Research on Properties of Polypropylene/Flake Graphite Molded Composite Materials

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Abstract: PP/FG composite materials were prepared by compressing moulding under high temperature through high-speed mixer, mixing mill and vulcanization machine taking PP as the matrix resin, FG as the thermal conductive filler, and NDZ-201 as the coupling agent. Effects of PP proportion, FG content and particle size on the thermal conductivity and mechanical properties of composite materials were studied. Results showed that PP proportion has little effect on the thermal conductivity of PP/FG composite materials, but it greatly affects the mechanical properties of the composite materials. Overall, the quality ratio of PP230 to K-4038 at 50:50 is more suitable. With the increasing of FG content, the thermal conductivity increases, and a significant critical value appears when the FG content is 50 wt%; The strength of the composite material first decreases and then increases, with an increase in modulus and a decrease in strain. As the FG particle size increases, the thermal conductivity of the composite material increases and the mechanical properties decrease.

Keyword: Polypropylene; Flake graphite; Compression molding; Composite materials; Thermal conductivity

1. Introduction

Polymer based thermal conductive composite materials can replace metal materials for manufacturing equipment such as condensers and heat exchangers due to their excellent mechanical properties, corrosion resistance, scale inhibition, easy processing, light weight, and low maintenance costs. They are widely used in fields such as chemical, pharmaceutical, construction, electronics, and seawater desalination[1-4]. At present, polymer based thermal conductive composites are usually prepared by adding fillers with high thermal conductivity to the matrix resin, such as nitrides, CFs, flake graphite, graphene, carbon nanotubes, etc[5-9]. Pan Shihao et al.[10] prepared AlN/PA6 thermal conductive composites by melt blending method and found that the thermal conductivity of the composite gradually increased with the increasing of AlN filling content. F Khodayaril et al.[11] prepared acrylic based nanocomposites with different metal oxide nanoparticles and multi walled carbon nanotubes (MWCNTs) content using a solvent mixing method. They found that the thermal conductivity of the composite material significantly increased with the addition of thermal conductive fillers. However, some high thermal conductivity fillers such as graphene and carbon nanotubes are expensive and prone to agglomeration, which limits the application of polymer based thermal conductivity composites. Therefore, the development of polymer based thermal conductivity composites with low cost and excellent performance has become a research hotspot.

With the rapid development of research and development technology for polymer based thermal conductive composites, high-performance polypropylene (PP)/flake graphite (FG) thermal conductive composites are receiving more attention. Wu et al.[12] prepared PP/graphite thermal conductive composite material with the graphite size of 20 μm and 2 μm. It was found that when the graphite filling amount was 40 wt%, the interlayer and interlayer thermal conductivity of the composite material were 1.125 W·m-1·K-1 and 2.897 W·m-1·K-1, respectively, also had certain mechanical properties. Xu et al.[13] prepared PA6/PP/FG composite materials through extrusion and injection methods, and found that the thermal conductivity reached 1.88 W·m-1·K-1 when FG content was 20 wt%. PP is a cost-effective matrix resin with low price, corrosion resistance, excellent mechanical properties, and good processing performance; Meanwhile, FG has a wide range of sources and high thermal conductivity, making it an ideal thermal conductive filler. However, FG and PP have poor compatibility and are difficult to mix evenly, making it difficult to increase the filling amount, resulting in low thermal conductivity of the composite materials.

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To attack these problems, high thermal conductivity PP/FG composite materials were prepared by compression molding method in this study. The compatibility between FG and PP was improved by adding coupling agents. The dispersion and filling amount of FG in PP were improved by utilizing the shear force of the open mill. In this research, the influence of PP ratios, FG content and particle size on the thermal conductivity and mechanical properties of composite materials were studied. This study provides a basis for the further preparation of composite materials with better comprehensive performance.

