CHEMICAL ENGINEERING TRANSACTIONS

VOL. 71, 2018

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Xiantang Zhang, Songrong Qian, Jianmin Xu

ISBN 978-88-95608-68-6; **ISSN** 2283-9216

DOI: 10.3303/CET1871184

Analysis on Preparation and Performance of PP/PP-g-MAH/CCW/MWCNTS Chemical Materials

Haifang Guo

Henan University of Science and Technology Sports Institu, Luoyang 471023, China
guo0379@126.com

This paper sheds new light on what effects the different dosage of Multi-walled Carbon Nanotube (MCN) plays on the mechanical properties of polypropylene/calcium carbonate whisker composites for seats. As a method, a twin roll mill is used to prepare the PP/ PP-g-MAH/CCW/ carbon nanotube composite with the surface modified MCN and modified calcium carbonate whisker, polypropylene (PP) and PP-g-MAH by melt blending mode, thereby to compare how the mechanical properties of PP/PP-g-MAH/CCW composite are subjected to different doses of modified MCN. The findings reveal that the multi-walled carbon nanotubes, if finished by mixed acid, will disperse uniformly in the composite, and well bond with the polymer substrate interface, toughing and strengthening the composite material; but when the mass fraction of carbon nanotubes gets higher, the agglomeration will appear, which in turn reduces the mechanical properties of the composite. When the mass fraction of carbon nanometer is 0.5% or so, the mechanical properties of the composite perform the best.

1. Introduction

PP, as a general-purpose thermoplastic, is made of propylene monomer by polymerization. It features low density, easy processing, non-toxicity, good mechanical properties, fatigue yield resistance, stress crack resistance, recyclability and reusability, so that it is commonly used as a seat material for stadiums. However, PP also has its own defects, for example, it has a high shrinkage rate, easy scoring on the surface, easy aging, and methyl group contained in molecular chain increases the rigidity of the whole chain, which reduces its impact resistance, restricts its application in the seats. In this context, the modification of PP is one of the hot topics for discussion in the field of sports seat materials (Lian et al., 2008; Bledzki et al., 2012). Inorganic whisker also features interface regularity, high aspect ratio, high strength, slender structure and high modulus. It can be modified to disperse uniformly in the polymer and plays a skeleton support role, so that a polymer-whisker composite is formed to further make the polymer present good mechanical properties (Zhou et al., 2005; Xu et al., 2013). Carbon nanotube is added as modified material to thermoplastics. It is expected that the overall properties of thermoplastics can be improved to expand their application in many fields.
This paper adopts the carbon nanotube added in PP/calcium carbonate whisker composites to investigate how it affects the mechanical properties of PP/calcium carbonate whisker composite for sports seats, hoping to provide the clues to the PP modification and application in the field of seat materials.

2. Test

2.1 Main materials

PP-g-MAH: KH PP-GMAH01, HKH National Engineering Research Center of Plastics Co., Ltd.;
Calcium carbonate whiskers: 0.5μm diameter and 10μm length, Shanghai Dianyang Industrial Co., Ltd;
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, colorless liquid, Nanjing Daoning Chemical Co., Ltd.

Please cite this article as: Guo H., 2018, Analysis on preparation and performance of pp/pp-g-mah/ccw/mwcnts chemical materials, Chemical Engineering Transactions, 71, 1099-1104 DOI:10.3303/CET1871184

2.2 Major equipment and instruments

Pendulum Impact Tester: ZBC7501-B, MTS Industrial Systems (China) Co., Ltd.;
Precision open mill: ZG-120, Dongguan Zhenggong Precision Testing Equipment Factory;
Box type resistance furnace: SX2-2.5-10, Shangyu Hunan Electric Furnace Oven Factory, Zhejiang;
Plastic pulverizer: SWP/l60, Jiaozhou Hongda Plastic Auxiliary Machinery Plant, Qingdao;
Flat vulcanizing machine: TP1400, Shanghai Wodi Technology Co., Ltd.;
Universal sample machine: ZHY-W, Hebei Chengde Experimental Machine Factory;
High-speed mixer: SHR-10A, Zhangjiagang City Spark Degradation Equipment Machinery Plant;
Electronic universal tester: CMT-4304, MST Industrial Systems (China) Co., Ltd.;
SEM: JEOL-2010, JEOL Ltd.

