Research Article

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Flexible MXene/copper/cellulose nanofiber heat spreader films with enhanced thermal conductivity

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Abstract: To deal with the heat dissipation problem produced by a high integrated circuit, the preparation of heat spreaders with excellent heat transportation performance is increasing in demand. The Ti3C2 MXene sheets and copper particles were fully contacted with cellulose nanofibers by a high-speed mixer, and the composite film was prepared as a heat spreader under the action of the vacuum-assisted filtration. The MXene sheets are connected by the esterification of the carboxyl group in MXene and the hydroxyl group in cellulose nanofibers to form a chemical bond and consist of the main skeleton of the composite film. Due to the synergistic effects of MXene and copper particles, the in-plane and out-of-plane thermal conductivities of the composite film reach 24.96 and 2.46 W m⁻¹ K⁻¹, respectively. Compared with the pure cellulose nanofiber films, the thermal conductivity of composite films increased by 2819.2 and 187.6%, respectively. By designing two applications of composite films in the actual use process, the excellent heating conduction abilities in two directions have been proved. This measure to improve the thermal conductivities of composite films by MXene-copper binary fillers also provides ideas for the novel heat spreader.

Keywords: Ti3C2 MXene, copper powders, cellulose nanofibers, thermal conductivity, synergistic effect
1 Introduction

With the electronic equipment tend to be integrated and lightweight in the fields of aerospace and aviation and microelectronics, higher temperature will result in a decline of the lifetime of electronic equipment and a decrease in work efficiency. Therefore, it is urgent to prepare a suitable heat spreader to dissipate the heat generated from the sustained working electronic equipment. In practical applications, the heat spreader used for heat dissipation needs excellent thermal conduction ability not only in the in-plane direction but also in the through-plane direction. Polymers with their advantages of low weight, low cost, and simple preparation process are widely used in thermal management [1–4]. But their thermal conductivities of about 0.1–0.5 W m⁻¹ K⁻¹ restrict their use in the thermal management field [5–8]. Thermal conductivities of polymer composite films are usually enhanced by adding fillers, which include graphene [9–13], boron nitride (BN) sheets [14–16], and few-layer Ti₃C₂ MXene [17–19].

MXene is a two-dimensional transition metal carbide, which has been applied in many fields by its excellent electromagnetic shielding, energy storage, high thermal conductivity, and other properties [20–22]. The intrinsic thermal conductivity is still in the theoretical calculation stage, and the thermal conductivity of monomolecular Ti₃C₂Fₓ reaches 108 W m⁻¹ K⁻¹ at the room temperature [23]. There are many methods for preparing polymer composite films, such as vacuum-assisted filtration [24,25], hot-pressing process [26,27], layer-by-layer spraying technique [28], multiple casting [29], and spin coating process [30]. Zhu et al. fabricated MXene and polyamide (PI) solution into a three-dimensional structure by freeze-drying, for the sake of making MXene sheets fully in contact with polymer macromolecules [27]. And then, the MXene/PI films with the thermal conductivity of 5.12 W m⁻¹ K⁻¹ is prepared by the hot-pressing process. Gao et al. successfully fabricated MXene/thermoplastic polyurethane films using the layer-by-layer spraying technique, which exhibit the thermal conductivities of 6.31 W m⁻¹ K⁻¹ in the in-plane direction and 0.42 W m⁻¹ K⁻¹ in the through-plane direction [28]. Jiao et al. prepared the MXene/CNF films using the vacuum-assisted filtration method, which achieves thermal conductivity of 14.93 W m⁻¹ K⁻¹ in the in-plane direction [25]. It can be found that the MXene as the single filler to fabricate polymer composite films do not achieve the expected high thermal conductivity. Furthermore, the enhancement of thermal conductivity in the through-plane direction is very limited.

The synergistic effect of fillers has a significant impact on the thermal conductivity of polymer composites [31–37]. Compared with the single filler, the distribution of fillers in the polymer matrix is more complex. If the structure is orderly, it will be more conducive to heat transfer. He et al. reported a work on the synergistic effect of GO and BN for enhanced thermal conductivity of the composite films [31]. With the filler content of GO being 1 wt%, the thermal conductivities of the polymer composite films increase from 6.12 to 11.20 W m⁻¹ K⁻¹ as the filler content of BN increases from 0 to 20 wt%. Barani et al. prepared an isotropic polymer composite of an epoxy matrix using graphene and copper particles, which exhibits a thermal conductivity of 13.5 W m⁻¹ K⁻¹ with the synergistic effect of 40 wt% graphene and 35 wt% copper particles [32]. Hence, we are trying to find a way by using the synergistic effect to improve the thermal conductivities of polymer composite films not only in the in-plane direction but also in the through-plane direction.

