

Preparation and Mechanical Properties of Polypropylene Composite for Seats

Mingzhe Yang

Zhengzhou Institute of Science and Technology, Zhengzhou 450064, China
 litymz@hotmail.com

This paper describes the effects of the Multiwalled Carbon Nanotubes (MCNs) of different masses on the mechanical properties of polypropylene/calcium sulfate whisker composites for seats. With a twin roller open mill, a kind of composite PP-g-MAH/CSW/NWNTS may be made from surface-modified MCNs and modified calcium sulfate whiskers, polypropylene (PP), maleic anhydride grafted polypropylene (PP-g-MAH) using melt blending method, thereby to compare which effects the modified MCN of different doses plays on the mechanical properties of the PP/PP-g-MAH/CSW/NWNTS composites for sports seats. This study shows that the MCNs that have a mix-acid treatment on the surface uniformly disperse in the composite material, and well bond with the interface of the polymer matrix, thus playing a function for toughening and strengthening composite material. But worse, when the mass fraction of carbon nanotubes is higher, there is a phenomenon of agglomeration occurred, which in turn worsens the mechanical properties of the composite material. The carbon nanotubes at approx. 0.5% make the mechanical properties of the composite the best.

1. Introduction

Polypropylene as a universal thermoplastic polymer is polymerized from propylene monomer. It is commonly used as a material for sports stand seats because it features small density, easy machining, non-toxicity, good mechanical properties, fatigue resistance yield, stress cracking resistance, and recovery for reuse. However unfortunately, polypropylene has a stronger shrinkage, easy scoring on the surface, and quick aging, as well as a molecular chain containing a methyl group which will increase the rigidity of the whole molecular chain, thereby reducing its impact property, limiting its applications in special sports seats with high strength and wear resistance. In this sense, the modification of polypropylene is one of the hot topics in the field of current sports seats (Lian et al., 2008; Bledzki et al., 2012).

The Calcium Sulfate Whisker (CSW) is an acicular monocrystal fiber material developed in recent years. It has regular arranged atoms in the monocrystal, which almost fills the gaps of many polycrystalline materials. Thanks to its interface regularity, high draw ratio, high strength, fine structure, and high modulus, modified CSW can uniformly disperse in the polymer to serve as a skeleton support. Beyond that, this kind of modified CSW can form a polymer-whisker composite material by which the polymer will exhibit good mechanical properties (Yang et al., 2015; Sun et al., 2015). As a new material, MCNs have unique tubular structure that allows special properties physically and chemically, including high specific surface area and aspect ratio, improved mechanical strength, good thermal stability and thermal conductivity, as well as unallowable deformation under stress. If MCN acts as a modified material added to engineering plastics, it is expected to further improve the overall properties of engineering plastics with its excellent performance and expand the fields where the engineering plastics can be used.

Here, a kind of PP/PP-g-MAH/CSW/NWNTS composite for sports seats is prepared by adding MCNs to polypropylene/CSW composites, and what effects the MCNs play on the composites is also investigated. It is hoped that this study may be used as a reference for currently developing the high-performance sports seats and provide the clues to the application of sports seats.

2. Experiment

2.1 Raw materials

Polypropylene: K8003, Dushanzi Petrochemical Co., Ltd;

Maleic anhydride grafted polypropylene: KH PP-GMAH 01, HKH National Engineering Research Center of Plastics Co., Ltd;

Calcium sulphate whisker: white flocculent powder, whiteness: 90% or more, fineness: ≤ 80 mesh, density: 2.69 g/cm^3 , diameter: $1\text{-}4\ \mu\text{m}$, Mohs hardness: 2-4, Shanghai Fengzhu New Material Technology Co., Ltd.

Multiwalled carbon nanotubes: ID: 5-10 nm, OD: 10-20 nm, length: 10-30 nm, Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences;

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

2.2 Major equipment

Pendulum Impact Tester: ZBC7501-B, MTS Systems (China) Corporation;

Precision open mill: ZG-120, Dongguan Zhenggong Precision Testing Instrument Factory;

Box-type resistance furnace: SX2-2.5-10, Shangyu City, Zhejiang Province, Hu Nan Electric Oven Factory;

Plastic pulverizer: SWP/l60, Qingdao JiaozhouHongda Plastic Auxiliary Machinery Plant;

Flat vulcanizer: TP1400, Shanghai Wodi Technology Co., Ltd.;

Universal sampling machine: ZHY-W, Hebei Chengde Experimental Machine Plant;

High-speed mixer: SHR-10A, Zhangjiagang Spark Degradation Equipment Factory;

Electronic universal tester: CMT-4304, MTS Systems (China) Corporation;

SEM: JEOL-2010, JEOL Ltd.