2. Experimental

2.1 Materials

The raw materials are as follows: PP230(powder form) and PPK4038 (granular form) were purchased from Maoming Shihua Dongcheng Chemical Co., Ltd and Taiwan Chemical Fiber Co., Ltd, respectively; FG with a carbon content of 99% (particle sizes of 17 μm、27 μm、37 μm、74 μm or 148 μm) was supplied by Hebei Aoteng Trading Co., Ltd; Titanate coupling agent of NDZ-201 and Anhydrous ethanol were obtained from Dinghai Plastic Chemical Co., Ltd and Tianjin Yongda Chemical Reagent Co., Ltd, respectively; Antioxidant 1010 and Antioxidant PLM-168 were purchased from Aladdin Reagent Company; Zinc stearate was got from Aladdin Reagent Company.

2.2 Instruments

Double-roll open mill (ZG-180, Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd); Electrothermal drum drying box (101-3AB, Tianjin Taisite Instrument Co., Ltd); Plate vulcanizing press machin (ZG-200T, Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd); Universal prototype (WZY-240, Chengde Hengtong Test Instrument Co., Ltd); Thermal constant analysing(TPS-2500S was produced by Sweden Hot disk Co., Ltd); Electronic universal testing machine (104C,Shenzhen Wance Testing Machine Co., Ltd.).

2.3 Characterization

Thermal conductivity was test according to GB/T 32064-2015, the probe radius is 3.189mm, the test temperature is 25℃, and the specimen size is 40×40×3±0.2mm。The tensile properties of the FG/PP composites were tested according to GB/T 1040.1-2006. Sample thickness: 3±0.2mm, 1B； The bending properties of the composites were tested according to GB/T 9341-2008. Sample thickness: 3±0.2mm, with testing speed of 2mm/min.

2.4 Preparation of PP/FG composite materials

NDZ-201 was dissolved with anhydrous ethanol and mixed evenly with FG. System was dried in a 120℃ oven. A certain amount of PP, antioxidant, and zinc stearate were mixed in a high-speed mixer for 3 times, each time for 1 minute. During the mixer mixing process, the roller gap multiple times was adjusted to ensure uniform mixing of the materials. The temperature of the mixer is 180℃ for the front roller and 175℃ for the rear roller. Place the mixed material slices in a heated mold for preheating, melting, and molding to obtain composite materials. The molding conditions are: the upper template of 193℃, the lower template of 190℃, exhaustion of 3 times. Then the formed composite material was obtained after cooling to room temperature under a pressure of 12 MPa.

3. Results and discussions

3.1 Effect of PP proportion on the properties of PP/FG composite materials

Two different PPs were mixed to prepare composite materials under the condition of FG content of 70 wt%, a graphite particle size of 37 μm and coupling agent FG content dosage of 0.7 wt%. And thermal conductivity and mechanical properties were tested. The results are shown in Figure 1 and Table 1.

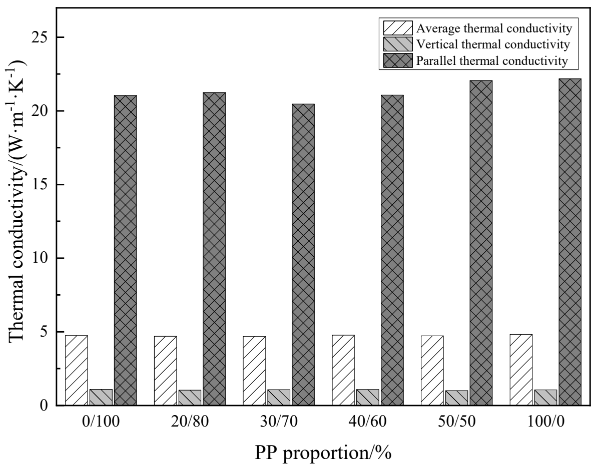

Figure 1 Effect of PP proportion on the thermal conductivity of PP/FG composite materials

As shown in Figure 1, there was no significant change in the thermal conductivity of composite materials prepared with different PP proportion. When the matrix is all PP-230, the average, vertical, and parallel thermal conductivity of the composite material are 4.74 $W \cdot m^{-1} \cdot K^{-1}$, 1.09 $W \cdot m^{-1} \cdot K^{-1}$ and 21.1 $W \cdot m^{-1} \cdot K^{-1}$, respectively. As the PP K-4038 amount increases, the thermal conductivity of the material does not change significantly, indicating that PP proportion have no obvious effect on the construction of thermal conductivity pathways in the composite material.