2.3 Sample preparation

Weigh 4g silane coupling agent KH560 and mix it with 980ml absolute ethanol for 40^{o}C water bath, stir it for 10min, and silane coupling agent / ethanol solution is available, then weigh 200g calcium carbonate whiskers, place it into the coupling agent / ethanol solution for water bath at 50 ° C, and remove it after 1.5 h, let it dry in an oven at 80 °C, and finally the modified calcium carbonate whisker from silane coupling agent KH560 is available (Zhang et al., 2016).
300 ml mixed acid is prepared by V (concentrated H2SO4): V (concentrated HNO3) =1:1, placed in a 3-necked flask, add 2g MCN and connect a reflux unit with it. Then, a 3-necked flask is placed on a heating device to treat it for 3h at 120 °C, filtrate it, wash it with deionized water to be neutral. Finally dry off it in a vacuum oven at 80 °C for 4h to obtain finished MCN (Duan et al., 2012).
The PP, PP-g-MAH and modified calcium carbonate whiskers are added to the high-speed mixer for a homogeneous mixing, and front and rear rolls of the twin-roll mill are set to 174^{o}C and 170^{o}C, respectively. After the mill reaches the preset temperature, according to the formula in Table 1 below, the evenly mixed PP, PP-g-MAH and modified calcium carbonate whiskers are added to have a blending in the mill for 5 min, and then the carbon nanotube is added for melting and kneading. After 3 min, the flaky materials are taken out from the mill, then pulverized in a pulverizer, placed into a mold. A press vulcanizer is used to crimp it into the plate (hot pressing conditions: the upper and lower plates are set to 180 °C, preheated and melted for 10 min, and hot pressed for 8 min, cold pressed for 10 min at 10 MPa). In the end, a universal sampling machine cuts the pressed plate into standard sample strips of the specified size for property testing.

Table 1: Components of composite materials

No.	PP	PP-g-MAH	CCW	MWCNTS	MWCNTS 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 is tested in accordance with GB/T 1843-2008; the tensile strength in accordance to the GB/T 1040.1-2006; the flexural strength in accordance with the GB/T9341-2008; SEM, the voltage is maintained at 20Kv, and the sample surface is gold-plated.

3. Results and discussion

3.1 Effect of carbon nanotubes on flexural strength of PP/calcium carbonate whisker composites for seats

As shown in Figure 1, the curve represents the effect of the dose of MCNs on the flexural strength of a PP composite for seats.
It is obvious that the flexural strength of the composite builds up as the dose of carbon nanotubes increases. When the mass fraction of carbon nanotubes is about 0.5%, the flexural strength of the composite reaches a maximum of 59.69 MPa, and then turns to weaken as the dose of carbon nanotubes continues to increase. A major reason for this is that, modified carbon nanotube will build up the bonding strength with the polymer substrate, and improve its dispersibility in the composite material; furthermore, the proper amount of calcium carbonate whiskers in the composite material uniformly disperse and interweave each other into a mesh structure, while the carbon nanotubes can play a bridging role, further improving the mesh structure, reducing the defects formed in the composite material due to anisotropy. In return, the network structure can improve

the energy transfer. When composite material is subjected to external stress, it can effectively transmit it to the whiskers and the carbon nanotubes. The carbon nanotubes have a higher mechanical strength thanks to the tubular structure, not easily deformed, thereby significantly improving the mechanical strength of the composite (Liu et al., 2007; Cheng et al., 2014; Wu et al., 2008; Wang et al., 211). Although the carbon nanotube is finished, as its dosage increases, the carbon nanotubes will agglomerate in the polymer substrate and weaken in the locale of agglomeration. When it is subjected to external forces, the composite material is first destroyed at the defects, thus reducing its flexural strength (Zhang et al., 2014; Luo, 2018).

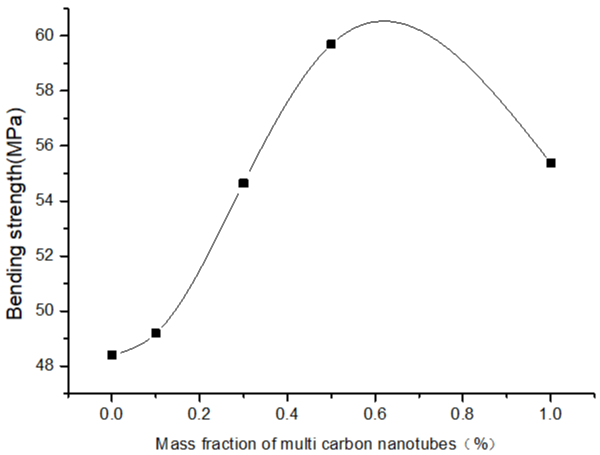


Figure 1: Flexural strength of composite under different content CNTS

3.2 Effect of carbon nanotubes on tensile strength of pp/calcium carbonate whisker composites for seats

As shown in Figure 2, a curve gives the change in the effect of the dose of MCNs on the tensile strength of PP composites.

