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Epoxy Composites with High Thermal Conductivity by Constructing Three-Dimensional Carbon Fiber/Carbon/Nickel Networks Using an Electroplating Method

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Carbonizing → Electroplating Ni → Epoxy

ABSTRACT: Heat dissipation problem is the primary factor restricting the service life of an electronic component. The thermal conductivity of materials has become a bottleneck that hinders the development of the electronic information industry (such as light-emitting diodes, 5G mobile phones). Therefore, the research on improving the thermal conductivity of materials has a very important theoretical value and a practical application value. Whether the thermally conductive filler in polymer composites can form a highly thermal conductive pathway is a key issue at this stage. The carbon fiber/carbon felt (CF/C felt) prepared in the study has a three-dimensional continuous network structure. The nickel-coated carbon fiber/carbon felt (CF/C/Ni felt) was fabricated by an electroplating deposition method. Three-dimensional CF/C/Ni/epoxy composites were manufactured by vacuum-assisted liquid-phase impregnation. By forming connection points between the adjacent carbon fibers, the thermal conduction path inside the felt can be improved so as to improve the thermal conductivity of the CF/C/Ni/epoxy composite. The thermal conductivity of the CF/C/Ni/epoxy composite (in-plane $K_\parallel$) is up to 2.13 W/(m K) with 14.0 wt % CF/C and 3.70 wt % Ni particles (60 min electroplating deposition). This paper provides a theoretical basis for the development of high thermal conductivity and high-performance composite materials urgently needed in industrial production and high-tech fields.

INTRODUCTION

With the rapid development of the electronic information industry, especially the development of the 5G information industry in recent years, the application of electronic components is gradually developing in the direction of high power, high integration, and high density. However, a large amount of heat will be generated during the operation of electronic equipment. If the excess heat cannot be exported in time, it will directly affect the service life and operation efficiency of electronic components. The heat dissipation problem of polymer packaging materials has become a huge obstacle to the development of the electronic information industry.[1,2] The thermal conductivity of polymer composites is mainly determined by the resin matrix, the filler, and the microstructure or interfacial bonding between the resin and the filler. Due to the low thermal conductivity of polymer packaging materials, the thermal conductivity of the polymer is usually improved by adding high thermal conductivity fillers. The filler-filled thermal conductive polymer materials are mainly prepared by adding high thermally conductive metal

materials (such as copper powder,[3,4] silver powder,[5−8] metal sheet, and wire[9−14]), carbon materials (such as carbon fiber,[15−22] graphene,[23−27] graphite,[28−30] carbon nanotube,[31−34] and carbon black[35−37]) or high thermal conductive inorganic fillers (such as aluminum nitride,[38,39] boron nitride,[40−43] silicon nitride,[44,45] silicon carbide,[46−50] magnesium oxide,[51,52] silicon oxide,[53] alumina,[54−59] barium titanate,[60] and zinc oxide[61]) and other high thermal conductivity fillers (such as MXene[62−68]). Filler-filled thermal conductive polymer composites have the advantages of a simple preparation method, low cost, suitable types of polymers, and fillers. However, the thermal conductivity of the polymer itself is low (epoxy is about 0.15−0.25 W/(m K)). If we want

to achieve the ideal thermal conductivity, the amount of fillers should be very high to form a thermal conduction path between the fillers. However, the increase of processing viscosity, the interface thermal resistance between the fillers, and the decline of mechanical properties hinder the development of these filler-filled composites.

The thermal conductivity of polymer composites is mainly determined by the resin matrix, the filler, and the microstructure or interfacial bonding between the resin and the filler. When the matrix and the filler are fixed, the structure of the composite determines the performance of the composite. The problem of low thermal conductivity of materials can be solved only by improving the thermal conduction path by constructing the material structure. Recently, researchers have carried out extensive research by constructing a three-dimensional (3D) filler network structure in the resin matrix,[69−83] which is considered as a promising strategy in many fields. By assembling some fibrous one-dimensional fillers with a high aspect ratio (metal silver, carbon nanotubes, and carbon fibers) or two-dimensional fillers (graphite flakes, graphene) to form a 3D network heat conduction structure, direct low thermal resistance and rich heat conduction paths can be provided in the resin matrix. Shahil et al.[84] fabricated a graphene−multilayer graphene (graphene−MLG) nanocomposite by ultrasonication of natural graphite in an aqueous solution of sodium cholate. The thermal conductivity of the nanocomposite is improved significantly due to the change of the filler network structure of the nanocomposite from graphite to graphene−MLG network structures, which could reach 24 times that of the matrix material under the conditions of the maximum filler content (10 vol % graphene−MLG). Guo et al.[85] prepared an epoxy composite by filling with microparticle ZnO and tetrapod-shaped ZnO (T-Zn) into the epoxy resin. The experimental results show that the epoxy composite with the T-Zn network structure has higher thermal conductivity (4.38 W/(m K)), which is about 2.7 times that of the composite with the ZnO network structure. Moreover, the MXene material was selected as the reinforced filler to add into the epoxy composite to improve the 3D thermal conductive network structure by Guo.[86] The thermal conductivity was enhanced by 36.7 compared with that of the CF composite. This phenomenon indicates that filler flexibility and thermal network density and continuity have great effects on the thermal conductive percolation pathway and play a leading role in the thermal conductivity of the composite.[87−91] In addition, the excellent orientation structure of fillers is another important consideration, which can obtain higher thermal conductivity in specific directions. Although it is one of the most complex methods to construct a 3D interconnection filler network in the polymer matrix, it is also the most effective method to improve the thermal conductivity of composites. The methods of constructing the 3D interconnected packing network include the freeze-drying method,[92−95] electrophoretic deposition method (EPD),[96−99] electrostatic flocking,[100−102] spatial confining forced network assembly method" (SCFNA),[103] hydrogen bonding self-assembly method,[104] and other orientation assembly methods.[105] Zeng et al.[94] prepared epoxy/CF composites by the freeze-drying orientation method, and the thermal conductivity reached 2.84 W/(m K) with 13.0 vol % CF. Yu et al.[95] fabricated PMDS/CF composites using the freeze-drying orientation method to make short carbon fibers oriented, and the thermal conductivity reached 6.04 W/(m K) (12.8 vol %). Wang et al.[106] used carbon fiber to insert