Herein, the few-layer Ti₃C₂ MXene sheets and copper particles with high thermal conductivities were utilized to fabricate polymer composite films. MXene sheets, copper particles, and cellulose nanofibers (CNFs) were sheered mixing by a high-speed mixer, and then the composite films were obtained after the vacuum-assisted filtration process. CNF can not only provide a certain bonding effect to combine the MXene layer with the layer (the possible bonding principle is shown in Figure 1) but also has a slightly higher thermal conductivity compared with other amorphous polymers, which also contributes more to the improvement of thermal conductivity of composite films [38]. In comparison to composite films under the synergistic effect of copper particles in different diameters and MXene sheets, it can be seen that composite film with copper particles in 1 μm diameter possesses the highest thermal conductivities of 24.96 W m⁻¹ K⁻¹ in the in-plane direction and 2.46 W m⁻¹ K⁻¹ in the through-plane direction, respectively.

2 Experimental section

2.1 Materials

Few layer Ti₃C₂ MXene colloid solution (concentration of 5 mg mL⁻¹) was purchased by Xiyan New Material Technology Co., Ltd (Shandong, China). Copper powders (0.1, 0.5, 1, 2, and 5 μm in diameter, purity of 99.999%)
were supplied by Nangong Lijia Metal Materials Co., Ltd. (Hebei, China). Cellulose nanofiber (CNF) solution (1.0 wt%, 4–10 nm in diameter, 1–3 μm in length) was offered by Qihong Technology Co., Ltd. (Guangxi, China).

2.2 Preparation of composite films

MXene colloid solution and copper powders were blended and dispersed in deionized water. The mixed dispersion was put into the SpeedMixer (DAC 150.1 FVZ-K, FlackTek SpeedMixer™, USA) at 3,500 rpm for 5 min. Afterward, the CNF solution was added to the blended solution, and the action was repeated using the SpeedMixer. The obtained dispersion was placed in the ultrasonic cleaner all the time to render the copper powders standing at a dispersing state. The obtained MXene/Cu/CNF dispersion was dropped onto a polycarbonate (PC) filter membrane by a vacuum filtration after the former layer of dropped dispersion dried. The 3 mL dispersion absorbed by a disposable drop tube was dropped into the vacuum filtration glass. After the solution in the glass dried up, the other 3 mL dispersion was dropped into it. Repeat the above process until all the solution is completely moved into the vacuum filtration device, the MXene/Cu/CNF film was formed on the filter membrane. Especially, the filler content of the MXene and copper particles is 27.94 and 23.74 vol%, respectively. The schematic diagram of the preparation of the MXene/Cu/CNF films is shown in Figure 1. The film-forming mechanism is depicted in the bottom left corner of Figure 1. During the whole vacuum filtration process, the carboxyl of CNF and the hydroxyl of the MXene sheet were dehydrated and esterified, which constituted the skeleton of the MXene film [39,40].

2.3 Characterization

The morphologies of Ti$_3$C$_2$ MXene, copper particle, the pure CNF film, and the prepared MXene/Cu/CNF films were observed using a scanning electron microscope (SEM, S4800, Hitachi, Japan) working at an accelerating voltage of 4 kV. High-resolution image of Ti$_3$C$_2$ MXene was characterized by a transmission electron microscope (TEM, Talos F200X, Thermo Fisher, USA) with an accelerated voltage of 200 kV. X-ray diffraction patterns (XRD, D8 Advance, Bruker AXS, Germany) were used to analyze the diffraction peaks of the Ti$_3$C$_2$ MXene and copper particles. The thermal conductivity $\lambda$ was calculated by the formula: $\lambda = \alpha \times \rho \times C_p$, where $\alpha$, $\rho$, and $C_p$ are thermal diffusivity, density, and heat capacity, respectively. The thermal diffusivity was tested by laser flash analysis (LFA, LFA 467 HyperFlash® system, NETZSCH, Germany). The density was calculated by the water-draining method. The heat capacity was measured and calculated by a differential scanning calorimetry (DSC, DSC214, Netzsch, Germany) machine. The infrared (IR) camera (Ti400, Fluke, USA) was utilized to record the IR images.
3 Results and discussions

The Ti₃C₂ MXene solution presents a strong Tyndall effect as shown in Figure 2(a), indicating well dispersion of the MXene. The SEM and TEM images of the MXene sheets are exhibited in Figure 2(b) and (c), respectively. The size of a single-layer MXene sheet is about 1 μm obtained by the SEM image, which is also identified by the TEM image. In addition, it can be seen from the TEM image that the number of layers of the MXene sheets is small verifying the existence of few-layer MXene sheets. The XRD spectra of MXene and copper are displayed in Figure 2(d). The MXene of the XRD curve described by the upper image of Figure 2(d) presents the character peak located at 6.86° corresponding to the (002) plane [40,41]. The XRD spectrum of copper particles includes three sharp peaks that are located at 43.32°, 50.45°, and 74.12°, corresponding to the (111), (200), and (220) planes of copper, respectively [42,43]. The morphological images of copper particles with the sizes of 0.1, 0.5, 1, 2, and 5 μm are shown in Figure 2(e) and Figure S1 (available in the Supplementary Materials). The digital pictures of composite films prepared with the copper in 1 μm diameter and in bending and folding states are exhibited in Figure 2(f), respectively. And it can be proved that the composite film has a certain process capability.