2.3 Sample preparation

Weigh 4g silane coupling agent KH550, place it in 980ml anhydrous ethanol, heat it up by water bath at 50°C , and stir them for 15min, the silane coupling agent / ethanol solution is then prepared. Then weigh 200gCSW, place it in a coupling agent / ethanol solution, heat it up by water bath at 60°C , and stir them at 60°C for 2h. In the end, it is dried in an oven at $84\ 84^\circ\text{C}$ to obtain a CSW modified with a silane coupling agent KH550 (Zhang et al., 2016).

300 ml mix-acid is prepared at a ratio of $V(\text{conc. H}_2\text{SO}_4): V(\text{conc. HNO}_3)=1:1$. Place it in a three-necked flask, then add 2g to the MCNs connected with a reflux device. The three-necked flask is placed in a heating device and treated at 120°C for 3h, then filtered, washed with deionized water until it turns into the neutral. Eventually, it is dried in a vacuum oven at 80°C for 4h to prepare surface-treated MCNs (Duan et al., 2012).

Polypropylene, maleic anhydride grafted polypropylene and modified CSW are added into a high-speed mixer to mix with each other uniformly. Now the front and rear rollers of the twin roller open mill are set to 173°C and 170°C , respectively. After the temperature of the open mill reaches the preset temperature, according to the formula in the following Table 1, the uniform mixture of the above three is added to an open mill for mixing. After 6 min, the MCNs are then placed in the open mill for melting and mixing. After 4 min, take out the sheet from the open mill, crush them in a pulverizer. The crushed material is placed in a mold and pressed into a plate using a flat vulcanizer (hot press conditions: 175°C on the upper and lower plates, 12 min preheating, 9 min hot pressing, 12 min cold pressing, 12 MPa pressure). At last, a universal sampling machine is used to cut the pressed plate into a standard sample strips of the specified size for performance test.

Table 1: Mass ratio of composites

Number	PP	PP-g-MAH	CSW	NWNTS	NWNTS 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 Test and characterization

Impact strength is tested in accordance with the GB/T 1843-2008; tensile strength in accordance with the GB/T 1040.1-2006; bending strength in accordance with GB/T9341-2008; SEM, the voltage is maintained at 20Kv, the sample surface is plated with gold.

3. Results and discussion

3.1 Effect of MCNs on flexural strength of PP/PP-g-MAH/CSW/NWNTS composites for sports seats

Figure 1 shows a curve of the flexural strength of polypropylene composites for sports seating as a function of mass fraction of MCNs. It is obvious that the flexural strength of composites beefs up as MCNs increase. When the mass fraction of MCNs is 0.5% or so, the flexural strength of composites reaches the peak of 60.57MPa, then lets up as the mass of MCNs continues to increase since the modified MCNs improves its bonding strength with the polymer matrix and the dispersibility in the composites; besides, a moderate CSWs in the composite material must uniformly disperse therein and interweave into a network structure by virtue of bridging effect as it has. In this way, some defects that the polymer has in the composite material due to anisotropy are eliminated. A perfect network structure can also advance the energy transfer. When external stress is applied to the composite material, it can be effectively transferred to the whiskers and carbon nanotubes. With tubular structure, the carbon nanotubes have a high mechanical strength since they are not subjected to the stress (Liu et al., 2007; Li et al., 2016; Wang et al., 2011). Although the carbon nanotubes are finished, the carbon nanotubes agglomerate in the polymer matrix as their mass fraction thereof gradually increases. There are also defects appeared at the agglomeration. When they are subjected to the external stress, the composite material is first destroyed at the defect, thus worsening the bending strength of composites (Zhang et al., 2014).