the graphite material in the Z-direction, and the thermal conductivity of the composite reached 6.20 W/(m K). Wang et al.[83] used a carbon felt (C felt) as the 3D skeleton, electroplated copper on the surface of the C felt to construct the 3D copper film network, which can be used as a continuous high-speed heat conduction path, and made the epoxy composite with the 3D interconnected Cu network, and the thermal conductivity reached 30.69 W/(m K). In our previous study,[107] we also prepared 3D all-carbon networks composed of carbon fibers (1D) and graphite sheets (2D) to improve the thermal conductivity of epoxy resin by air flow and solution dipping methods. The carbon/carbon fiber/graphite networks show an anisotropic structure. The thermal conductivity of the epoxy/carbon/carbon fiber/graphite composite was about 6.2 W/(m K) with 17.48 vol % carbon fibers and only 6.34 vol % graphite adhesive. By constructing the heat conduction structure of a 3D network filler to improve the connection between the fibers, the heat transfer ability of the heat conduction network can be greatly improved, and then the thermal conductivity of the composite can be improved. Therefore, it is one of the most effective ways to improve the thermal conductivity of the composites to construct the 3D interconnection filler network in the polymer matrix. Carbon fiber is easy to form the thermal conduction path in composites and has excellent mechanical properties. The combination of carbon fiber and polymer materials has become a research hotspot in the preparation of thermally conductive composites. The continuous carbon fiber structure has inherent advantages in heat conduction. It can directly utilize the high thermal conductivity of carbon fiber in the axial direction. At the same time, there is no difficulty in processing using the vacuum-assisted molding method. The main problems to be solved are to improve the connectivity between the fibers to further improve the connectivity of thermal conduction paths in all directions.

In this paper, the CF/C felt with the 3D skeleton structure was prepared by an air-laid and needle-punching method—liquid impregnation and solidification method—a high-temperature pyrolysis and carbonization method. The nickel heterographene-coated carbon fiber/carbon felt (CF/C/Ni felt) was fabricated by an electroplating deposition method. Three-dimensional (3D) CF/C/Ni/epoxy composites were manufactured by vacuum-assisted liquid-phase impregnation. The thermal conductivity and mechanism of the composites were studied. In the process of preparing the 3D CFC/Ni framework by electroplating, there is no need to modify the surface of the CF/C felt. The CF/C felt itself has good conductivity; therefore, the CF/C felt is directly connected with the copper electrode and the CF/C felt is used as the electrode. Then, the CF/C felt connected to the electrode is dipped into the electroplating liquid, that is, the electroplating can be carried out. By controlling the electroplating time, the amount of electroplating can be controlled so as to control the size of the thermal conduction path and then the thermal conductivity. In addition, by controlling the amount of nickel plating, the contact between the fibers increases, and the thermal conduction paths in all directions increase. The thermal conductivity of the composite is improved in all directions, thus forming an efficient 3D thermal conduction path. The thermal conductivity of the CF/C/Ni/epoxy composite is up to 2.13 W/(m K) with 14.0 wt % CF/C and 3.70 wt % Ni particles (60 min electroplating deposition).

This paper will provide a new idea for the preparation of 3D skeleton high thermal conductivity composites.

RESULTS AND DISCUSSION

Composition and Micromorphology of CF/C/Ni/ Epoxy Composites. The structure of the polymer composite determines the properties of the polymer composite. The structure of the polymer composite includes the composition and the microstructure of the polymer composite. The composition of the thermally conductive polymer composite includes the epoxy resin and thermally conductive filler, and their composition ratio. The 3D framework thermal conductive filler CF/C/Ni in this paper is composed of CF/C and nickel microparticles; therefore, the content of CF/C and nickel in CF/C/Ni will directly determine the thermal conductivity of the final composite. Table 1 exhibits the composition of the

Table 1. Composition of the CF/C/Ni Felt in CF/C/Ni/ Epoxy Composites

| samples	CF/C (wt %)	Ni (wt %)
CF/C	14.0	0
CF/C/Ni-15	14.0	1.85
CF/C/Ni-30	14.0	2.29
CF/C/Ni-45	14.0	3.17
CF/C/Ni-60	14.0	3.70

CF/C/Ni felt in CF/C/Ni/epoxy composites. It can be seen from Table 1 that with the increasing electroplating time, the nickel content in the CF/C/Ni/epoxy composites increases gradually from 1.85% (CF/C/Ni-15) to 2.29% (CF/C/Ni-30), 3.17% (CF/C/Ni-45), and 3.70% (CF/C/Ni-60), indicating that nickel can be electrodeposited on the CF/C felt skeleton step by step by an electroplating method. This is because the CF/C felt has very good conductivity, which ensures that it can be used as an electrode to provide electrons. After receiving electrons, nickel cations carry out a reduction reaction, and nickel atoms are gradually deposited on the CF/C composite framework. The nickel deposited on the CF/C felt can increase the contact probability of the adjacent carbon fibers, shorten the distance between the adjacent carbon fibers, broaden the thermal conduction path, and finally improve the thermal conductivity of the epoxy composite. At the same time, nickel microparticles also increase the surface area of the CF/C felt, thus improving the bonding strength between the CF/C/Ni felt and the epoxy resin.

In the case of a certain material composition of the polymer composite, the microstructure of the thermally conductive filler will directly determine the performance of the polymer composite. The most direct way to observe the microstructure of materials is to observe it using an SEM. The CF/C/Ni felt prepared in this paper has a 3D thermal conductivity network structure; therefore, it is necessary to observe its micro-structure to reveal the influence of its microstructure on the thermal conductivity of the prepared composite. Figure 1 indicates the micromorphology of the CF/C/Ni felt and the CF/C/Ni/epoxy composite. Figure 1a illustrates the SEM of the soft CF felt. The carbon fibers have a straight rod structure and randomly cross each other in the X−Y plane. The surface of carbon fibers is smooth and almost free of impurities. The diameter of most carbon fibers is about 7 μm. The diameter distribution is narrow, and the smooth surface structure is often not closely combined with the resin, and the interface
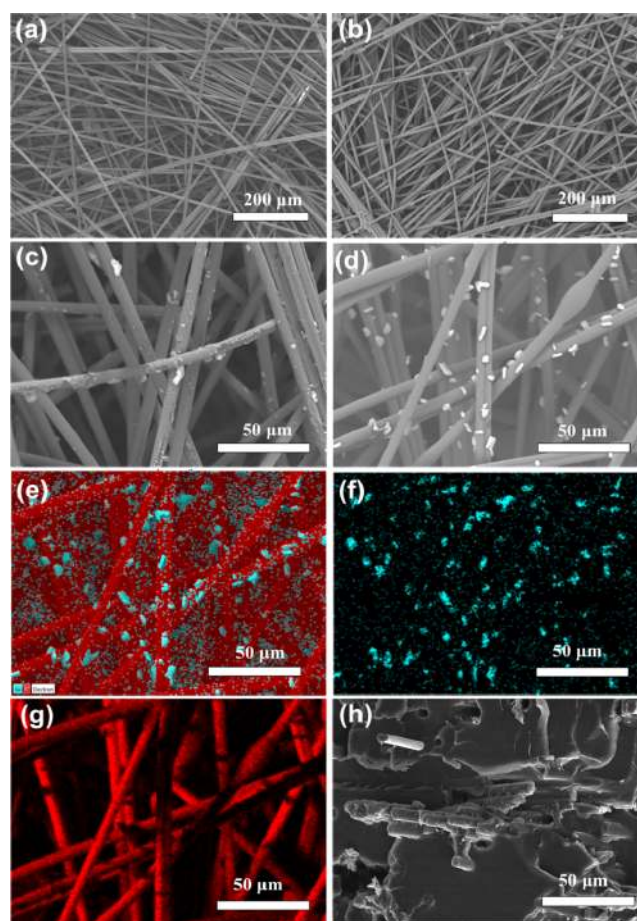
Figure 1. Micromorphology of the CF/C/Ni felt and CF/C/Ni/ epoxy composites: (a) the soft CF felt, (b) the CF/C felt, (c) the SEM image of the CF/C/Ni-30 felt, (d) the SEM image of the CF/ C/Ni-60 felt, (e) the mapping diagram of Ni and C elements in the CF/C/Ni-60 felt, (f) the Ni element mapping diagram of the CF/ C/Ni-60 felt, (g) the C element mapping diagram of the CF/C/Ni-60 felt, (h) SEM of the CF/C/Ni-60/epoxy composite.

