Hindawi Publishing Corporation
International Journal of Polymer Science
Volume 2015, Article ID 305317, 6 pages
http://dx.doi.org/10.1155/2015/305317

Research Article

Thermal Analysis of NR Composite with MWCNTs Aligned in a Magnetic Field

Jin Xu and Yan He

College of Electromechanical Engineering, Qingdao University of Science and Technology, No. 99 Songling Road, Qingdao, Shandong 266061, China

Correspondence should be addressed to Yan He; heyan_sd@163.com

Received 1 September 2015; Revised 11 November 2015; Accepted 12 November 2015

Academic Editor: Yiqi Yang

We got the aligned carbon tube in the rubber matrix through magnetic field. TEM shows that Fe_3O_4 is 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 content of carbon tube. If the magnetic field is larger and the direction time is longer, a greater thermal conductivity of composites can be obtained.

1. Introduction

Carbon nanotubes (CNTs), a kind of typical one-dimensional nanocarbon materials with a seamless nanotube structure which seem to be curled up by a single layer or multilayer graphite flake, show a variety of excellent properties such as electrical, thermal, mechanical, and optical properties and have attracted much attention due to their outstanding properties and significant potential application in so many fields since Iijima's observations in 1991 [1]. CNTs are becoming a focus and leading edge in the study of science and industry since Ajayan et al. [2] used the carbon nanotubes for reinforcing polymer composite. Therefore, many 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 on carbon nanotubes reinforced rubber composite mainly focused on mechanics, thermal stability, and 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 non-free movement. However, CNTs make heat transfer come true mainly via the vibration of the phonon. So CNTs own a higher thermal conductivity as shown in the related articles; it was reported 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 excellent thermal conductivity itself, its ability of improving the rubber's heat conduction was just limited. 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].

Orientation distribution and different existing state have an obvious effect on formation of thermal conductive network chain structure, for carbon nanotubes, special thermal conductive materials, have the particularity of 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 et al. [13] found that the thermal conductivity of epoxy resin composites filled with 17% of orient carbon nanotubes increased by 18%. Park et al. [14] found that if carbon nanotubes in epoxy are oriented by mechanical method, the thermal conductivity of composites rises up to 100 W/(m·K), compared with epoxy resin composites with an arbitrarily arrangement for carbon nanotubes at room temperature, which owned a thermal conductivity of the 55 W/(m·K). Abdalla et al. [15] made carbon nanotubes aligned in the resin in a magnetic field and found that thermal conductivity of resin composites along the direction of carbon nanotubes orientation is much bigger than that in vertical directions. Haggenmueller et al. [16] studied the thermal conductivity of polyethylene composites filled with carbon nanotube and found that thermal conductivity was obviously increasing with the increase of orientation coefficient in the axial orientation.

In this paper, magnetic nanocomposites formation of Fe_3O_4-CNTs is reported firstly, which was prepared by hydrothermal process, with multiwalled carbon nanotubes as the carrier. And the analysis of microstructure, magnetism of Fe_3O_4-CNTs, and homogeneity of Fe_3O_4 on CNTs surface are presented. Then, carbon nanotubes were made to be aligned in the nature rubber adopting a method of solution blending in a magnetic field [17], and the rubber was cross-linked at room temperature. Then NR polymer composites are presented; along with that was 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.

2. Experimental

2.1. Materials. Materials are as follows: nature rubber (the total solids content of 61.5); multiwalled carbon nanotube (diameter: 20–40 nm; length: 5–15 μm; 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 dithiocarbamate (ZDC); other rubber curing auxiliaries.

2.2. 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 nanocarbon materials can be obtained from it, which contains large amounts of catalyst particles, amorphous carbon, nanocarbon 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 bonded or noncovalent interactions between CNTs and Fe_3O_4. So it is quite necessary to make CNTs surface with enough charge groups. Now, 10 g original CNTs to 500 mL of concentrated sulfuric acid and nitric acid mixture (volume ratio 1 : 1) are added, and it was purified for 6 h at 60°C under ultrasonic processing, and then it is filtered and washed with deionized water again and again until neutral. And then it got dried in vacuum under 80°C.