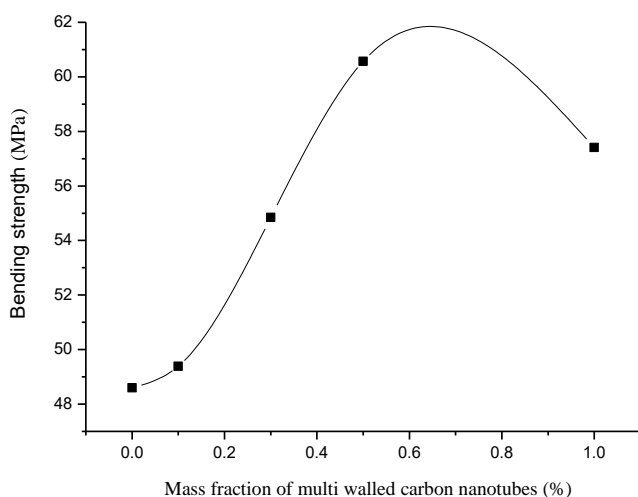


Figure 1: Flexural strength of composite under different content NWNTS

3.2 Effect of MCNs on tensile strength of PP/PP-g-MAH/CSW/NWNTS composites for sports seats

Figure 2 is a curve of the tensile strength of PP/PP-g-MAH/CSW/NWNTS composites for sports seats as a function of mass fraction of MCNs. It is obvious that the tensile property of polypropylene composites for sports seats is significantly improved by the added MCNs. When the mass fraction of MCNs is 0.5% or so, the tensile strength of propylene composite reaches a maximum of 50.84 MPa for the following reasons: the modified carbon nanotubes improve their dispersion in the polypropylene matrix, further increase the network skeleton support capacity of CSWs in the composite material; it is also tightly clad by the polypropylene matrix; the interface is well bound. When the composite material is subjected to external stress, most fractures appears between the polypropylene cladding and the substrate, so that the carbon nanotubes can absorb a huge mass of energy, which suggests that the carbon nanotubes can further boost the toughness of the polypropylene composite for sports seats and is conducive to improve the deformation resistance of composites (Yu et al., 2003). Although the carbon nanotubes are finished and the surface activity somewhat lessens, the specific surface area is substantial. As their mass fraction increases, their dispersion gets worse. Agglomeration also occurs, resulting in stress concentration, relative displacement on the interface between the two. Hence, the stress cannot be effectively transferred, weakening the exertion of the potential strength of carbon nanotubes, so that the tensile strength of polypropylene composites for sports seating gradually lets up (Zhang et al., 2014).

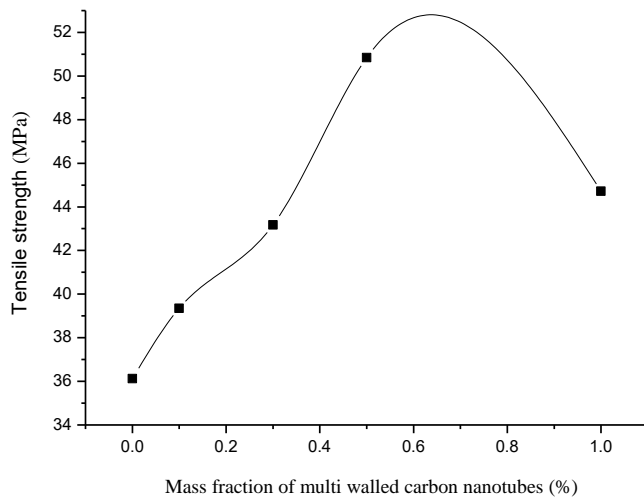


Figure 2: Tensile strength of composite under different content NWNTS

3.3 Effect of MCNs on impact strength of PP/PP-g-MAH/CSW/NWNTS composites for sports seats

Figure 3 is a curve of the impact strength of PP/PP-g-MAH/CSW/NWNTS composites for sports seats as a function of mass fraction of MCNs. As shown above, the impact strength of the composite material is significantly improved by adding the surface-treated carbon nanotubes. As compared to PP/PP-g-MAH/CSW composites, about 0.5% carbon nanotubes as added will boost the impact strength of the composites from 30.5KJ/m² to 45.56KJ/m², up by 49.4%, since carbon nanotubes treated with mixed acid reduce their surface energy and improve their dispersibility in the polypropylene matrix. Moreover, they can act as crystal nuclei, lowering the rampart against PP's crystallization into nucleation energy, and increasing the crystallinity of the matrix. As there are the bulk of carbon nanotubes, the crystal grains in the growth process are easily encountered by each other to stop generation, so it has a grain refinement effect, overcomes the stress concentration between many grain interfaces. When subject to external impacts, the stress is more easily dispersed. It is suggested that carbon nanotubes have a good toughening effect on polypropylene composites (Li et al., 2012; Zhou and Liang, 2015). As the mass fraction of carbon nanotubes gradually builds up, agglomeration occurs, resulting in structural defects and the formation of stress cracking points, which in turn leads to reduced toughness of the composite (Zhang et al., 2014).

