

Preparation and Thermal Conductivity of FG/PP Composites

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Abstract: The surface modified flake graphite (FG) was filled into polypropylene (PP) and mixed by a double-roll open mill. FG/PP composites with high thermal conductivity were prepared by compression molding. Studies had shown that the modification of FG by coupling agent was beneficial to the dispersion in FG/PP composites. The effect was better when the amount of NDZ-201 was 0.7wt%. With the increase of FG particle size, the thermal conductivity of FG/PP composites increased obviously. Compared with 17 μ m FG, the average, vertical and parallel thermal conductivity of FG/PP composites prepared with 148 μ m FG increased by 65.9%, 87.7% and 47.0% respectively. The thermal conductivity of FG/PP composites were improved with the increase of FG content. When FG content was 70wt%, the thermal conductivity increased significantly, the average, vertical and parallel thermal conductivity reached 4.16 W·m⁻¹·K⁻¹, 0.938 W·m⁻¹·K⁻¹ and 18.4 W·m⁻¹·K⁻¹.

Key word: Flake graphite, Polypropylene, Composites, Thermal conductivity

1. Introduction

Polypropylene (PP) is a general plastic with regular structure and high crystallinity. Its working temperature is between -10°C~125 °C, with good chemical stability and excellent mechanical properties. Since there are no free electrons in PP, only atoms, groups and chains can vibrate at room temperature, so the thermal diffusion ability of PP is poor. Its thermal conductivity is only about 0.2W·m⁻¹·K⁻¹, and its thermal conductivity is far lower than that of metal, so its application is limited in heat exchanger, radiator, condensate cooler and other heat transfer equipment [1-5]. Relatively speaking, graphite has good thermal conductivity, high heat resistance and low price, so it has been widely applied in thermal conductive composites. Moreover, China is rich in graphite resources, and it is 90 % of world production. There are many kinds of graphite, which provides us with unique conditions for the study of FG/PP composites [6-8].

The thermal conductivity of Graphite Filled PP composites is attributed to the mechanism of thermal conduction path. Graphite contacts each other to form a three-dimensional thermal conduction path, and then forms a bi-continuous composites with PP. Therefore, graphite is the key factor in the construction of heat conduction path. When the filling amount is low, the composites are coated by polypropylene to form a "sea-island" structure, and the thermal conductivity of the composite has little change. With the increase of the filling amount, the probability of graphite contact in the

composite increases. When the filling amount increases to a certain critical value, the heat conduction path is gradually improved, and a three-dimensional heat conduction path of the interpenetrating "sea-sea" structure is formed. Thus, the filling form and amount of graphite become the key to the research of thermal conductive composites [9-11].

In this study, the coupling agent was used to modify the surface of FG to improve its dispersion in PP and further increase the filling amount in FG/PP composites. By designing the molding structure and adjusting the orientation degree of graphite, more complete three-dimensional network heat conduction paths were constructed, so as to meet the use requirements of heat transfer equipment, reduce the amount of metal, control the production cost, save energy, and expand its application in chemical industry, metallurgy, new energy and seawater desalination [12-17].

2. Experimental methods

2.1 Materials

Flake graphite (FG, 99%) with the particle size of 17 μ m, 27 μ m, 37 μ m, 74 μ m and 148 μ m were purchased from Hebei Haoteng Trading Co., Ltd; Polypropylene (PP, 230#) was obtained from Sinopec Maoming Petrochemical Company; Silane coupling agents (KH-560, KH-570) and Titanate coupling agent (NDZ-101, NDZ-201) bought from Dinghai Plastic Chemical Co.,

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Ltd; Absolute ethanol (analytical pure) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd; Antioxidant 1010 and Zinc stearate were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2 Equipments

Double-roll open mill (ZG-180) was produced by Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd; Electric drying oven (101-3AB) was produced by Tianjin Taisite Instrument Co., Ltd; Flat vulcanizer (ZG-200T) was produced by Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd; Universal prototype (wzy-240) was produced by Chengde Hengtong Test Instrument Co., Ltd; Thermal constant analysing (TPS-2500S) was produced by Sweden Hot disk Co., Ltd.

2.3 Preparation of FG/PP composites

The coupling agent was dissolved in anhydrous ethanol, and then mixed well with FG. The mixture was dried in an oven at 140°C. A certain amount of PP, zinc stearate, antioxidant and treated FG were pre-mixed in a high-speed mill, then mixed in a double-roll open mill, and finally molded by the flat vulcanizer to prepare FG/PP composites.

