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Preparation and Properties of HGM and CCF Co-filled Polypropylene Chemical Composites

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The purpose of this paper is to study the effects of different amount of hollow glass microspheres (HGM) on the flame retardancy and mechanical properties of polypropylene (PP)/ reinforced nitrogen-phosphorus compound intumescent flame retardant (IFR)/ Chopped carbon fiber (CCF) composites for electric meter turnover boxes. To this end, the melt blending method was used by taking the CCF, reinforced IFR, and flame-retardant PP composite as the matrix. Then, the modified HGM was added to obtain the PP/IFR/CCF/HGM flame retardant reinforced composites for electric meter turnover box. Through the analysis of its performances in combustion, bending, impact, tensile strength and hardness, the results show that with certain amount of HGM, the flame-retardant properties and mechanical properties of the composite materials for meter turnover box can be improved; with more addition of HGM, the mechanical properties of the composite material would be significantly reduced; when 10 times of HGM amount is added, the mechanical properties of the composite material are optimal.

1. Introduction

Polypropylene (PP) is a commonly used general-purpose plastic, which has low price, easy processing and wide source. Therefore, it has been widely used as the structure material of electric meter turnover box. However, it also has some disadvantages, such as insufficient strength, easy combustion, and serious dripping during the burning. So, reinforcement and flame retardancy are the research hotspots in the application field of PP composites (Bledzki et al., 2012; Monteiro et al., 2009; Idicula et al., 2010; Xu et al., 2013).

At present, the flame retardant of PP is often added; but as the added amount of flame retardant increases, the mechanical properties of PP decrease. Chopped carbon fiber is an inorganic non-metallic material with excellent performance. It can be modified to have a good bonding force with the resin interface. Filling it into the resin can improve the mechanical properties of the composite (Jiang et al., 2015). HGM have large volume, low thermal conductivity, high compressive strength and good self-flowability. Due to the characteristics of isotropic and high filling amount, the material has a very high dimensional stability; with the appropriate filling ratio, the flame retardancy of the composite material can be improved, and the mechanical strength is also remarkably promoted.

Based on this, this paper intends to use the HGM to modify the PP/CCF composite material for the turnover box, and studies the effect of HGM on the flame retardancy and mechanical properties of PP/CCF composites for electric meter turnover boxes. It is expected to provide reference for PP modification and guide the application of the meter turnover box.

2. Experiments

2.1 Main raw materials

Polypropylene: K8003, Dushanzi Petrochemical Co., Ltd.;
Chopped carbon fiber: 0.1MM, Shanghai Liso Composite Material Technology Co., Ltd.;
Hollow glass microspheres: effective density of 0.15-0.60g/cc, average particle size between 30-80um, New Material Technology Co., Ltd, Maanshan Mine, Sinosteel;

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Silane coupling agent: KH-570, Nanjing Daoning Chemical Co., Ltd.; Nitrogen and phosphorus compound flame retardant: FR-101, Qingdao Lianmei Chemical Co., Ltd.;
Maleic anhydride grafted polypropylene: KH PP-GMAH 01, Haier kehua;

2.2 Main equipment and instruments

Pendulum Impact Tester: ZBC7501-B, MTS Industrial Systems (China) Co., Ltd.;
Horizontal vertical burner: Model CZF-3F, Nanjing Jiangning District Analytical Instrument Factory;
Precision open mill: ZG-120, Dongguan Zhengong Precision Testing Equipment Factory; High-speed mixer: SHR-10A, Zhangjiagang Xinghuo Degradation Equipment Machinery Plant; Oxygen Index Tester: JF-3, Nanjing Jiangning District Analytical Instruments plant;
Box type resistance furnace: SX2-2.5-10, Shangyu Hunan Electric Furnace Oven Factory, Zhejiang Province;
Rubber shore durometer: LX-D type, Laizhou Lean Test Instrument Co., Ltd;
Plastic pulverizer: SWP/l60, Qingdao Jiaozhou Hongda Plastic Auxiliary Machinery Factory;
Flat vulcanizing machine: TP1400, Shanghai Wodi Technology Co., Ltd;
Electronic universal testing machine: CMT-4304, MTS Industrial Systems (China) Co., Ltd;
Universal sample machine: ZHY-W, Hebei Chengde Experimental Machine Factory;