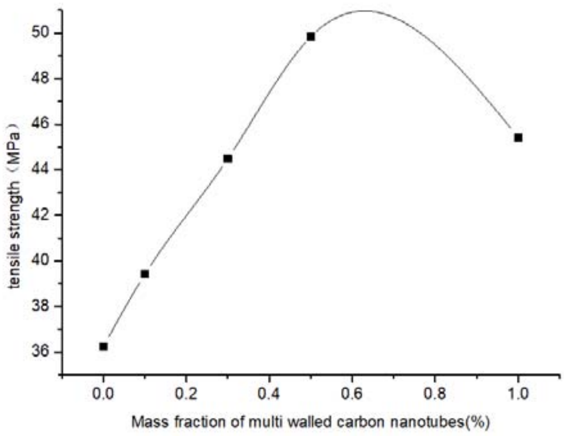


Figure 2: Tensile strength of composite under different content MWCNTS

It is clear that the tensile properties of PP composites are significantly improved by the addition of carbon nanotubes. When the mass fraction of carbon nanotubes is 0.5% or so, the tensile properties of PP composites reach a maximum of 49.84 MPa. It is likely that due to the modified carbon nanotubes, their dispersibility in the PP substrate is improved to further enhance the bearing capacity of the meshed-shaped skeleton of calcium carbonate whiskers in the composite material. They are also tightly wrapped by the PP substrate material, and well bonded with interface. When the composite is subjected to external stress, most of the fracture surface appears between the PP cladding layer and the substrate, so that the carbon nanotube can absorb a lot of energy, which suggests that it can further increase the rigidity of the PP composite material, and is conducive to improving non-deformability of composite material. Although the carbon nanotubes is finished, the surface activity is reduced. Due to its large specific area, its dispersibility decreases as its mass fraction increases, the agglomeration occurs, resulting in the stress concentration which succumbs to the relative displacement between the interfaces. In this way, the stress can not be effectively transmitted, so that the strength potential of the carbon nanotubes weakens, leading the tensile strength of the PP composite to a gradual decrease (Zhang et al., 2014; Yang, 2018).

3.3 Effect of carbon nanotubes on impact strength of PP/calcium carbonate whisker composites for seats

As shown in Figure 3, a curve shows the effect of the dose of MCN on the impact strength of PP composites.

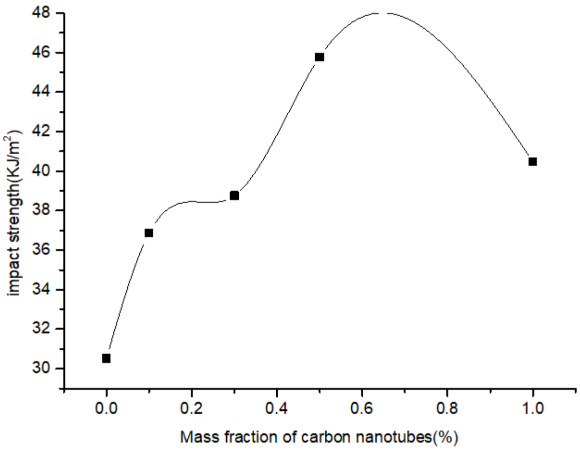
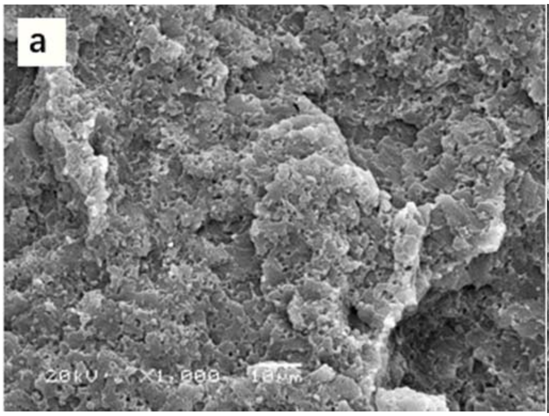