Table 1 Effect of PP proportion on the mechanical properties of PP/FG composite materials

PP proportion 230/K-4038	Tensile strength /MPa	Elastic tensile modulus /GPa	Breaking tensile strain /%	Bending strength /MPa	Elastic bending modulus /GPa	Fracture bending strain /%
0/100	23.4	6.34	0.48	39.9	8.36	0.68
20/80	24.3	7.86	0.39	41.2	9.59	0.53
30/70	26.3	8.38	0.38	42.1	10.4	0.51
40/60	27.1	8.88	0.36	45.0	10.6	0.49
50/50	29.6	9.10	0.34	50.8	11.7	0.48
100/0	34.8	10.3	0.30	63.0	17.8	0.32

As shown in Table 1, the mechanical properties of composite materials with different PP ratios are significantly different. When the matrix is all PP-230, the tensile and bending strengths of the composite materials are 23.4 MPa and 39.9 MPa, the tensile and bending elastic modulus are 6.34 GPa and 8.36 GPa, and the tensile and bending strains at break are 0.48% and 0.68%, respectively; With the increasing of PP K-4038 dosage, the strength and modulus of the composite material increase, while the breaking tensile strain and fracture bending strain decrease. Considering the comprehensive mechanical properties, the ratio of the two types of PP is optimal at 50: 50.

3.2 2.2 Effect of FG content on the properties of PP/FG composite materials

Composite materials with different FG contents were prepared taking FG with particle size of 17 μm and coupling agent NDZ-201 was 1 wt% of FG content. And thermal conductivity and mechanical properties were tested. The results are shown in Figure 2 and Table 2.

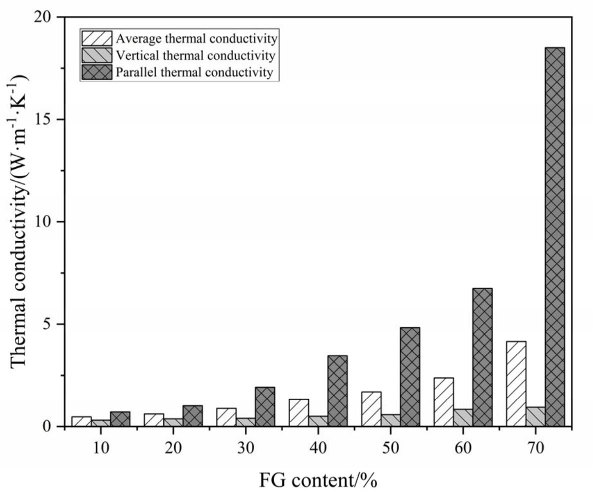

Figure 2 Effect of FG content on the properties of PP/FG composite materials

As shown in Figure 2, with the increase of FG content, the thermal conductivity of the composite material also increases. When the FG content is 10 wt%, the average, vertical, and parallel thermal conductivity of the composite material are 0.475 $W\cdot m^{-1}\cdot K^{-1}$、0.318 $W\cdot m^{-1}\cdot K^{-1}$ and 0.710 $W\cdot m^{-1}\cdot K^{-1}$, respectively. When the FG content increased to 70 wt%, the average, vertical, and parallel thermal conductivity were 4.16 $W\cdot m^{-1}\cdot K^{-1}$、0.938 $W\cdot m^{-1}\cdot K^{-1}$ and 18.4 $W\cdot m^{-1}\cdot K^{-1}$, respectively, corresponding to increasing of 7.76 times, 1.95 times, and 24.9 times, respectively. Through comparison, the parallel thermal conductivity of composite materials has significantly improved, which is closely related to molding. The graphite layer in the vertical state is prone to tilt and collapse when pressure is applied in the vertical direction; Meanwhile, the molten material flows towards fewer parts and promote the orientation of FG along its flow direction under the action of pressure. Therefore, with the increase of FG content, the parallel thermal conductivity of the composite material increases much more than the vertical thermal conductivity. In addition, when the FG content is below 50 wt%, the thermal conductivity of the composite material increases slowly with the increase of FG content, because of the continuous phase in the composite material is mainly PP, making it difficult to form a relatively complete thermal conductivity path; When the FG content exceeds 50 wt%, FG is the mainly continuous phase in the composite material, and the opportunity for FG to overlap with each other greatly increases. It is easy to construct more complete thermal conductivity paths in the composite material, resulting in a sharp increase in thermal conductivity.

