Journal of Applied Science and Engineering Innovation, Vol.8, No.1, 2021, pp. 8-12
ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

The Effect of Carbon Nanotubes on the Structure and Properties of Natural Rubber Composites

Zhenxu Li, Lining Song, Lina Yang, Jie Zhao, Ning Wang, Zheng Gu*, Peiyao Li, Li Wang

Qingdao University, 266071 , China

Abstract: Natural rubber (NR) is widely used in military industry, aerospace industry, medical equipment and other fields. Carbon nanotubes (CNTs) were selected as nano fillers and NR / CNTs nanocomposites were prepared by mechanical mixing method. Based on the relationship between structure and properties, the effects of CNTs addition on the micro properties, vulcanization properties, mechanical properties, wear resistance and solvent resistance of the nanocomposites were investigated by means of mechanical property test, transmission electron microscopy (TEM), thermogravimetric analysis (TG), dynamic mechanical property test (DMA). The results showed that: TEM observation showed that CNTs dispersed uniformly in NR matrix, and the two phases had good compatibility; with the increase of CNTs content, the mechanical properties and solvent resistance of the nanocomposites increased significantly TG analysis showed that the nanocomposites had excellent thermal stability, and the comprehensive properties showed that the optimal amount of CNTs was 3 phr.

Keywords Carbon nanotubes; Natural rubber; Styrene butadiene rubber; Mechanical mixing; Nanocomposites.

INTRODUCTION

Natural rubber (NR) is a widely used renewable biological resource. It has the characteristics of high production capacity, low cost, excellent strength,high flexibility and abrasion resistance[Li et al.,2020].It is widely and important in the military industry, aerospace, medical equipment and other fields, so NR has a huge effect on national economic construction that cannot be ignored. However,NR also has obvious shortcomings in some aspects, for example,its mechanical properties are relatively poor,At the same time, it is easy to be affected by external conditions and cause it to lose its function.[Zhang et al.,2017;Lv et al.,2010;Peng et al.,2014].Studies have shown that mixing nano-fillers uniformly into NR can simultaneously realize the functionalization of polymers and improve the mechanical properties of NR.Therefore, NR nanocomposites are one of the most active research fields in materials science[Luo et al.,2014].Among the many inorganic Nano fillers, carbon nanotubes (CNTs) have excellent potential value [Wen et al.,2013].CNTs are composed of concentric cylinders formed by crimping a single-layer or multilayer graphite sheet structure. They have the advantages of high aspect ratio, low density, excellent mechanical properties, heat resistance and thermal conductivity. Therefore, CNTs are used to fill NR to improve Its mechanical properties have broad prospects [Zhu et al.,2016; PATOlE et al.,2012;Peng et al.,2018]. L. X. Li et.al [Li et al.,2019] studied the effects of multi-walled carbon nanotubes and graphene on the mechanical properties of natural rubber. The study showed that both graphene and multi-walled carbon nanotubes can improve the performance of composite materials, However, there is a problem that multi-walled carbon nanotubes do not improve the mechanical properties of composite materials .J. P. Song et.al [Song et al.,2019] studied the effect of the ratio of carbon black/carbon nanotubes on the physical and thermal conductivity of natural rubber composites by using the combined method of carbon black/carbon nanotubes. The study showed that the combined ratio of carbon black/carbon nanotubes was 28/7 that we have Optimal performance. This method gives full play to the role of CNTs filler, but it has strict process requirements and is not conducive to industrial production.

At present, the preparation methods of CNTs/NR composites mainly include mechanical blending, solution blending, emulsion blending and in-situ polymerization [Wang et al.,2015].The solution blending method can reduce molecular agglomeration, which is beneficial for CNTs in the NR matrix. Medium dispersion, but a variety of organic solvents are used during preparation, which is easy to cause pollution; emulsion blending can improve the dispersion of CNTs, but cannot change its agglomeration in the NR matrix; in-situ polymerization can make CNTs fully dispersed In the NR matrix, but the added filler will increase the viscosity of the polymer and complicate the polymerization reaction; the mechanical blending method can not only make the CNTs uniformly dispersed, but also save costs while reducing pollution [Jia et al.,2019;Chou et al.,2019]. Therefore, in this experiment, the mechanical blending method was used to prepare CNTs/NR nanocomposites without changing the process. At the same time, the related mechanism research of CNTs/NR nanocomposites was carried out on this basis.

