DYNAMIC PROPERTIES AND TIRE PERFORMANCES OF COMPOSITES FILLED WITH CARBON NANOTUBES

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"CARBON NANOTUBES"

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ABSTRACT

Carbon nanotubes (CNTs) have been widely studied in rubber goods and tire compounds to improve, for example, antistatic and thermal conductivity performances. CNTs were applied in passenger tire tread compounds to improve comprehensive tire performances, especially wet traction. High frequency dynamic properties of CNT-filled compounds were revealed for the first time. There was good correlation between compound dynamic properties and vehicle tire test results. The influence of CNTs on tire performances and their mechanisms was investigated and explained by the dynamic properties and master curve analysis in the frequency domain. Substituting 50 phr carbon black N234 by 20 phr CNTs could maintain hardness but increased static and dynamic moduli, which was beneficial for the tire handling, with 0.25 point improvement in the subjective testing. For the CNT-filled compounds, 1.5% traction improvement on a dry road and 6.5% traction improvement on a wet road can be explained successfully by the increased hysteresis loss (tan δ) and decreased storage modulus (G') at high frequency domain (10^4–10^8 Hz). It is implied by Williams–Landel–Ferry law calculation that a strong interaction between CNTs and rubber resulted in higher temperature dependence; however, the trade-off was a 7% higher tire rolling resistance coefficient and 33% worse wear resistance for the CNT tires. CNT-filled compounds were demonstrated to have superior handling and traction performances suitable for racing and sports car tires. [doi:10.5254/rct.18.82599]

INTRODUCTION

It is necessary to provide a modern vehicle tire with low rolling resistance, good dry and wet tractions, secure braking, reasonable service life, excellent handling, good tear resistance, and other special properties such as low electrical resistance and high thermal conductivity.[1,2] Traction, especially wet traction, is the most important tire performance from a safety point of view, and much effort has been devoted by tire makers to improving traction. Traction refers to the frictional resistance generated on the tread surface by the roughness of the road surface.[3] Traction is directly related to energy loss in each deformation cycle: each point in the tire goes through a stress–strain cycle once every rotation. Because of the viscoelastic nature of the rubber compound, the deformation leads to energy loss in the form of heat in each cycle.[4]

Carbon nanotubes (CNTs) are excellent candidates for multifunctional rubber reinforcement because of their high strength (~100 times stronger than steel), high modulus (~1 TPa), high thermal conductivity (about twice as high as diamond), excellent electrical capacity (1000 times higher than copper), and thermal stability (2800 °C in vacuum).[5–9] Thus, the future of CNT application lies mainly in the fabrication of high-end materials ranging from reinforced composites to electrical sensors. Many studies have reported on CNT/rubber nanocomposites regarding preparation techniques and vulcanization characteristics as well as mechanical, electrical, and thermal properties. For example, Ata[9] reported a general approach to fabricate elastomeric composites possessing high electrical conductivity for applications ranging from wireless charging interfaces to stretchable electronics. Galano[10] studied the potential role of CNTs as free-radical scavengers, an ongoing area of research. Park[8] investigated the effect of diameter and content of CNTs on the physical properties of SBR/CNTs nanocomposites. But there are no reports about the application of CNTs in tire compound to improve their comprehensive performances or no reports

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สำเนาเพื่อใช้ในการศึกษาเท่านั้น

TABLE I
TECHNICAL DATA OF CNT COMPOUND

Item	Technical index
Diameter, nm	12–15
Length, μm	3–12
Layers	8-15
Weight loss at 875 °C, %	100
Moisture at 105 °C, %	0.20
Specific surface area, m^2/g	260

that have investigated the correlation between the CNT tire performances and laboratory test results, especially for dynamic properties. Wu[11] studied the use of CNTs and graphene in tire tread compound. Lu[12] studied multi-wall CNT bundles (MWCNTBs) with the same orientation and high surface defects that can be directly incorporated into the elastomer matrix through the melt compounding technique. But all of these published studies had no further study on the correlation between the CNT tire performances and laboratory results, especially for the effect of the CNT incorporation on the dynamic properties of the compound and its tire performances. The CNT working mechanism was therefore unknown.

