Book Chapter

Thermal Analysis of MWCNTs / NR Polymer Composite Aligned in a Magnetic Field

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Abstract

We got the aligned carbon tube in the rubber matrix through coated Fe_3O_4 on the carbon tube. TEM shows Fe_3O_4 are symmetrically coated on the outer surface of MWCNTs. Diffraction peaks corresponding to Fe_3O_4 cubic crystal also appeared in the X-ray diffraction spectra. Thermal conductivity of composites increases by filling the appropriate modification of carbon tube. The magnetic field is larger, the direction time is longer, the thermal conductivity of composites is greater.

Introduction

Carbon nanotubes (CNTs), a kind of typical one-dimensional nano carbon materials with a seamless nano tube structure curled up by a single layer or multi-layer graphite flake, show a variety of excellent properties such as electrical, thermal, mechanical and optical properties and so on, have attracted much attention due to their outstanding properties and significant potential application in many fields since Iijima's observations in 1991 [1]. CNTs has becoming a focus and leading edge in the study of the scientific and industry since Ajayan [2] used the carbon nanotubes for reinforcing polymer composite. Therefore, the domestic and foreign scholars have conducted a lot of research and exploration, and have achieved gratifying results. However, these studies mainly focused on the resin, plastic and other composite materials. The research of carbon nanotubes reinforced rubber composite was lately, and mainly focus on mechanics, thermal stability, conductive and electromagnetic work. The research on the performance of thermal conductivity of carbon nanotube filled rubber was even limited.

Rubber is a typical viscoelastic polymer. Its thermal conductivity is very small (about 0.2 W/(m·K)) because of the existence of phonon scattering caused by the lattice defects and its chain segment not free movement. However, CNTs make heat transfer come true mainly via the vibration of the phonon. So CNTs own a higher thermal conductivity, as the related articles showed that the theoretical value of thermal conductivity of carbon nanotube is as high as 6600 W/(m·K) [3], and the experimental value can also achieve 3000 W/(m·K)[4]. Research on thermal conductivity of rubber filled with carbon nanotube has also made some achievements in recent years [5-6]. But our team [7] found that although carbon nanotube owned a higher thermal conductivity itself, its ability of improving the rubber's heat conduction was far beyond the reach of its thermal conductivity. The reason mainly is that the thermal properties of carbon nanotube based composite material are very closely related to the distribution, structure characteristics of carbon nanotubes in the composite material, microscopic state and the rule of heat transfer [8-12].

The influence of orientation distribution and different existing state on thermal conductive network chain structure formation is very great, for carbon nanotubes, a special thermal conductive materials, have the particularity one dimensional structure, compared with the other thermal conductive filler, which is bound to bring a greater impact on the performance of thermal conductivity of the composite. Marconnet [13] found that filled with 17% orient carbon nanotubes, thermal conductivity of epoxy resin composites increased by 18%. Park [14] found that making carbon nanotubes in epoxy resin orientation arrangement by mechanical method, thermal conductivity composites rised up to 100 W/(m·K), compared with carbon nanotubes arbitrarily arrangement in epoxy resin composites at room temperature, which owned a thermal conductivity of the 55 W/(m·K). Abdalla [15] made carbon nanotubes aligned in the resin in a magnetic field, and found that thermal conductivity of resin composites in the direction of carbon nanotubes orientation is much bigger than those vertical directions. Haggenmueller[16]studied that the thermal conductivity of polyethylene composites filled with carbon nanotube, and found that thermal conductivity is obviously increasing with the increase of orientation coefficient in the axial orientation.

In this paper, a magnetic nanocomposites formation of Fe_3O_4-CNTs is reported firstly, which was prepared by hydrothermal process, with multi-walled carbon nanotubes as the carrier. And the analysis of microstructure, magnetic of Fe_3O_4-CNTs, and the homogeneity of Fe_3O_4 on CNTs surface are presented. Then, carbon nanotubes are made to be aligned in the nature rubber adopted the method of solution blending in a magnetic field [17], and cross-linked curing at room temperature. Then NR polymer composites are presented, along with the results of a study on microstructure of CNTs aligned in nature rubber, and the relationship between magnetic field intensity, orientation time and thermal conductivity of nature rubber composites are explored.