2.3 Sample preparation

20ml of silane coupling agent KH570 was taken and dissolved in 980ml of ethanol to prepare the KH570/ethanol solution with 2% volume concentration. Then, 200g of chopped carbon fiber was weighed and placed in the 2% KH570/ethanol solution for 12h, and dried in an oven at 80°C to obtain the modified CCF. According to the ratio of the composite materials in Table 1 below, the PP and the modified CCF, the nitrogen-phosphorus compound IFR, and the maleic anhydride grafted polypropylene (PP-g-MAH) were first added to the high-speed mixer and uniformly mixed; when the double roll temperature of precision open mill reached 170℃, the mixture was added to the open mill for melting and mixing; after 3 minutes, the hollow glass microbeads were added. Finally, with the mixture uniformly mixed, the sheets were made. The obtained sheet material was pulverized on a plastic pulverizer, and then the pulverized material was pressed at a flat vulcanizing machine at 180°C to be the 200mm × 200mm × 3mm sheets (hot pressing condition: preheating and melting for 14 minutes, hot pressing for 12 minutes, cold pressing for 12 minutes, pressure 10MPa). Next, the sheet material was cut into the sample with the specified size on a universal sample machine, which were used for various flame retardant performance and mechanical properties tests (Zhang and Wei, 2016).

Table 1: Ratio of composite materials used in electric meter turnover box

No.	PP/PP-g-MAH/CCF/IFR (g)	HGM (g)
1#	75/15/25/25	0
2#	75/15/25/25	10
3#	75/15/25/25	15
4#	75/15/25/25	20
5#	75/15/25/25	25

2.4 Testing and characterization

The pressed sheets of PP composite material with different compositions were cut into samples at specified size. Then, in accordance with the methods specified in GB/T 2408-2008 and GB/T2406.2-2009, the horizontal combustion performance and the vertical combustion performance were measured by the horizontal vertical burning instruments respectively, and the oxygen index was measured by an oxygen index meter (Liu et al., 2013). The testing of the hardness, the impact strength, tensile strength, and bending strength for the composite material followed national standard GB/T 531, national standard GB/T 1043-1993, national standard GB/T 1040-1992, and GB/T. T9341-1988 respectively.

3. Results and analysis

3.1 Combustion behaviour of composite materials

Table 2 lists the horizontal and vertical combustion performance of PP/IFR/CCF/HGM composites. It can be seen from Table 2 that the flame-retardant performance of the 1# composite material is lower than that of the 2#, 3#, 4#, and 5# composite materials. Comparing the components of each group, it’s found that by adding HGM to the matrix of 1# composite material, the flame retardant performance of the composite material was significantly improved, indicating that the HGM had significantly improved the flame retardant properties of the composite during the combustion process.

Table 2: Horizontal and vertical burning properties of PP/IFR/CCF/HGM composites

No.	drip	self-extinguishing	The horizontal combustion	The vertical combustion
1#	drip	self-extinguishing	FH-2	FV-1
2#	None	self-extinguishing	FH-1	FV-1
3#	None	self-extinguishing	FH-1	FV-0
4#	None	self-extinguishing	FH-1	FV-0
5#	None	self-extinguishing	FH-1	FV-0

