

Effect of Multi-walled Carbon Nanotubes on Properties of MSW Filled PP / PP-g-MAH Chemical Blend System

Bin Gu*

Zhengzhou Electric Power College, Zhengzhou 450000, China
 zdlgubin@sina.com

The purpose of this paper is to study the effects of different amounts of multi-walled carbon nanotubes (MWCNT) on the mechanical properties of polypropylene (PP)/magnesium sulfate whisker (MSW) composites for electric meter turnover boxes. To this end, the melt-blending method was adopted to blend the surface-modified MWCNTs with the modified MSW, PP, and maleic anhydride grafted polypropylene (PP-g-MAH), and then two-roll mill was used to obtain the PP/PP-g-MAH/MSW/MWCNT composite materials for electric meter turnover box by melt blending. Finally, the effects of different amounts of modified MWCNT on the mechanical properties of PP/PP-g-MAH/MSW composites for electric meter turnover boxes were compared. The results show that after mixed acid treatment, the MWCNT surface is uniformly dispersed in the composite, and the interface with the polymer matrix is well combined, which can strengthen the composite material; when the mass fraction of MWCNT is high, agglomeration occurs, reducing the mechanical properties of the composite; when the mass fraction is about 0.3%, the mechanical properties of the composites are the best.

1. Introduction

Polypropylene is made of propylene monomer. It has low density, easy processing, non-toxicity, good mechanical properties, fatigue and yield resistance. It can be recycled and reused, and often used as a material for electric meter turnover boxes.

The research on the PP modification is one of the hot topics in the packaging containers field of electric meter (Lian et al., 2008; Bledzki et al., 2012). Inorganic whiskers are needle-shaped single crystal fibre materials developed in recent years. Its atoms in the single crystal are arranged neatly, which can almost overcome various defects of polycrystalline materials.

After modification, it can be uniformly dispersed in the polymer, so as to ensure the good mechanical property of the polymer (Zhou et al., 2005). As a new material, multi-walled carbon nanotubes have the advantages of large specific surface area, long aspect ratio, high mechanical strength, good thermal stability and good thermal conductivity. Based on this, by adding MWCNTs in the PP/MSW composites for electric meter turnover box, this paper studies the effect of MWCNTs on the mechanical properties of PP/MSW composites. It's expected to provide reference for PP modification.

2. Experiments

2.1 Main raw materials

Polypropylene: K8003, Dushanzi Petrochemical Co., Ltd;

Maleic anhydride grafted polypropylene: KH PP-GMAH 01, Haier Kehua;

Magnesium sulfate whiskers: NP-YW2, whiteness: ≥ 93 (fluorescence whiteness); bulk density: 0.1 to 0.3; water content: $< 1.0\%$; pH: 9 to 10.5; purity: $\geq 96\%$; length L: 3.5 to 120 μm ; diameter D: $< 2\mu\text{m}$; length-diameter ratio L/D: 8 to 70, Jiangxi Fengzhu New Material Technology Co., Ltd;

Multi-walled carbon nanotubes: ID: 5-10nm, OD: 10-20nm, length: 10-30nm, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences;

Silane coupling agent: KH-550, colourless liquid, Nanjing Daoning Chemical Co., Ltd.

2.2 Main equipment and instruments

Pendulum Impact Tester: ZBC7501-B, MTS Industrial Systems (China) Co., Ltd.;
 Precision open mill: BP-8175-A, Dongguan Baopin Precision Instrument Co., Ltd.;
 Box type resistance furnace: SX2-2.5-10, Shangyu Hunan Electric Furnace Oven Factory, Zhejiang Province;
 Plastic pulverizer: SWP/I60, Qingdao Jiaozhou Hongda Plastic Auxiliary Machinery Factory;
 Plate vulcanizing machine: TP1400, Shanghai Wodi Technology Co., Ltd.;
 Universal sample machine: ZHY-W, Hebei Chengde Experimental Machine Factory;
 High-speed mixer: SHR-10A, Zhangjiagang Xinghuo Degradation Equipment Machinery Plant;
 Electronic universal testing machine: CMT-4304, MTS Industrial Systems (China) Co., Ltd.

2.3 Sample preparation

4g of silane coupling agent KH550 was weighed in the 980ml of absolute ethanol, and stirred for 15min in the 45°C water bath to obtain the silane coupling agent/ethanol solution. Then, 200g of MSW was weighed, put in coupling agent/ethanol solution, and stirred for 1.5h in the 50°C water bath. Finally, it was dried in an oven at 75 ° C to obtain the modified MSW of KH550 silane coupling agent (Zhang et al., 2016; Duan et al., 2012).