In this study, we investigated the advantages of CNTs when used in tire tread compounds, including their mechanical, thermal, and electrical properties and tire performances. Furthermore, through the correlation between the dynamic properties of the rubber compounds and the actual tire performances, the CNT working mechanism in the tire tread compound was proposed for the first time.
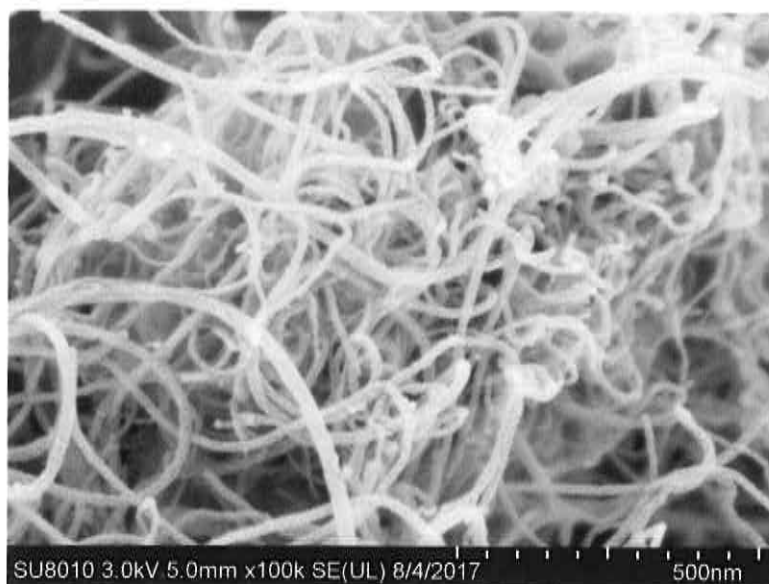

SU8010 3.0kV 5.0mm ×100k SE(UL) 8/4/2017   500nm

FIG. 1. — Scanning electron microscopic image of CNTs (magnified 100 000 times).

Ingredient	Reference compound	CNT compound
TSR20	20	20
SBR1739	110	110
N234	95	45
CNT		20
HD115MP	10	10
TESPT	0.5	0.5
C9 resin	24	24
Stearic acid+ZnO	5.5	5.5
Wax+6PPD+CBS+S	7.9	7.9

EXPERIMENTAL

MATERIALS

SBR1739 (Shenhua Chemical Industry Co., Ltd., Nantong, China) was used as the rubber matrix. MWCNTs were obtained from Shandong Dazhan Nano Materials Co., Ltd. (Binzhou, China). The technical data for CNTs are shown in Table I and Figure 1. The coupling agent used was bis(triethoxysilylpropyl)tetrasulfide (TESPT; Nanjing Shuguang Chemical Group, Nanjing, China). HD115MP (Quechen Silicon Chemical Co., Ltd., Wuxi, China) and carbon black (CB) ISF N234 (Cabot Co., Ltd., Boston, MA, USA) were used as the reinforcement fillers. Stearic acid, the antioxidant N-(1,3-dimethylbutyl)-N'- phenyl-p-phenylenediamine (6PPD; Shandong Yanggu Huatai Chemical Co., Ltd., Liaocheng, China), sulfur (China Sunsine Chemical Holdings Ltd., Heze, China), the accelerator N-cyclohexy-2-benzothiazole sulfonamide (CBS; China Sunsine Chemical Holdings), and zinc oxide (ZnO; Dalian JinShi Zinc Oxide Co., Ltd., Dalian, China) were used as additives.

COMPOUND FORMULAS

Compound formulas used in this study are listed in Table II. The reference compound was a typical CB-filled compound for passenger tire treads. CNT compound was a composite filled by 20 phr CNT to replace 50 phr N234 compared to the reference compound.

Time or temperature	Action
0 min	Add rubber, ZnO, stearic acid, wax, 6PPD
1 min	Add silica, TEPST, N234
2 min	Add resin
3 min	Ram up and down
155 °C	Dump

FIG. 2. — Information of tires.

MIXING PROCESS

The compounds were mixed in two steps, unless otherwise indicated. The nonproductive step was carried out in a 370 L internal mixer (Tangential Mixer XM370; Dalian Rubber and Plastics Machinery Co., Ltd., Dalian, China). The mixing process used is shown in Table III. The starting temperature was 50 °C, and the mixer temperature was kept at 50°C. The dump temperature was 155 °C. The productive step was carried out on an automatic two-roll mill. The accelerators and sulfur were added during this step.

