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Review on Thermal Conductivity of the Graphene Reinforced Resin Matrix Composites

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Abstract. Graphene is a two-dimensional nanostructure filler with high thermal conductivity (5000 W/mK) and excellent mechanical properties, which has a very wide application prospect. Graphene is with super high specific surface area, which provides a greater contact area with polymer matrix. Then it is more easy to form the thermal conductive heat channels, which could improve the thermal conductivity of composite materials. The concentration, the ratio of geometrical diameters, the dispersion in the matrix and the interfacial bonding between graphene and the matrix materials will greatly affect the thermal conductivity of graphene reinforced composites. However, the graphene nanosheets can be easy to stack together and difficult to be dispersed into the solvent and polymer matrix. In order to improve the interfacial combination between graphene nanosheets and the matrix so as to reduce the interfacial thermal resistance of the composites, it is usually to modify the surface of graphene nanosheets, which mainly includes non-covalent modification and covalent modification. In this paper, researches on the thermal conductivity of graphene were reviewed, and the existing problems and the future research focus were also discussed.

1. Introduction

With the development of scientific technology, researchers have embedded some information electronic devices into aerospace materials to ensure the structure stability of the composites to better control the safety and intelligence of airliners and warplanes [1-4]. However, a considerable amount of heat can be generated when the electronic components are running. It will even seriously destroy the structure stability and greatly reduce the use life of the composites if the generated heat does not be dissipated in time [5-10]. Therefore, it is urgent to create an effective method to highly improve the thermal conductivity of composites.

The traditional thermal conductive materials are mainly filled with particles, which are composed of thermal conductive resins and composites [11]. The commonly used thermal conductive particles are mainly metallic nanoparticles with high thermal conductivity [12-16], such as Ag(429 W/mĸ), Al(237 W/mĸ), Cu(317 W/mĸ). In order to form a continuous thermal conductive network in the polymer, the volume content of particles should reach to 60% [22-25]. However, the composites are particularly heavy with filling content [26-30]. Moreover, the mechanical properties of the composites can be greatly reduced with the poor interface binding between metal particles and resin matrix. Therefore, it is urgent to find one filler with low density and high thermal conductivity to solve the current problems.

In recent years, the discovery of fullerenes and carbon nanotubes has inspired leading research passion of scientists. In 2004, Novoselov and colleagues first successfully prepared graphene by

mechanical stripping method [31]. Graphene was considered to be an ideal nanomaterial with Young's modulus and strength are high up to 1TPa and 130GPa respectively [32-34]. Graphene with good thermal conductivity(5000W/mK) [35]. Studies show that the two-dimensional geometry and large specific surface area of graphene are beneficial to the strong coupling with the matrix [36]. Teng et al. [37]showed the thermal conductivity of composites increased 37.5% higher than the pure epoxy resin after addition of graphene. Yu et al. [38] added 5wt% graphene, the thermal conductivity of composites was 4 times of neat. Researches [39-45] showed that the addition of graphene significantly increase the thermal conductivity of composites. In this paper, researches on the thermal conductivity of graphene were reviewed, and the existing problems and the future research focus were also discussed.

2. The Thermal Conductive Mechanism of Graphene

Some people difine graphene as semi-metal material, so the graphene has the two mechanisms of electron conduction and phonon conduction [47], and is dominated by phonon conduction. The thermal conductivity of phonons κ_s is:

$$k_s = \frac{1}{2} v_s l_s C_V^s$$

(1)

v_s—the average velocity of the phonon;

l_s—the mean free path of the phonon;

C_V^s—the volume heat capacity of the phonon.

According to the equation, the thermal conductivity of graphene is mainly determined by the mean path and the volume heat capacity of the phonons. l_s is basically determined by two scattering processes: the scattering caused by collisions between phonons, and the scattering between phonons and crystals, various defects, and impurities. At higher temperature, the phonon vibration intensifies, and the interaction between phonons is enhanced, thus l_s is decreasing, so the thermal conductivity decreases with the increase of temperature. And it is the opposite of the lower temperature [48]. The carbon atoms will be kept on larger vibration amplitude, and the most important is that the lattice vibration of graphene can seriously affect its thermal properties. With the temperature rising, the lattice vibrations of graphene is strengthened, and the phonon motion is especially intense. Moreover, with the number of phonons in the heat flow increasing, the interaction between phonons is more frequent, so the scattering of phonons is increasing. Correspondingly, The mean free path of phonons decreases with the thermal conductivity of graphene becoming weaker [49-50]. Electronic motion has a certain contribution to the thermal conductivity of graphene, but at higher temperature, the lattice vibrations plays a leading role to the thermal conductivity of graphene.

