Study on Polypropylene Composites with High Thermal Conductivity and Its Preparation

Haijun Zhou [1], Mengmeng Zhou [2], Xiaolei Zhang [3,*], Yating Zhao [4], Lu Bai [1], Xiaoqi Chen [1], Fen Zhang [1], Yantao Li [1]

[1] Institute of Energy Resource, Hebei Academy of Sciences, Shijiazhuang, 050081, China
[2] Shi Jiazhuang Polymer Composite Technological Innovation Center, College of Chemical Engineering, Shijiazhuang University, Shijiazhuang, 050035, China
[3] Hebei University of Science and Technology, Shijiazhuang, 050018, China
[4] Hengshui ZhongYuTieXin Waterproof Technology Co., Ltd, Hengshui, 053000, China

Abstract. Polypropylene (PP) composite materials were prepared through two molding methods of injection and compression molding, taking PP, FG as the matrix and thermal conductive filler. The effects of molding methods and FG content on the thermal conductivity of composite materials were studied, and the SEM, XRD, and thermal expansion properties of the materials were further analyzed. Results showed that thermal conductivity of the composite material increases with increasing of the FG content. When the FG content was 75 wt%, the average thermal conductivity of the composite materials prepared by injection molding and compression molding is 9.88 W·m-1·K-1 and 6.03 W·m-1·K-1, respectively. The axial thermal conductivity is 16.6 W·m-1·K-1 and 1.35 W·m-1·K-1, and the radial thermal conductivity is 5.88 W·m-1·K-1 and 26.9 W·m-1·K-1, respectively. In composite materials formed by injection molding, the flaky FG is mainly oriented vertically, while in compression molding, the flaky FG is mainly oriented horizontally.

Keywords: Thermal conductivity; Polypropylene; Composite material; Injection; Molding

1. Introduction

Thermal conductive materials are widely used in many fields such as chemical engineering, pharmaceuticals, metallurgy, etc. Metal materials have long been used as thermal conductive materials. However, due to their poor corrosion resistance, easy scaling, and high maintenance costs, their application range is limited. Metal materials have long been used for thermal conductivity because of good thermal conductivity and fast thermal conductivity. However, due to their poor corrosion resistance, easy scaling, and high maintenance costs, their application scope is limited. Therefore, polypropylene composite materials with high thermal conductivity, which have many advantages such as corrosion resistance, scale inhibition, easy processing, and low cost, have become a research hotspot in this field. They are considered an ideal material to replace stainless steel, enamel, graphite, glass in the fields of chemical, pharmaceutical, dyeing, metallurgy, new energy, and seawater desalination treatment to manufacture heat exchangers and condensers[1-6]. At present, the thermal conductivity of this type of thermal conductive composite material in China is not high, especially in the process of processing and forming, where graphite is prone to form a single horizontal orientation, resulting in a higher radial thermal conductivity, while the axial (vertical) thermal conductivity is generally not high, and even increasing the thermal anisotropy, thereby limiting the application in heat exchange technology. Therefore, how to improve the axial orientation of flake graphite in polypropylene composite materials and the axial thermal conductivity, axial heat exchange efficiency of composite materials has become the key to improving the application value of PP composite materials[7-10].

To prepare high thermal conductivity polypropylene composite materials, two processes, injection molding and compression molding were used in this study. The effects of molding method and graphite content on the thermal conductivity are studied. SEM analysis, XRD analysis, and thermal expansion analysis were used to study the orientation of graphite in composite materials and the impact on thermal conductivity pathways.

2. Experimental

2.1 Materials

The powder PP230# and granular PPK4038 were obtained from Maoming Shihua Dongcheng Chemical Co., Ltd and Taiwan Chemical Fiber Co., Ltd, respectively; FG with a carbon content of 99% with particle sizes of 37 μm was purchased by Hebei Aoteng Trading Co., Ltd; Titanate coupling agent of NDZ-201

* Corresponding author: zhangxl_2021@hebust.edu.cn

and Anhydrous ethanol were supplied by Dinghai Plastic Chemical Co., Ltd and Tianjin Yongda Chemical Reagent Co., Ltd, respectively; Antioxidant 1010, Zinc stearate and Antioxidant PLM-168 were purchased from Aladdin Reagent Company.