2.4 Testing methods

The thermal conductivity was tested according to GB / T 32064-2015. The radius of probe was 3.189mm, the test temperature was 25°C, and the sample size was 40×40×3mm.

3. Results and discussion

3.1 Types of coupling agents

The inorganic filler treated by coupling agent has better compatibility with polymer, which can effectively improve the properties of composites. FG was treated with two silane coupling agents and two titanate coupling agents. When FG content of 17μm was 50wt% and the coupling agent dosage (measured by FG content) was 1wt%, the FG/PP composites were prepared and their thermal conductivities were tested (Fig.1). It can be seen from Fig. 1 that the thermal conductivities of FG / PP composites prepared by FG treated with four different types of coupling agents had no obvious change. The coupling agent basically had no effect on the orientation of FG, so the thermal conductivity changed little.

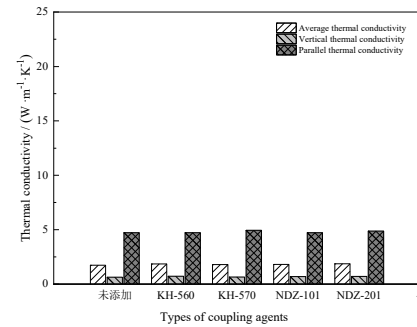


Fig.1 Effect of coupling agent on thermal conductivities of FG/PP composites

3.2 Content of coupling agents

When the FG content of 37μm was 70wt%, the FG/PP composites were prepared by changing the amount of NDZ-201 and their thermal conductivities were tested (Fig.2).

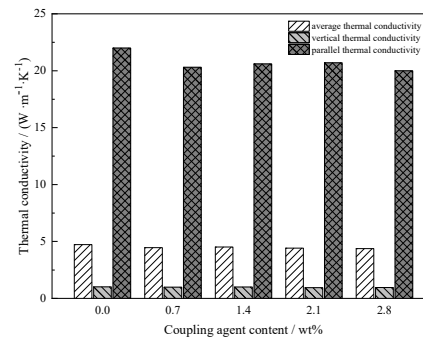


Fig.2 Effect of coupling agent dosage on thermal conductivities of FG/PP composites

As shown in Fig.2, the thermal conductivities of FG/PP composites prepared by FG treated with NDZ-201 were slightly lower than that of composites without coupling agent. The average, vertical and parallel thermal conductivities of the composites without NDZ-201 were 4.73W·m⁻¹·K⁻¹, 1.01W·m⁻¹·K⁻¹ and 22.0W·m⁻¹·K⁻¹, respectively. When the addition of NDZ-201 was 2.8wt%, the average, vertical and parallel thermal conductivities of the composites were 4.37 W·m⁻¹·K⁻¹, 0.951 W·m⁻¹·K⁻¹ and 20.0 W·m⁻¹·K⁻¹. Thermal conductivities of composites decreased slightly with the increase of coupling agent content. The possible reason is that the thermal conductivity of the coupling agent itself is very low. When the coupling agent is coated on the surface of FG, the internal resistance of the composite increases, which hinders the heat transfer in the composite and reduces the heat conduction flux of the composite.

3.3 Content of FG

In order to investigate the effect of FG content on the properties of the composites, FG/PP composites with different FG content were prepared by 17μm FG and 1wt⁰ NDZ-201 coupling agent. Fig. 3 shows the results.