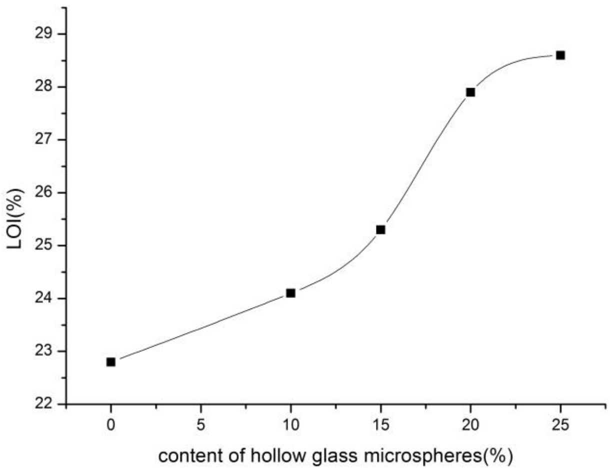

Figure 1: Hollow glass microspheres with different content on the composite effect of limiting oxygen index

Figure 1 shows the limiting oxygen index curve of different HGM amounts-added composites for electric metering boxes.

It can be seen from Figure 1 that with the HGM amount increasing, the limiting oxygen index of the composite increases; when the HGM addition is less than 15 grams, the limiting oxygen index of the composite increases ; when it reaches 20 grams, the limiting oxygen index increases significantly. With the continuous addition of HGM, the limiting oxygen index starts to increase slowly. With no addition of HGM, the nitrogen-phosphorus compound IFR will foam on the PP surface and form the dense expanded carbon layer during the combustion process, thereby achieving the purpose of heat insulation and air-insulation; besides, the carbon layer can flame retardant, heat insulated and oxygen insulated, which can prevent the formation of droplets and achieve the effect of flame retardant. With HGM added, the HGM will adhere to the surface of the carbon layer during combustion, increasing the stress of the carbon layer skeleton; furthermore, due to the thermal insulation of HGM, the heat transfer can be decreased, and the decomposition of the internal polymer can be reduced, which has the flame retardation effect (Feng et al., 2009; Li et al., 2013).

3.2 Effect of different addition amount of HGM on the mechanical properties of composite materials for electric meter turnover box (Cai et al., 2010)

3.2.1 Effect of different addition amount of HGM on bending strength of composite materials for electric meter turnover box

Figure 2 shows the effect of different amounts of HGM on the bending strength of the composite.

It can be seen from Figure 2 that with the HGM addition increasing, the bending strength of the composite increases first and then decreases; when the added amount of HGM is 10 times of the addition amount, the bending strength of the composite reaches the maximum value, increasing by 30.57% more than that of the PP/CCF composite. Whereas, when the addition of HGM increases. the bending strength of the composite decreases slowly; when the added amount is more than 20 times of the addition, the bending strength of the composite decreases sharply (Shang et al., 2011).

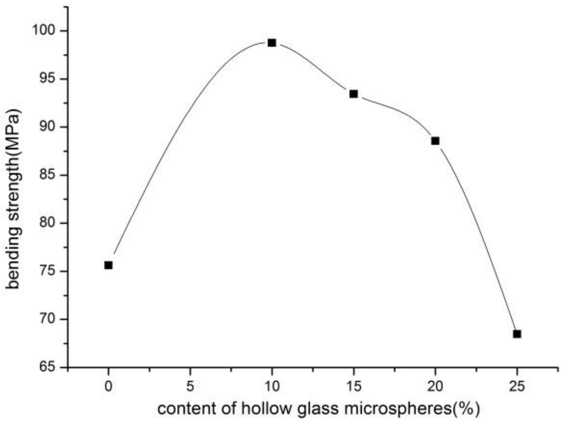

Figure 2: Content of bending strength of composite hollow glass Microsphere

3.2.2 Effect of different addition amount of HGM on impact strength of composite materials for meter turnover box

Figure 3 shows the effect of different added amounts of HGM on the impact strength of composite materials for electric meter turnover boxes.