Curing properties of the compounds were determined by using a D-MDR3000 rheometer (MonTech Rubber Testing Solutions, Buchen, Germany) at 150 °C for 60 min. The compounds were vulcanized at 150 °C and 100 bar for 40 min. All the tires were manufactured in Shandong Fengyuan Tire Manufacturing Co., Ltd (Zaozhuang, China). The size of tires was 205/45ZR17 88W (Figure 2).

CHARACTERIZATIONS

The dynamic properties of composites were tested by using a Metrivib DMA+1000 machine (01db-Metravib, Limonest, France) and included strain sweep, temperature sweep, and frequency sweep. Tire tests were performed according to the ECE R117 regulation, and the vehicle model was Chevrolet Sail. For the dry braking distance test, the velocity was from 100 to 0 km/h, and the velocity of wet braking distance test was from 80 to 20 km/h. Other testing methods and standards are shown in Table IV.

TABLE IV
TESTING METHODS AND STANDARDS

Testing method	Reference standard
Mooney viscosity	ASTM D1646-2007
Mooney scorch	ASTM D1646-2007
Hardness/Shore A	ASTM D2240-2010
Tensile properties	ASTM D412-2006
Tear resistance	ASTM D624-2007

TABLE V
PHYSICAL PROPERTIES FOR REFERENCE AND CNT COMPOUNDS

	Reference	CNT
ML_{1+4} @ 100 °C	76	95
Mooney Scorch, min	18.7	21.2
Ts2, min	8.1	6.0
T90, min	24.0	21.8
Minimum torque (S'_{min}), dN·m	3.43	6.48
Maximum torque (S'_{max}), dN·m	13.43	17.72
$S'_{max} - S'_{min}$, dN·m	10.00	11.24
Tensile strength, MPa	18.6	20.7
Elongation at break, %	508	568
Tear resistance, kN/m	61.6	66.5
Hardness, Shore A	73	74
MA10, MPa	7.03	9.03
MA100, MPa	2.29	3.09
MA300, MPa	2.54	2.46
MA300/MA100	1.11	0.80
Akron abrasion, cm^3	0.262	0.259

RESULTS AND DISCUSSION

COMPOUND PHYSICAL PROPERTIES

The influence of 50 phr CB N234 substituted by 20 phr CNTs on the processability and physical properties is shown in Table V and Figure 3. Because of the extremely high specific surface area of CNTs, the interactions between filler–filler and filler–elastomer were very strong, resulting in increased Mooney viscosity as well as minimum torque (S'min) from the vulcanization curve. This was not beneficial for the processability. There was improvement in tensile strength,
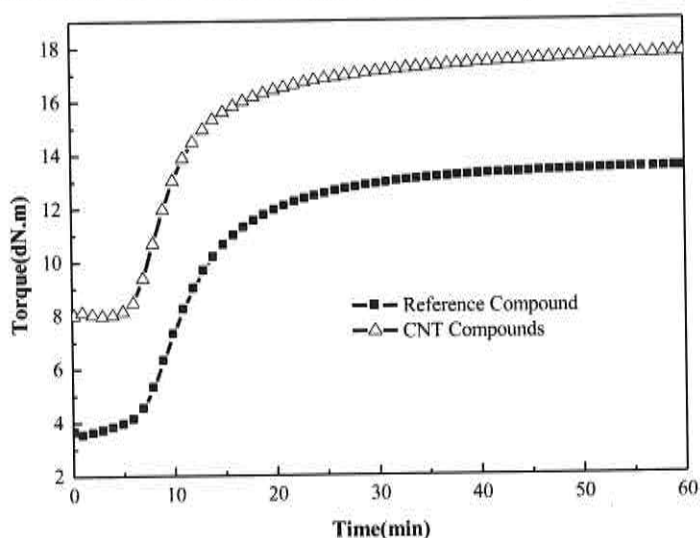