bonding is poor. It is not easy to form a connecting path between the adjacent fibers and only through the straight fibers for heat conduction. Figure 1b displays the SEM of the CF/C felt. Carbon fibers overlap each other randomly, and many overlapping positions are adhered to by some carbon. The adherent carbon materials are residual carbon materials from pyrolysis and carbonization of the phenolic resin. Due to the influence of surface tension, a phenolic solution with high viscosity and low fluidity tends to stay in the overlapping and crossing position of carbon fibers during impregnation. The bonded carbon can improve the strength of the CF/C felt and promote the stability of the in-plane orientation structure of the CF/C felt. On the other hand, it can enhance the contact interface between carbon fibers, increase the thermal conduction path in the CF/C felt, and improve the thermal conductivity of the final composite. Figures 1c and 3d reveal the typical SEM images of the CF/C/Ni-30 felt and CF/C/Ni-60 felt. The nickel particles uniformly adhere to the carbon fiber surface of the CF/C felt, indicating that the electro-chemical deposition is more uniform, which is conducive to the formation of uniform and stable composite materials. The size of nickel microparticles is smaller than the diameter of the carbon fiber, and many tiny microparticles adhere to the
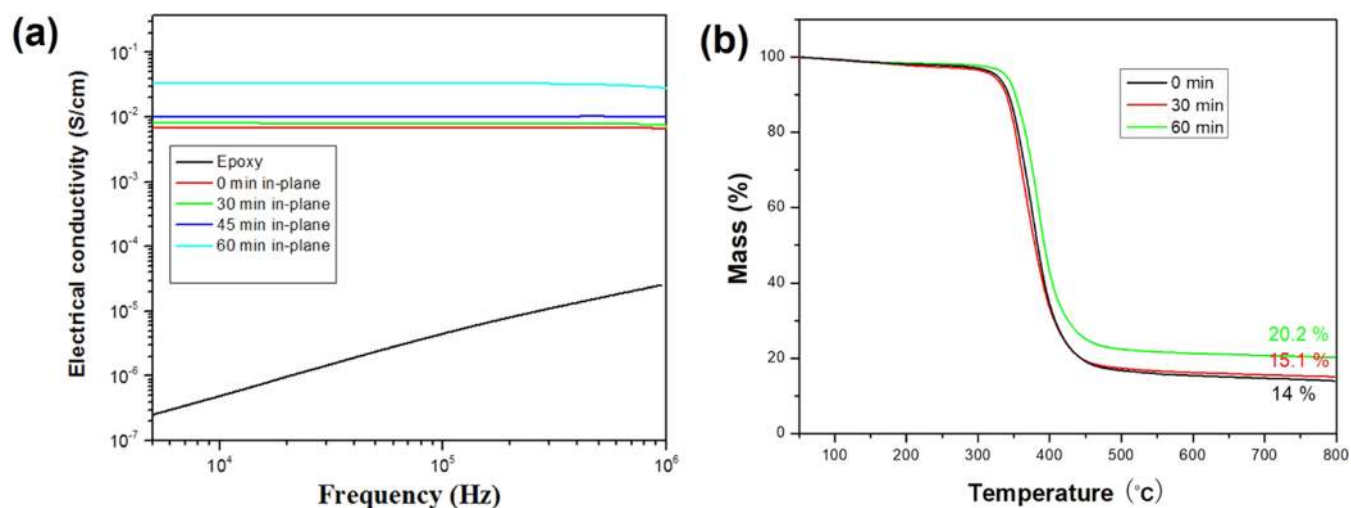
Figure 2. Curves of electrical conductivity and thermogravimetric performance of CF/C/Ni/epoxy composites: (a) electrical conductivity and (b) thermogravimetric curve.

surface of the carbon fiber. The nickel microparticles of the CF/C/Ni-60 felt, as shown in Figure 1d, are obviously more than those of the CF/C/Ni-30 felt, as shown in Figure 1c, indicating that the deposition of nickel on the surface of the carbon fiber increases with the increasing electroplating time. In particular, the increase of nickel microparticles between different carbon fibers can significantly increase the thermal conduction path between the carbon fibers, which is conducive to the improvement of the thermal conductivity of the subsequent composite.

To further characterize the structure of the CF/C/Ni-60 felt, the element analysis of the CF/C/Ni-60 felt was carried out. Figure 1e displays the mapping diagram of Ni and C elements in the CF/C/Ni-60 felt. Figure 1f,g exhibits the Ni element and C element mapping diagram of the CF/C/Ni-60 felt. As seen from the above three figures, the element C is the basic frame element in the CF/C/Ni-60 felt, which constitutes the basic frame of the CF/C/Ni-60 felt. In the process of heat conduction, the carbon skeleton is the main channel of heat transfer, and the widening of this channel will be conducive to the transfer of more heat. In Figure 1f, the Ni element mapping diagram of the CF/C/Ni-60 felt shows that the nickel deposited by electroplating is evenly distributed on the whole CF/C frame, which widens the heat conduction path to a certain extent, shortens the distance between carbon fibers. At the same time, some nickel microparticles connect the adjacent carbon fibers, increasing the bridge between the carbon fibers and increasing the heat conduction path. The thermal conductivity of the CF/C/Ni-60 felt can be improved by widening the path, shortening the distance between the carbon fibers, and increasing the bridge point, and then the thermal conductivity of the subsequent epoxy composite can be increased.