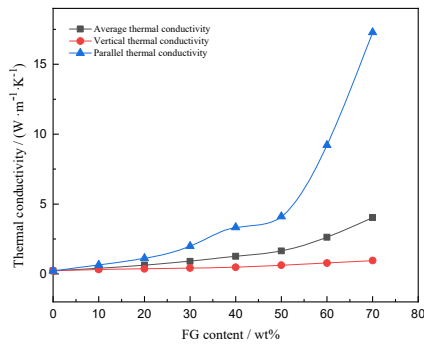


Fig.3 Effect of FG content on thermal conductivities of FG/PP composites

The thermal conductivities of the composites increased with the increase of FG content. When the FG content is 10wt%, the average, vertical and parallel thermal conductivity of the FG/PP composites were $0.475 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $0.318 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $0.710 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively. When the FG content increased to 70wt%, the average, vertical and parallel thermal conductivity were $4.16 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $0.938 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $18.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which improved by 7.76, 1.95 and 24.9 times, respectively. By contrast, it was found that the parallel thermal conductivities were improved most obviously, which was closely related to the molding method. Before pressing, the molten materials in the mold cavity are unevenly distributed. When pressure is applied in the vertical direction, the graphite sheets in the vertical state are easy to tilt and fall down. At the same time, the molten materials flow to the parts with less materials and lower pressure, which promote the orientation of FG. Therefore, FG is difficult to orientate in the vertical direction and cannot form a good heat conduction path. On the other hand, FG has a high degree of orientation parallel to the surface of the material, and the layers come into contact with each other to form more complete stacking structures, which provides more heat conduction paths for the transfer of heat flux, so the improvement of parallel thermal conductivity of the composites is much greater than that of vertical thermal conductivity. In addition, When FG content was less than 50wt%, the continuous phase in the composite was PP, the thermal resistance was very large, and the thermal conductivity increased slowly. When FG content exceeded 50wt%, FG transformed into continuous phase, and the chance of overlapping between FG was greatly increased, which made it easy to construct more complete thermal conduction paths, thus sharply increasing thermal conductivity.

3.4 Particle size of FG

To explore the effects of FG with different particle sizes on the thermal conductivity of composites, FG with particle sizes of 17, 27, 37, 74 or 148 μm was selected to prepare FG/PP composites under the condition of FG content of 50wt%, NDZ-201 dosage of 1wt% and the thermal conductivities were tested (Fig.4).

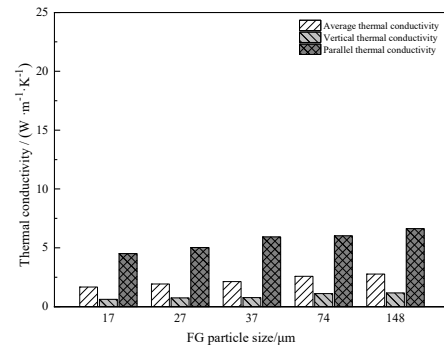


Fig.4 Effect of FG particle size on thermal conductivities of FG/PP composites

It can be observed from Fig.4, the thermal conductivities of the FG/PP composites increased with the increase of FG particle size. The average, vertical and parallel thermal conductivities of the composites with FG particle size of 17 μm were $1.67 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $0.618 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $4.51 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively. When FG particle size was 148 μm , the average, vertical and parallel thermal conductivities of the composites were $2.77 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $1.16 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $6.63 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, increasing by 65.9%, 87.7% and 47.0%, respectively. The reason is that when the FG particle sizes are small, the particles are coated by PP melt film. During molding, they are not easy to be flattened and crushed; Meanwhile, because the FG particles are small, the specific surface area is large, and there are many PP diaphragms between FG particles, which hinder the formation of heat conduction path, the thermal conductivities are low. On the contrary, when the FG particles are large, the PP melt film between the particles is thick and uneven. FG particles are easy to be separated and contact with each other under compressive shear stress, which provides the possibility to form more complete thermal conductivity network. At the same time, the number of gaps between FG particles is less, which is more conducive to the overlapping contact of uncoated FG particles to form the complete heat conduction path, so as to improve the thermal conductivities of FG/PP composites.

4. Conclusion

In this paper, PP was filled with FG modified by coupling agent, and FG/PP composites with high thermal conductivity were prepared by molding method. The effects of the type and amount of coupling agent, FG content and particle size on the thermal conductivity of the composites were investigated. The results were as follows:

- (1). The use of coupling agent NDZ-201 to modify FG was beneficial to the dispersion in the materials, but the thermal conductivities of FG/PP composites decreased slightly.
- (2). With the increase of FG content, the thermal conductivities of FG/PP composites increased. When the FG content was more than 50wt%, the thermal

conductivities of the composites had an obvious critical value, in which the parallel thermal conductivities improved most significantly.

(3). The thermal conductivities of FG / PP composites increased dramatically with the increment of FG particle sizes. Compared with 17 μ m FG, the average, vertical and horizontal thermal conductivity of the FG/PP composites prepared by 148 μ m FG increased by 65.9%, 87.7% and 47.0%, respectively.

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