3. Study on Thermal Conductivity of Graphene Reinforced Composites

As an ideal nanometer fillers, graphene's higher surface area is beneficial to the strong coupling effect with the matrix, which can improve the thermal conductivity, electrical conductivity and mechanical properties of the composites. The concentration, the ratio of geometrical diameters, the dispersion in the matrix and the interfacial bonding between graphene and the matrix will greatly affect the thermal conductivity of composites [51-53]. If graphene combines with the matrix interface well, it will greatly increase the contact area between graphene and the matrix, which can reduce the thermal resistance of the interface and promote the heat transfer, but there will still be problems of phonon scattering. The mismatch of the phonon spectrum of the graphene with the interface of the matrix causes the scattering of the phonons, resulting in the delay of the heat flow transfer [50,54]. On the one hand, the excellent interface combination between the graphene and the matrix can reduce the interfacial thermal resistance. On the other hand, the maximum physical contact between graphene nanosheets can also to some extend solve the phonon-scattering problem by designing the whole composite system. The connection among the graphene nanosheets provides a pathway for the phonons diffusion, while is accompanied by the smallest phonon scattering [55-56]. The adding of graphene in the matrix could found a thermal conductive pathway, but the mechanical properties of composites were sacrified.

Due to vander Waals force, the graphene nanosheets can be easy to stack together. In order to improve the interfacial combination between graphene nanosheets and matrix so as to reduce the interfacial thermal resistance of composites, it is usually to modify the surface of graphene nanosheets, which mainly includes non-covalent modification and covalent modification.

The non-covalent modification of graphene is realized by using the Vander Waals force between the surfactants and graphene nanosheets. It does not destroy the structure of graphene nanosheets and guarantees the integrity of graphene properties. The non-covalent modifiers utilizes the π conjugate structure to interact with the π electrons of graphene to weak the Vander Waals force between the graphene nanosheets. Conjugated polymers [57], surfactant molecules [58] and biomolecules [59] are commonly used. However, the non-covalent modification of graphene is weak, which is still not beneficial to connection between modifier and interface of the matrix, and therefore the covalent modification of graphene is necessary.

The functional groups of the modifier molecules react with the functional groups of graphene to form a stable covalent bond, which is the covalent modification. Since pure graphene has few functional groups on its surface, graphene should be oxidized and a large number of carboxyl, hydroxyl and epoxy groups should be induced. Then the groups could react with other functional groups to modify the graphene nanosheets [60-63]. Silane coupling agent is a good modifier [64-65]. The hydroxyl groups are formed after the alkanoxy groups of silane coupling agent molecules hydrolysis. Then it reacts with hydroxyl group on the surface of graphene to form Si-O bond, and the graphene's surface would be grafted with amino or epoxy groups. Therefore, the functional graphene will participate in the curing reaction of the epoxy resin to form a stable bond in the interface. The literature [66] showed that covalent modified graphene destroyed its own structure and reduced its thermal conductivity, but the coupling effect between graphene and polymer is strengthened. The inner layer of the graphene nanosheets works as the high thermal conduction pathway for heat-transfer, and the outer layer is connected with the resin matrix by covalent bond, which promotes the transmission of phonons from graphene to resin matrix. Then the thermal conductivity of the composites could be improved effectively by reducing the thermal resistance and phonons scattering, while the mechanical properties of the composites could be also greatly improved.

4. Influence Factors for Thermal Conductivity of Graphene Reinforced Composites

Graphene provides a greater contact area with matrix due to its super high specific surface area. Then it is more easy to form the thermal conductive heat channels in the composites. The addition content, the ratio of geometric diameter and dispersion in the matrix directly affect the thermal conductivity of composites. Here the influencing factors will be described in detail.

