



From nano to giant? Designing carbon nanotubes for rubber reinforcement and their applications for high performance tires



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ABSTRACT

Carbon nanotubes (CNTs) attract considerable scientific and engineering interest because of their excellent mechanical, electrical and thermal properties. Today, when manufacturers use CNTs, purification, chemical modifications and dispersion techniques are usually applied rendering them cost-effective in large-scale applications. Our research shows that multi-wall CNTs bundles (MWCNTBs) with the same alignment, orientation and high surface defects for each CNT can be directly incorporated into the elastomer matrix through melt compounding. A uniform dispersion of CNTs and strong interfacial interactions between elastomers and CNTs due to the silane-coupling agent can be simultaneously produced. The resulting elastomer/MWCNTBs nanocomposites demonstrate excellent mechanical properties, high thermal conductivity and low volume resistivity. Note that this nanocomposite is achieved using common compounding equipment that is easy to industrialize. Through further scale-up, we confirmed that this elastomer/MWCNTBs nanocomposite has the most optimized comprehensive performance with practical applications for fuel-savings and engineering tires. These advantages include fuel efficiency, anti-static electricity and long-time fatigue resistance. In light of the large number of tires used worldwide, this work is promising for future large-scale industrial applications of CNTs.

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1. Introduction

Carbon nanotubes (CNTs) are unique one-dimensional nanostructures with carbon atoms belonging to sp^2 hybridization [1], and have good mechanical, electrical and thermal properties. For instance, theoretical and experimental results show that individual single-wall carbon nanotubes (SWCNT) have high tensile modulus (640 GPa to 1 TPa) [2] and tensile strengths (150–180 GPa) [3]. Past studies of CNT have gained great scientific and technological interest [4]. Recently, long, vertically aligned multi-walled nanotubes exhibited viscoelastic behavior and outstanding fatigue resistance

under repeated high compressive strain [5,6]. A viscoelastic material composed of a random network of long interconnected carbon nanotubes was found to have an operational temperature range from -196° to 1000°C with thermal stability resulting from energy dissipation through the zipping and unzipping of carbon nanotubes at contacts [7]. Methods of mass production of CNTs increased over the past 20 years including several production lines with annual capacities of over several hundred tons of CNTs [8]. However, large-scale industrial applications of CNT are still needed even though CNTs are commercially produced for lithium ion batteries [9], flexible touch screens [10], and CNT-based transistors [11], of which only 10 tons are used each year.

Introducing CNT into polymer matrices to simultaneously enhance the mechanical properties and achieve new functional characteristics such as thermal and electrical conductivity, wave-adsorbing, electric-magnetic shielding, is one promising direction for its application [12,13]. For instance, high performance elastomer composites with both high elasticity and conductivity have been successfully fabricated for the first time by using carbon nanotubes

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array (CNTA) as nanosprings [14]. Meanwhile, the fabrication of graphene reinforced rubber tailored for tire has also been illustrated through the rational design of covalent interfaces [15].

and a simple, environment-friendly latex co-coagulation method [16]. A bio-based elastomer nanocomposites aimed for the application of tire is also reviewed [17]. In addition, Winey et al. [18] reviewed the effects of size, aspect ratio, loading, dispersion state and alignment of nanotubes within polymer matrices on the resulting mechanical, electrical, rheological, thermal and flammable properties. However, to overcome the difficulties of homogeneous dispersion of CNTs [19] and weak interfacial bonding between CNT and polymer matrices [20], researchers developed various approaches for improving dispersion, such as acid modification [21], ultrasonic dispersion [22], liquid compounding such as solution and latex compounding [23], in-situ polymerization [24] and melt compounding [25]. Most compounding methods are complicated and are cost-prohibitive, which hinders the large-scale industrial applications of CNT.

Industries view melt compounding as the most environmentally friendly technique. However, the uniform dispersion of CNTs in polymer matrices is difficult in melt compounding because the synthesized CNTs are highly entangled. Our study designed and synthesized a new kind of CNT bundles that can be uniformly dispersed and have strong interfacial interactions.

2. Experimental

2.1. Materials

We used the following materials: high-defect multiwall carbon nanotubes (HD-CNT, FloTube™ 9000, Beijing Cnano Technology Co., Ltd, > 95%, length ~10 μm, diameter ~11 nm), high-defect multi-wall carbon nanotube bundles (HD-CNTB, FloTube™ 7000, Beijing Cnano Technology Co., Ltd, > 93%, length ~ up to 50 μm, diameter ~6–8 nm), NR (cloud mark 1, Yunnan Natural Rubber Co., Ltd).

2.2. Measurements

(Scanning electron microscope: SEM) The morphology of the surface was observed under an S-4800 scanning electron microscope (SEM, Hitachi Corp., Japan).

(Transmission electron microscope: TEM) High-resolution transmission electron microscope (HR-TEM) observation of MWCNTs was carried out using a JEM-3010 TEM (JEOL, Japan) operating with an accelerating voltage of 300 kV.

(Atomic force microscopy: AFM) Atomic force microscopy (AFM) studies were conducted under the tapping mode on a Veeco Digital Instrument Multi-Mode SPM.