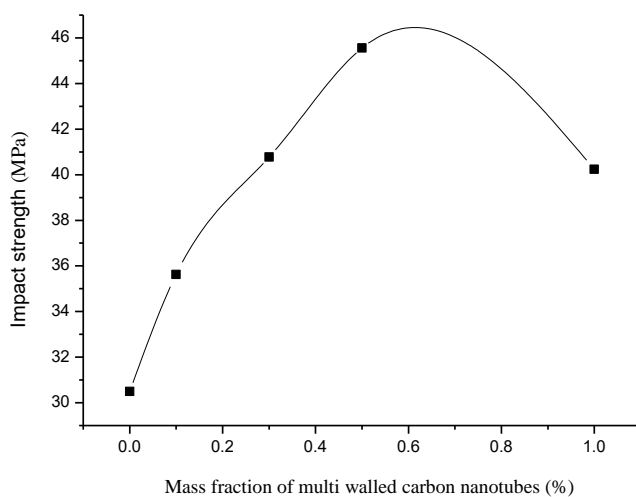


Figure 3: Impact strength of composite under different content NWNTS

3.4 SEM analysis of impact section of PP/PP-g-MAH/CSW/NWNTS composites for sports seats

As shown in Figure 4, the SEM image is taken for impact section of PP/g-MAH/CSW/NWNTS composite used for sports seats as a function of MCN's mass fractions. It can be seen that the CSWs are wrapped by the polymer matrix and can uniformly disperse and effectively transmit stress. In Figures 4(b), 4(c), 4(d), and 4(e), there are carbon nanotubes of different mass fractions. The white dots in the figures are carbon nanotube bosses surrounded by a polypropylene matrix. When the mass fraction of carbon nanotubes is low, the distance between the bosses is wide. It is suggested that the carbon nanotubes uniformly disperse in and tightly wrapped by the polypropylene matrix, no agglomeration occurred. Both are well-bonded, which suggests that the carbon nanotubes play a certain role in strengthening and strengthening the composite material. When the mass fraction of carbon nanotubes gets higher, the phenomenon of agglomeration appears, as is evident in Figure 4(e). The composite material forms a structural defect at the agglomeration and easily ruptures resulting from the defect when it is subjected to external stress. This coincides with the above test results.