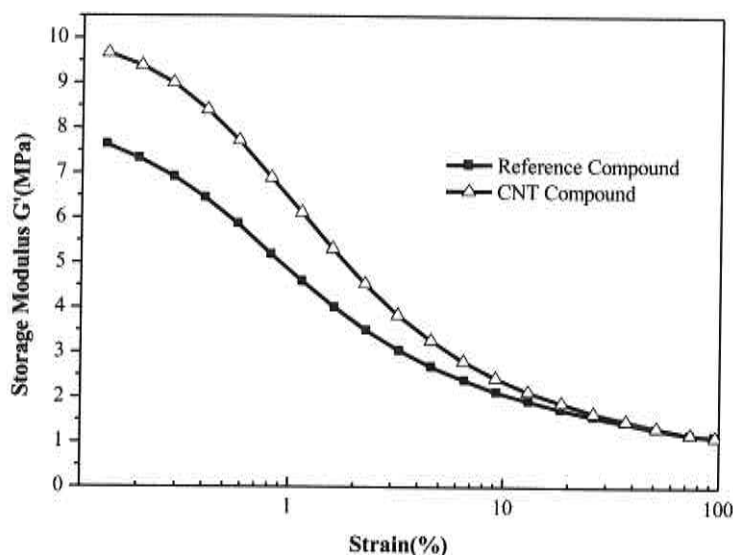FIG. 3. — Vulcanization curves of compounds at 150 °C.

FIG. 4. — Strain sweep curves of storage modulus (G') at 40 °C for reference and CNT compounds.

elongation at break, and tear resistance that could be contributed by the high reinforcement of CNTs[13] and the synergistic effect of CNTs and CB.[14]

HANDLING

Hardness and modulus at 10% (MA10) are generally used as indicators of capacity in resisting exterior forces that relate to the tire stiffness or rigidity. It was found that although the Shore A hardness was similar, the MA10 was much higher for the CNT compound than that of the reference. Increased MA10 rigidity probably resulted from the reinforcement effect of the CNTs and higher extents of cross-linking of rubber[8] as it is well known that dynamic rigidity is relevant to tire handling performance. The storage modulus of strain sweep at 40 °C was performed to predict the handling performance of the tire, and the results are shown in Figure 4. The storage modulus decreases upon increasing the strain amplitude, known as the Payne effect, and is related to the filler–filler interaction.[15] Because of the nano size of CNTs, large surface, area, and large aspect ratio, it had higher CNT–elastomer and CNT–CNT interaction than that of CB, resulting in increased storage modulus. One of the important functions of the tire is transferring engine torque to generate traction and direction, so sufficient rigidity is necessary for the tire tread compounds, especially for racing and sports tires. As mentioned, the rigidity of tread compounds was enhanced

TABLE VI
HANDLING AND COMFORT SUBJECTIVE TEST RESULTS FOR REFERENCE AND
CNT TIRES

	Reference	CNTs
Comfort	6.5	6.25
Wet handling	6.5	6.75
Dry handling	6.5	6.75

TABLE VII
WET AND DRY BRAKING DISTANCES FOR REFERENCE AND CNT TIRES

	Reference	CNTs
Wet braking distance (80 to 20 km/h), m	29.2	27.3
Dry braking distance (100 to 0 km/h), m	39.8	39.2

by the incorporation of CNTs; hence, the handling performance of the vehicle test was improved (Table VI).

TRACTION

Tires with CNT compounds showed better wet and dry tractions compared to CB compounds. The braking distances were reduced by 6.5 and 1.5%, respectively (Table VII). The mechanism of wet traction improvement with CNTs requires further investigation. The friction coefficient of rubber sliding on the road surface depends strongly on temperature and frequency. The data obtained at different frequencies and temperatures can be transformed into a master curve by multiplying the frequency with a suitable shift factor (α_T) based on the time–temperature superposition principle [also known as Williams–Landel–Ferry (WLF) law]. The master curve could be used to describe the properties of the materials over a wide range of frequencies, especially high frequency ranges up to megahertz and gigahertz.[16]