Experimental

Materials

Nature Rubber(the total solids content of 61.5); mutil-walls carbon nanotube(diameter: 20-40 nm; length: 5-15μm; specific surface area: 90-120 m^2/g; Shenzhen port of nano Co., LTD); Sodium dodecyl sulfate(SDS); $FeCl_3{\cdot}6H_2O$; $FeSO_4{\cdot}7H_2O$; toluene; Potassium Ethyl Xanthate; Zinc diethyl dithiocarbamaate(ZDC); other rubber curing auxiliaries.

Fabrication of Fe_3O_4-CNTs

The pretreatment of the MWCNTs: The CNTs used in the experiment were prepared by chemical vapor deposition (CVD), a mixture of nano carbon materials, which contains large amounts of catalyst particles, amorphous carbon, nano carbon particles and other impurities. These impurities seriously affect the performance of carbon nanotubes, and limit the application of carbon nanotubes. Therefore, raw carbon nanotubes need to be purified. Moreover, due to CNTs' smooth surface, there is no direct keyed effect and no non covalent bonds attract role between CNTs and Fe_3O_4. So it is quite necessary to make CNTs surface with enough charge groups. Now, 10g original CNTs to 500mL of concentrated sulfuric acid and nitric acid mixture (volume ratio 1:1)are added, and it purified for 6h at 60℃ under ultrasonic processing, and then it is filtered, washed with deionized water again and again until neutral. And then it got dried in vacuum under 80℃.

Preparation of magnetic nanocomposites CNTs-Fe_3O_4[16]: added 0.004mol $FeCl_3 \cdot 6H_2O$ and 0.002mol $FeSO_4 \cdot 7H_2O$ to 400mL deionized water, added 1g of purified CNTs, and dispersed by ultrasound for 0.5h at room temperature. Then stirred under Nitrogen protection, rised temperature up to 50℃, reacted for 0.5h. Then heated up again to 65℃, added 6mol/L NaOH solution and adjusted solution PH>12. After reacted 1h, continue to heat up to 85℃, and added 0.25g sodium dodecyl sulfate (SDS), then cooled to room temperature under stirring. Filtered, and got sediment, washed to neutral with deionized water. And then used magnet separated out Fe_3O_4-CNTs magnetic composite materials. Placed into the vacuum oven to dry and grinded.

Fabrication of Fe_3O_4-CNTs/NR Composite

The formulation of NR composites used in experiments is shown in Table 1. NR was dissolved in toluene solution, stirring and dispersing for 1 h. At the same time, Fe_3O_4/MWNTs was dispersed in toluene solution using ultrasonic dispersion machine for 1h. In order to obtain well-mixed mixture, we mixed the above two kinds of solution for 2 h. The mixed solution of rubber addtives was added to the mixed solution of NR and Fe_3O_4/MWNTs. Then we put the mixture in a culture dish and removed bubbles 0.5 h under vacuum condition. Put the dish in a magnetic field for a certain period of time to make Fe_3O_4/MWNTs oriented.

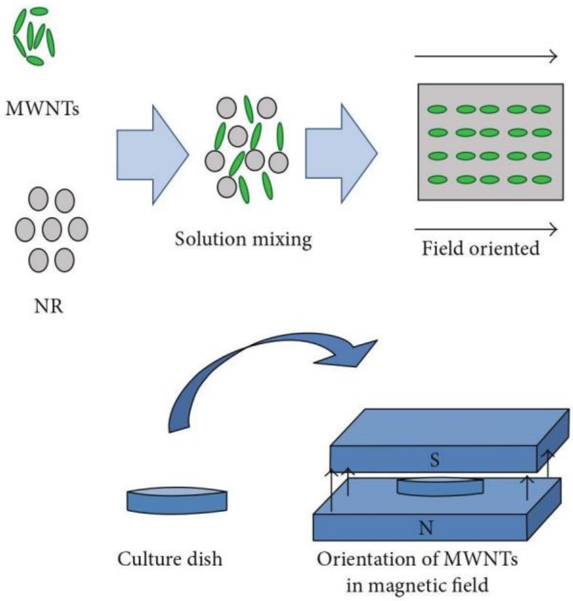

Figure 1: the orientation of MWNTs in NR in magnetic field.