(Bound rubber: BR) The content of BR was measured using an extraction method with toluene as a solvent. About 1 g of the composite was stored for two weeks after it was cut into 1 mm³ pieces and placed in a 300 mesh steel wire basket and was immersed in 100 mL of toluene at room temperature for seven days. The prepared MWCNT/NR gel was named gel-RT, and the extracted rubber bound on the MWCNTs in the gel-RT was named BR. After 4 days, the solvent was completely recovered. Then, the gel-RT was collected and dried to a constant mass in a vacuum oven. The dried gel-RT was analyzed using a thermal gravimetric analyzer (TGA) (Mettler-Toledo Group, Switzerland). The test conditions were as follows: temperature range, 25–600 °C; increase rate, 10 °C/min; atmosphere, nitrogen. During the pyrolysis process, the insoluble rubber on the MWCNTs surface decomposed, and the fraction of the rubber in the gel-RT was calculated. Then the BR contents were calculated using equation (1):

$$\text{BR} (\%) = [M_2 w_2 / M_1 w_1] \times 100, \quad (1)$$

where M_1 and M_2 are the dry weights of the sample before and after extraction, respectively; w_1 is the fraction of the rubber in the composite before extraction in theory, and w_2 is the fraction of the rubber in the extracted sample, which was measured using TGA. The obtained dried gel-RT products were extracted with toluene at high temperature (110 °C) for 48 h by using Soxhlet extractor. Then as prepared, MWCNT/NR gel was named as gel-HT, and the extracted rubber bound on the MWCNTs in the gel-HT was named as TBR. The insoluble parts were dried until the mass remained constant. The formula used for the computation of TBR contents was the same as that of the BR.

(Solid-state nuclear magnetic resonance: NMR) The low-field solid-state nuclear magnetic resonances (LFSNMR) transverse magnetization relaxation (T_2) experiments for the TBR, BR, net NR were measured using a XLDS-15 LFSNMR spectrometer (IIC Innovative Imaging Corp. KG, Germany). The measurement temperature was (60 ± 0.1) °C.

(Rubber processing analysis: RPA) The strain amplitude dependence of the dynamic storage modulus (G') of a mixed compound was measured with a RPA2000 rubber processing analyzer (RPA, Alpha Technologies Ltd., USA) to evaluate the filler network effect. A strain sweep from 0.28% to 400% was performed at 60 °C and 1 Hz.

(Thermal conductivity) Thermal conductivity was measured by an HC-110 thermal conductivity tester (Laser Comp, USA) under steady state conditions. The disc-shaped specimens were 60 mm in diameter and 6.0 mm in thickness. Measurements were carried out with the specimens clamped between the cooling calorimeter and heating calorimeter, whose temperatures were 20 °C and 30 °C, respectively. Additionally, the contact pressure was 414 kPa.

(Electrical conductivity) The volume resistivity values of rubber samples (80 mm diameter and 2 mm thickness) were measured by digital insulated resistor tester (PC68, Shanghai, PR China). The measured resistances R_v were then converted into volume resistivity R_v by using the equation:

$$\rho_v = R_v \frac{S}{h}, \quad (2)$$

where S is the area of electrodes; h is the thickness of sample.

(Mechanical properties) Tensile tests were performed on a CTM4104 tensile tester (SANS, Shenzhen, China) at a cross-head speed of 500 mm/min⁻¹ at room temperature.

(Raman spectroscopy: RS) RS was performed to determine the defects of pure MWCNTs and MWCNTs in the composites using a Raman spectrometer (JY-HR 800, HORIBA Ltd., France) with a laser excitation at 514 nm.

(Fourier Transform infrared spectroscopy: FTIR) FTIR was recorded using a Bruker Tensor 27 IR spectrometer (Bruker Optics) with a resolution of 4 cm⁻¹.

(X-ray Photoelectron Spectroscopy: XPS) XPS analysis was carried out using an ESCA LAB 250 (Thermo Fisher Scientific Corp., USA) with an Al Ka X-ray source (1486.6-eV photons).

2.3. Preparation of nanocomposites

(Preparation of structure tire) To obtain the fuel-efficient tire tread, we mixed 55 phr SSBR 5025-2, 30 phr SSBR 2305 and 30 phr rare-earth polybutadiene rubber together using a mixing mill at room temperature. We then added silica at 50 phr into the rubber matrix with 5 phr silane coupling agent. After adding CNTs and other agents, the composites on the mill are heated for a while.