Figure 1h shows the SEM of the CF/C/Ni-60/epoxy composite. The carbon fibers and epoxy resin are tightly bonded, and carbon fibers are tightly covered by resin in the CF/C/Ni-60/epoxy composite, as shown in Figure 1h. After impregnation with epoxy resin, the air and holes in the CF/C/Ni-60 felt are completely filled by the epoxy resin. According to the cross-section of the fractured CF/C/Ni-60/epoxy composite, the carbon fibers have good adhesion to the epoxy resin, and no obvious interfacial holes and cracks are

observed. The newly added nickel particles did not hinder the formation of the composites. After molding, the CF/C/Ni framework embedded in the epoxy resin can form a good thermal conduction path, which reduces the thermal resistance of the interface. Phonons, electrons, and other heat transfer media can transfer heat rapidly in the 3D framework.

In the conventional case, when the filler is added to the epoxy resin, the viscosity will increase, which brings difficulties to the processing. At the same time, due to the difference in density between the epoxy resin and the filler, the epoxy resin will appear as a settlement phenomenon in the curing process, resulting in uneven dispersion of the filler in the composite. The thermally conductive filler is not easy to form a high thermal conductivity network in the resin system, resulting in the low thermal conductivity of the composite. However, in the CF/C/Ni/epoxy composite, there are no difficulties in molding, filler settlement, uneven dispersion, and other phenomena, but the CF/C/Ni felt forms a high thermal conductivity path in the epoxy resin, which reflects the advantages of the CF/C/Ni thermal conductivity network with the 3D skeleton structure in composite molding and improving the thermal conductivity of the composite.

Electrical Conductivity and Thermal Stability of CF/C/Ni/epoxy composites. The CF/C felt is an all-carbon framework structure, which has certain electrical conductivity. After electroplating nickel microparticles on the CF/C felt, the overall electrical conductivity of the CF/C/Ni structure will be improved. The electrical conductivity often has a positive correlation with the improvement of thermal conductivity. Therefore, it is necessary to study the electrical conductivity of CF/C/Ni/epoxy composites. It is also necessary to study the thermal properties of polymer composites because polymer materials should have certain thermal stability in the service process. Figure 2 shows the curves of electrical conductivity and thermogravimetric performance of CF/C/Ni/epoxy composites. Figure 2a indicates the electrical conductivity of CF/C/Ni/epoxy composites from 5×10^3 to 10^6 Hz. The electrical conductivity of pure epoxy resin was also tested and compared with that of the composite. From Figure 2a, pure epoxy resin is highly electrically insulated. After adding the CF/C felt to the epoxy resin matrix, the electrical conductivity of the CF/C/epoxy composite (in-plane) can significantly be
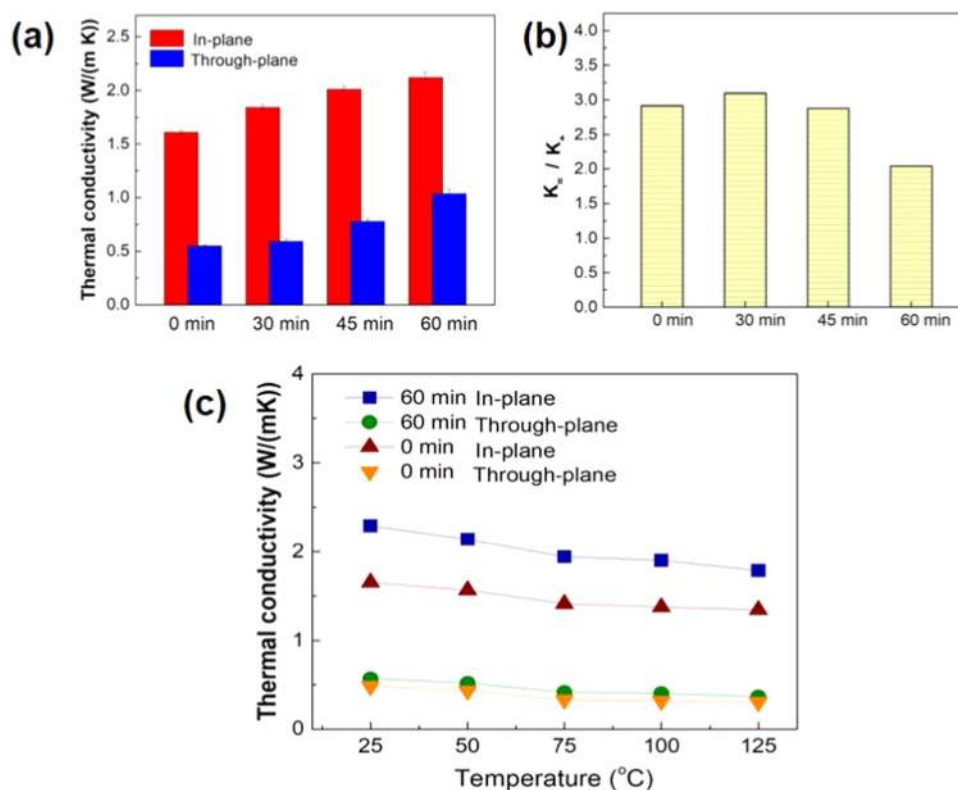
Figure 3. Thermal conductivity of the CF/C/Ni/epoxy composites: (a) in-plane ($K_\parallel$) and through-plane ($K_\perp$) thermal conductivity of the composites at 25 °C, (b) $K_\parallel/K_\perp$, and (c) temperature-dependent K of the epoxy nanocomposites.

improved by several orders of magnitude, which can be attributed to the excellent electrical conductivity of carbon fibers and the staggered stacking contact structure of carbon fibers in the $X-Y$ plane. With the change of the carbon network from CF/C to CF/C/Ni (CF/C/Ni-30 and CF/C/Ni-60), the electrical conductivity (in-plane) is further improved. This is mainly because Ni microparticles attached to the overlapping position of the adjacent carbon fibers can enhance the contact area of carbon materials and provide more conductive channels. The longer the plating time, the more Ni microparticles are deposited, and the more conductive the conductive path will increase; therefore, the electrical conductivity of the CF/C/Ni-60 epoxy composite is higher than that of the CF/C/Ni-30 epoxy composite. It is worth noting that the electrical conductivity of the CF/C/Ni-60 epoxy composite is further improved, especially the electrical conductivity of the CF/C/Ni-60 epoxy composite (through-plane) is more than 10^{-2} S/cm, due to the fact that the structure of the CF/C/Ni-60 epoxy composite is anisotropic. In the $X-Y$ plane, the electrons mainly propagate in the axial direction of carbon fibers. In addition, the carbon and nickel microparticles between the carbon fibers increase the conductive path, forming an $X-Y$ plane conductive network with high electrical conductivity.

The thermal stability of polymer composites is related to the stability of polymer materials in the service life, which is very important for the application of materials in the actual thermal management. Therefore, it is necessary to analyze the thermal weight loss of polymer composites. Figure 2b displays the thermogravimetric curve of CF/C/Ni/epoxy composites. The thermal decomposition temperatures of CF/C/Ni/epoxy composites are all higher than 300 °C, indicating that the

composites have very good thermal stability. After adding the CF/C/Ni felt, the microstructure of the CF/C/Ni network will restrict the thermal movement of epoxy resin molecules at high temperatures; therefore, adding the CF/C/Ni network can improve the thermal stability of CF/C/Ni/epoxy composites. In addition, with the increase of plating time, the content of nickel increases, and the residual mass content of CF/C/Ni/epoxy composites also increases, which is consistent with the quality change trend, as shown in Table 1, exhibiting that nickel can be well combined with carbon fibers by electroplating.

