoxy resin has brittle cracks and tear off, forming rough wear surface, leading to large shear resistance. So its friction coefficient is large, wear is serious, and the wear type is fatigue wear. It can be seen from Fig. 9 (b), there are many pits, cracks, furrows, and a small amount of debris in some areas of the worn surface of epoxy-Ti₃C₂ 3DNS 0 composites, and the wear forms are mainly abrasive wear and fatigue wear. The scratch surfaces morphologies of epoxy-Ti₃C₂ 3DNS composites filled with Ti₃C₂ MXene in Figs. 9(c)–9(f) are similar with a lot of flaky debris which has been compacted to varying degrees but there is no obvious furrow trace. Hence, the wear type under this condition is mainly fatigue wear.

The above analysis shows that the introduction of pure CNF with three-dimensional network could not significantly improve the friction and wear performance of epoxy matrix, and the wear form has not changed. When fatigue wear occurs, the main wear form is peeling wear, and the wear debris is mostly irregular block, which is similar to epoxy resin. This is because in the curing process of epoxy resin, the linear molecular chain reacts with the curing agent to form a three-dimensional network cross-linking structure, which is hard and brittle. Under the condition of alternating stress, there is a distribution point of the maximum shear force under the surface, where cracks are most likely to form [32]. With the back and

Fig. 9 SEM images of the worn surfaces of (a) epoxy resin and epoxy- Ti_3C_2 3DNS composites with (b) 0 g, (c) 0.5 g, (d) 1.0 g, (e) 2.0 g, and (f) 3.0 g few-layer Ti_3C_2 MXene nanosheets.

forth movement of the friction process, the cracks propagate [33]. Because of the network cross-linking structure of the molecular chain, its propagation direction is disordered, and finally extends to the surface, forming irregular block debris with the rough surface. Moreover, the thermal performance of epoxy resin is poor, and the accumulation of heat in the process of friction will cause surface defects. Therefore, the friction coefficient and wear rate of epoxy resin are relatively high. Epoxy- Ti_3C_2 3DNS 0 composites did not significantly improve the friction and wear properties, because the CNF was involved in the curing process and had no obvious effect on the properties of epoxy matrix.

In epoxy- Ti_3C_2 3DNS composites, although the interface between Ti_3C_2 MXene and the matrix is good, it is still not as strong as the bonding strength formed by curing reaction of epoxy matrix itself. So, the directional distribution of the few-layer of Ti_3C_2 MXene as a weak layer exists in the epoxy matrix. In the friction process, with the action of alternating stress, cracks parallel to the wall layer are easy to form at the wall layer of the few-layer Ti_3C_2 MXene. With the friction process going on, the cracks propagate along the wall layer direction, forming large flake debris

and delamination. The layered debris exists between the friction pairs. Some of the debris is compacted and some of them are sliding which is equivalent to sliding friction, reducing the friction coefficient and wear rate to a large extent. In addition, there is a weak van der Waals force between the layers of Ti_3C_2 MXene. The multi-layer Ti_3C_2 MXene is sheared to form a thin sheet layer under the shear force, which makes the shear strength in the process of friction lower and thus has a certain effect on friction reduction. However, when with few Ti_3C_2 MXene, as shown in Fig. 4(c), for epoxy- Ti_3C_2 3DNS 0.5 composites, there are few Ti_3C_2 MXene on the CNF surfaces. So the effect in guiding the directional crack growth is not obvious. The hardness of the composites is relatively small and the deformation is large, so the wear rate and wear volume are larger, even larger than that of epoxy resin, but the friction coefficient is significantly reduced because the debris has a better self-lubricating effect.

With the increase of Ti_3C_2 MXene content, the hardness and thermal properties are gradually improved. The deformation and damage of the composites are small in the friction process, and the defects caused by heat accumulation are reduced, so

the wear rate is gradually reduced with the content of filler. Another point that deserves attention is that with the increase of Ti_3C_2 MXene content, the friction coefficient increases only slightly. Therefore, the content of Ti_3C_2 MXene is not the more the better. It may be because with the increase of filler, the hardness of wear debris increases, and the effect of lubrication and friction reduction is slightly worse under repeated rolling.

4 Conclusions

In this work, the few-layer Ti_3C_2 MXene with three-dimensional network was constructed by freeze-drying method, and epoxy- Ti_3C_2 3DNS composites were prepared with the few-layer Ti_3C_2 MXene nanosheets. Epoxy- Ti_3C_2 3DNS composites have the better CTE, TC, and higher microhardness compared with epoxy resin. Furthermore, these properties are better with the increase of the few-layer Ti_3C_2 MXene content. When the nanosheets was 3 g, TC can get up to 0.262 W/(m·K), the CTE is 41.9 ppm/K at 40 °C, and the hardness was 74.9% higher than that of epoxy resin. The friction and wear properties of the composites with different nanosheets contents were improved to different degrees. When the nanosheets content is 1.0 g, the friction coefficient of the composites is 0.170, which is 76.3% lower than that of epoxy resin. When the nanosheets content was 3.0 g, the wear rate of the composites is $9.9 \times 10^{-5} \text{ mm}^3/(\text{m} \cdot \text{N})$, which is 67.3% lower than that of epoxy resin. In brief, epoxy- Ti_3C_2 3DNS composites with three-dimensional network can effectively improve the thermal performances and the properties of friction and wear, which play an important role in the research of composite materials of high-performance devices.

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