Table 2 Effect of FG content on the mechanical properties of PP/FG composite materials

FG particle size/μm	Tensile strength /MPa	Elastic tensile modulus /GPa	Breaking tensile strain /%	Bending strength /MPa	Elastic bending modulus /GPa	Fracture bending strain /%
10	31.2	3.12	1.92	52.8	3.47	2.15
20	26.7	3.24	1.42	47.0	3.95	1.69
30	30.7	4.27	1.19	49.9	5.45	1.33
40	33.7	5.91	1.01	53.0	7.57	0.96
50	34.4	6.02	0.66	51.5	9.10	0.73
60	37.1	10.5	0.47	61.2	11.8	0.64
70	36.1	10.7	0.32	59.0	13.7	0.49

As shown in Table 2, with the increasing of FG content, the tensile strength and bending strength of the composite material first decrease and then increase. When the FG content is 20 wt%, the tensile strength and bending strength of the composite material decrease to the minimum of 26.7 MPa and 47.0 MPa, respectively. As the FG content further increases, the tensile strength and bending strength increase. When the FG content is 60 wt%, the tensile strength and bending strength reach 37.1 MPa and 61.2 MPa, respectively. The tensile and bending elastic modulus of composite materials increase with the increase of FG content. The tensile and bending elastic modulus are 3.12 GPa and 3.47 GPa with 10 wt% FG, respectively; When the FG content increases to 70 wt%, the tensile modulus and elastic bending modulus of elasticity increase to 10.7 GPa and 13.7 GPa, respectively. The breaking tensile strain and fracture bending strain of composite materials decrease with the increase of FG content. The breaking tensile strain and fracture bending strain are 1.92% and 2.15% when FG content was 10 wt%. And the breaking tensile strain and fracture bending strain decreased to 0.32% and 0.49%, with the FG content increased to 70 wt%. The reason was that the dispersion concentration of FG in the composite material is too low under lower FG content. Meanwhile, PP matrix bears most of the stress, and the plastic deformation energy that the composite material can absorb is very small; However, with the increase of FG content, according to the reinforcement effect of rigid particles [20], FG, as a rigid inorganic particle, has a reinforcement effect on the material, resulting in higher mechanical properties of the composite material.

3.3 Effect of FG particle size on the properties of PP/FG composite materials

Under the condition of a fixed FG content of 50 wt% and a coupling agent NDZ-201 dosage of 1 wt% of FG content, FG particle size of 17μm、27 μm、37 μm、74 μm、148 μm were selected to prepared composite materials, and the thermal conductivity and mechanical properties were tested. The results are shown in Figure 3 and Table 3.

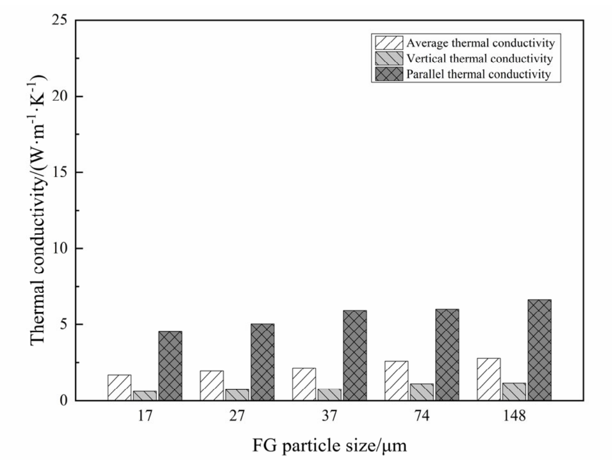

Figure 3 Effect of different particle sizes of FG on the thermal conductivity of PP/FG composite materials