Corresponding Author: Zheng Gu, Qingdao University, No.308 Ningxia Road, Qingdao, 266071, China

MATERIALS AND METHODS

Materials and experimental formula

NR, No. 1 standard rubber, Hainan; CNTs, GT-304, Shandong Zouping Dazhan New Material Co., Ltd.; ZnO, SA, 4010NA, CZ, DM, and S are all commercially available.

Formula: NR 100 phr, SA 2 phr, ZnO 4 phr, CZ 0.7 phr, 4010NA 1 phr, S 1.5 phr, and the mass parts of CNTs are variable: 0 phr, 1 phr, 2 phr, 3 phr, 4 phr.

Rubber compound preparation process

Add NR on the double-roll mill. After the NR is completely wrapped, add ZnO, SA, CZ, 4010NA, CNTs and mix in sequence. After 10 minutes of milling, add S. After the filler is evenly dispersed, extruded from a two-roll mill, Cut a part of the obtained material to vulcanize in a flat vulcanizer according to the vulcanization curve, and the vulcanization condition is 145℃*T90.

Rubber compound test standards and methods

1) TEM test

The rubber compound was vulcanized and embedded in epoxy resin and ultra-thin sectioned. The sections were placed under a transmission electron microscope (JEM-2000EX, Japan JEOL) to scan high-magnification images and low-magnification images respectively.

2) Mechanical performance test

Use an electronic tensile testing machine (Model DXLL/50000, Shanghai Dejie Instrument Equipment Co., Ltd.) to test the tensile properties of the samples according to GB/T528/1998, and test the tear properties of the samples according to GB530/1981. The stretching speed is controlled at 500mm/min.

3) Wear resistance test

Use a roller abrasion machine (DIN/40 type, Yangzhou Xinhong Testing Machine Factory) to test the wear resistance of the vulcanizate according to GB-9867-2008.

4) Determination of solvent resistance

Measured according to GB/T1690-92, the temperature is 27±2℃, and the gasoline immersion period is 4±0.5h.

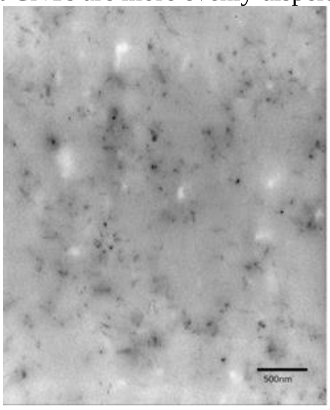
5) TGA test

A thermogravimetric analyzer (TGA/STDA851, Mettler/Toledo) was used to determine the performance change of the rubber compound. The heating rate was controlled at 10℃/min, and the test temperature was maintained at 25-700℃ in an air atmosphere.

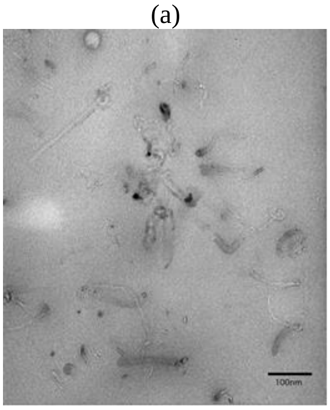
RESULTS AND DISCUSSION

TEM analysis of NR/CNTs nanocomposites

Fig. 1 shows the TEM photos of NR / CNTs nanocomposites with 3 phr of CNTs, in which figure (a) is a high magnification image, and figure (b) is a low magnification image. In the figure, the black dot linear substance is CNTs, and the white structure is NR matrix. It can be seen from figure (a) that the interface between CNTs and NR matrix is fuzzy, indicating that the two phases have good compatibility. From figure (b), it can be found that CNTs exist in all positions in NR matrix, which indicates that CNTs are more evenly dispersed.