Figure 3(a) and (d) exhibits sectional SEM of pure CNF film at low and high magnifications. It can be found that the surface of the pure CNF is smooth and the stripes formed by brittle fracture are obviously arranged in order. The sectional morphologies of MXene/Cu/CNF films with different copper particle diameters are shown in Figure 3(b, c, g, h, and i), in which enlarged SEM images are located under them. When the copper particles are 0.1 μm in diameter, as displayed in Figure 3(b) and (e), the agglomeration of copper particles is serious, due to the particle size attaining nanometer level. Under the action of vacuum filtration equipment, MXene sheets are propped up with many flat holes with thick middle and thin sides. As the sizes of copper particles increase, the number of copper particles in agglomeration status decreases. But the diameter of the copper particles after agglomeration increases, the holes propped by particles become round and more ordered. When the particle size increases to 1 μm, the shape of the propped holes is closest to the circle, and the distribution of holes is more uniform. As the sizes of copper particles increase to more than 1 μm, the agglomeration phenomena have been alleviated. Because the sizes of particles become bigger, the diameters of the holes propped up by the particles become longer and larger, and the distribution of the holes becomes more disordered. In summary, as exhibited

![Figure 2: (a) Digital picture of Tyndall phenomenon of MXene colloidal solution. (b) SEM and (c) TEM images of MXene. (d) XRD curves of MXene and copper powders. (e) SEM image of copper powders in 1 μm diameter. (f) Digital pictures of the MXene/CU/CNF film and bending and folding abilities of the composite film.](image-url)
from the sectional SEM images, the holes obtained and propped by copper particles in 1 μm diameter have the best morphological structure in shape and distribution.

The model of heat conduction of the composite films is shown in Figure 4(a). The effect of synergistic filler was reported by the previous works. Two or more kinds of filler to the composite were introduced, and the mutual effect of which can lead to higher thermal conductivity. For the in-plane direction, MXene sheets play a dominant effect on the thermal conductivity because of forming an orientation continuous pathway using the vacuum filtration method. Meanwhile, for the through-plane direction, copper particles play a main role in thermal conductivity after agglomeration and the formation of the heating conduction pathway. The thermal diffusivities and conductivities of the pure CNF film and the MXene/Cu/CNF films with different copper particles diameters at the in-plane direction are exhibited in Figure 4(b), in which it can be seen that the thermal diffusivities and conductivities in the in-plane direction both present the trend of first rising and then falling. The thermal diffusivities and conductivities in the in-plane direction achieve a summit at 1 μm with 13.64 mm² s⁻¹ and 24.96 W m⁻¹ K⁻¹, respectively. A similar trend for the through-plane direction is displayed in Figure 4(c), in which the thermal diffusivity and conductivity are 1.35 mm² s⁻¹ and 2.46 W m⁻¹ K⁻¹, respectively. Compared with the reported thermal conductivity of the MXene/CNF films [17,34,44,45], the composite films with the synergistic effect of MXene sheets and copper particles of 0.1–5 μm show a higher heating conduction ability. Although the MXene sheets and the copper particles play dominant effects on thermal conductivities in the in-plane and through-plane directions, respectively, the more excellent heating conduction abilities of the MXene/Cu/CNF films are led by their synergistic effects and formation of continuous heating conduction networks. To quantify the difference between the thermal conductivities of the pure polymer and the polymer composite, the thermal conductivity enhancement (TCE) rates of the composite films with different

Figure 3: Sectional and their enlarged SEM images of (a and d) pure CNF film and MXene/Cu/CNF films with different copper powder diameters of (b and e) 0.1, (c and f) 0.5, (g and j) 1, (h and k) 2 and (i and l) 5 μm, respectively.
copper particles diameters are introduced and shown in Figure 4. The TCE rate is calculated by the following equation,

\[ \text{TCE} = \frac{\lambda_1 - \lambda_0}{\lambda_0}, \]