Table 1: Formula of Fe_3O_4-CNTs/NR composite.

Raw material	mass fraction phr/g
NR	100
S	3
ZnO	3
ZDC	1
SA	2
RD	1
potassium ethyl xanthate	1
Fe_3O_4-CNTs	variable

Results and Discussion

TEM Analysis of Fe_3O_4/MWNTs Composite Particles

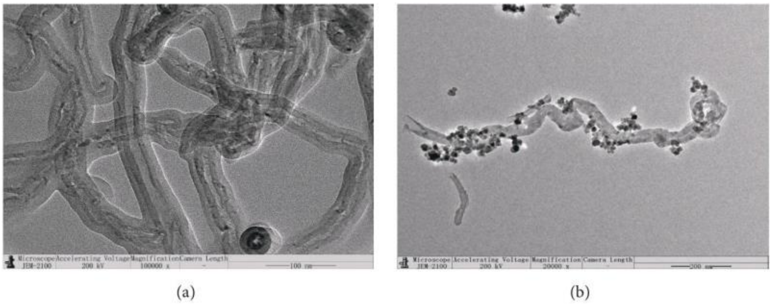

Figure 2: TEM images of O-MWNTs and Fe_3O_4/MWNTs; a. O-MWNTs; b. Fe_3O_4/MWNTs.

Figure2 is O-MWNTs under optimum acidification condition and Fe_3O_4/MWNTs nano-magnetic composite particles prepared by chemical co-precipitation. Figure(a) show that MWNTs was cut shorter, with its end caps open, while MWNTs surface become cleaner for amorphous carbon generated during its preparation and nano carbon particles and other impurities have been cleared after the acid-treated. Those variations all provide skeleton for Fe_3O_4. The TEM image shows MWNTs being coated by Fe_3O_4 magnetic particles. It is clear that a large number of black particles of its size about 20nm are symmetrically coated on the outer surface of MWNTs. In the preparation and washing process, Fe_3O_4 particles are still relatively evenly adsorbed on the MWNTs surface without falling after a relatively long period of ultrasonic oscillation and mixing treatment. This indicates that a negative charge was produced on its surface by purified MWNTs, so that a certain degree of electrostatic attraction make Fe_3O_4 particles firmly adsorbed on the surface of MWNTs.

X-ray Diffraction Spectra of MWNTs Coated by Fe_3O_4

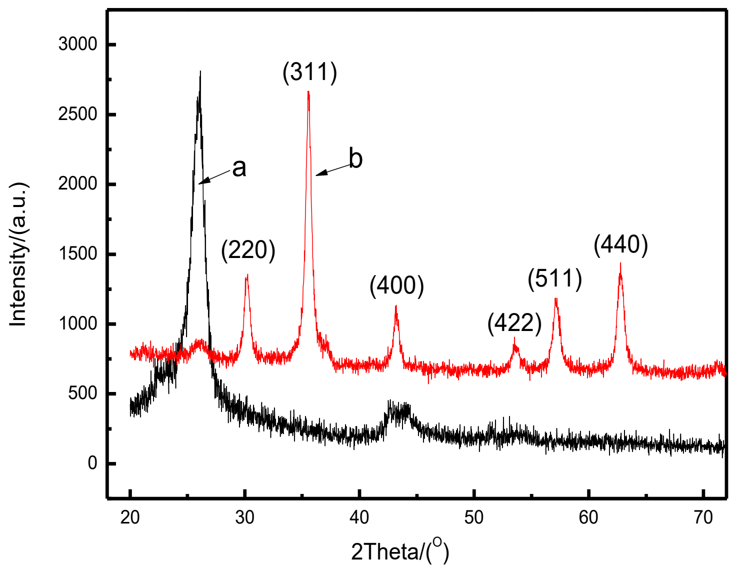

Figure 3: X-ray diffraction spectra of O-MWNTs and Fe_3O_4/MWNTs.