(a)



(b)

Fig. 1 TEM photo of NR/CNTs nanocomposite when the amount of CNTs added is 3 phr

Mechanical properties of NR / CNTs Nanocomposites

Table 1 shows the mechanical properties of NR / CNTs nanocomposites. It can be seen from table 1 that the tear strength, tensile strength and elongation stress of the composites increase significantly with the increase of CNTs content. The constant elongation stress is the ability of the material to resist external forces under certain deformation, which mainly indicates the strength of the rubber macromolecular chain limited by the filler, so the filler has a stronger restrictive effect on the rubber macromolecular chain, indicating that the greater the fixed elongation stress of the filler [Tan et al.,2006]. Fig. 2 shows the comparison of stress-strain curves of nanocomposites containing 3 phr of CNTs and pure NR. it can be seen from the figure that after adding CNTs, the stress-strain curve of nanocomposites changes significantly, and the tensile strength is higher than that of pure NR. As the strain increases, the rate of stress increase increases significantly, and the tensile modulus also increases significantly. It can also be seen from the figure that the stress of NR/CNTs nanocomposites increases rapidly when the strain is about 400%, while the pure NR system shows a significant increase at about 500%.

Table 1. Various mechanical properties of NR/CNTs nanocomposites

Content (phr)	300% fixed elongation stress (MPa)	500% fixed elongation stress (MPa)	Tensile Strength (MPa)	Tear strength (KN/m)	Elongation at break (%)
0	2.43	8.77	18.92	33.54	629
1	2.92	10.55	21.32	37.72	614
2	3.94	13.31	22.72	44.32	588
3	4.64	14.90	23.03	46.25	572
4	6.26	18.60	24.38	48.50	554

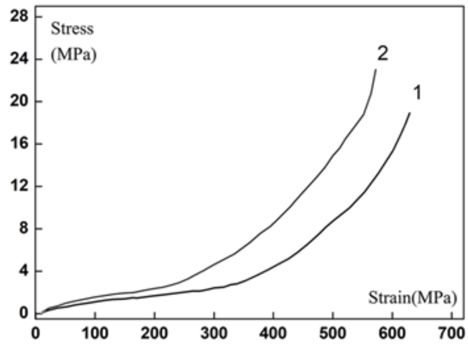


Fig. 2 The stress-strain curve of nanocomposites when the amount of CNTs added is 0 phr and 3phr

According to the chart, the tensile strength of NR / CNTs nanocomposites increases with the increase of CNTs content. When the content of CNTs is 4 phr, the tensile strength of the composite increases by 28.9% compared with pure NR, which indicates that the effect of CNTs filling and reinforcing rubber is very excellent; at the same time, the tear strength of the composite also increases with the increase of CNTs content, Compared with pure NR, the tear strength of the composites increased by 44.6%. The results show that When the addition amount of CNTs increases, the affinity between the NR matrix and CNTs increases, and the probability of CNTs and NR macromolecular chains compounding increases. At the same time, they are evenly distributed in the rubber matrix after mixing to limit the stretching, movement and crystallization of the rubber macromolecular chains, thereby Improve the overall tear strength and tensile strength of the nanocomposite.

Fig.3 shows the abrasion volume data of NR/CNTs nanocomposites. It can be seen from Figure 3 that as the content of CNTs increases, the wear volume of the nanocomposite shows a decreasing trend. When the amount of CNTs added is 3 phr, the abrasion volume of the composite material is reduced by 17.3% compared with pure NR, It shows that the wear resistance of composite materials is greatly improved, and the service life of the prepared rubber products is prolonged. Analysis believes that increasing the amount of CNTs added will have a better affinity for CNTs and NR macromolecules, and CNTs are easier to compound with NR macromolecular chains. The composite copolymer greatly restricts the rubber macromolecular chain, so the wear resistance of nanocomposites is greatly improved.

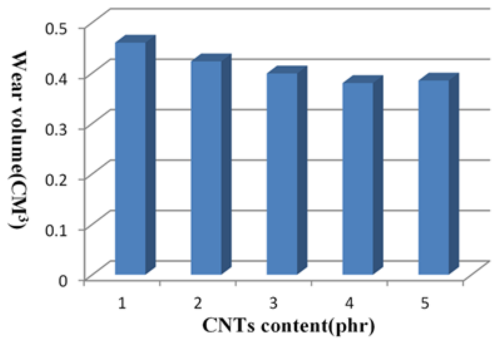


Fig.3 Wear resistance of NR/CNTs nanocomposites

Solvent resistance of NR/CNTs nanocomposites

Fig.4 shows the swelling index data of NR/CNTs nanocomposites. It can be seen from the figure that the swelling index of NR/CNTs nanocomposites decreases with the increase of CNTs content. When the amount of CNTs added is 3 parts, the swelling index is reduced to 2.30 relative to 2.98 of pure NR. When the CNTs content is 4 parts, the swelling equilibrium is reached. Because CNTs have a high display energy and aspect ratio, they have a strong restrictive effect on the NR macromolecular chain, which restricts the entry of solvent molecules, so the NR/CNTs nanocomposite has excellent solvent resistance.