2.2 Instrument

The main instruments were as follows: 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.); X-ray diffraction (XRD, Uitima IV type, Rigaku Corporation, Japan); Scanning electron microscope (SEM, Inspect-S50, American FEI Company); Thermomechanical Analyzer (TMA-450, TA Instruments Waters, USA).

2.3 Characterization

Thermal conductivity was test according to GB/T 32064-2015, the probe radius is 3.189 mm, the test temperature is 25℃, and the specimen size is 40×40×3±0.2 mm.

SEM observed the morphology of different samples after quenching in liquid nitrogen and spraying gold treatment on the cross-section.

XRD was tested in conditions: 40 kV, 40 mA, scanning speed of 5°/min, and scanning range of 10°~70°.

The thermal expansion performance is tested using TMA-450 according to GB/T 2572-2005 for the average linear expansion coefficient of composite materials, under nitrogen atmosphere and a heating rate of 3℃/min.

2.4 Preparation of PP/FG composite materials

NDZ-201 was dissolved in anhydrous ethanol, mixed evenly with FG, and dried in a 140℃ oven. Then a certain amount of PP, antioxidant and zinc stearate were added into the high-speed mixer to mix for 3 times (1 min each time), and then mixed in the open mill to obtain master batch for standby.

(1) Preparation of molded composite materials: The weighed masterbatch was added to the preheated molding mold, and the molding conditions are as follows: the temperature of upper and lower template is of 193℃ and 190℃,respectively. And the pressure is 12 MPa. Keep the pressure and cool to room temperature to obtain the formed composite material.

(2) Preparation of injection composite materials: The weighed masterbatch was added to the core in the middle of the preheated pressure injection mold, and apply pressure to the masterbatch through the pressure injection core to fill the cavity uniformly through the narrow mold opening and trapezoidal flow channel. Maintain pressure and cool to room temperature to obtain the formed composite material.

3. Results and discussions

3.1 Effect of molding method and FG content on the thermal conductivity of composite materials

This study investigates the differences in thermal conductivity of composite materials prepared by different molding methods and FG content. A particle size of 37 μm FG was selected and NDZ-201 were used as coupling agents (with a dosage of 0.7 wt% of FG content). Composite materials with different FG content were prepared using injection molding and compression molding processes, respectively. The thermal conductivity results are shown in Figure 1, Figure 2 and Figure 3.

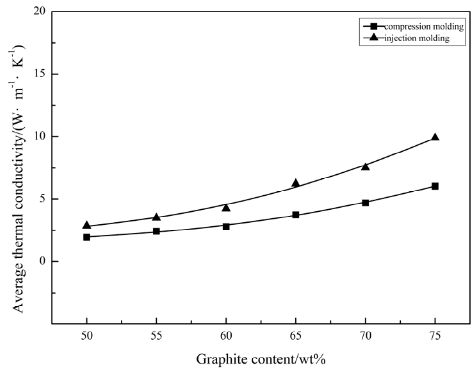


Figure 1 Effect of molding method and FG content on the average thermal conductivity of composite materials

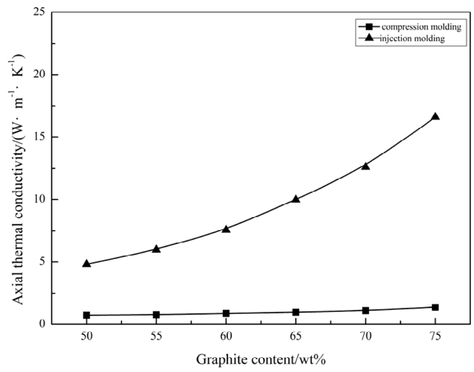


Figure 2 Effect of molding method and FG content on the axial thermal conductivity of composite materials