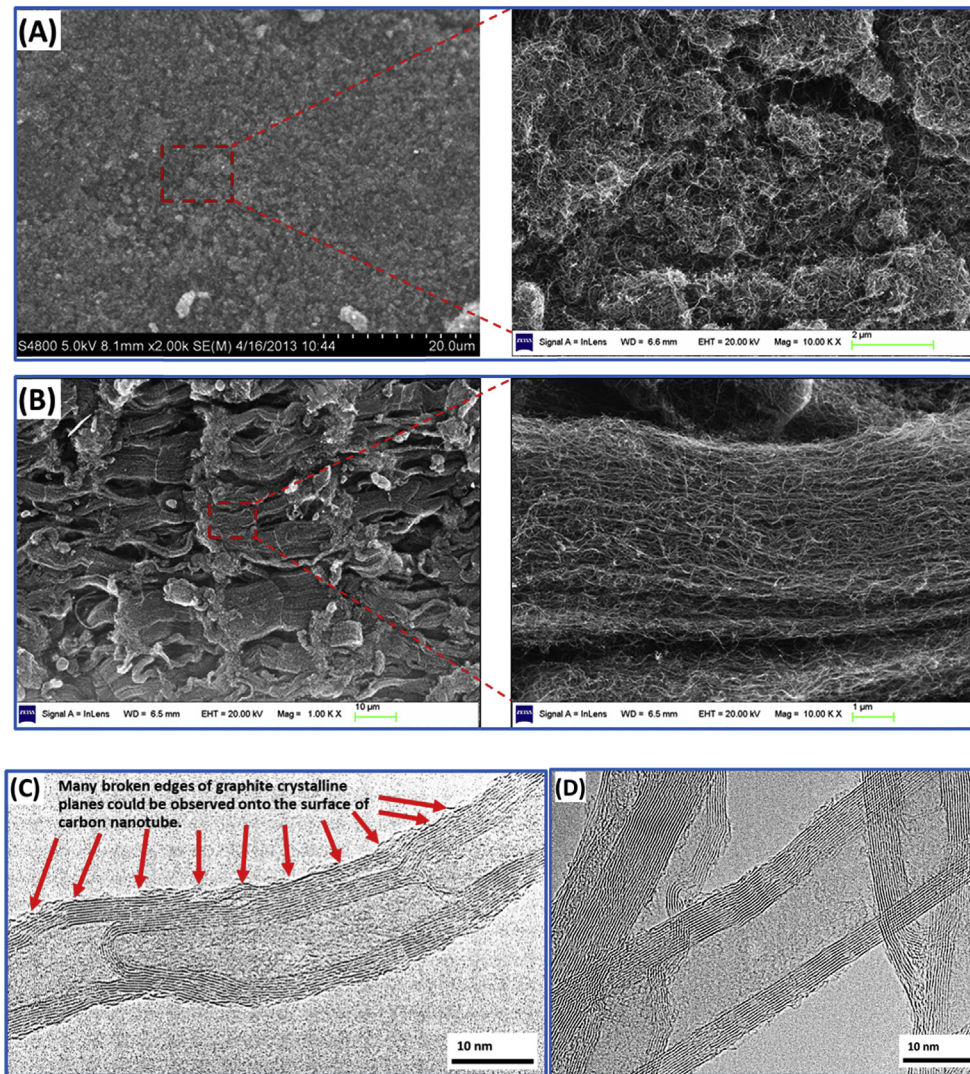


Fig. 1. Comparison of SEM images between (A) high-defect multiwall carbon nanotubes (HD-CNT, FloTube™ 9000); (B) high-defect multi-wall carbon nanotube bundles (HD-CNTB, FloTube™ 7000) and of HRTEM images between (C) HD-CNT (FloTube™ 9000) and (D) Low-defect multiwall carbon nanotubes (LD-CNT, GM3).

After cooling for an hour, we added the other agents.

(Preparation of engineering tire) To obtain the energy-saving tires and engineering tires, we mixed 3 phr carbon nanotubes in 100 phr NR using an internal mixer (XSM-05/10-200). To obtain low dynamic compression fatigue and high thermal conductivity, we added 100 phr nano- α alumina into the natural rubber matrix. The heat treatment temperature was held at 120 °C and mixed for 3 min. The silane coupling agent in-situ modification of the packing can be complete and promote the interface bonding.

3. Results and discussion

First, we characterized the morphology of CNTs through SEM as shown in Fig. 1A and B. These present the array of high-defect multiwall carbon nanotubes (HD-CNT, FloTube™ 9000) and high-defect multi-wall carbon nanotube bundles (HD-CNTB, FloTube™ 7000). Obviously, their micro-structures are remarkably different. The CNTs in the HD-CNTB all orientate and align in a one-dimension that is perpendicular to the catalyzed loading LDH nano-sheet. The high resolution SEM (HRSEM) showed that some curvatures and entanglements exist between CNTs in the HD-CNTB, but far fewer than CNTs in the HD-CNT as presented in Fig. 1B.

During the compounding process of HD-CNTB and rubber, a single CNT was ripped off from the catalyzed loading LDH, and it then became dispersed in the rubber matrix. Because there was less entanglement between CNTs, the dispersion was better, and the CNTs also had a higher aspect ratio that maintains structural integrity.

Carbon black has been used in rubber for over 100 years [26]. As such, we adjusted the preparation process of CNTs to produce an abundance of graphite with staggered floors on the surface of CNTs, similar to carbon black, to improve the surface roughness and the number of the high active points. The HD-CNT had many surface defects as indicated by the high resolution TEM photograph in Fig. 1C. Because of the literal alignment of graphite crystal layers of CNTs, many staggered floors-like structures were formed on the surface of CNTs. These were very common on the surface of carbon black. On the contrary, the surface of the low defect carbon nanotubes (LD-CNT) possessed few defects of MWCNTs, although some amorphous carbons existed, and the entire structure of MWCNTs was intact as shown in Fig. 1D.

Next, we examined the dispersion state of CNTs. As shown in Fig. 2A, the TEM graphs of NR/CNT (100/5) by mechanical mixing indicated that HD-CNTBs are dispersed randomly in the NR matrix.