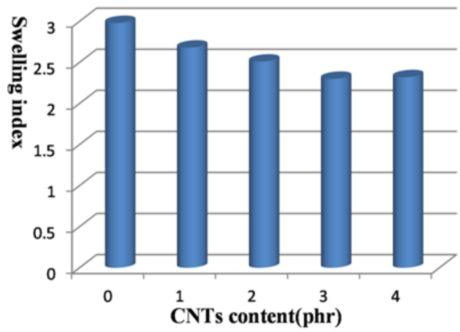


Fig.4 Solvent resistance of NR/CNTs nanocomposites (room temperature×4h, gasoline)

DMA analysis of NR/CNTs nanocomposites

Figure 5 shows the trend of the loss factor of NR/CNTs nanocomposites with temperature. It can be seen from Figure 5 that when the glass transition temperature is reached, the internal friction of pure NR is significantly higher than that of NR/CNTs nanocomposites. The analysis suggests that the dispersed phase of CNTs in the NR matrix has a larger specific surface area and deformation coefficient when it is near the glass transition temperature, which restricts the rubber macromolecular chain. Therefore, although the thermal movement ability of the rubber macromolecule is strengthened, it is still Not enough to support its movement; the loss coefficient of the composite material is similar to pure NR at 0 ℃, and slightly lower than pure NR at about 60 ℃, indicating that the rolling resistance of NR/CNTs nanocomposites is slightly reduced while the wet skid resistance no change.

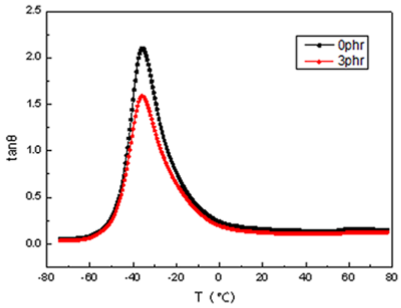


Fig.5 Comparison of loss coefficients of NR/CNTs nanocomposites

TG analysis of NR/CNTs nanocomposite

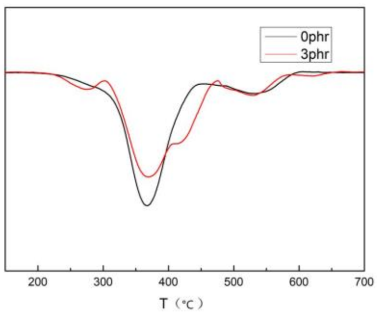


Fig. 6 Thermal weight loss of nanocomposites

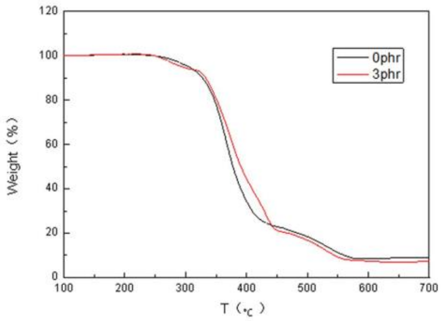


Fig.7 Differential graph of thermal weight loss curve of nanocomposite

Figure 6 is the thermal weight loss curve when the CNTs is added at 0 parts and 3 parts, and Figure 7 is the differential diagram of Figure 6. It can be seen from the two figures that the initial degradation temperature difference between nanocomposites and pure NR is not large. The maximum thermal degradation rate temperature of composite materials increases from 368 ℃ of pure NR to 373 ℃ when the amount of CNTs added is 3 parts, indicating that NR/CNTs Nanocomposite materials have more excellent thermal stability.The analysis believes that NR/CNTs nanocomposites produce small molecules during high temperature decomposition, and CNTs limit the small molecules produced during thermal decomposition of the material. At the same time, CNTs can form a barrier layer with good airtightness and effectively prevent O2 from entering the reaction. NR/CNTs nanocomposite has excellent thermal stability.