Frequency sweeps of viscoelastic properties were measured at different temperatures. Tan δ curves are shown in Figures 5 and 6 for reference and CNT compounds, respectively. The tan δ curves at different temperatures were shifted to a reference temperature of 30 °C by using the time–temperature superposition principle. Empirically determined α_T values are shown in Figure 7 as a function of temperature.[4] The CNT-filled compound had an α_T value that was more temperature dependent than that of the CB compound. Consequently, when the CNT and CB compounds had the same glass-transition position under the temperature sweep test, the tan δ curve would shift to the higher frequency domain (10^4–10^8 Hz) with the incorporation of CNTs, which was considered as the working zone for grip (Figure 8). By contrast, storage modulus (G') at high frequency (Figure
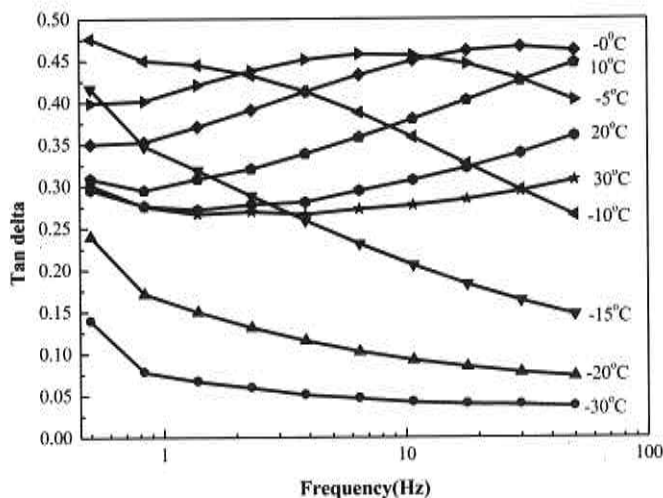

FIG. 5. — Frequency sweep of tan δ at different temperatures for reference compound.
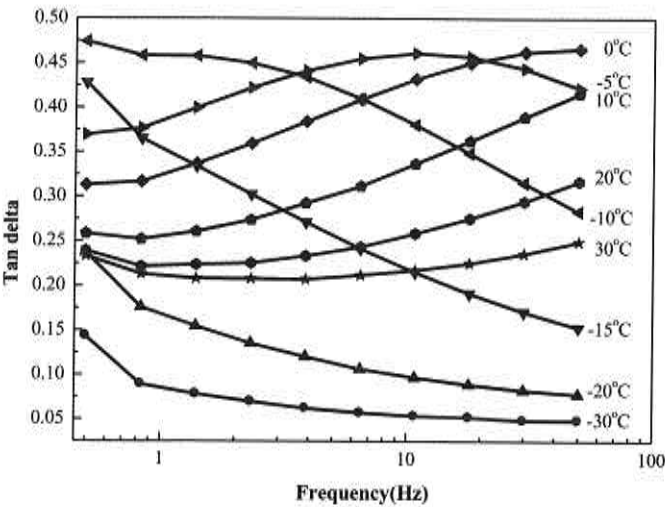
FIG. 6. — Frequency sweep of tan δ at different temperatures for CNT-filled compounds.

9) is related to the microscopic deformation when the tire contacts the road. A lower storage modulus would induce large deformation that is also beneficial to the friction. From the master curve dynamic properties, we can explain the improved wet and dry tractions for the CNT compound because of its higher hysteresis loss (higher friction) and lower modulus (higher contact area) at high frequency domain for grip.

The empirically determined $\log(\alpha_T)$ was used to calculate the WLF constants C_1 and C_2 in Eq. 1:

$$\log(\alpha_T) = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \qquad (1)$$

where $(T - T_0)/\log(\alpha_T)$ was plotted against $(T - T_0)$ and C_1 and C_2 were determined by the slope and intercept of the fitted line.[16] The constants C_1 and C_2 were calculated according to the WLF equation[17]
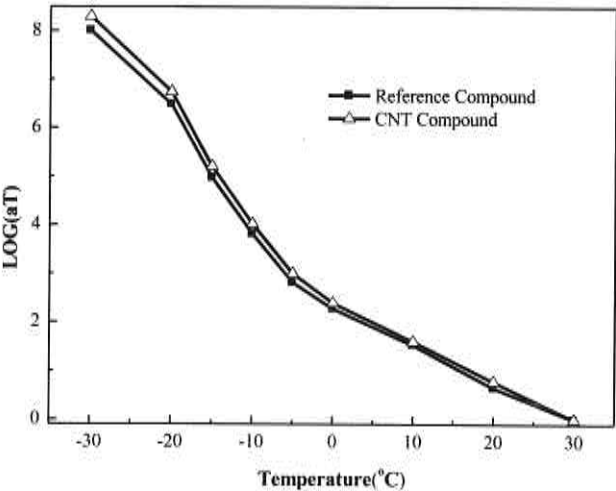