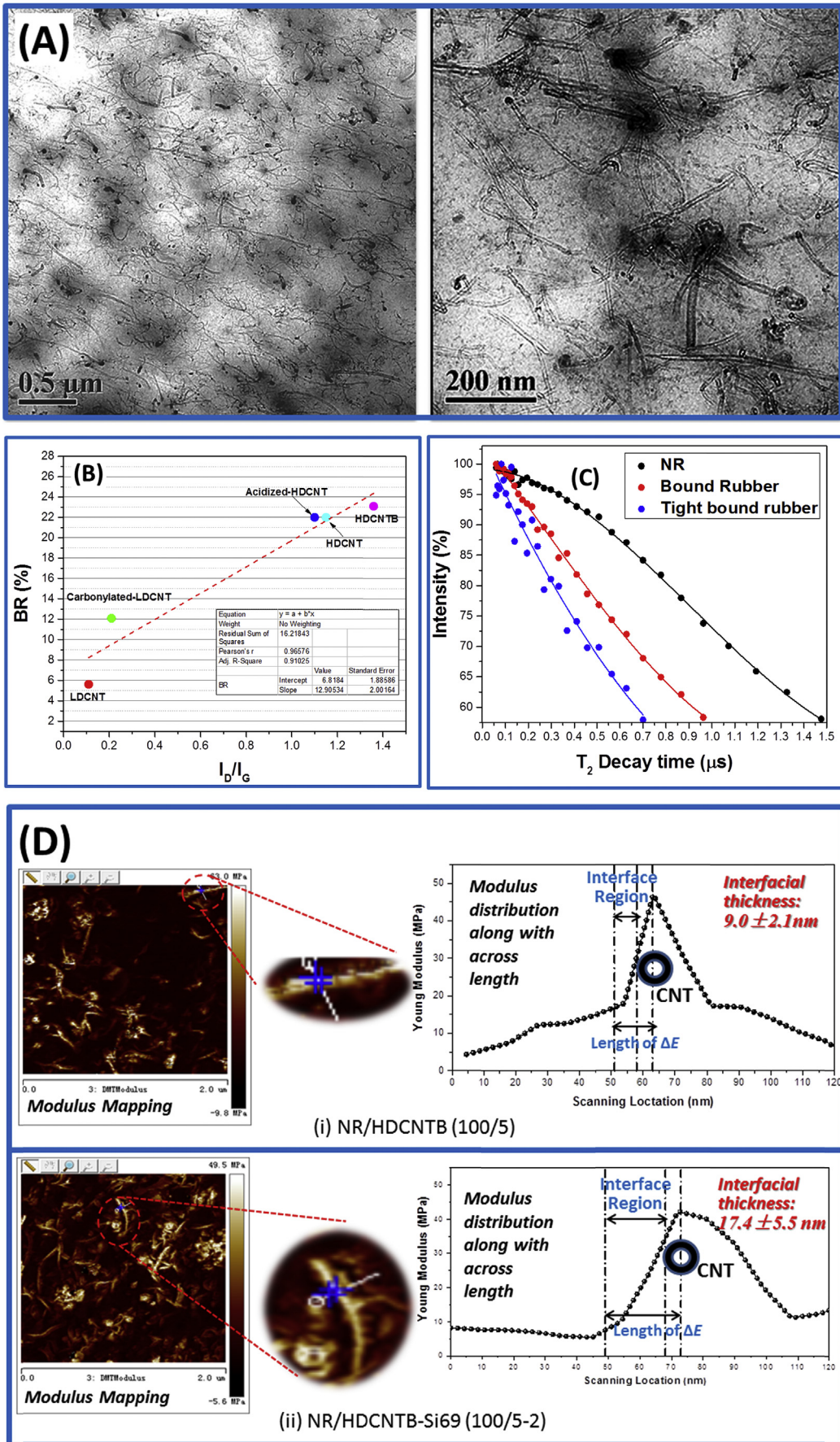


Fig. 2. Microstructural characterizations on NR/MWCNTs: (A) TEM images of NR/HDCNTB (100/5); (B) Correlation between bound rubber content and I_D/I_G of MWCNTs; (C) Proton T_2 relaxation curves of net NR, bound rubber and tight bound rubber of NR/HDCNTB (100/5) mixing compound; (D) Measurement of interfacial thickness for (i) NR/HDCNTB (100/5) and (ii) NR/HDCNTB-Si69 (100/5-2) by using AFM quantitative nano-mechanics technique. The resulting values were averaged from 50 experimental data.