Figure 3 shows that the O-MWNTs is treated by mixed acid(a) and MWNTs coated with Fe_3O_4. Typical Bragg peaks appears at 2θ=26.018° in curve a, which also appears at curve b in the same position. But its strength is significantly less than O-MWNTs curve for the weaken role. Contrast JCPDS card(No.88-315)， in 30.258°、35.519°、43.213°、53.517°、57.101°、62.770°at diffraction peaks corresponding to Fe_3O_4 cubic crystal (220)、(311)、(400)、(422)、(511)、(440) six crystal faces.

Magnetic Analysis of Fe_3O_4/MWNTs

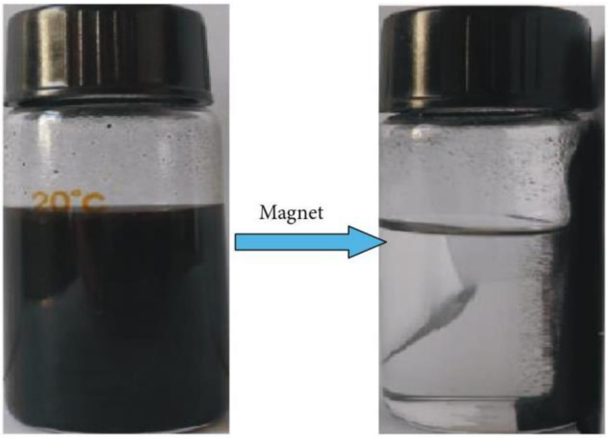

Figure 4: Photos of Fe_3O_4/MWNTs under a magnetic field.
The left photo shows that magnetic nanocomposite particles Fe_3O_4/MWNTs are added to the water by ultrasonic vibration and evenly are dispersed. Then the right photo is obtained by putting mixed solution in a magnetic field. It is found that Fe_3O_4/MWNTs composite particles quickly settled in one side beaker wall, which shows that MWNTs coated with Fe_3O_4 enhance magnetic itself.

SEM Analysis of NR Composites Filled with Aligned Fe_3O_4/MWNTs

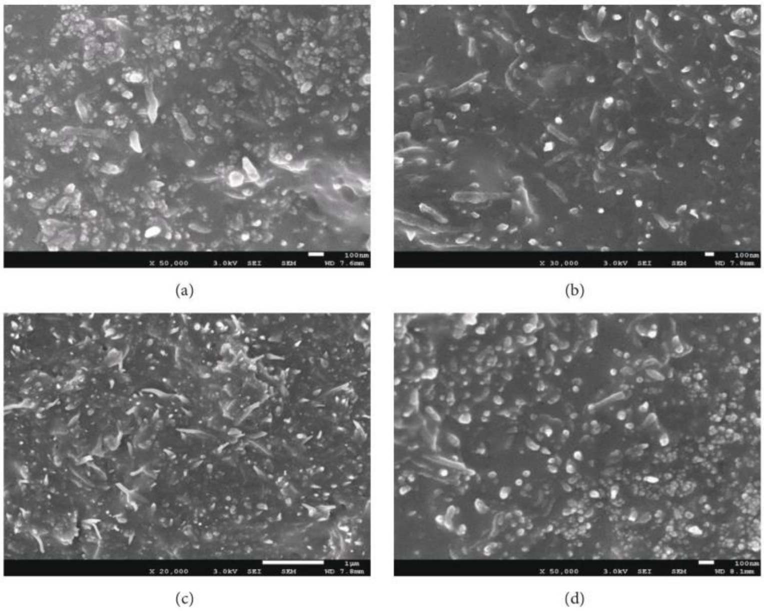

Figure 5: SEM images of NR composites.

a. 6 % 0 B 0 h; b. 10 % 1 B 0 h; c. 10 % 1 B 2.5 h; d. 10 % 2 B 2.5 h

As can be seen from Figure5, the probability of contact between Fe_3O_4 and MWNTs increases with the increasing filling fraction of particles, also promoted a more perfect thermal network chain. Fe_3O_4 particles in contact with each other on the surface of carbon tube serves as a bridge between MWNTs. The longer time orientation or the larger magnetic field strength, the greater degree of orientation of Fe_3O_4/MWNTs. The particles are arranged in parallel in the orientation direction which reduces thermal resistance. So the thermal conductivity of composites increases with directional time and magnetic field intensity.