300 ml of mixed acid was prepared at the V (concentrated H₂SO₄): V (concentrated HNO₃) = 1:1, placed in the three-necked flask, and then 2g of MWCNT were added while being connected to a reflux unit. The flask was placed in a heating unit and treated at 120°C for 3 h. After drying and washing with deionized water to the neutrality, finally it's dried in a vacuum oven at 80°C for 4h so as to prepare the surface-treated multi-walled carbon nanotubes (Liu et al., 2007; Cheng et al., 2014; Wu et al., 2008; Zhang et al., 2014).

PP, PP-G-MAH, and modified MSW were added to the high-speed mixer and mixed uniformly. The front and rear roll temperatures of the two-roll mill were set to 172 °C and 170 °C respectively, and after the temperature of the mill reached the set temperature, the uniformly mixed PP, PP-G-MAH, and modified MSW were added to the open mill for 4 min according to the formula in Table 1 below. Then, the MWCNT were added to the mill for melting and mixing; after 5 minutes, the sheet was made from the mill. Next, the sheet material was pulverized in a pulverizer, and the pulverized material was placed in a mould and pressed into a plate using a flat vulcanizing machine (hot pressing conditions: upper and lower plate temperature of 175°C, preheating and melting for 10 min, and hot pressing for 7 min, cold pressing for 10 min, and pressure of 10 MPa). Finally, the universal sample machine was used to cut the pressed sheet into a standard sample of the specified size for performance testing (Li et al., 2012).

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

No.	PP	PP-g-MAH	MSW	MWNT	MWNT mass fraction
1	100	10	10	0	0%
2	100	10	10	0.12	0.1%
3	100	10	10	0.36	0.3%
4	100	10	10	0.6	0.5%
5	100	10	10	1.21	1%

2.4 Testing and characterization

The impact strength was tested according to GB/T 1843-2008;
 The tensile strength was tested according to GB/T 1040.1-2006;
 The bending strength was tested according to GB/T9341-2008;
 The SEM, The voltage was kept at 20Kv;
 The sample surface was gold-plated.

3. Results and discussions

3.1 Effect of MWCNT on tensile strength of PP/MSW composites for electric meter turnover boxes

Figure 1 is the changing curve showing the effect of the MWCNT content on the tensile strength of PP composites for electric meter turnover boxes.

It can be seen from the figure that with the addition of MWCNT, the tensile properties of the composites are significantly improved. When the mass fraction of MWCNT is about 0.3%, the tensile strength of the composites reaches the maximum value of 45.09 MPa, which is 24.83% higher than that of the composite material without adding MWCNT. The reasons are mainly: the modified MWCNTs have improved their dispersibility in the PP matrix, which can further enhance the bearing capacity of the MSW skeleton in the

composite material. Besides, it's also tightly wrapped by the PP matrix and bonded well on the interfaces. In this way, when the composite material is subjected to external stress, the fracture surface mostly appears between the PP coating layer and the matrix, so that the MWCNT can absorb a large amount of energy, indicating that it can further increase the rigidity of the PP composite material. This is beneficial to improve the resistance of composites (Zhou and Liang., 2015; Xiong et al., 2009; Zhang and Wei , 2016; Hua et al., 2011; Yi et al., 2008). As its mass fraction increases, its dispersibility begins to decrease, and agglomeration begins to occur, resulting in a gradual decrease in tensile strength of PP composites.

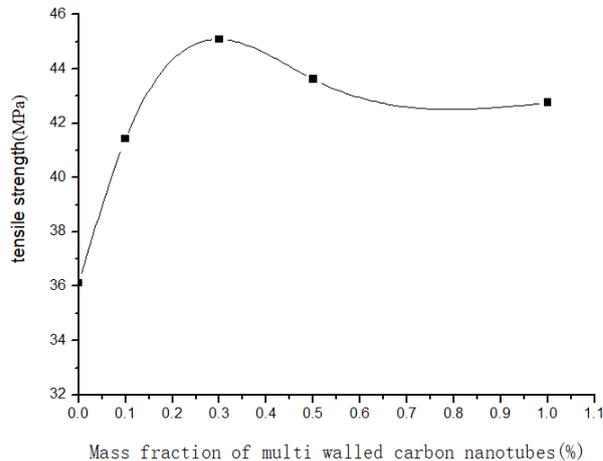


Figure 1: Tensile strength of composite under different content CNTS

3.2 Effect of MWCNT on bending strength of PP/MSW composites for electric meter turnover boxes

Figure 2 is the chging curve showing the effect of the MWSNT content on the bending strength of PP composite for an electric meter turnover box.