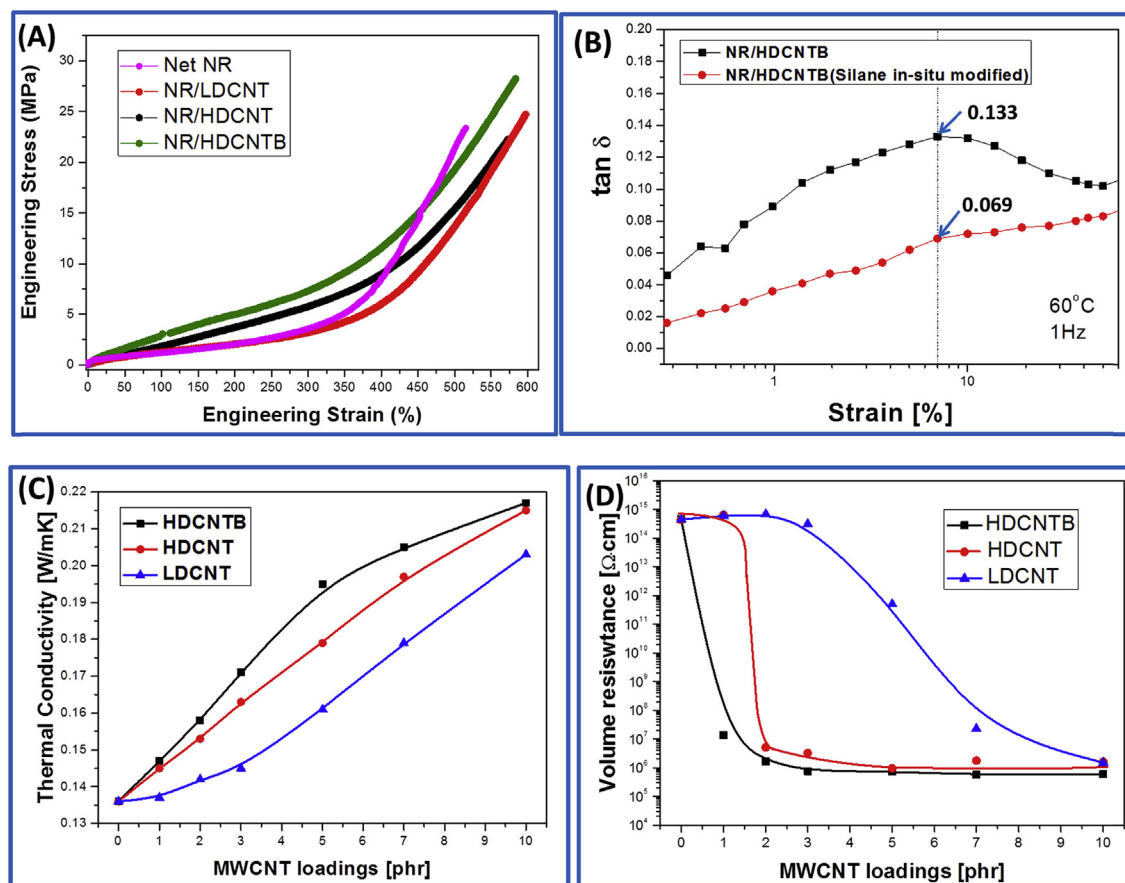


Fig. 3. Comprehensive properties of NR reinforced by various types of MWCNTs: (A) Comparison of strain-stress curves among various NR/CNT (100/5) nanocomposites; (B) Influence of silane in-situ modification on hysteresis (i.e., strain amplitude dependences of loss index ($\tan \delta$)) of NR/HDCNTB (100/5); (C) Plots of thermal conductivity as function of loading of CNTs for NR nanocomposites reinforced with different types of MWCNTs; (D) Plots of electronic volume resistance as function of loading of CNTs for NR composites reinforced by different types of MWCNTs.

We noted that the dispersion state had insignificant change, even when the coupling agent was introduced, as shown in Fig. S2. In addition, we have compared the tube length distribution between HDCNTs and HDCNTBs in the rubber matrix after the mechanical mixing, finding that a relatively longer aspect ratio is maintained for HDCNTBs (Fig. S3). This further confirms that HDCNTBs can be better candidates.

We investigated interfacial interactions by measuring the content of the bound rubber (BR) using five different kinds of CNT such as low-defect carbon nanotubes (LDCNT), carbonylated-LDCNT, acidized-high defect carbon nanotubes (acidized HDCNT), high defect carbon nanotubes (HDCNT) and high defect carbon nanotube bundles (HDCNTB). The bound rubber was the content of the non-extractable rubber after being immersed in a good solvent for a long enough time. More bound rubber leads to stronger interfacial interactions [27–29]. To ensure accurate measurements, no other additives were used other than CNT and rubber. The BR content was measured through the toluene extraction at ambient temperature. The relationship between the BR content and graphite defects I_D/I_G (Raman spectra) is shown in Fig. 2B and shows a positive linear correlation. Meanwhile, the spin-spin relaxation T_2 of the low-field solid state nuclear magnetic resonances was used to probe the dynamics of rubbery chains with relaxation rates in the following order TBR > BR > net NR. This indicated that the CNTs had the strongest constraint on the mobility of the polymer chains of TBR in Fig. 2C.

The atomic force microscope (AFM) was used to analyze the

modulus change of polymer with respect to the distance away from the CNT to reflect the thickness of the interfacial region as shown in Fig. 2D. We noted that the interfacial thickness could be increased to become 17.4 ± 5.5 nm with the in-situ modification by silane coupling agent Si69 for the natural rubber filled with high defect CNTB, compared to the interfacial thickness equal to 9.0 ± 2.1 nm of the system without Si69. Therefore, interfacial interaction was enhanced by improving the graphite structure of CNTs.

Next, we focused on the strain-stress curves of various CNTs filled NR and pure NR as shown in Fig. 3A. In the range of the strain smaller than 300%, the value of the stress exhibited the following order: HDCNTB > HDCNT > LDCNT. The up-turn of stress greater than 300% may have resulted in part from the orientation and crystallization of the macromolecular chains, including the pure system. Meanwhile, the loss factor as a function of the strain amplitude was further decreased by Si69 in Fig. 3B such as the loss factor at the strain equal to 7% at 60°C reduced by silane modification from 0.133 to 0.069. We compared the thermal conductivity (Fig. 3C) and volume resistance (Fig. 3D) as a function of the MWCNT loading for three different kinds of CNT such as HDCNTB, HDCNT and LDCNT, which indicated that the change trend was the most significant for HDCNTB, and the least for LDCNT. Generally, HDCNTB has more structural defects and leads to excellent mechanical, thermal conductivity and volume resistance properties compared to other types of CNTs, because of better dispersion of CNTs and stronger interfacial adhesion.