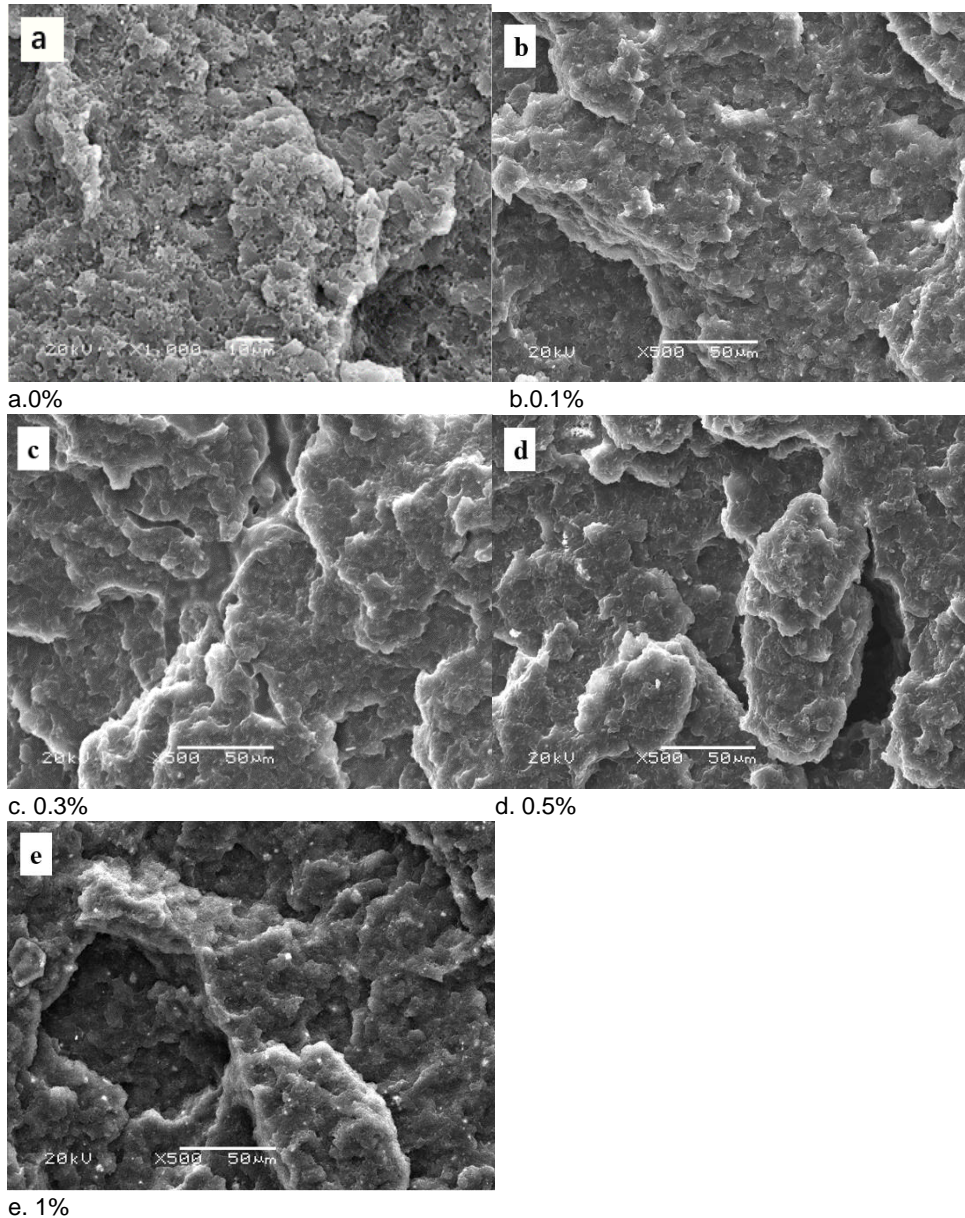


Figure 4: The SEM images of the cross-section of composite with different content of NWNTS

4. Conclusions

(1) Carbon nanotubes have a good compatibility with composites after mixed acid treatment, fully exert their own good physical and chemical properties, and significantly improve the mechanical properties of PP/PP-g-MAH/CSW composites.

(2) A proper mass fraction of carbon nanotubes can improve the toughness and strength of PP/PP-g-MAH/CSW composites. Unfortunately, when the mass fraction of carbon nanotubes gets higher, a phenomenon of agglomeration occurs, resulting in structural defects that worsen the mechanical properties of the material instead.

(3) When the mass fraction of carbon nanotubes is approximate 0.5%, the mechanical properties of PP/PP-g-MAH/CSW/NWNTS composites for sports seats present the best.

Acknowledgments

This work is supported by Project of scientific and technological breakthrough in Henan (182102311103).

References

- Bledzki A., Heim H.P., Paßmann D., Rise A., 2012, Manufacturing of Self-Reinforced All-PP Composites, Synthetic Polymer-Polymer Composites, 719-738, <https://doi.org/10.3139/9781569905258.022>
- 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.
- Li S.Y., Yan D.G., Wang J.L., 2012, Preparation and Study on Carbon Nanotubes/Polypropylene Composite Materials, GuangZhou Chemical Industry and Technology, 40(19), 43-44.
- Li Y., Yuan S., Zhang Q., Wen J., Yin L., 2016, Study on Preparation and Properties of Modified Calcium Sulfate Whisker Filled PP/EPDM Composite, plastics technology, 44(1), 35-38.
- Lian R., 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.
- Sun X., Fei D.J., Liu X.F., Ren J., Gu Z.C., Zhang A.M., Wu J.X., 2015, The effect of calcium sulphate whisker on the properties of EPDM/PP thermoplastic elastomer, plastics industry, 43(5), 102-105.
- 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.
- Yang X.L., Yu L., Zhang X.C., Li L.X., Qin W., 2015, Mechanical properties and thermal stability of PBS filled with calcium sulfate whisker, plastic, 44(02), 48-51.
- Yu Y., Jia Z.J., Zeng Y., Zhang P., 2003, Study on Reinforced Mechanism of Carbon Nanotubes on PA6 Composites, Polymer Materials Science and Engineering, 19(3), 198-200.
- 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., Han J., Lan R., 2014, Research Progress of Carbon Nanotubes Modification and Polypropylene/Carbon Nanotubes Composites, Shanghai Plastics, (4), 1-6.
- 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, 43(11), 81-84.