It can be seen from the figure that the bending strength of the composite increases gradually with the increase of the MWSNT content. When the mass fraction of MWSNT is about 0.3%, the bending strength of the composite reaches the maximum value of 60.75 MPa. As the content of MWSNT continues to increase, the bending strength of the composite material gradually decreases. Compared with the composite material without MWSNT, the bending strength is increased by 25% with about 0.3% of the MWSNT mass fraction. The main reasons are: For the modified MWCNT, its interfacial bonding strength with the PP matrix is increase, so as to improve the dispersibility in the composite material; the appropriate amount of MSW in the composite material in the composite material must be uniformly dispersed and interwoven into a network structure, so that when the composite material is under external stress, it can be effectively transmitted to MSW and MWCNT, thereby significantly improving the mechanical strength of the composite (Monteiro et al., 2009; He and Gu, 2007; Zhang et al., 2016; Yang et al., 2009). As its content increases, MWCNT begin to agglomerate in the polymer matrix, reducing the bending strength of the composite.

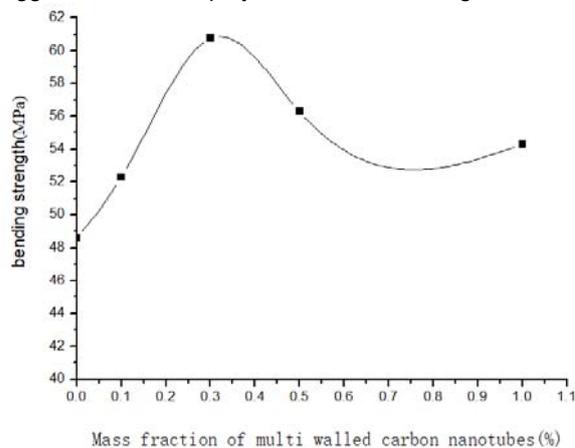


Figure 2: Bending strength of composite under different content MWNTS

3.3 Effect of MWCNT on impact strength of PP/MSW composites

Figure 3 is the changing curve showing the effect of the MWCNT content on the impact strength of the PP composite material for an electric meter turnover box.

It can be seen from the figure that the impact strength of the composite material is significantly improved by adding the surface treated MWCNT. Compared with the composite material without MWCNT, the impact strength of the composite added with about 0.3 mass fraction of MWCNT increased from 30.5 KJ/m² to 44.28 KJ/m², increasing by 45.18%. The reasons are mainly: With mixed acid treatment of MWCNT, it can reduce its surface energy, improve its dispersibility in the PP matrix, lower the crystallization nucleation energy barrier of PP, and enhance the crystallinity of the PP matrix; thus, the MWCNT has a good toughening effect on PP composites. (Ni et al., 2001; Jing et al., 2008; Gao et al., 2014) As the mass fraction of MWCNT continues to increase, agglomeration tends to occur, resulting in a decrease in the toughness of the composite (Wei and Jia, 2015)

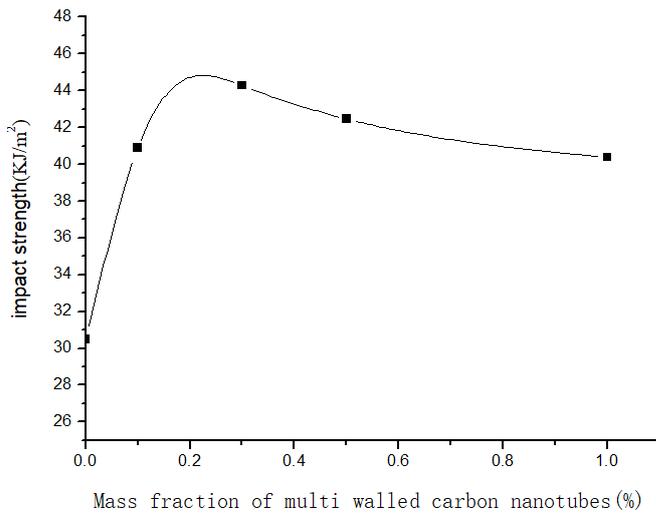
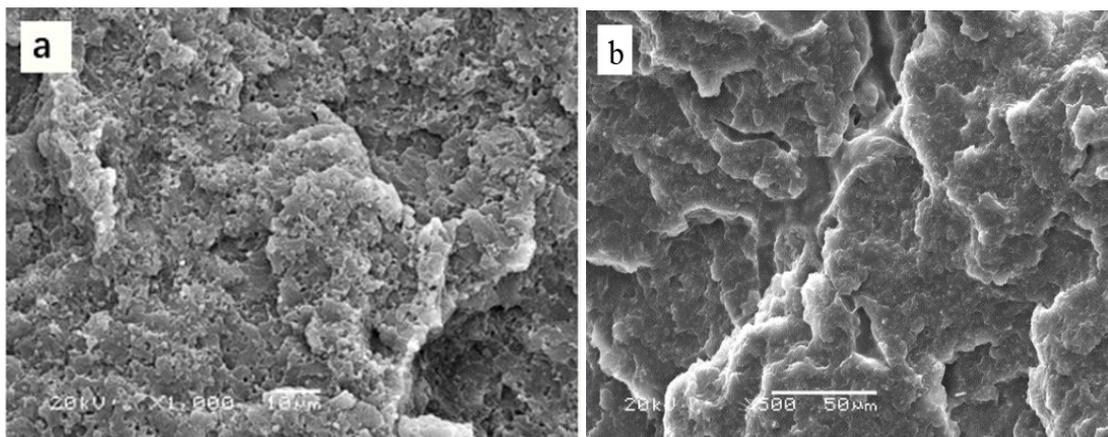