Thermal Conductivity of CF/C/Ni/Epoxy Composites. In the service life of electronic components, most of the energy is dissipated by heat; therefore, whether the heat dissipation material can transfer the heat is very important, and the thermal conductivity is a crucial performance parameter. Therefore, it is very necessary to study the thermal conductivity of materials, and the thermal conductivity of anisotropic materials in all directions needs to be further studied. Figure 3 reveals the thermal conductivity of CF/C/Ni/epoxy composites. To study the thermal conductivity of CF/C/Ni/epoxy composites, the thermal conductivity of CF/C/Ni/epoxy composites at 25 °C was studied. The thermal conductivity of epoxy composites (in-plane $K_\parallel$ and through-plane $K_\perp$) with the CF/C/Ni network with different nickel microparticle contents (electroplating time) were measured by a laser flash technique, as shown in Figure 3a. Pure epoxy resin is a well-known poor thermal conductivity (0.18 W/(m K)). Due to the inherent high thermal conductivity of carbon fiber and the orientation structure of carbon fiber, the thermal conductivity of the epoxy composites will be improved with the increase of the CF/C/Ni content in the epoxy resin matrix.

Table 2. Previously Reported Thermal Conductivity Values of Polymer Composites

material	method	thermal conductivity	reference
PDMS/CF	solution blending method	2.73 W/(m K) (20 wt % CF)	Wei[108]
PDMS/CF	freeze-dried orientation method	6.04 W/(m K) (20 wt % CF)	Hou[109]
paraffin/CF	direct carbonization of biomass sisal fibers	1.73 W/(m K) (12.8 wt % CF)	Sheng[110]
CF/epoxy resin	freeze-dried orientation method	19.4 W/(m K) (19.4 wt % CF)	Ma[111]
PDMS/CF	spatial confining forced network assembly method	2.95 W/(m K) (18 wt % CF)	He[103]
graphene/CF/PAI	liquid-phase impregnation method	0.53 W/(m K) (4.25 wt % graphene)	Xu[112]
Al$_2$O$_3$/CF/epoxy resin	solution blending method	3.84 W/(m K) (6.4 wt % CF/74 wt% Al$_2$O$_3$)	Wang[18]
graphene/epoxy resin	liquid-phase-exfoliation method	5.1 W/(m K) (18 wt % graphene)	Shahil[84]
graphene/epoxy resin	solution blending method	11 W/(m K) (60 wt % graphene)	Kargar[87]
graphene/Cu/epoxy resin	solution blending method	13.5 W/(m K) (40 wt % graphene/35 wt % Cu)	Barani[88]
MXene/CF/epoxy resin	freeze-dried orientation method	9.68 W/(m K) (10.2 wt % CF/20 wt % MXene)	Guo[86]
ZnO/epoxy resin	solution blending method	4.38 W/(m K) (50 wt % ZnO)	Guo[85]

The through-plane thermal conductivity ($K_\perp$) of the epoxy composites with the CF/C/Ni network structure is improved to a certain extent under the action of Ni electroplating metal particles. The thermal conductivity changes from 0.55 W/(m K) (0 min) to 0.6 W/(m K) (30 min), 0.5 W/(m K) (45 min), and 1.0 W/(m K) (60 min), indicating that Ni electroplating microparticles are beneficial to improve the thermal conductivity of CF/C/Ni/epoxy composites. This is because the Ni microparticles attached to the CF/C structure increase the contact opportunities between the CF/C framework layers and increase the thermal conductivity path. The longer the electroplating time of Ni microparticles is, the more the amount of Ni particles is, the more the contact opportunities are, and the more the thermal conductivity is improved. In addition, especially in the $X–Y$ plane, the thermal conductivity (in-plane, $K_\parallel$) increases more obviously. The thermal conductivity of CF/C/Ni/epoxy composites in-plane ($K_\parallel$) increases from 1.6 W/(m K) (0 min) to 1.8 W/(m K) (30 min), 2.0 W/(m K) (45 min), and 2.13 W/(m K) (60 min), which are 8.89 times (0 min), 10 times (30 min), 11.1 times (45 min), and 11.8 times (60 min) of that of pure epoxy resin, respectively. This is mainly due to the following reasons. (a) In the $X–Y$ plane, it is easier for heat to propagate along the carbon fiber axis, and the direction of heat conduction is just in the $X–Y$ plane of the carbon fiber axis. (b) The bonded carbon structure widens the heat conduction path, while the nickel-plated microparticles further widen the heat conduction path. Especially the nickel-plated microparticles between the adjacent carbon fibers can enhance the contact area between the carbon fibers. Thus, a connected heat conduction network with low thermal resistance is formed. Finally, the CF-C-Ni network connected structure with carbon fibers as the backbone is formed. The more Ni microparticles are plated, the wider the thermal conduction path and the more obvious the thermal conductivity increases.

To study the relationship between the thermal conductivity anisotropy of epoxy composites and the CF-C-Ni network, we calculated the value of thermal conductivity anisotropy of epoxy resin composites with the CF-C-Ni network, that is, the ratio of thermal conductivity (in-plane) to thermal conductivity (through-plane) ($K_\parallel/K_\perp$). Figure 3b reveals $K_\parallel/K_\perp$ of CF/C/Ni/epoxy composites. As shown in Figure 3b, the thermal anisotropy value of epoxy resin composites with different carbon networks increases significantly first and then decreases with the increasing electroplating time due to the anisotropy of the CF/C skeleton itself. The CF/C felt is composed of layers of carbon fibers with the $X–Y$ plane

structure through needling. For the carbon fibers in the $X–Y$ plane cross-stack and composite, the contact probability of carbon fibers is higher but the contact area between the planes is less. However, with the increasing electroplating time, the number of nickel-plated microparticles increases gradually, and the nickel-plated microparticles preferentially improve the fiber connection in the $X–Y$ plane, especially the cross-composite point connection. However, the distance between the different $X–Y$ planes is not close enough, and the nickel microparticles can play a certain role in the connection of carbon fibers in the different $X–Y$ planes, but the effect is not significant. Therefore, in the early stage of electroplating, one effect ($K_\perp$) is large, the other ($K_\parallel$) is small, and the ratio increases gradually. However, when the nickel-plated microparticles increase to a certain extent, the nickel microparticles can act between the carbon fibers in the different $X–Y$ planes, and the contact area in the Z-direction ($K_\parallel$) will increase significantly; therefore, the final thermal conductivity ratio ($K_\perp/K_\parallel$) will decrease. The thermal conductivity anisotropy of the epoxy composites decreases, and the difference in the thermal conductivity in all directions decreases. The formation of isotropic high thermal conductivity has always been a hot topic in the field of thermally conductive composites.