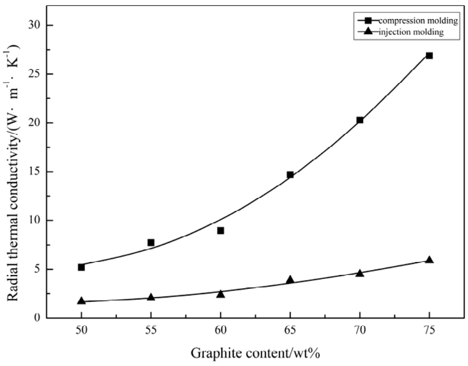


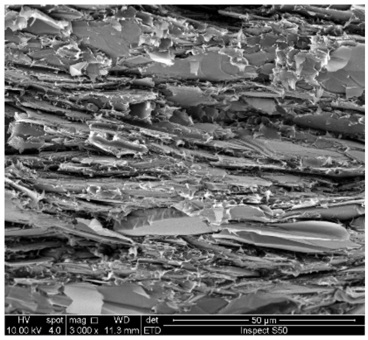
Figure 3 Effect of molding method and FG content on the radial thermal conductivity of composite materials

It can be seen from figures 1, 2 and 3, as the FG content increases, the thermal conductivity of the composite materials prepared by both molding methods shows an increasing trend. This is because with the increasing of FG content, the FG in the composite material is more likely to form a complete thermal conductivity pathway in the vertical, horizontal, and overall directions. Moreover, when FG content is 50 wt%, the average thermal conductivity of the composite materials prepared by injection molding and compression molding is 2.86 $W \cdot m^{-1} \cdot K^{-1}$ and 1.95 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 1.47; The axial thermal conductivity of the composite material is 4.80 $W \cdot m^{-1} \cdot K^{-1}$ and 0.73 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 6.56; The radial thermal conductivity of the composite material is 1.70 $W \cdot m^{-1} \cdot K^{-1}$ and 5.19 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 0.33; However, when the FG content increased to 75 wt%, the average thermal conductivity of the composite materials prepared by injection molding and compression molding increased to 9.88 $W \cdot m^{-1} \cdot K^{-1}$ and 6.03 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 1.64. The axial thermal conductivity of the composite material increased to 16.6 $W \cdot m^{-1} \cdot K^{-1}$ and 1.35 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 12.3; The radial thermal conductivity of the composite material increased to 5.88 $W \cdot m^{-1} \cdot K^{-1}$ and 26.9 $W \cdot m^{-1} \cdot K^{-1}$, respectively, with a ratio of 0.22.

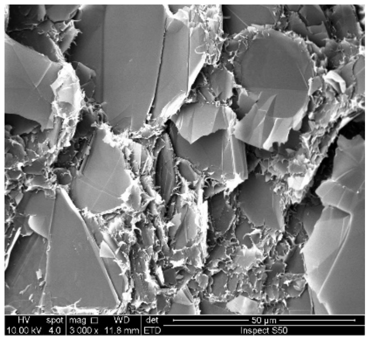
The above results indicate that the average thermal conductivity and axial thermal conductivity of composite materials prepared by injection molding are higher than those of compression molding composite materials, while the radial thermal conductivity of composite materials prepared by injection molding is higher. This is because during the injection molding process, the molten material enters the mold cavity and folds. At this time, the sheet shaped FG is mainly oriented vertically, which means that the thermal conductivity path of the composite material in the vertical direction is more and more complete. Meanwhile, a more complete three-dimensional thermal conductivity pathway is constructed, so the average and axial thermal conductivity of composite materials prepared by compression molding are higher. During the molding process, the molten material is subjected to vertical pressure, and the material flows horizontally into the mold cavity. At this time, the flaky FG is mainly oriented horizontally, and the thermal conductivity path of the composite material is more complete in the horizontal direction. Therefore, the composite material prepared from it has a higher radial thermal conductivity.