Thermal Performance Analysis of NR Composites Filled with Fe3O4/MWNTs

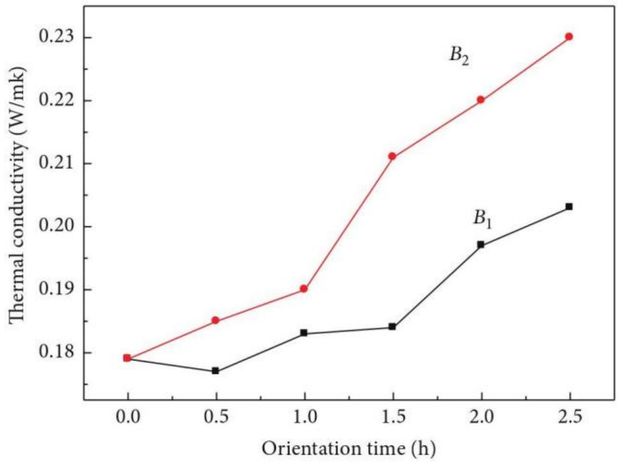

Figure 7: Effect of orientation time and magnetic intensity on thermal conductivity of composite (volume fraction=6%, at 80℃ test temperature).

The degree of orientation of Fe_3O_4/MWNTs in NR matrix increases, which is likely to lead to anisotropy of NR composites along the direction of magnetic field. NR composites obtains higher thermal conductivity and growth rate along orientation direction in strong magnetic field(B_1=400 mT, B_2=600 mT). Strong magnetic field works are done on Fe_3O_4/MWNTs, which attributes high anisotropic degree of NR composites.

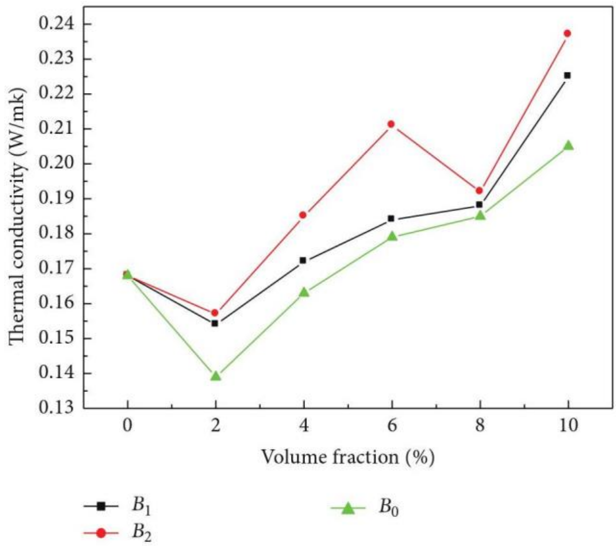

Figure 8: Impact of volume fraction on thermal conductivity of Fe_3O_4/MWNTs/NR composite(at 80℃ test temperature).

We get curves of thermal conductivity of NR composite under different magnetic field intensity at 1.5 hours. With the increase of Fe_3O_4/MWNTs filling fraction, thermal conductivity of NR composites increases gradually and strong magnetic field (B_2) has greater effect on improving thermal conductivity. Thermal conductivity of composites is better in B_2 because of higher orientation degree of Fe_3O_4/MWNTs.

Conclusions

- TEM shows Fe_3O_4 are uniformly coated on the outer surface of MWNTs. Diffraction peaks corresponding to Fe_3O_4 cubic crystal also appeared in the X-ray diffraction spectra.
- In the absence of magnetic field, thermal conductivity of composites with different Fe_3O_4/MWNTs content increases followed with test temperature. As the amount of fillers increases, the formation of heat transfer network chain become more and more perfect, which attribute composites have higher thermal conductivity.
- Thermal conductivity of composites increases by filling the appropriate modification of carbon tube. The magnetic field is larger, the direction time is longer, the thermal conductivity of composites is greater.

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