4.1. The Addition Content of Graphene

The thermal conductivity of graphene is the same as the principle of conductive property, which could be explained by percolation theory. The network has a critical probability Pc, and when the probability is no more than Pc, the network is consisted of isolated node clusters. But when the probability is more than Pc, the large cluster of nodes expand to the entire network. As the graphene concentration increases, the thermal conductivity of composites is increasing, and when the concentration of graphene is to a critical point, the graphene nanosheets interconnect to form the conductive network path [68], then the thermal conductivity of composites will be greatly improved. It is separated from each other in the matrix when the graphene concentration is low, so the the thermal conductivity of composites is not improved. When the graphene concentration reaches up to the threshold, there is an effective contact between graphene nanosheets to form the thermal conductive pathway. And the heat transfer is founded through the graphene nanosheets quickly without the matrix, the thermal conductivity of composites can jump sharply. Then the graphene concentration continues to increase, the thermal conductivity of composites will continue to increase. Wang et al. [69]added 5wt% graphene nanosheets into the polymer matrix, the thermal conductivity of composites was four times higher than the neat. Yu et al. [70]showed that when the addition of graphene was 25vol%, the thermal conductivity of composites was 30 times higher than the pure epoxy resin. Some researches [71-73] also showed that graphene nanosheets and carbon nanotubes could be orientated in the direction of

electric field in low content, which could form the conductive path by head-to-tail ligation. Both the thermal conductivity of composites and the mechanical properties of composites were improved.

4.2. The Number of Layers of Graphene
The number of layers and transverse dimensions of graphene make a crucial effect on the properties of graphene [74]. The number of layers and the particle size of graphene could greatly affect the heat transfer. With the length increase of particle size, the mean free path of the phonons in the direction of heat flow increases, and the thermal conductivity of graphene nanosheets also increases [75]. Studies have shown that the thermal conductivity of graphene in free state decreases with the number of layers increasing, but it's opposite when the graphene is wrapped in the matrix [76]. Then with the increasing of the number of layers, the thermal conductivity in the direction of the plane and the entire interface will increase. The heat transfer of graphene in different state is different, because the surrounding matrix materials can reduce the phonon energy of graphene. In other words, the thermal conductivity of graphene is decreased when it is embedded in the matrix [77]. And in the case of the same diameter ratio, the thermal conductivity of the matrix could be improved by the multi-layer graphene than the single-layer graphene, because the diameter of multi-layer graphene is far larger than that of single-layer graphene, the mean free path of the phonons in the direction of heat flow increases, and the thermal conductivity of graphene nanosheets also increases correspondingly.

4.3. The Dispersion in the Matrix of Graphene
The graphene is very difficult to be dispersed in the resin matrix because its surface has almost no functional groups. Solution blending method, melting blending method and in-situ polymerization are mainly the methods of preparing graphene reinforced composite materials, and the dispersion degree is totally different by different mixing ways [78]. However, the agglomeration of graphene results in the poor bonding interface with the resin matrix, then the thermal interface resistance is large and it is not enough to improve the thermal conductivity of composite materials. As is known to all, if the modified graphene can be better connected with resin matrix, it is beneficial to the phonon transmission, thus the thermal conductivity of composite materials could be effectively improved. In the same way, there is an strong intermolecular force between the modified graphene and polymer molecules, which is beneficial to the dispersion of graphene in resin matrix effectively. Song et al. [79] showed that the thermal conductivity of composite materials reached up to 1.53 W/mK when the modified graphene were added into epoxy resin. Hu et al. [80-81] showed that the thermal conductivity of composite materials reached up to 0.49 W/mK after the graphene modified by benzidine. The above researches showed that there is a strong coupling effect between the modified graphene and resin matrix, good dispersion in the resin matrix could be achieved and the thermal interface resistance is reduced accordingly, so the thermal conductivity of composite materials could be improved greatly.

5. Conclusion
Graphene is a two-dimensional nanostructure filler with high thermal conductivity (5000 W/mK) and excellent mechanical properties, which has a very wide application prospect. However, the dispersion of graphene in the matrix remains a great challenge. The agglomeration of graphene reduces the mechanical properties and the large thermal interface resistance reduces the thermal conductivity of composites, and therefore there are still some difficulties in the application of heat dissipation materials. Researches [82]showed that the lower content of graphene could be used in electric field to form graphene networks and both the thermal conductivity and mechanical properties of composites could be improved to replace the high content addition of graphene. These enhanced properties of composites can further be used for various industrial applications and a lot of research work could be done in future.

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