Figure 3: Impact strength of composite under different content CNTS

3.4 SEM analysis for impact section of PP/PP-g-MAH/MSW/MWNT composites for electric meter turnover box

Figure 4 shows the SEM images of the impact section for the 0% and 0.3% MWCNT-added composite.



a. 0%

b. 0.3%

Figure 4: The SEM images of the cross-section of composite with 0%, 0.3% content of MWNTS

It can be seen from Figure 4a that the MSW are wrapped by the polymer matrix and are capable of being uniformly dispersed to transfer stress. Figure 4b contains the 0.3% MWCNT-added composite, in which the

white dots are MWCNT protrusions wrapped by the PP matrix; at the low mass fraction, the distance between the protrusions is large, indicating that the MWCNT were uniformly dispersed in the pp matrix without agglomeration.

The MWCNTs are uniformly dispersed in the matrix of the composite material and tightly wrapped by the matrix, and the interface is well bonded, indicating that the MWCNTs have a certain toughening and reinforcing effect.

4. Conclusions

- (1) After the mixed acid treatment of MWCNTs, its compatibility with the composite material is better, which significantly improves the mechanical properties of the PP/MSW composite for electric meter turnover box.
- (2) The MWCNT with appropriate mass fraction have certain toughening and strengthening effect on the PP/MSW composite of the electric meter turnover box. However, when its mass fraction is large, agglomeration can occur, thereby forming structural defects and decreasing the mechanical properties of the composite material.
- (3) When the mass fraction of MWCNT is about 0.3%, the mechanical properties of PP/MSW/MWCNT composites for electric meter turnover boxes are the best.

Acknowledgments

This work is supported by Project of mass innovation and achievement application plan of Henan electric power company in 2018 (no.72).