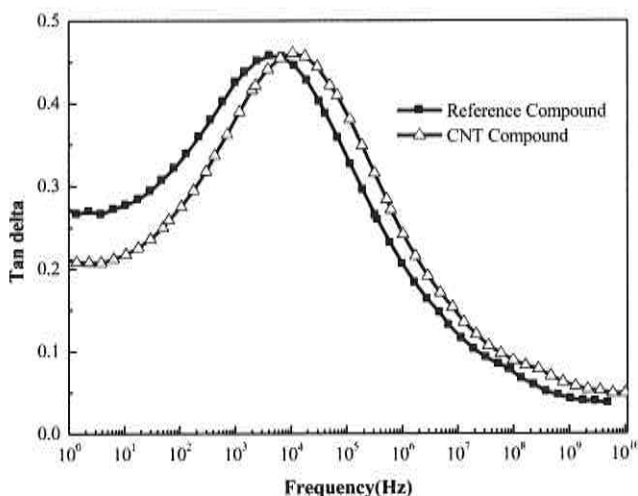FIG. 7. — Temperature dependence of shift factor (α_T) (reference temperature $T_0 = 303$ K).

FIG. 8. — Frequency sweep master curves of tan δ for reference and CNT compounds.

and are shown in Table VIII. The calculated WLF constants C_1 and C_2 appear to reflect reinforcement since the CNT compound had a larger value than the reference. Since the molecular chains in CNT-filled compound were less mobile than those in the CB compound, the temperature dependence would increase.

WEAR RESISTANCE

Tire wear is a consequence of sliding under friction. It is a complex process that depends on a range of factors such as abrasion, surface structure, texture, force, and tread compounds.[18] MA300/MA100 (Table V) and Akron abrasion of compounds are always used to predict the wear resistance of a tire.[19] However, it was found that they had a paradoxical conclusion, with 33% lower mileage for the CNT tire (Table IX). This might be due to the difference in abrasion conditions between
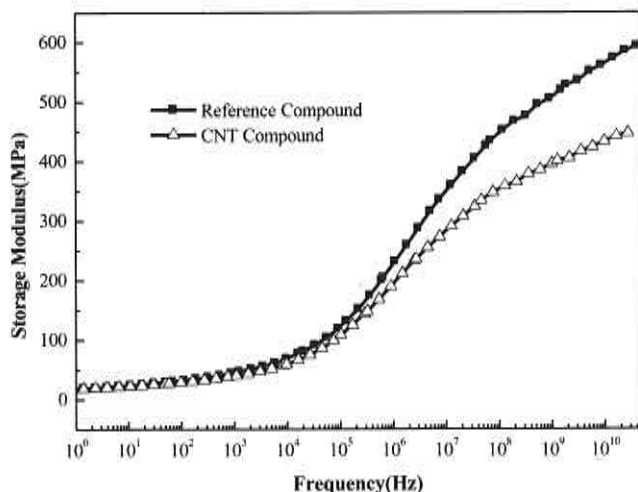

FIG. 9. — Frequency sweep master curves of G' for reference and CNT compounds.

TABLE VIII
CALCULATED WLF CONSTANTS C_1 AND C_2

Constant	Reference compound	CNT compound
C_1	9.9	26.2
C_2	157	348

Akron and real tire use. Akron abrasion was performed at a force of 26.7 N. At this force it was difficult to induce large deformation, so the results had no significant difference between reference and CNT compounds. By contrast, MA300/MA100 compounds are always used to characterize the molecular chain slipping ability and strength on the filler surface. They are related to the reinforcement of fillers at large deformation. CNT-filled compounds showed a lower MA300/MA100 ratio than the reference compound because the regular surface of CNT had fewer functional points to archer the elastomer chains than that of CB.