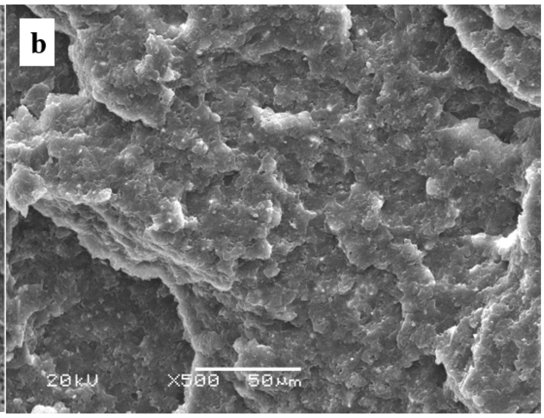
Figure 3: Impact strength of composite under different content MWCNTS

It is obvious that the impact strength of the composite material is significantly improved by doping with the finished carbon nanotubes. In relation to the PP/calcium carbonate whisker composite, the impact strength of the composite material increases from 30.52KJ/m^{2}to 45.78KJ/m^2 if doped with 0.5 % carbon nanotubes, up 44.78%. The reason is that the finished carbon nanotubes reduce the surface energy and disperse in the PP substrate more evenly; furthermore, the carbon nanotubes can act as crystal nuclei, remove the barrier from the PP crystal nucleation energy, thus improve the crystallization of the PP substrate. Due to the large mass of carbon nanotubes, the crystal particles stop to generate due to the easy collision with each other during the growth process. That is to say, they have effects of refining the particles, overcoming the stress concentration between the large crystal boundaries. Subjected to external impact, the stress more easily diffuses. In this case, carbon nanotube has a good toughening effect on the PP composite material. As the mass fraction of carbon nanotubes continues to increase, the agglomeration tends to occur, causing structural defects and stress cracks, which in turn leads the composite toughness to weakening (Zhang et al., 2014).

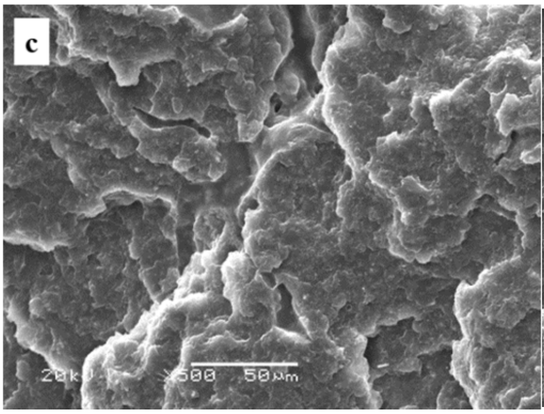
3.4 SEM analysis of Impact fracture of PP/PP-g-MAH/CCW/MWCNTS composite for seats

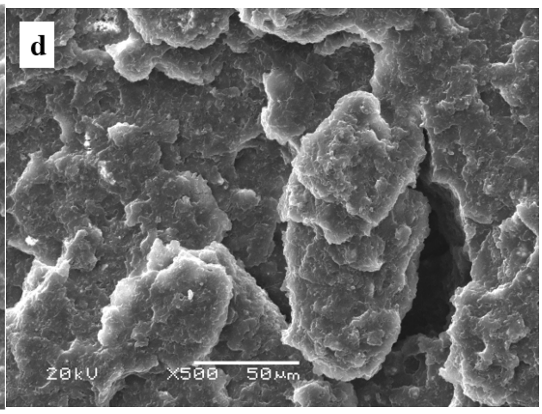
As shown in Figure 4, a SEM image is taken for impact fracture of the composite with different mass fractions of carbon nanotubes. As shown in Figure 4a, the calcium carbonate whiskers are wrapped by the polymer substrate and evenly dispersed to effectively transfer the stress. As shown in Figure 4b, 4c, 4d, and 4e, carbon nanotubes of different mass fractions are contained. The white dots in the figure are raised heads of carbon nanotubes wrapped by a PP substrate. When the mass fraction of carbon nanotubes is low, the larger distance between raised heads shows that the carbon nanotubes are evenly dispersed in the PP substrate. There is no sign of agglomeration. The fact that carbon nanotubes are uniformly dispersed in the substrate of the composite material and tightly cladding by it, and well bonded with each other between two interfaces shows that they play a certain toughening and strengthening effect on the composite material. When the mass fraction of carbon nanotubes is high, agglomeration occurs, as shown in Figure 4e. As composite material forms structural defects around the agglomeration, it is very easy to fracture from the defected structure when subjected to external stress, as coincided with the above test results (Wei et al., 2018).