Preparation of magnetic nanocomposites CNTs-Fe_3O_4 [16]: 0.004 mol $FeCl_3 \cdot 6H_2O$ and 0.002 mol $FeSO_4 \cdot 7H_2O$ were added to 400 mL deionized water, as well as 1 g of purified CNTs, and then dispersed by ultrasound for 0.5 h at room temperature. Firstly, the mixture solution was stirred under nitrogen protection at 50°C for 0.5 h. Secondly, 6 mol/L NaOH solution was added to adjust the PH of mixture solution was alkaline at 65°C. After reacting for 1 h, 0.25 g sodium dodecyl sulfate (SDS) was added to the mixture solution at 85°C. Finally, the mixture solution was cooled to room temperature under stirring and then filtered to get sediment. The sediment was washed to neutral with deionized water. Fe_3O_4-CNTs magnetic composite materials were separated out using a magnet, dried in a vacuum oven, and then ground.

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

2.3. 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, stirred and dispersed for 1 h. At the same time, Fe_3O_4/MWNTs were dispersed in toluene solution using ultrasonic dispersion machine for 1 h. In order to obtain well-mixed mixture, we mixed the two kinds of solution above for 2 h. The mixed solution of rubber additives 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 for 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).

3. Results and Discussion

3.1. TEM Analysis of Fe_3O_4/MWNTs Composite Particles. Figure 2 is O-MWNTs under optimum acidification condition and Fe_3O_4/MWNTs nanomagnetic composite particles prepared by chemical coprecipitation. Figure 2(a) shows that MWNTs were cut shorter, with their end caps open, while MWNTs' surface became cleaner for amorphous carbon generated during their preparation and nanocarbon particles and other impurities have been cleared after the acid treatment. 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 size about 20 nm 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 their surface by purified MWNTs, so that a certain degree of electrostatic attraction makes Fe_3O_4 particles firmly adsorbed on the surface of MWNTs.

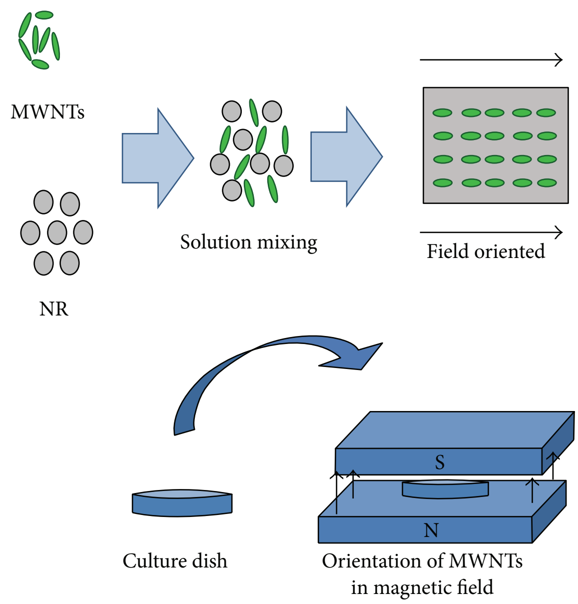


FIGURE 1: The orientation of MWNTs in NR in magnetic field.

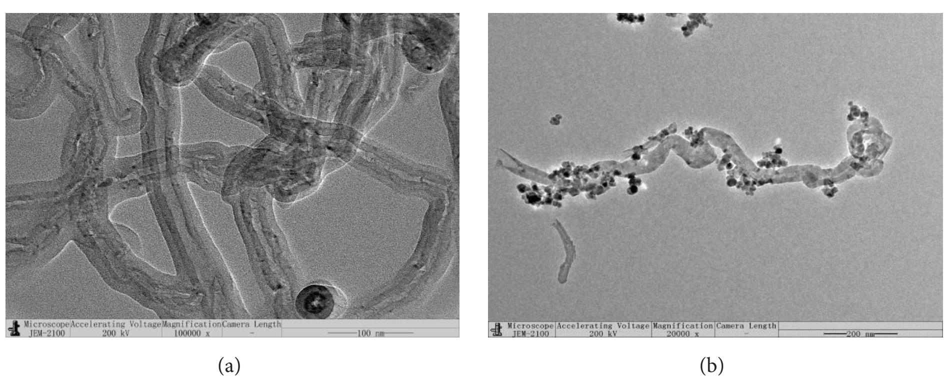


FIGURE 2: TEM images of O-MWNTs and Fe_3O_4/MWNTs: (a) O-MWNTs and (b) Fe_3O_4/MWNTs.