Figure 3c exhibits temperature-dependent K of the epoxy composites. It can be found that all of the in-plane and through-plane thermal conductivities of epoxy composites show a slight decreasing change as the temperature increases from 25 to 125 °C. The through-plane thermal conductivity of the CF/C/Ni-60/epoxy composite decreases more obviously at 125 °C, but the thermal conductivity remained at 1.8 W/(m K) with only a 20% decrease. This is due to the volume expansion of the CF/C/Ni/epoxy composite caused by the increasing temperature. The volume expansion of the interface between the CF/C/Ni network and epoxy resin will increase with the increasing temperature, resulting in the increase of interface thermal resistance and the decrease of thermal conductivity. This phenomenon is common in the polymer composites. The through-plane thermal conductivity of the CF/C/Ni-60/epoxy composite prepared in this paper remains at a high level with the increasing temperature (about 2.0 W/(m K)), indicating that the CF/C/Ni framework structure can improve the heat transfer performance of the polymer composites.

Table 2 displays the previously reported thermal conductivity of polymer composites. Compared with the preparation methods used in these works, the method adopted in this study is relatively simple and benefits the product on a

big scale. Moreover, the thermally conductive filler content is relatively small, but the thermal conductivity of the CF/C/Ni composite is significantly improved compared to that of pure epoxy resin in this study.

Thermal Management Application of CF/C/Ni/Epoxy Composites. To study the thermal management application of epoxy composites with CF/C/Ni felts, the surface temperature distribution and its change with time during the heating process of the composite were captured by a hand-held infrared thermal imager in this paper. Figure 4 illustrates the
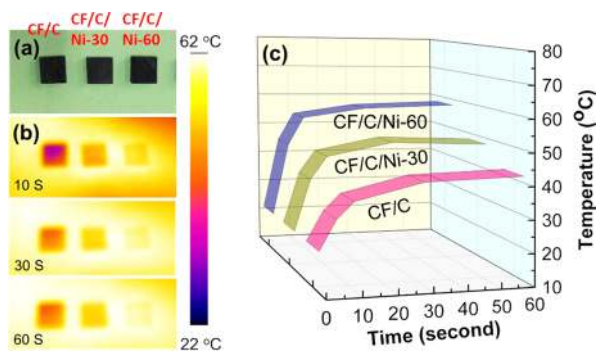
Figure 4. Infrared imaging of CF/C/Ni/epoxy composites: (a) optical photos of composites under different carbon fiber networks, (b) thermal images of temperature distribution of composites with different carbon fiber networks; (c), (b) surface temperature curves of composites with different carbon fiber networks.

infrared imaging of CF/C/Ni/epoxy composites. As shown in Figure 4a, polymer composites with CF/C, CF/C/Ni-30, and CF/C/Ni-60 networks of the same size from left to right were placed on the same heating table at the same time. Figure 4b,c exhibits the thermal images of temperature distribution and surface temperature curves of composites with different carbon fiber networks. From the infrared thermal images, the epoxy composites with CF/C/Ni-30 and CF/C/Ni-60 networks show a faster temperature rising trend with time than those with CF/C networks, showing that the composite with CF/C/Ni has a higher heat dissipation capacity. The surface temperature of the epoxy composite with the CF/C/Ni-60 network is higher than that of the epoxy composite with the CF/C/Ni-30 network, showing that the more the nickel microparticles are, the better the thermal management ability of the material is. After heating for 60 s, the surface temperature of the epoxy composite with the CF/C/Ni-60 network is about 56 °C, which is very close to the surface temperature of the heating table, showing great thermal management ability. The heat transfer ability of the three kinds of epoxy composites is consistent with that of the thermal conductivity of the three kinds of composites, that is, the higher the thermal conductivity of the composites, the higher the heat transfer ability of the composites.

To further understand the excellent thermal management ability of the epoxy composites with the CF/C/Ni network, the heat transfer diagram of the composites was drawn. Figure 5 displays the mechanism of the heat conduction in the CF/C/epoxy composite and the CF/C/Ni/epoxy composite. All CF/C and CF/C/Ni form a 3D thermal network in the epoxy resin. The heat conduction mechanism in the carbon fiber network can explain the following two phenomena. (1) The in-plane thermal conductivity of the CF/C/epoxy composite is higher than the through-plane thermal conductivity of the CF/
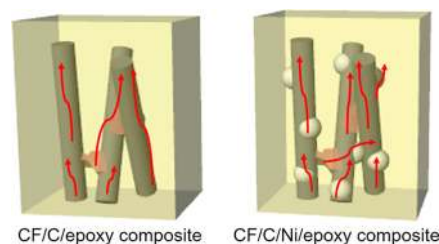
Figure 5. Mechanism of the heat conduction in the CF/C/epoxy composite and the CF/C/Ni/epoxy composite.

C/epoxy composite. The thermal conductivity of the epoxy composite with the CF/C/Ni thermal conduction network has the same phenomenon. These phenomena are caused by the tensile crystalline orientation of carbon fibers and the thermal resistance of the interfaces in the composites. In the production process of carbon fiber, spinning, preoxidation, carbonization, and graphitization are carried out under a certain traction force, so the carbon fiber produced is easier to have the carbon crystal orientation in the direction of the traction force (that is, the axial direction of carbon fiber). The crystalline orientation is more favorable for the heat transfer of phonons or electrons. The thermal conductivity of carbon fibers in the axial direction is much higher than that in the nonaxial direction. The axial thermal conductivity of carbon fiber can even reach 518 W/(m K) or higher.[113] In addition, the main long fiber (120 mm) used in the preparation of the CF/C felt is much larger than the size of the thermal conductivity testing sample, so it can be considered that the carbon fiber in any direction is continuous carbon fiber. Therefore, there is no interface thermal resistance in the axial direction when heat is transferred in a single fiber, which is more conducive to the improvement of the thermal conductivity of the epoxy composite. However, there are a lot of interfaces between the carbon fibers and the epoxy resin, especially between the Z-direction carbon fibers and the epoxy resin, which is not conducive to the phonon heat conduction. From the SEM images in Figure 1, it can be seen that the axial direction of carbon fiber is mainly distributed in the $X-Y$ plane, with little anisotropy in the Z-direction. In the $X-Y$ plane, the carbon fibers are arranged crosswise, and the probability of arrangement in all directions is the same, so the thermal conductivity of the epoxy composite in all directions will be the same. Therefore, whether in the CF/C/epoxy composite or the CF/C/Ni/epoxy composite, heat is more easily transmitted in the $X-Y$ plane, especially in the axial direction of carbon fiber, which is attributed to the high axial thermal conductivity and the continuity of carbon fiber. In the Z-direction, the thermal conductivity of the epoxy composite is low, which is due to the thermal resistance between the carbon fibers and the epoxy resin. Therefore, the higher the orientation degree of carbon fibers, the less the thermal resistance inside the fibers or between the fibers and the epoxy resin, and the better the thermal conductivity and thermal management performance of the epoxy composite. (2) The epoxy composite with the 3D CF/C/Ni thermal conduction network has higher thermal conductivity and better thermal management ability than that of CF/C/epoxy composite in the same direction. Because the nickel plating particles between the carbon fibers increase the thermal conduction path between the carbon fibers, the thermal conductivity of the composites and the thermal management ability of the
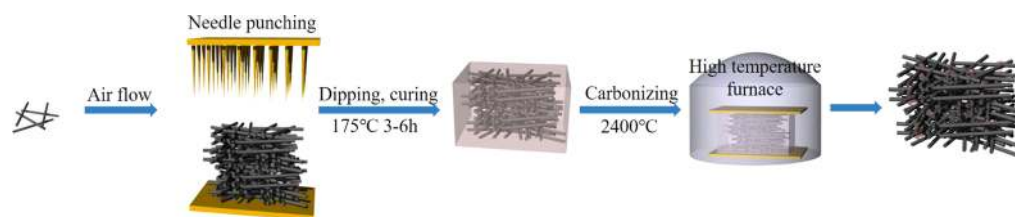
Figure 6. Preparation process of the CF/C felt.