ROLLING RESISTANCE

Tire rolling resistance arises from the deformation of all tire components under the rotational contact with the road surfaces. From the tire prospective, rolling resistance comes from a combined effect of component material hysteresis loss, tire architecture, inflation pressure, and tire stiffness. According to Futamura's deformation index analysis, the energy hysteresis loss of the passenger car tire is approximately proportional to tan δ of the tire compounds.[20] The existence of a strong filler–filler network between CNTs is clearly evidenced from a larger Payne effect (Figure 4), but interestingly lower tan δ at small strains and higher tan δ at large deformation above 5% (Figure 10).[21] Because of the strong CNT entanglement network, the hysteresis loss (tan δ) of the CNT compounds is low at small deformation. However, when the deformation level becomes large and the CNT entanglement network starts to break down, the elastic modulus of the compounds drops significantly and the hysteresis loss (tan δ) increases dramatically. The tan δ value of temperature sweep from 40 to 80 °C could also be used as an indicator of rolling resistance. Figure 11 shows that tan δ of CNT compound was higher than that of the reference. From the above-mentioned dynamic property results, rolling resistance was expected to increase with incorporation of CNTs, and the rolling resistance of the tires showed that the CNT tire was 0.9 N/kN (Table X).

CONCLUSIONS

Substituting 50 phr CB N234 by 20 phr CNTs could maintain hardness but increase static and dynamic moduli due to the strong interaction between CNT–CNT and CNT–rubber. This was beneficial for the tire handling, with 0.25 point improvement in the subjective testing. For the CNT-

TABLE IX
TIRE WEAR RESISTANCE FOR REFERENCE AND CNT COMPOUNDS

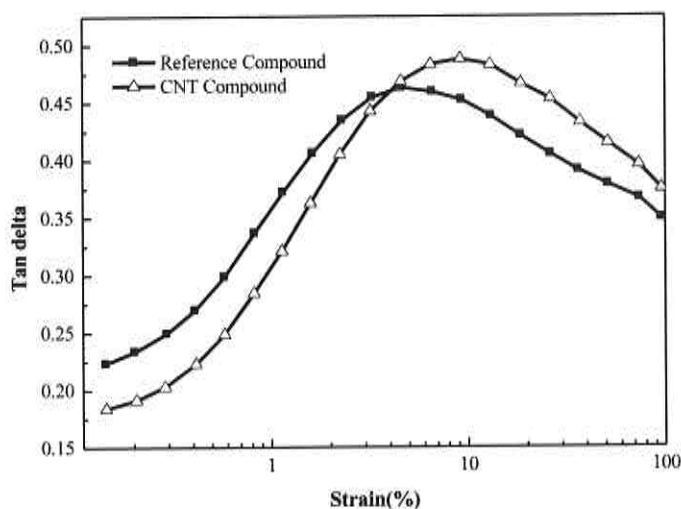|	Reference	CNTs
Tire weight change, wt%	2.8	4.1
Groove wear depth, mm	0.82	1.26
Expecting mileage (front wheel), km	60 000	40 000

FIG. 10. — Strain sweep of tan δ at 40 °C for reference and CNT compounds.

filled compound, 1.5% improvement on a dry road and 6.5% improvement on a wet road can be explained successfully by the increased hysteresis loss (tan δ) and decreased storage modulus (G′) at high frequency domain (10^4–10^8 Hz). However, the reinforcement factor MA300/M100 decreased with the incorporation of CNTs, and the wear resistance of tire was reduced by 33%. The reinforcement of CNTs was not as good as that of CB because there were fewer defects on the CNT surface than those on the CB surface for elastomer molecular bonding. The high specific surface area and strong filler–filler interaction of CNTs led to the trade-off of rolling resistance by 7%. CNT-filled compounds were demonstrated to have superior handling and traction performances that were suitable for racing and sports car tires.