3.2. X-Ray Diffraction Spectra of MWNTs Coated by Fe_3O_4. Figure 3 shows that the O-MWNTs are treated by mixed acid (a) and MWNTs coated with Fe_3O_4. Typical Bragg peaks appear at $2\theta = 26.018^\circ$ in curve (a), which also appear at curve (b) in the same position. But its strength is significantly less than O-MWNTs curve for the weaken role. Contrast JCPDS card (number 88-315) in 30.258°, 35.519°, 43.213°, 53.517°, 57.101°, and 62.770° at diffraction peaks corresponds to Fe_3O_4 cubic crystal (220), (311), (400), (422), (511), and (440), six crystal faces.

3.3. Magnetic Analysis of Fe_3O_4/MWNTs. The left photo of Figure 4 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 of Figure 4 is obtained by putting mixed solution in a magnetic field. It is found that Fe_3O_4/MWNTs composite particles quickly

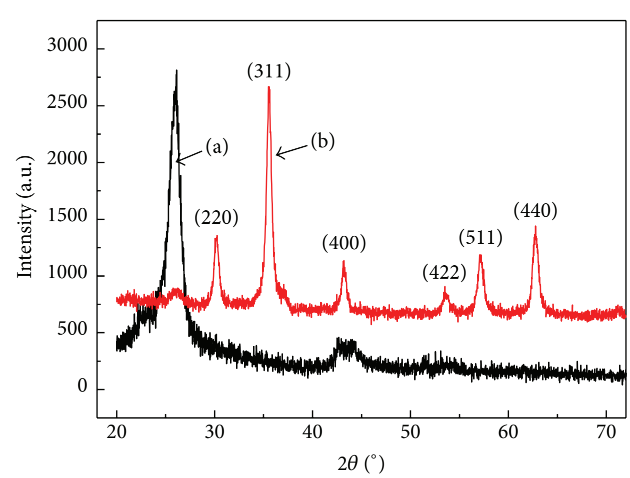


FIGURE 3: X-ray diffraction spectra of O-MWNTs and Fe_3O_4/MWNTs.

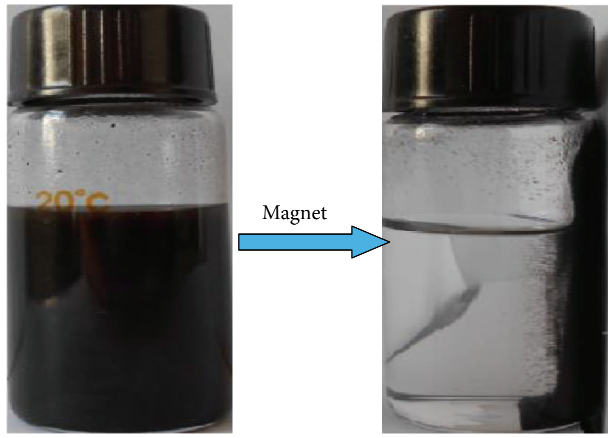
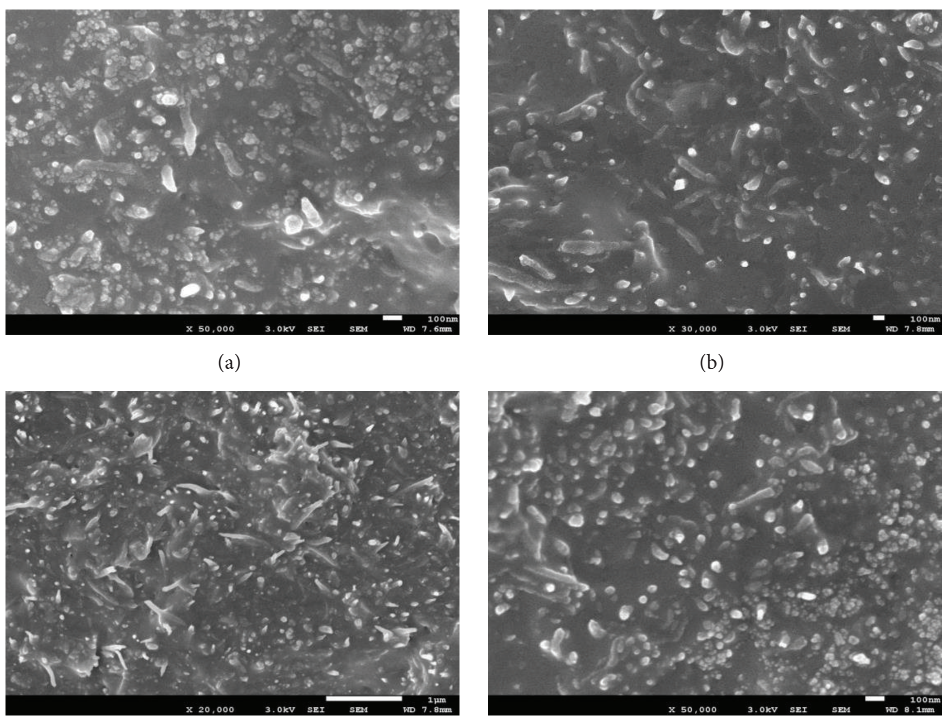


Figure 4: Photos of Fe_3O_4/MWNTs under a magnetic field.