composites are improved. As can be seen from Figure 4, the heat conduction capacity of the CF/C/Ni/epoxy composite is much higher than that of the CF/C/epoxy composite. According to the fractal theory,[114−116] the thermal conductivity of the composites can be significantly improved by increasing the connecting path of the thermally conductive filler in the composites. In this paper, the increase of nickel particles is equivalent to increasing the connecting path between fillers, so the phenomenon in this paper is based on the composite fractal theory. In Figure 5, in the CF/C/epoxy composite, due to the lack of contact between the carbon fibers and the small contact area, the heat flow is mainly transmitted through the carbon fibers, while the paths between the fibers are less, the interface thermal resistance between the fibers is larger, so the thermal conductivity is lower, and the thermal management ability is poor. Therefore, the surface temperature of the CF/C/epoxy composites during heating shows that the thermal conductivity is low, as shown in Figure 4. In contrast, the heat transfer performance of the CF/C/Ni/epoxy composite is better, and the heat flux is mainly distributed in carbon fiber and nickel. The presence of nickel particles makes the contact area between the carbon fibers larger, especially the presence of nickel particles in the cross-contact position of carbon fibers, which makes the thermal resistance and thermal scattering in the three-dimensional thermal skeleton smaller, and the thermal conductivity increases accordingly. The more nickel particles are electroplated, the more conductive the paths are, and the more conductive the composite is. When the composite is applied to the thermal management devices in the vertical direction, the temperature of the upper surface of the composite almost reaches the temperature of the heat source, and the heat energy of the heat source can be effectively transferred to the top through rich heat conduction channels, dense carbon networks, and low interface thermal resistance. With excellent thermal management ability, polymer composites can ensure the rapid release of heat generated inside the device, thus ultimately improving the efficiency of electronic devices and the service life of equipment.

From the above analysis, it can be seen that the "CF axial increasing heat transfer effect", "bonded Ni microparticles increasing heat conduction path effect" improve the thermal conductivity of the CF/C/Ni/epoxy composite and the thermal management ability of the CF/C/Ni/epoxy composite. It is hoped that the epoxy composite with the 3D CF/C/Ni thermal conduction network can give some suggestions for the application of the carbon fiber/polymer composite.

■ EXPERIMENTAL SECTION

Materials. Carbon fiber (SYT45 12K) was obtained from Zhongfu Shenying Carbon Fiber Co., Ltd, China. $NiSO_4 \cdot 6H_2O$ (AR), $NiCl_2 \cdot 6H_2O$ (AR), H_3BO_3 (AR), and $C_{12}H_{25}SO_4Na$ (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Ethanol (AR) was supplied from Sigma-Aldrich.

Phenolic resin (PF-5408) was obtained from Jinan Shengquan Group Co., Ltd, China. The solid content, free phenol, and moisture of phenolic resin are 65, 9.5−11.8, and 2.5−4.0 wt %, respectively. Epoxy resin (Araldite LY 1564) and polyamine hardeners (Aradur 3486) with a weight ratio of 3:1 were purchased by Huntsman.

Preparation of Samples. *Preparation of the CF Felt and CF/C Felt.* The CF/C felt with a 3D skeleton structure is the basic 3D thermally conductive filler in the epoxy composite, and its structure directly affects the thermal conductivity of the epoxy composite. The preparation process of the CF/C felt mainly includes air-laid and needle punching—liquid impregnation and solidification—high-temperature pyrolysis and carbonization. Figure 6 shows the schematic diagram of the preparation process of the CF/C felt. (a) The air-laid and needle-punching method. Carbon fibers with an average length of 120 mm were placed into the air flow web forming machine for air flow web forming. Carbon fibers were loosely arranged in the X−Y plane and can move freely to destroy the original in-plane stacking structure. To enhance the mechanical stability, the carbon fibers with the X−Y structures were needle punched in the needling machine to obtain the soft CF felt with an X−Y−Z three-dimensional structure. Through the process of needle punching, about 1% of carbon fibers in the X−Y plane were pushed to the vertical plane by the Z needle. In the carbon fiber felt, the Z-direction carbon fibers can restrain the movement of X−Y fibers so as to enhance the structural stability. The weight of the soft CF felt is about 700 g/m^2 and the thickness is 10 mm. (b) Liquid impregnation and solidification. The CF felt with an X−Y−Z structure was completely immersed in the phenolic alcohol solution (solid content 35 wt %). After liquid-phase impregnation, the soft felt was transferred to an oven at 80 °C for 2 h to volatilize ethanol. Then, the impregnated and dried felt was transferred to the mold on the hot pressing machine, and the temperature was adjusted to 175 °C for 5 h to make the phenolic resin cured completely. (c) High-temperature pyrolysis and carbonization. The cured samples were transferred to a high-temperature furnace. The temperature in the furnace increased from room temperature to 400 °C at a speed of 75 °C per hour and then increased from 400 to 500 °C at a speed of 25 °C/h. Then, the temperature of the furnace was maintained at 500 °C for 2 h. Finally, the temperature is increased to 2400 °C and maintained for 1 h to pyrolyze and carbonize the phenolic resin in the composite to obtain an anisotropic CF/C felt.