It can be seen From Figure 3 the thermal conductivity of the composite material increases accordingly with the FG particle size increases. With FG particle size of 17 μm, the average, vertical, and parallel thermal conductivity of composite materials are1.67 $W·m^{-1}·K^{-1}$、0.618 $W·m^{-1}·K^{-1}$and 4.51 $W·m^{-1}·K^{-1}$, respectively. while the average, vertical, and parallel thermal conductivity of composite materials with FG particle size of 148 μm reached 2.77 $W·m^{-1}·K^{-1}$、1.16 $W·m^{-1}·K^{-1}$and 6.63 $W·m^{-1}·K^{-1}$, which were 65.9%, 87.7%, and 47.0% higher than the former. The larger FG particle size, the smaller specific surface area, and the PP melt film between the FG particles is thick and uneven, FG particles are easily separated by squeezing and shearing resulting in contact with each other under compressive and shear stress, forming a more complete thermal conductivity network. When FG particle size is larger, the number of gaps between FG particles in the same space is relatively small, which is more conducive to the overlapping of uncoated FG particles to form a relatively complete thermal conductivity path, thereby improving thermal conductivity.

Table 3 Effect of FG particle size on the mechanical properties of PP/FG composite materials

FG particle size/μm	Tensile strength /MPa	Elastic tensile modulus /GPa	Breaking tensile strain /%	Bending strength /MPa	Elastic bending modulus /GPa	Fracture bending strain /%
17	34.4	7.85	0.70	53.0	9.87	0.69
27	32.5	6.74	0.91	50.4	7.79	0.93
37	30.5	6.53	0.77	49.0	8.01	0.86
74	27.9	6.48	0.80	44.3	7.35	0.87
148	25.1	6.83	0.54	43.0	7.12	0.86

Table 3 showed that the strength and modulus of the composite material gradually decrease with the increase of FG particle size. When the particle size of FG is 17 μm, the tensile strength of the composite material is 34.4 MPa, the tensile modulus of elasticity is 7.85 GPa, the bending strength is 53 MPa, and the bending modulus of elasticity is 9.87 GPa; The particle size of FG is 148 μm, its tensile strength decreased to 25.1 MPa, tensile modulus of elasticity decreased to 6.83 GPa, flexural strength decreased to 43.0 MPa, and flexural modulus of elasticity decreased to 7.12 GPa. It is relatively difficult for FG and PP with large particle sizes to mix evenly, and defects such as voids and cracks are prone to occur. This material is prone to cracking when subjected to stress, leading to material fracture, thereby reducing the mechanical properties. In addition, due to the different expansion coefficients of PP and FG, the interface between the two is easy to separate during the cooling process of the material. The larger the FG particle size, the more obvious the separation, and the greater the internal stress generated, thereby reducing the mechanical properties of the material.

4. Conclusion

PP/FG composite materials were prepared through molding process. And the compatibility between FG and PP was improved through the coupling agent NDZ-201, also increase the dispersion and filling amount of FG in PP with the shear force of the open mill. Effects of PP ratios, FG content and particle size on the thermal conductivity and mechanical properties of composite materials are as follows:

(1) Different PP proportion have little effect on the thermal conductivity of PP/FG composite materials, but have a significant impact on the mechanical properties of the composite materials. Overall, the ratio of 50:50 between PP230 and K-4038 is more suitable.

(2) The thermal conductivity of the composite material increases with the increasing of FG content, and a significant critical value appears with FG content of 50

wt%; The tensile strength and bending strength of the material first decrease and then increase, and the tensile modulus and bending modulus also increase with the increase of FG content. The breaking tensile strain and fracture bending strain at break decrease. When the FG content with particle size of 17 μm is 70 wt%, the average, vertical, and parallel thermal conductivity of the material are 4.16 $W \cdot m^{-1} \cdot K^{-1}$、 0.938 $W \cdot m^{-1} \cdot K^{-1}$and 18.4 $W \cdot m^{-1} \cdot K^{-1}$, respectively. The tensile strength and bending strength are 36.1 MPa and 59.0 MPa, and the tensile and bending modulus of elasticity are 10.7 GPa and 13.7 GPa; The breaking tensile strain and fracture bending strain are 0.32% and 0.49%, respectively.