References

- Bledzki A., Heim H.P., Paßmann D., Ries A., 2012, Manufacturing of Self-Reinforced All-PP Composites, *Synthetic Polymer–Polymer Composites*, 8, 719-738.
- Cheng F., Jiang Q., Zhang Z., 2014, Potassium titanate whisker application in polymer composites, *Engineering plastics applications*, 12, 123-126.
- Di Y., Cui X., Nan N., Zhou C., 2018, Hydration reaction of cementitious materials prepared with molybdenum tailings, *Chemical Engineering Transactions*, 66, 7-12, DOI: 10.3303/CET1866002
- Duan Z.W., Jie X.H., Zhang Y.M., 2012, Research on Acid Treatment of Multi-walled Carbon Nanotubes, *Materials review*, 828-830.
- Gao J., Yuan Z.K., Yu J.H., Lu S., Rao B., Jiang N., 2014, Preparation and Thermal Properties Study of Boron Nitride/Epoxy Resin Composite, *Insulating Materials*, 2, 17-24.
- He C.X., Gu H.Y., 2007, Progress in research of poplymer composites filled with inorganic nano particles, *China Synthetic Resin and Plastics*, 2, 69-72.
- Hua M.Y., Li Y.M., Li X., 2011, First-principles Calculation of the Geometric Configuration, Energies and Electronic Structures of Potassium Hexatitanate Whisker, *Journal of Synthetic Crystals*, 6, 1574-1579.
- Jing X.M., Lu J.M., Ma C., Jing K.Y., 2008, Present Situation and developing prospect for the research of potassium titanate whiskers, *Journal of Southwest University for Natural sciences*, 34, 540-544.
- Li S.Y., Yan D.G., Wang J.L., 2012, Preparation and Study on Carbon Nanotubes/Polypropylene Composite Materials, *Guangzhou Chemical Industry and Technology*, 19, 43-44
- Lian R.B., Xu M.Z., Li Q., Huang R., 2008, Study on Properties of Glass Fiber Reinforced Polypropylene Composite, *Plastic science and technology*, 8, 40-44.
- Liu J., Xu W.C., Zeng G.R., Li D., 2007, Study on the graft modification of polypropylene, *Packaging engineering*, 9, 33-35.
- Lu T.J., Yu Y., Fan P., Chang H., Li X., Li Y., Zheng X.W., Wang Y.Q., 2001, Study on Magnesium Sulfate Whisker Reinforced Flame Retardant Polypropylene, *China Plastics*, 9, 66-68.
- Luo D., 2018, Study on the influence of superconducting carbon black on the mechanical and antistatic properties of wood powder /pvc composites, *Chemical Engineering Transactions*, 66, 127-132, DOI: 10.3303/CET1866022
- Monteiro S.N., Lopes F.P.D., Ferreira A.S., Nascimento D.C.O., 2009, Natural Fibre Polymer Matrix Composites: Cheaper, Tougher and Environmentally Friendly, *Journal of the Minerals Metals and Materials Society*, 61, 17–22, DOI: 10.1007/s11837-009-0004-z
- Ni H.C., Liu Y., 2009, Influence of TiO₂ composite nanoparticles on the anti-ultraviolet ability and crystallization of PP, *Chemical Research and Application*, 21(10), 1404-1407.
- Shen L.J., Zhao P., Zhu W.H., 2010, A ratiometric hydrophilic fluorescent copolymer sensor based on benzimidazole chromophore for microbioreactors, 89, 236-240, DOI: 10.1016/j.dyepig.2010.03.016

- Tae Y.J., Narinder S., Gang W.L., 2007, Benzimidazole-based ratiometric fluorescent receptor for selective recognition of acetate, 48(50), 8846-8850, DOI: 10.1016/j.tetlet.2007.10.060
- Wu Y., Zheng A., Han F., 2008, A new type of short fiber reinforced polymer composites, Journal of high polymer, 6, 46-47.
- Xiong L., Ma H.Y., Wang R., Liang H.B., Guan J., 2009, Study on Multi-Walled Carbon Nanotubes Modified with KH550 on Toughening Epoxy Resin, Journal of Aeronautical Materials, 29(4), 63-66.
- Xu Z., Huang J., Chen M., Tan Y., Wang Y.Z., 2013, Flame retardant mechanism of an efficient flame-retardant polymeric synergist with ammonium polyphosphate for polypropylene, Polymer Degradation and Stability, 98(10), 2011-2020.
- Yang Q., Zhang B., Mao Z., Xu H., Qian F., Hang J., 2009, Preparation and Properties of PP/Modified Nano-TiO₂ Composites, Polymer Materials Science and Engineering, 1, 48-51.
- Yin H.Y., Shu M.Y., 2008, The Latent heat of crystallization and Crystallization temperature of HDPE /PP, Packaging Engineering, 31(9), 64-67.
- Zhang J.L., Wei F., 2016, Effects of six Potassium titanate whiskers on mechanical properties of polypropylene composite, Journal of high polymer, 3, 14-18.
- Zhang J.L., Wei F.J., Zhang Y.F., 2016, Different coupling agent modified effect of PTW on PP/GF properties of composite, Packaging Engineering, 6, 80-83.
- Zhang R., Liu Z., Fu Y.Q., Zhang Y.F., Han J., Lan R., 2014, Research Progress of Carbon Nanotubes Modification and Polypropylene/Carbon Nanotubes Composites, Shanghai Plastics, 4, 1-6.
- Zhou J., Wang Y., Meng H., 2005, Study on property of PP modified with potassium titanate whisker, Engineering plastics applications, 11, 21-24.
- Zhou T.Y., Liang J.Z., 2015, Effects of Multi-walled Carbon Nanotubes Content on the Thermal Stability and Crystallization of PP/Multi-walled Carbon Nanotube Composites, China Plastics Industry, 11, 81-84.
- Wei, F., & Jia, Q. 2015. Synthesis and luminescence of A₃Bi(PO₄)₃:Eu²⁺(A= Ba and Sr) powders. Journal of Materials Science: Materials in Electronics, 26(1), 262-266.