Preparation of CF/C/Ni 3D Networks. In the CF/C felt, carbon fibers are bonded by a small amount of pyrolysis carbon, and there are not enough bonding points between the carbon fibers, so it is necessary to broaden the 3D thermal conduction path to improve the thermal conductivity of the final composite. In this study, the CF/C/Ni felt was prepared by electroplating nickel on the surface of the CF/C skeleton. The electroplating process of the CF/C felt is displayed in
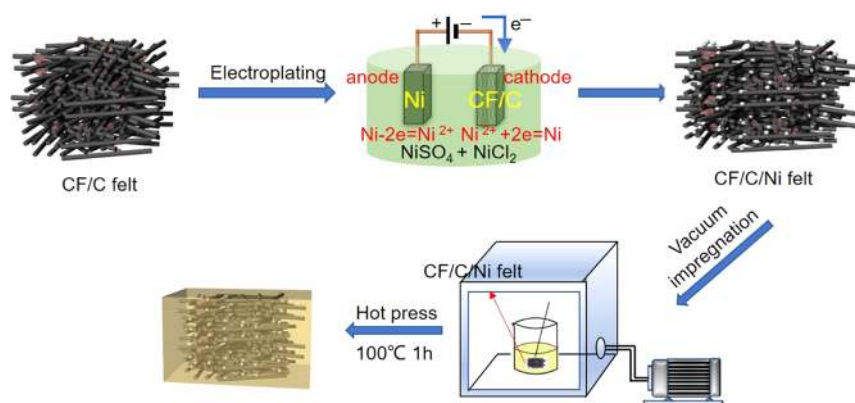
Figure 7. Preparation process of the CF/C/Ni felt and CF/C/Ni epoxy composite.

Figure 7. Because the CF/C felt is all-carbon material with good conductivity, it can be directly fixed on the cathode as the cathode electrode. The anode is a nickel sheet, and the solution is the aqueous solution of $NiSO_4 \cdot 6H_2O$ (240 g/L), $NiCl_2 \cdot 6H_2O$ (40 g/L), H_3BO_3 (30 g/L), and $C_{12}H_{25}SO_4Na$ (0.2 g/L). The solution temperature is 60 °C. Then, the power with the current 200 mA and the voltage 1.5 V was turn on to electroplated nickel on the CF/C felt. The electroplating time was set to 15, 30, 45, and 60 min, respectively, so as to control the amount of nickel plating. Finally, after the washing process, the obtained CF/C/Ni felt was washed with ionic water and ethanol to remove free ions and then placed into the oven for drying. The CF/C/Ni felts electroplated for 15, 30, 45, and 60 min were labeled as CF/C/Ni-15, CF/C/Ni-30, CF/C/Ni-45, and CF/C/Ni-60, respectively.

Preparation of CF/C/Epoxy Composite and CF/C/Ni/ Epoxy Composites. When the powdered thermally conductive filler is compounded with epoxy resin, there are many problems, such as the increase of viscosity, the settling of the filler, the uneven dispersion of the filler, and the difficulty of forming the thermal conductive network. The epoxy composites with the CF/C and CF/C/Ni felts (Figure 7) were prepared by vacuum-assisted liquid-phase impregnation and molding. The CF/C/Ni felt was completely immersed in a liquid epoxy resin system containing a 75 wt % epoxy resin (Araldite LY 1564) and a 25 wt % curing agent (Aradur 3486) for 1 h in a vacuum. Then, the impregnated composite system was transferred into a mold in a hot pressing machine for curing. The curing temperature was 100 °C for 1 h and the curing pressure was 10 MPa. Finally, the CF/C/epoxy composite and CF/C/Ni/composites were prepared.

Characterization. A scanning electron microscope (SEM, Hitachi S-2150, Japan) was used to observe the micromorphology of CF/C, CF/C/Ni, and CF/C/Ni/epoxy composites. The samples were brittle and broken in liquid nitrogen, and the surfaces of the samples were sprayed with gold.

At room temperature, the electrical conductivity of the composite samples in a different frequency ranging from 5×10^3 to 10^6 Hz was tested by an impedance analyzer (Agilent E4991) equipped with a 16453 dielectric testing device. The upper and lower sides of the composite needed to be sprayed with gold to be used as electrodes.

Thermogravimetric analysis (TGA) of CF/C/Ni/epoxy composites was carried out in a thermal analysis instrument (Netzsch TG209 F3, Germany) with a heating rate of 20 °C/ min from 50 to 800 °C in a nitrogen atmosphere.

The thermal diffusivity of the composites was characterized using a laser thermal analyzer (Netzsch Nanoflash, LFA 457, Germany). The sample size was about 10 mm × 10 mm × 2 mm. The specific heat capacity of epoxy composites was measured using a differential scanning calorimeter (DSC) of Netzsch 200 F3 in Germany. The thermal conductivity (λ) can be calculated by the product of thermal diffusivity (α), density (ρ), and specific heat capacity (C_ρ).[117]

An infrared thermal imager (Fluke Ti480) was used to detect the thermal management performance of the composites. The sample size was about 10 mm × 10 mm × 2 mm. The temperature of a hot table was 60 °C. The sample surface temperature with increasing time was recorded.

■ CONCLUSIONS

In this paper, the carbon fiber/carbon felt (CF/C felt) with a 3D skeleton structure was prepared by an air-laid and needle-punching method—liquid impregnation and solidification method—high-temperature pyrolysis and carbonization method. The Nickel heterographene-coated CF/C felt was fabricated by an electroplating deposition method. Three-dimensional (3D) CF/C/Ni/epoxy composites were manufactured by vacuum-assisted liquid-phase impregnation. The thermal conductivity and mechanism of the composites were studied. The main conclusions are as follows.

(1) The thermal conductivity of the epoxy composites increases obviously with the increasing nickel electroplating particles in the in-plane direction ($K_\parallel$). The thermal conductivity ($K_\parallel$) increases from 1.6 W/(m K) (0 min) to 1.8 W/(m K) (30 min), 2.0 W/(m K) (45 min), and 2.13 W/(m K) (60 min), which are 8.89 times (0 min), 10 times (30 min), 11.1 times (45 min), and 11.8 times (60 min) of pure epoxy resin, respectively. These are due to the fact that in the in-plane direction ($K_\parallel$), the heat is conducted in the direction of carbon fibers, and the bonded carbon structure widens the heat conduction path, while the nickel-plated metal particles further widen the heat conduction path, especially the nickel-plated metal composite particles at the cross position of carbon fibers or between adjacent and parallel fibers can enhance the contact area between carbon fibers. Finally, the 3D CF-C-Ni network connected structure with carbon/carbon fibers as the backbone is formed. The more the Ni particles are plated, the wider the thermal conduction path, and the more obvious the thermal conductivity increases.

(2) The epoxy resin composite with the CF-C-Ni network has a much better thermal response, which indicates that the composite has great potential in the application of thermal management in electrical equipment and electronic devices. The research content of this paper provides a new idea for the preparation of the high thermal conductivity carbon fiber/polymer composite.

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Notes

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