CONCLUSION

1) After adding CNTs, CNTs are uniformly dispersed in the NR matrix, and the two phases have good compatibility;

2) With the increase of the amount of CNTs added, the tensile stress, tear strength and tensile strength of the nanocomposite all increase; With the addition of CNTs, composite copolymers greatly restrict the NR macromolecular chain, and the wear resistance of nanocomposites increases.

3) The addition of CNTs significantly enhances the solvent resistance of NR/CNTs nanocomposites; CNTs can limit the small molecules generated during thermal decomposition of the material, and at the same time can form a good barrier layer, so NR/CNTs nanocomposites have excellent Thermal stability.

4) When the amount of CNTs added is 3phr, the overall performance of the nanocomposite is the best

ACKNOWLEDGMENT

Thank the helpful comments and suggestions from my teachers and colleagues in intelligent detection and control lab of HIT at Weihai. And also thank Beijing Up-tech to provide part hardware .This work is supported by the study fund of HIT at Weihai (No.IMVQ02020003 and IMJQ21080002).

REFERENCES

Jia Chengyun,Zhou Xincong,Wang Chao,Kuang Fuming, 2019, “Study on friction and wear properties of nitrile butadiene rabber/multi-walled carbon nanotube bearing materials”, China ShiprepairVol.32,No.5,pp.37-41.

Li Lixia,Ren Jinzhong,Qi Shuangchun,Li Wenjuan,2020, “Thermal degration kinetics of GE/NR and MWCNT/NR composites”, New Chemical Materials, vol.48,No.2, pp 136-139.

Li Lixia,Ren Jinzhong,Zhao Xiaoya,2019, “Study on Mechanical Properties of Natural Rubber by Multiwall Carbon Nanotubes and Graphene”, Shandong Chemical, Vol.48,No.21,pp.9-10+14.

Luo Yongyue,Zhao Pengfei,Lv Zhen, 2014, “Study of the microstructure and properties of graphene / natural rubber composites”, Chemical Research and Application , vol.26, No.12, pp 1898-1903.

Lv Mingzhe,Zeng Zongqiang,Li Puwang,Huang Maofang, 2010, “Thermal Degradation of the Nano-SiO2/ Natural Rubber Compound”, Chinese Journal Of Tropical Agriculture, vol.30, No.11, pp 1-4.

Patole A S,Patole S P,Jung S, 2012, “Self—assem—bledgraphene/carbon nanotube/poIystyrene hybrid nano—composite by in situ microemulsion polymerization”, European Polymer Journal, vol.48, No.2,pp.252—259.

Peng Zheng,Zhong Jieping, Liao Shuangquan, 2014, “Development of Modification of Natural Rubber”, Polymer Bulletin, China, No.5, pp 41-48.

Peng Wenli,Zhang Xuewen, Huang Anping,Gao Lin, 2018, “Research progress of polypropylene/carbon nanotubes composites” Chemical Industry and Engineering Progress, Vol.37,No.12,pp.4735-4743.

Qiu Liu,Ding Guoxin, 2019, “Graphene oxide modification and its application in rubber”, Applied Chemical Industry, Vol.48,No.8,pp.1970-1973+1984.

Song Junping,Tian Kaiyan, Li Xiteng,Wang Yiwen, 2019, “Effect of Carbon Black/Carbon Nanotubes Blend Ratio on Physical Properties and Thermal Conductivity of NR Composites”,China Rubber Industry,vol.66,No.6,pp.430-434.

TanYingjie,Liang Yurong ,Zhang Liqun,2006, “Structure and properties of OMMT/NBR nano-composites”, China Rubber Industry, Vol.53,No.7,pp.393-396.

Wang Feng,Zheng Jucheng,Yang Qibo, 2015, “Research progress in carbon nanotube/rubber composites”, China Elastomerics, vol.25,No.6,pp82-85.

Wen B, Cao M S, Hou Z L, 2013, “Temperature dependent microwave attenuation behavior for carbon—nanotube/siIica composites”, Carbon, vol.65, pp 124-139.

Zhang Tao,Yan Xiangjie,Wang Linyan,Liang Yurong, 2017, “Structure of graphene oxide/NR nanocomposite and its performance research”, New Chemical Materials, vol.45, No.12, pp 49-52.

Zhu Changcai,Yang Kun,Zhang Tingting,ZhangPing,Zhao Shugao,2016, “Mechanism of carbon nanotube reinforced natural rubber”, China Elastomerics, vol.26,No 6,pp 1-6.