For the first time, high frequency dynamic properties of CNT-filled compounds were revealed. All the tire performances can be explained using the master curves and common dynamic
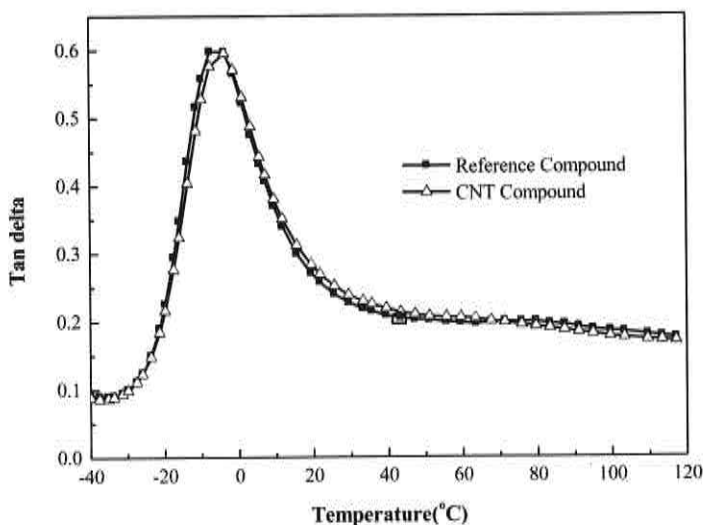

FIG. 11. — Temperature sweep of tan δ for reference and CNT compounds.

TABLE X

TIRE ROLLING RESISTANCE FOR REFERENCE AND CNT COMPOUNDS

	Reference	CNTs
Rolling resistance coefficient, N/kN	12.8	13.7

properties. It is implied by WLF law calculation that strong interaction between CNTs and rubber resulted in higher temperature dependence. Therefore, tan δ-frequency master curve was shifted to the high frequency. Further detailed studies are in progress and the results will be reported in the future.

ACKNOWLEDGEMENTS

REFERENCES

[1] W. Kaewsakul, K. Sahakaro, W. K. Dierkes, and J. W. M. Noordermeer, RUBBER CHEM. TECHNOL. 86, 313 (2013).

[2] M. Castellano, L. Conzatti, G. Costa, L. Falqui, A. Turturro, B. Valenti, and F. Negroni, Polymer 46, 695 (2005).

[3] G. Heinrich and H. B. Dumler, RUBBER CHEM. TECHNOL. 71, 53 (1998).

[4] S. Maghami, W. K. Dierkes, T. V. Tolpekina, S. M. Schultz, and J. W. M. Noordermeer, RUBBER CHEM. TECHNOL. 85, 513 (2012).

[5] W. K. Park and J. H. Kim, Macromol. Res. 13, 206 (2005).

[6] A. A. Abdul-Lateef, M. Al-Harthi, and M. A. Atieh, Arab. J. Sci. Eng. 35, 49 (2010).

[7] Y. X. Zhou, P. X. Wu, Z.-Y. Cheng, and S. Jellani, Express Polym. Lett. 2, 40 (2008).

[8] Y. S. Park, S. Hub, S. J. Kang, S. I. Yun, and K. H. Ahn, Carbon Lett. 10, 320 (2009).

[9] S. Ata, T. Mizuno, A. Nishiza, C. Subramaniam, D. N. Futaba, and K. Hata, Sci. Rep. 4, 7232 (2014).

[10] A Galano, Nanoscale 2, 373 (2010).

[11] Y. P. Wu and L. Q. Zhang, Chin. Sci. Bull. 61, 3371 (2016).

[12] Y. Lu, J. Liu, G. Hou, J. Ma, W. Wang, F. Wei, and L. Zhang, Compos. Sci. Technol. 137, 94 (2016).

[13] D. Ponnamma, K. K. Sasasivuni, Y. Grohens, Q. Guo, and S. Thomas, J. Mater. Chem. C 2, 8446 (2014).

[14] Y. He, J. Gao, X. Gong, and J. Xu, Results Phys. 7, 4352 (2017).

[15] S. S. Sarkawi, W. K. Dierkes, and J. Noordermeer, Rubber World 247, 26 (2012).

[16] H. Mouri and K. Akutagawa, RUBBER CHEM. TECHNOL. 72, 960 (1999).

[17] P.-S. He, Polym. Bull. 2, 75 (2002).

[18] D. P. Gerrard and J. Padovan, RUBBER CHEM. TECHNOL. 75, 29 (2001).

[19] M. J. Wang, Tire Ind. 19, 280 (1999).

[20] P. Zhang, M. Morris, and D. Doshi, RUBBER CHEM. TECHNOL. 89, 79 (2016).

[21] F. Clement, L. Bokobza, and L. Monnerie, RUBBER CHEM. TECHNOL. 78, 232 (2005).