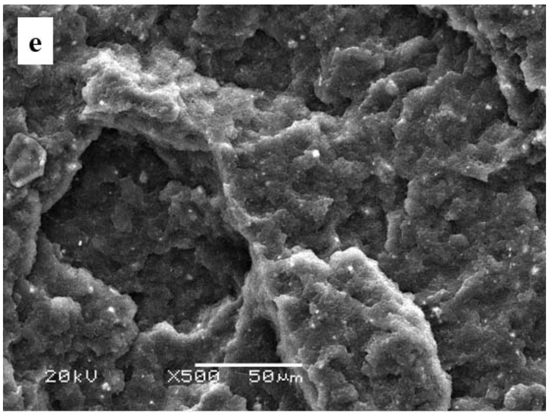


a. 0%   b. 0.1%





c. 0.3%   d. 0.5%



e. 1%

Figure 5: The SEM images of the cross-section of composite with different content of MWCNTS

4. Conclusion

(1) After the treatment with the mixed acid, the carbon nanotube has a good compatibility with the composite material, fully exerting the physicochemical properties, so that the mechanical properties of the PP/calcium carbonate whisker composite material for the seat are substantially improved.
(2) The carbon nanotubes with proper mass fraction have the toughening and strengthening effect on the PP/calcium carbonate whisker composite for the seat. However, the high mass fraction of the carbon nanotubes will lead to the agglomeration which contributes to the structural defects. The mechanical properties of the material are instead reduced.
(3) When the mass fraction of carbon nanotubes is 0.5% or so, the mechanical properties of PP/calcium carbonate whisker/carbon nanotube composites for seats perform the best.

Acknowledgments

The research project of the Henan Social Science Association (SKL-2017-2814)

References

Bledzki A., Heim H.P., Paßmann D., Ries A., 2012, Manufacturing of Self-Reinforced All-PP Composites, Synthetic Polymer–Polymer Composites, 719-738.

Cheng F.W., Jiang Q.B., Zhang Z.J., 2014, Potassium titanate whisker application in polymer composites, Engineering plastics applications, 42(12), 123-126.

Duan Z.W., Jie X.H., Zhang Y.M., 2012, Research on Acid Treatment of Multi-walled Carbon Nanotubes, Materials review, 26(8), 28-30.

Lian R.B., Xu M.Z., Li Q., Huang R., 2008, Study on Properties of Glass Fiber Reinforced Polypropylene Composite, Plastic science and technology, 36(8), 40-44.

Liu J., Xu W.C., Zeng G.R., 2007, Study on the graft modification of polypropylene, Packaging engineering, 28(9), 33-35.

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

Wang B.C., Zhou X., Yin J.S., 2011, Investigation on mechanical properties of carbon nanotubes hybrid epoxy/T700 composites, Journal of Solid Rocket Technology, 34(6), 789-793.

Wei F., Jiang B., Pan B., 2018, Frictional wear of potassium titanate whisker filled carbon fabric/epoxy composites, Chemical Engineering Transactions, 66, 115-120, DOI: 10.3303/CET1866020

Wu Y., Zheng A.J., Han F.Y., 2008, A new type of short fiber reinforced polymer composites, Journal of high polymer, 29(6), 46-47.

Xu Z.Z., Huang J.Q., Chen M.J., 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, DOI: 10.1016/j.polymdegradstab.2013.07.010

Yang M., 2018, Preparation and mechanical properties of polypropylene composite for seats, Chemical Engineering Transactions, 66, 133-138, DOI: 10.3303/CET1866023

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.Z., Fu Y.Q., Zhang Y.F., Han J., Lan R.C., 2014, Research Progress of Carbon Nanotubes Modification and Polypropylene/Carbon Nanotubes Composites, Shanghai Plastics, (4), 1-6.

Zhou J., Wang Y.Q., Meng H., 2005, Study on property of PP modified with potassium titanate whisker, Engineering plastics applications, 33(11), 21-24.