It can be seen from Figure 3 that with the HGM addtion increasing, the impact strength of composite materials first increases and then decreases; when the added amount is more than 10 grams, its impact strength decreases sharply; as it is above 15 grams, it tends to be decreasing gently. With the 10g addition amount of HGM, the impact strength value is 23.54KJ/m^2, which is 11.81% higher than that of PP/CCF composite. This is mainly because the modified HGM has a good compatibility with PP material, and the impacted HGM are deformed and broken to absorb certain amount of energy, further improving the impact strength of the composite material (Cockburn et al., 2012; Fernandez et al., 2014).

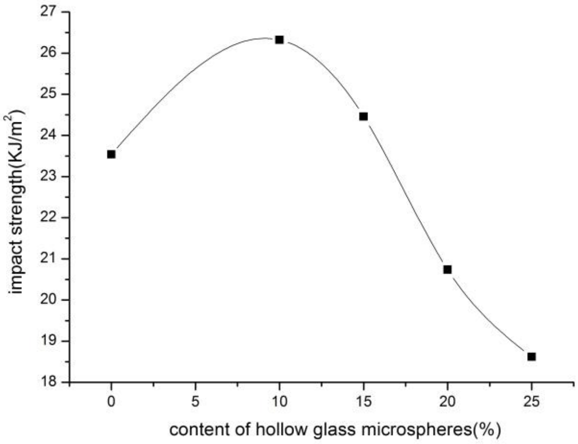

Figure 3: Content of impact strength of composite hollow glass Microsphere

3.2.3 Effect of different addition amount of HGM on the hardness of composite materials for electric meter turnover box

Figure 4 shows the effect of different additions of HGM on the hardness of the composite.

It can be seen from the curve of Figure 4 that the hardness of the composite increases with the addition of HGM. With the addition amount of 10 grams, the hardness reaches the maximum of 68HD, which is 4.26% higher than that of the PP/CCF composite. Then, when the amount of addition continues to increase, the hardness of the composite shows a decling trend. This is mainly due to the isotropy and the high filling volume of HGM, which improves the stability of the composite material. On one hand, the surface hardness of the composite material can be significantly improved at a proper filling ratio; on the other hand, the HGM can also serve as nucleating agent, increasing the hardness of the composite (Lu et al., 2010; Feng et al., 2009; Lin et al., 2014; Gao et al., 2014; Wei et al., 2018).

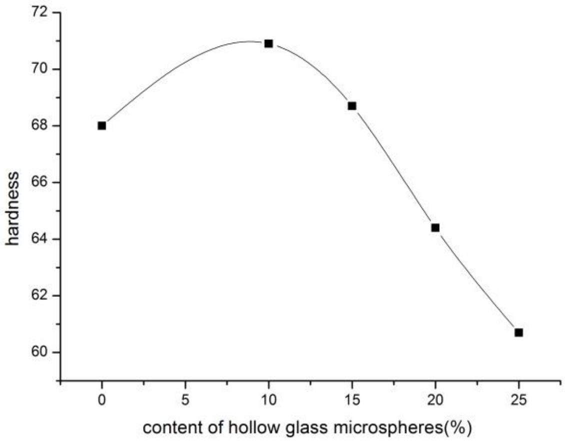

Figure 4: The hardness of composite under different contents of hollow glass microspheres

4. Conclusions

(1) HGM are small spheres with large sphericity, which can improve fluidity and reduce internal stress of composites. Due to their isotropic and high filling characteristics, the addition of certain amount of HGM to the PP/CCF composites can further improve their mechanical properties such as tensile strength, bending strength and hardness.
(2) As a halogen-free material, HGM are difficult to burn and heat-insulated. The added HGM to the composite material can cause the surface of the carbon layer to be heat and oxygen insulated during the combustion process. It can also enhance the support of the large carbon layer skeleton, which is flame retardant and environmentally friendly.
(3) The density of HGM is only a fraction of the density of the resin, which can reduce the weight of the composite material while significantly reducing the cost.

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