3.2 Scanning electron microscopic image characterization of composite materials

In order to visually observe the distribution and orientation of FG in the composite materials prepared by two different molding methods, scanning electron microscopic (SEM) was used to observe the cross sections of the two composite materials with FG content of 70 wt%. The results are shown in Figure 4.



a) compression molding material cross section



b) injection molding material cross section

Figure 4 SEM images of composite materials formed by molding and injection molding:

Figure 4 shows that FG in compression and injection molding composite materials exhibits significantly different orientations. Figure 4a) shows that the composite material formed by compression molding exhibits a stacked arrangement of FG layers perpendicular to the heat flow direction, and the horizontal orientation of FG is higher than the vertical orientation. From Figure 4b), it can be seen that the orientation direction of FG in the composite material formed by injection molding is consistent with the direction of heat flow in the direction perpendicular to the material surface, fully confirming that the horizontal direction of the composite material formed by compression molding has more and more complete thermal conductivity paths, and the vertical direction of the composite material formed by injection molding has more and more complete thermal conductivity paths, while constructing a more complete three-dimensional thermal conductivity path.

3.3 XRD analysis of composite materials

When the FG (with particle size of 37 μm) filling amount is 70 wt%, XRD was used to analyze the orientation of FG in the compression and injection molding composite materials, and the results are shown in Figure 5.

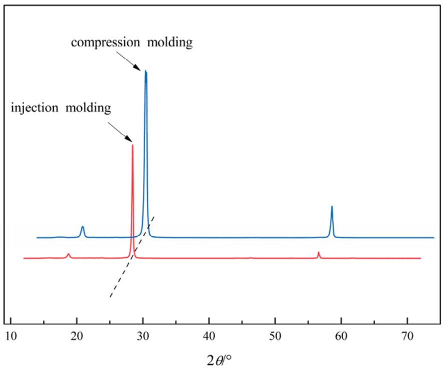


Figure 5 XRD analysis of composite materials formed by compression and injection molding

From Figure 5, it can be seen that the characteristic diffraction peak of the (002) crystal plane of graphite appears at 2θ=26.4°. The intensity of this characteristic peak is used to describe the orientation of FG in the material[11]. When FG is oriented horizontally in the material, there are more planes that satisfy Bragg's law at 2θ=26.4 °, which results in a high intensity of the characteristic diffraction peak of the (002) crystal plane in the XRD results; When FG is vertically oriented in the material, there are fewer planes that satisfy Bragg's law at 2θ=26.4 °, resulting in a decrease in the intensity of the characteristic diffraction peak of the (002) crystal plane in the XRD results. The characteristic diffraction peak of the (002) crystal plane of FG in the compression molding composite material appears at 2θ=26.4 °, with a peak of 97099. The characteristic diffraction peak of the (002) crystal plane of FG in the injection composite material appears at 2θ=26.44 °, with a peak of 65710. This fully indicates that FG in the compression molding composite material is mainly oriented horizontally, while FG in the injection composite material is mainly oriented vertically.

3.4 Analysis of thermal expansion performance of composite materials

When the FG (with particle size of 37 μm) filling amount is 70 wt%, the thermal expansion curves of compression and injection molding composite materials were tested, and the results are shown in Figure 6.

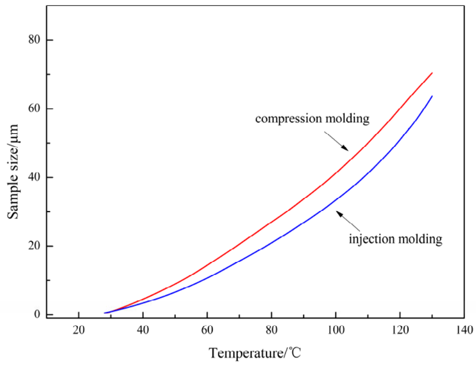


Figure 6 Thermal expansion curve of composite materials prepared by compression and injection molding

From the thermal expansion curve in Figure 6, it can be calculated that the average linear expansion coefficients of compression molding and injection molding composite materials at 30-130℃ are 261.36×10^{-6}/°C and 223.27×10^{-6} /°C, respectively. The average linear expansion coefficient of the compression molding composite material is lower than that of the injection composite material. This is due to the different orientation directions of FG in the two composite materials. FG in the compression molding composite material is mainly oriented horizontally, while FG in the injection composite material is mainly oriented vertically, which fully reflects the experimental results mentioned above.