The silane in situ modification can increase the interfacial layer

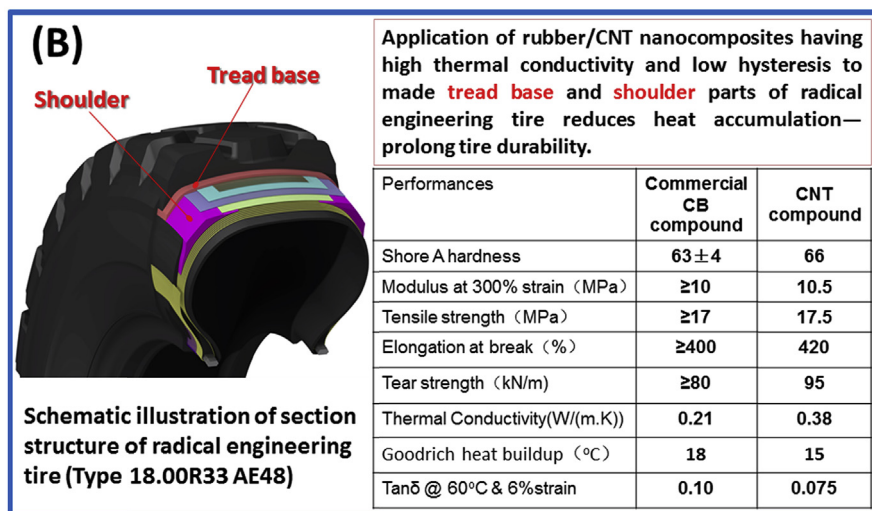
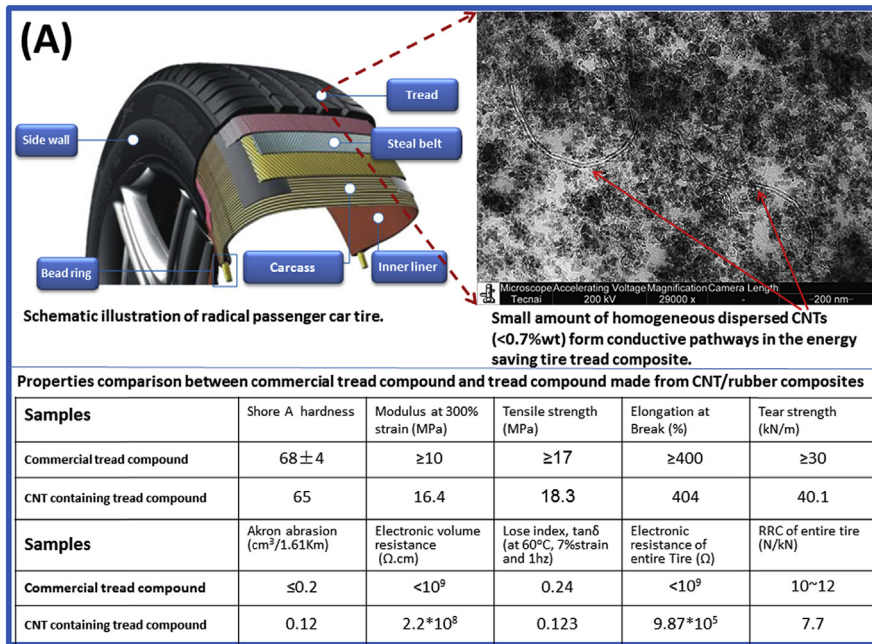


Fig. 4. Application of rubber/CNT nanocomposites in high-performance tires: (A) Using CNTs in the highly filled rubber/nano silica tread composite for solving the problem of electronic charge releasing of the energy-saving passenger tire; (B) Application of rubber/CNT nanocomposites in high-performance engineering tires for reducing heat accumulation; (C) End products of energy-saving tires and engineering tires containing rubber/CNT nanocomposite parts. The diameter of rim and cross width of the engineering tire is 33 inch and 18 inch, respectively, and its outer diameter is over 1.9 m.

thickness between carbon nanotubes and rubber matrices from 9 nm to 17.4 nm by strengthening the interfacial interactions, which promoted the efficiency of the stress transfer between CNT and rubber. This reduced the molecular friction between inter-tubes under dynamic loading and improved the static and dynamic mechanical properties such as the tear strength, crack resistance, fatigue, energy-savings and service life. These excellent properties can be well maintained even during the large-scale preparation process as shown in Fig. S7–9.

Finally, we focused on the scale-up application of CNTs. The first successful example was the preparation of the fuel-saving passenger tires by taking advantage of its mechanical reinforcing and electrical conductivity. Because of adverse environmental issues, the development of the fuel-saving tires is an important trend in the global tire industry. Recently, a key technology to produce the energy-saving tires is to use high loading of nano-silica instead of carbon black to reinforce the tire tread rubber materials, which reduces the rolling resistance of the tire. However, silica is an electrically insulating material, and it can cause electric shock from the accumulation of the static electricity caused by tire resistance, which far exceeds the safety value (GB/T26277-2010 prescribed tire resistance $<10^{10}\Omega$).