(a) (b) (c) (d)

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.

settled toward one side of beaker wall, which shows that MWNTs coated with Fe_3O_4 enhance magnetic itself.

3.4. SEM Analysis of NR Composites Filled with Aligned Fe_3O_4/MWNTs. As can be seen from Figure 5, the probability of contact between Fe_3O_4 and MWNTs increases with the increasing filling fraction of particles and also promoted a more perfect thermal network chain. Fe_3O_4 particles in contact with each other on the surface of carbon tube serve as a bridge between MWNTs. The longer the time for orientation or the larger the magnetic field strength is, the greater the degree of orientation of Fe_3O_4/MWNTs can be obtained. 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 (Figure 5).

3.5. Thermal Performance Analysis of NR Composites Filled with Fe_3O_4/MWNTs. 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 obtain higher thermal conductivity and growth rate along orientation direction in strong magnetic field (B_1 = 400 mT and B_2 = 600 mT). Strong magnetic field

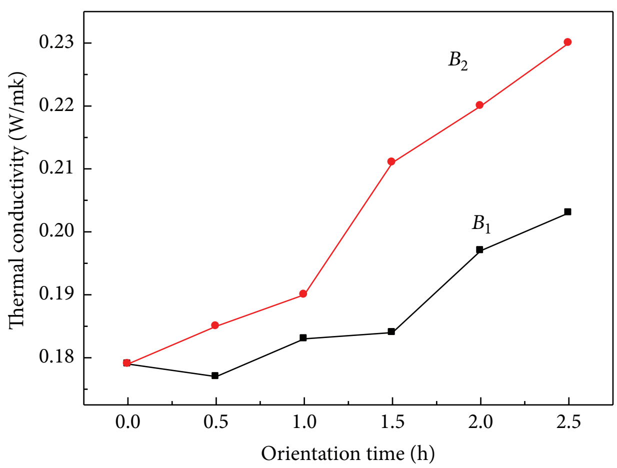


FIGURE 6: Effect of orientation time and magnetic intensity on thermal conductivity of composite (volume fraction = 6%, at 80°C test temperature).

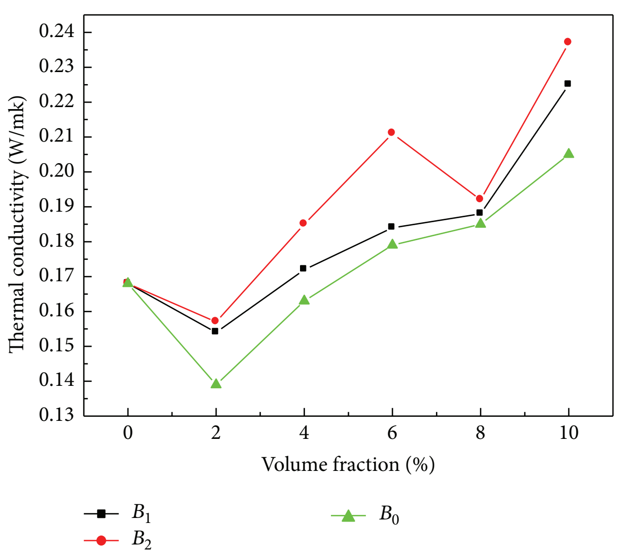


FIGURE 7: Impact of volume fraction on thermal conductivity of Fe_3O_4/MWNTs/NR composite (at 80°C test temperature).

works are done on Fe_3O_4/MWNTs, which is attributed to high anisotropic degree of NR composites (Figure 6).

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 (Figure 7).

4. Conclusions

(1) TEM shows that Fe_3O_4 is 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.

(2) 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 becomes more and more perfect, in which attribute composites have higher thermal conductivity.

(3) Thermal conductivity of composites increases by filling the appropriate modification of carbon tube. If the magnetic field is larger and the direction time is longer, the thermal conductivity of composites is greater.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work is supported by Grants from National Natural Science Foundation of China (no. 51276091) and Department of Science and Technology of Shandong Province, China (no. 2014ZZCX01503).