where \( \lambda_1 \) and \( \lambda_0 \) are thermal conductivities of the polymer composite and the pure polymer, respectively. The remarkable TCE rates of the MXene/Cu/CNF films with different copper particles diameters also present the same trend in comparison to the thermal conductivities, which is 2819.2\% in the in-plane direction and 187.6\% in the through-plane direction with copper particles in 1\( \mu \)m diameter. For the sake of testing the heating conduction stability of the composite films, the thermal conductivity of composite films at 25, 55, 85, and 100\( ^\circ \)C is measured and exhibited in Figure 4(e) (in-plane direction) and (f) (through-plane direction). With the temperature increasing, the thermal conductivities of composite films gradually rise in the in-plane direction and fall in the through-plane direction. In terms of composite films, the fillers playing the dominant effects on in-plane and through-plane directions are not uniform; hence, the different trends for the thermal conductivities as a function of temperature in two directions. Furthermore, the thermal conductivities of the composite films, obtained from Figure 4(e) and (f), have a low change rate. And, the thermal conductivity of composite film with copper particles in 1\( \mu \)m diameter has the lowest change rate of 6.91\% in the in-plane direction and 4.68\% in the through-plane direction.

To exhibit the excellent thermal conductivity of the MXene/Cu/CNF films with copper particles in 1\( \mu \)m diameter, two types of instrumentation were used to characterize the heating conduction abilities of the in-plane and through-plane directions, respectively. Figure 5(a) shows the mechanism diagram of the heated device that was utilized to test the thermal conduction ability of the in-plane direction. A direct-current power was linked to an annular heated ceramic plate, which was under the texted composite films. Above them, another annular ceramic plate of the same size was used to fix the composites films, and an infrared (IR) camera was used for capturing the surface temperature and IR images. The temperatures of margin and center points captured by the films as a function of time are shown in Figure 5(b) and (c), respectively. As presented in Figure 5(d), the IR images of the MXene/Cu/CNF films and the pure CNF film are located in the first and second rows, respectively. Every image was the temperature contour-line image drawn from the temperature under and after heating captured by the IR image in the upper left corner of the
With an increase in the heating time, the temperatures of the unheated part of the CNF film, the MXene/Cu/CNF films have a higher contour line of the films rose from the margin to the center, forming clear contour lines. In comparison to the pure at the same time, the composite film at the same position possesses a higher temperature after the same heating time. It can be seen that the temperature increasement rate of the MXene/Cu/CNF films is higher than that of the pure CNF film at either the margin point or center point, as shown in Figure 5(b) and (c). After heating for 120 s, the temperatures of the composites film at a margin point of 57.4°C and a center point of 74.7°C are 14.9 and 21.0°C higher than that of the pure CNF film, respectively. A cooling radiator model presented in Figure 5(e) was used to exhibit the heating conduction ability in the through-plane direction. The films to be tested were placed between the CPU and a cooling fan, and then, the power capacity of the CPU

Figure 5: (a) Mechanism diagram of the heated device. The time-temperature curve of (b) margin and (c) center points captured from the (d) corresponding temperature contour-line images of the MXene/Cu/CNF films with copper powders in 1 μm diameter and pure CNF film. The temperature contour-line images were drawn by the temperature data of the inset infrared images photographed by an infrared camera. (e) Mechanism diagram of a cooling radiator and (f) corresponding time-temperature curves of CPU.
was promoted to the apex. The CPU temperature curves as a function of time, which is revealed in Figure 5(f), are the confidence intervals and curves calculated by the temperature points, and the mean temperature during the whole CPU operating time is located in the bottom right corner of the picture. As the CPU began to work with a full load, the temperatures of the two films rose sharply and tend to be steady at about 300 s. The steady temperature under the action of the MXene/Cu/CNF films is lower than that of the pure CNF film obviously. And, the mean temperature under the action of the composite film is 5.2°C lower than that of the pure CNF film.

4 Conclusion

In this paper, the MXene/Cu/CNF films were prepared by high-speeding shear mixing and vacuum-assisted filtration of MXene sheets and copper particles of different sizes. The basic skeleton of the film was formed by dehydration and esterification of hydroxyl groups in MXene and carboxyl groups in CNF. Under the synergistic effect of two different fillers, the maximum in-plane thermal conductivity of 24.96 W m⁻¹ K⁻¹ and through-plane thermal conductivity of 2.46 W m⁻¹ K⁻¹ are obtained by composite films with the copper particles in 1 μm diameter. By calculating the TCE of the in-plane and through-plane directions with the formula, it can be found that the thermal conductivity of the composite films increased by 2819.2 and 187.6% at two thermal conduction directions, respectively. A heated device and a cooling radiator are utilized to visualize the thermal conductivities of the MXene/Cu/CNF films in the in-plane and through-plane directions. From the results of the designed test, the MXene/Cu/CNF film has an excellent thermal transfer performance in both the directions. In summary, by adding two kinds of fillers with a synergistic effect, the thermal conductivities of the polymer composite film in the in-plane and through-plane directions can be effectively increased simultaneously. This also provides a way for the preparation of thermally conductive polymer films with excellent thermal conductivity.

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