(3) As the FG particle size increases, the thermal conductivity of the composite material significantly increases, and the mechanical properties correspondingly decrease. Set FG content is 50 wt% in composite materials, And comparing composite material prepared by FG with a particle size of 148 μm with the materials containing FG particle size of 17 μm, the average, vertical, and parallel thermal conductivity increased by 65.9%, 87.7%, and 47.0%. The tensile strength and bending strength decreased from 34.4 MPa and 53.0 MPa to 25.1 MPa and 43.0 MPa, respectively.

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References

1. Hauser R A, King J A, Pagel R M, et al. Effects of carbon fillers on the thermal conductivity of highly filled liquid-crystal polymer based resins[J]. Journal of Applied Polymer Science, 2008, 109(4): 2145-2155.
2. Panwar V, Park J O, Park S H, et al. Electrical, dielectric, and electromagnetic shielding properties of polypropylene-graphite composites[J]. Journal of Applied Polymer Science, 2010, 115(3): 1306-1314.
3. Liu Z H. A study on the graphite/polymer composite bipolar plates in PEMFC[D]. Tianjin University, 2005.
4. Zhang L W. Manufacturing, property and application of thermal conductive polymer composites[D]. East China University of Science and Technology, 2010.
5. Donnay M, Tzavalas S, Logakis E. Boron nitride filled epoxy with improved thermal conductivity and dielectric breakdown strength[J]. Composites Science and Technology, 2015, 110: 152-158.
6. Li J, Ou B Q, Jiao L C, et al. Effects of compound filler contents on properties of polyamide 6 thermally conductive composites[J]. Engineering Plastics Application, 2015, 43(9): 134-137.
7. Zhao J, Ting O Y, Yang Y, et al. Thermal conductivity enhancement of phase change materials with form-stable carbon bonded carbon fiber network[J]. Materials & Design, 2018, 143: 177-184.
8. Hong Y Z, Zhu J, Feng Z M, et al. Preparation and research of thermally conductive PBT/CF composites[J]. Engineering Plastics Application, 2015, 43(4): 92-97.
9. Ma L, Chen K X, Mo D C, et al. Preparation, properties and mechanism of thermal conductive graphene/polymer composites[J]. CIESC Journal, 2017, 68(S1): 18-25.
10. Pan S H, Dai P G, Chen Y J, et al. Research on thermal conduction performance of AIN/PA6 composite material[J]. 2015, 43(11): 83-84, 108.
11. Khodayari F, Jamshidi M. Influence of Mwcts and nanometal oxide/Mwcts hybrids on the thermal conduction of their acrylic-based nanocomposites[J]. Iranian Polymer Journal, 2016, 25(3): 1-8.
12. Wu J W, Ji X Y, Yang J D, et al. Preparation and properties of polypropylene/graphite composites with high thermal conductivity[J]. Engineering Plastics Application, 2016, 44(8): 36-40.
13. Xu H G, Peng X T, Zhou J J, et al. Research of thermally conductive composites based on flake graphite filled in polyamide6/polypropylene[J]. Engineering Plastics Application, 2015, 43(9): 1-6.
14. Zhao M. New modified polypropylene materials[M]. Chemical Industry Press, 2021.
15. S N, Cao G Z, Wang X, et.al, Research of the Polypropylene Modification Methods[J]. 2011.39(4):57-59.
16. Hu M, Yu D, Wei J. Thermal conductivity determination of small polymer samples by differential scanning calorimetry[J]. Polymer Testing, 2007, 26(3): 333-337.
17. Yuan J Y. Preparation and properties of thermally conductive and electrically insulating polypropylene composites[D]. South China University of Science and Engineering, 2014.
18. Yan S. Preparation and properties of polypropylene-based thermal conductive composites[D]. Beijing University of Chemical Technology, 2012.
19. Mhike W, Focke W W, Mofokeng J P, et al. Thermally conductive phase-change materials for energy storage based on low density polyethylene, soft Fischer–Tropsch wax and graphite[J]. Thermochimica Acta, 2012, 527: 75–82.
20. Meng J R, Liang G Z, Qin H Y, et al. Toughening and reinforcing effect of rigid fillers for polymers[J]. Plastics, 2002, 31(2): 47-50.