References

[1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.

[2] P. M. Ajayan, O. Stephan, C. Colliex, and D. Trauth, "Aligned carbon nanotube arrays formed by cutting a polymer resin—nanotube composite," *Science*, vol. 265, no. 5176, pp. 1212–1214, 1994.

[3] S. Berber, Y.-K. Kwon, and D. Tománek, "Unusually high thermal conductivity of carbon nanotubes," *Physical Review Letters*, vol. 84, no. 20, pp. 4613–4616, 2000.

[4] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, "Thermal transport measurements of individual multiwalled nanotubes," *Physical Review Letters*, vol. 87, no. 21, Article ID 215502, 2001.

[5] J.-T. Luo, H.-C. Wen, W.-F. Wu, and C.-P. Chou, "Mechanical research of carbon nanotubes/PMMA composite films," *Polymer Composites*, vol. 29, no. 12, pp. 1285–1290, 2008.

[6] A. A. Abdullateef, S. P. Thomas, M. A. Al-Harthi et al., "Natural rubber nanocomposites with functionalized carbon nanotubes: mechanical, dynamic mechanical, and morphology studies," *Journal of Applied Polymer Science*, vol. 125, supplement 1, pp. E76–E84, 2012.

[7] Z.-P. Wang, "Experimental study on property of rubber composites filled with carbon nanotubes," *Advanced Materials Research*, vol. 87-88, pp. 110–115, 2010.

[8] J.-T. Di, Z.-Z. Yong, X.-J. Yang, and Q.-W. Li, "Structural and morphological dependence of carbon nanotube arrays on catalyst aggregation," *Applied Surface Science*, vol. 258, no. 1, pp. 13–18, 2011.

[9] Y. Bin, M. Kitanaka, D. Zhu, and M. Matsuo, "Development of highly oriented polyethylene filled with aligned carbon

nanotubes by gelation/crystallization from solutions," *Macromolecules*, vol. 36, no. 16, pp. 6213–6219, 2003.

[10] Y. A. Kim, T. Hayashi, M. Endo, Y. Gotoh, N. Wada, and J. Seiyama, "Fabrication of aligned carbon nanotube-filled rubber composite," *Scripta Materialia*, vol. 54, no. 1, pp. 31–35, 2006.

[11] I. Kang, M. Abdul Khaleque, Y. Yoo, P. J. Yoon, S.-Y. Kim, and K. T. Lim, "Preparation and properties of ethylene propylene diene rubber/multi walled carbon nanotube composites for strain sensitive materials," *Composites Part A: Applied Science and Manufacturing*, vol. 42, no. 6, pp. 623–630, 2011.

[12] H. Chen, A. Roy, J.-B. Baek, L. Zhu, J. Qu, and L. Dai, "Controlled growth and modification of vertically-aligned carbon nanotubes for multifunctional applications," *Materials Science and Engineering R: Reports*, vol. 70, no. 3–6, pp. 63–91, 2010.

[13] A. M. Marconnet, N. Yamamoto, M. A. Panzer, B. L. Wardle, and K. E. Goodson, "Thermal conduction in aligned carbon nanotube-polymer nanocomposites with high packing density," *ACS Nano*, vol. 5, no. 6, pp. 4818–4825, 2011.

[14] J. G. Park, Q. Cheng, J. Lu et al., "Thermal conductivity of MWCNT/epoxy composites: the effects of length, alignment and functionalization," *Carbon*, vol. 50, no. 6, pp. 2083–2090, 2012.

[15] M. Abdalla, D. Dean, M. Theodore, J. Fielding, E. Nyairo, and G. Price, "Magnetically processed carbon nanotube/epoxy nanocomposites: morphology, thermal, and mechanical properties," *Polymer*, vol. 51, no. 7, pp. 1614–1620, 2010.

[16] R. Haggenmueller, C. Guthy, J. R. Lukes, J. E. Fischer, and K. I. Winey, "Single wall carbon nanotube/polyethylene nanocomposites: thermal and electrical conductivity," *Macromolecules*, vol. 40, no. 7, pp. 2417–2421, 2007.

[17] K. A. Anand, T. S. Jose, R. Alex, and R. Joseph, "Natural rubber-carbon nanotube composites through latex compounding," *International Journal of Polymeric Materials and Polymeric Biomaterials*, vol. 59, no. 1, pp. 33–44, 2010.