4. Conclusion

(1) Composite materials with different FG contents were prepared using injection molding and compression molding processes, respectively. And the particle size of FG was 37 μm, and the coupling agent was NDZ-201(with a dosage of 0.7 wt% of the FG content). As the FG content increased, the thermal conductivity of the composite materials prepared by both molding methods increased.

(2) When the FG content is 75 wt%, the average thermal conductivity of the composite materials prepared by injection molding and compression molding is 9.88 $W\cdot m^{-1}\cdot K^{-1}$and 6.03 $W\cdot m^{-1}\cdot K^{-1}$, respectively. The axial thermal conductivity is 16.6 $W\cdot m^{-1}\cdot K^{-1}$ and 1.35 $W\cdot m^{-1}\cdot K^{-1}$, and the radial thermal conductivity is 5.88 $W\cdot m^{-1}\cdot K^{-1}$ and 26.9 $W\cdot m^{-1}\cdot K^{-1}$, respectively.

(3) The thermal conductivity test, SEM analysis, XRD analysis and thermal expansion analysis results show that the sheet-like FG in the composite material formed by injection molding is mainly oriented vertically, and there are more and more complete thermal conductivity pathways in the vertical direction of the composite material. At the same time, a more complete three-dimensional thermal conductivity pathway is constructed. The sheet-like FG in the composite material formed by compression molding is mainly oriented horizontally, and the thermal conductivity pathway in the horizontal direction of the composite material is more and more complete.

Acknowledgments

This work was financially supported by the Two-institute Cooperation Project of Hebei Academy of Sciences (Project No: 22713) and t he Fundamental Research Funds Pilot Project of the Hebei Academy of Sciences (Project No: 2023PF03-1).

References

1. Fan Wei, Feng Gang, Zhao Jiawei. Research and application development of thermal conductivity polymer composites[J]. Engineering Plastics Application, 2011, 39(12): 101-104.
2. Zhang Luwen. Preparation 、 property and application of thermal conductive polymer composites[D]. East China University of Science and Technology, 2010.
3. Rebecca A. Hauser, Julia A. King, Rachel M. Pagel, 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.
4. Yan Sha. Preparation and properties of polypropylene-based thermal conductive composites[D].Beijing University of Chemical Technology,2012.
5. Xu Shang. Molecular simulation study on thermal conductivity and microstructure optimization of polymer materials [D]. Southeast University, 2017.
6. Liu Han， Wu Hongwu. Research progress of thermal conductive polymer composites with fillers[J]. China Plastics Industry, 2011(4): 10-13.
7. Liu Ke, Liu Ying, Wu Daming, et al. The effect of flake graphite orientation on the thermal conductivity of flake graphite/polypropylene and flake graphite/nylon 66 composites[J]. Journal of Composite Materials, 2014, 31(3): 610-616.
8. Wang Zhengzheng, Liu Deju, Zhou Haijun, et al. Preparation and properties of polypropylene/flake graphite thermal conductive composites[J]. Engineering Plastics Application, 2020, 48(1): 30-34, 45.
9. Wu Jiawei, Ji Xinyu, Yang Jindi, et al. Preparation and properties of polypropylene/graphite composites with high thermal conductivity[J]. Engineering Plastics Application, 2016, 44(8): 36-40.
10. Xu Huagen, Peng Xintao, Zhou Junjie, et al. Research of thermally conductive composites based on flake graphite filled in polyamide 6/polypropylene[J]. Engineering Plastics Application, 2015, 43(9): 1-6.
11. Chen Guohua, Wang Haiquan, Zhao Weifeng. Fabrication of highly ordered polymer/graphite flake composite with eminent anisotropic electrical property. Polymers for Advanced Technologies, 2008, 19(8): 1113-1117.