To eliminate accumulated static electricity, some foreign tire companies use a particular kind of rubbery material with high electric conductivity, such as chimney gum, in the preparation of tire tread. However, this method not only complicates the manufacturing process, but also has adverse effects. Our study used a small amount of CNTs into high loading of silica reinforced energy-saving tire tread rubber composite to form a continuous conductive path to gain the anti-static property of tire tread with low dynamic hysteresis.

Our research group successfully implemented the industrial trial production of MWCNTs/rubber composites by using a 370-L Banbury mixer. A low hysteresis and anti-static tire tread that uses only about 0.7% weight fraction of MWCNTs was produced, as shown in Fig. 4A. The production capability of one batch is 360 kg. In Fig. 4A, TEM data shows that CNTs are uniformly dispersed in the industrial pilot production of HDCNTBs/rubber composites and form an electric pathway to solve the problem of the electric charge. Moreover, the data in the table of Fig. 4A shows that the mechanical performance meets or exceeds that commercial product by mixing carbon black with rubber for tire treads by comparing Shore A hardness, modulus at 300% strain, tensile strength, elongation at break, tear strength, Akron abrasion, volume resistance and loss factor. The data indicated that the dynamic loss was reduced by nearly 50%, and the volume resistivity can meet the anti-static requirement with the value smaller than $10^9\Omega\text{ cm}$.

Based on these results, a particular kind of carbon nanotube/rubber composite tailored for energy-saving tires are presently being trial-produced, among them the energy-saving of ES9000 205/55/R16. The rolling resistance coefficient reaches Level B, as prescribed by the tire labeling regulation of the European Union, with more energy-savings as compared other commercialized tires. The electrical resistance of the whole tire is $10^5\Omega$, which is defined as anti-static.

According to a rough estimation, China consumed around 84.25 million tons of gasoline in 2013. China could save 4 million tons of fuel and reduce 10 million tons emission of carbon dioxide each year by using energy-saving tires for all automobiles. Therefore, the large-scale application of energy-saving tires made of carbon nanotube reinforced rubber could provide a positive contribution to the energy conservation and gas emissions.

The second most successful large-scale industrial application of rubber/CNT nanocomposites is the fabrication of large high-performance engineering tires for use in mining and other field

operations, as shown in Fig. 4B. However, the rubber/CNT nanocomposites accelerate the accumulation of the heat in tires during the rolling process, and decreases the thermal conductivity, which adversely affects the service life of the tires. To resolve this issue, we introduced both carbon nanotube and nano- α alumina into the natural rubber matrix to obtain low dynamic compression fatigue and high thermal conductivity by using dually functionalized carbon nanotubes for improving rubber thermal conductivity. The size of the engineering tire is shown in Fig. 4C. We found that the dynamic heat production was lower than that of the commercialized aeolus tire, and the thermal conductivity increased by more than 50%. This demonstrated that the tires have improved durability, while promoting heat transfer during the vulcanization process by saving energy consumption during the manufacture of tires.

4. Conclusion

Our study introduced novel approach to prepare a particular kind of MWCNTs with good dispersion in the rubber matrix. First, MWCNTs were designed to grow along a fixed direction to lessen or reduce inter-entanglements. Then more graphite topology structures were introduced to CNT surfaces by controlling the experimental parameters. Further, in-situ silane modification improved the interfacial adhesion between CNTs and rubber matrix in the rubber/HDCNTBs system. The resulting rubber/CNT nanocomposite had excellent mechanical, thermal conductive properties as well as good crack-growth resistance and fatigue properties. Therefore, combined with the present facile compounding technique in the tire industry, such rubber/CNT nanocomposites are successfully applied to the scale-up production of high-performance fuel-saving and engineering tires. Our study demonstrated way to fabricate the next-generation of green tires, and on the other hand opens up a viable opportunity for the large-scale application of CNTs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.compscitech.2016.10.020>.

References

- [1] S. Iijima, *Nat. Lond.* 354 (1991) 56.
- [2] T. Uchida, S. Kumar, Single wall carbon nanotube dispersion and exfoliation in polymers, *J. Appl. Polym. Sci.* 98 (3) (2005) 985–989.
- [3] W.A. de Heer, *Nanotubes and the pursuit of applications*, *MRS Bull.* 29 (4) (2004) 281–285.
- [4] E.T. Thostenson, Z.F. Ren, T.W. Chou, *Advances in the science and technology of carbon nanotubes and their composites: a review*, *Compos. Sci. Technol.* 61 (13) (2001) 1899–1912.
- [5] J. Suhr, P. Victor, L.C.S. Sreekala, X. Zhang, O. Nalamasu, P.M. Ajayan, Fatigue resistance of aligned carbon nanotube arrays under cyclic compression, *Nat. Nanotechnol.* 2 (7) (2007) 417–421.
- [6] A.Y. Cao, P.L. Dickrell, W.G. Sawyer, M.N. Ghasemi-Nejhad, P.M. Ajayan, Super-compressible foamlike carbon nanotube films, *Science* 310 (5752) (2005)

- 1307–1310.
- [7] M. Xu, D.N. Futaba, T. Yamada, M. Yumura, K. Hata, Carbon nanotubes with temperature-invariant viscoelasticity from-196 degrees to 1000 degrees C, *Science* 330 (6009) (2010) 1364–1368.
- [8] Q. Zhang, J.Q. Huang, W.Z. Qian, Y.Y. Zhang, F. Wei, The road for nanomaterials industry: a review of carbon nanotube production, post-treatment, and bulk applications for composites and energy storage, *Small* 9 (8) (2013) 1237–1265.
- [9] B.J. Landi, M.J. Ganter, C.D. Cress, R.A. DiLeo, R.P. Raffaele, Carbon nanotubes for lithium ion batteries, *Energy Environ. Sci.* 2 (6) (2009) 638–654.
- [10] D. Jung, K.H. Lee, D. Kim, D. Burk, L.J. Overzet, G.S. Lee, Highly conductive flexible multi-walled carbon nanotube sheet films for transparent touch screen, *Jpn. J. Appl. Phys.* 52 (3) (2013) 03BC03.
- [11] M.M. Shulaker, G. Hills, N. Patil, H. Wei, H.Y. Chen, H.S. PhilipWong, S. Mitra, Carbon nanotube computer, *Nature* 501 (7468) (2013) 526.
- [12] M.T. Byrne, Y.K. Gun'ko, Recent advances in research on carbon nanotube-polymer composites, *Adv. Mater.* 22 (15) (2010) 1672–1688.
- [13] J.N. Coleman, U. Khan, Y.K. Gun'ko, Mechanical reinforcement of polymers using carbon nanotubes, *Adv. Mater.* 18 (6) (2006) 689–706.
- [14] N. Ning, L. Ji, L. Zhang, J. Liu, Y. Lu, S. Wu, H. Zou, M. Tian, T.W. Chan, High elasticity and conductivity of elastomer composites with arrayed carbon nanotubes as nanosprings, *Compos. Sci. Technol.* 118 (2015) 78–84.
- [15] Z. Yang, J. Liu, R. Liao, G. Yang, X. Wu, Z. Tang, B. Guo, L. Zhang, Y. Ma, Q. Nie, F. Wang, Rational design of covalent interfaces for graphene/elastomer nanocomposites, *Compos. Sci. Technol.* 132 (2016) 68–75.
- [16] H. Kang, K. Zuo, Z. Wang, L. Zhang, L. Liu, B. Guo, Using a green method to develop graphene oxide/elastomers nanocomposites with combination of high barrier and mechanical performance, *Compos. Sci. Technol.* 92 (2014) 1–8.
- [17] R. Wang, J. Zhang, H. Kang, L. Zhang, Design, preparation and properties of bio-based elastomer composites aiming at engineering applications, *Compos. Sci. Technol.* 133 (2016) 136–156.
- [18] M. Moniruzzaman, K.I. Winey, Polymer nanocomposites containing carbon nanotubes, *Macromol.* 39 (16) (2006) 5194–5205.
- [19] B.P. Grady, Recent developments concerning the dispersion of carbon nanotubes in polymers, *Macromol. Rapid Commun.* 31 (3) (2010) 247–257.
- [20] P.M. Ajayan, J.M. Tour, Materials science - nanotube composites, *Nature* 447 (7148) (2007) 1066–1068.
- [21] M.H. Liu, Y.L. Yang, T. Zhu, Z.F. Liu, A general approach to chemical modification of single-walled carbon nanotubes with peroxy organic acids and its application in polymer grafting, *J. Phys. Chem. C* 111 (6) (2007) 2379–2385.
- [22] A.I. Isayev, R. Kumar, T.M. Lewis, Ultrasound assisted twin screw extrusion of polymer-nanocomposites containing carbon nanotubes, *Polymer* 50 (1) (2009) 250–260.
- [23] A.K. Bhowmick, M. Bhattacharya, S. Mitra, K.D. Kumar, P.K. Maji, A. Choudhury, J.J. George, G.C. Basak, Morphology-property Relationship in Rubber-based Nanocomposites: Some Recent Developments, *Advanced Rubber Composites*, Springer-Verlag Berlin, Berlin, 2011, pp. 1–83.
- [24] C. Park, Z. Ounaies, K.A. Watson, R.E. Crooks, J. Smith, S.E. Lowther, J.W. Connell, E.J. Siochi, J.S. Harrison, T.L.S. Clair, Dispersion of single wall carbon nanotubes by in situ polymerization under sonication, *Chem. Phys. Lett.* 364 (3–4) (2002) 303–308.
- [25] W.D. Zhang, L. Shen, I.Y. Phang, T.X. Liu, Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding, *Macromolecules* 37 (2) (2004) 256–259.
- [26] G. Heinrich, M. Kluppel, T.A. Vilgis, Reinforcement of elastomers, *Curr. Opin. Solid State Mater. Sci.* 6 (3) (2002) 195–203.
- [27] S.S. Choi, E. Ko, Novel test method to estimate bound rubber formation of silica-filled solution styrene-butadiene rubber compounds, *Polym. Test.* 40 (2014) 170–177.
- [28] Y.L. Yue, H. Zhang, Z. Zhang, Y.F. Chen, Polymer-filler interaction of fumed silica filled polydimethylsiloxane investigated by bound rubber, *Compos. Sci. Technol.* 86 (2013) 1–8.
- [29] M. Qu, F. Deng, S.M. Kalkhoran, A. Gouldstone, A. Robisson, K.J. Van Vliet, Nanoscale visualization and multiscale mechanical implications of bound rubber interphases in rubber-carbon black nanocomposites, *Soft Matter* 7 (3) (2011) 1066–1077.