

# The Partial Replacement of Silica or Calcium Carbonate by Halloysite Nanotubes as Fillers in Ethylene Propylene Diene Monomer Composites

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**ABSTRACT:** The effect of partial replacement of silica or calcium carbonate ( $\text{CaCO}_3$ ) by halloysite nanotubes (HNTs) on the curing behavior, tensile properties, dynamic mechanical properties, and morphological characteristics of ethylene propylene diene monomer (EPDM) composites was studied. Five different compositions of EPDM/Silica/HNT and EPDM/ $\text{CaCO}_3$ /HNT compounds (i.e. 100/30/0, 100/25/5, 100/15/15, 100/5/25, and 100/0/30 parts per hundred rubber (phr)) were prepared on a two-roll mill. The results indicated that the replacement of  $\text{CaCO}_3$  by HNTs increased the tensile strength, elongation at break ( $E_b$ ), and tensile modulus of composites from 0 to 30 phr of HNTs whereas for silica, the maximum tensile strength and  $E_b$

occurred at 5 phr loading of HNTs with an enhanced stress at 300% elongation (M300). The curing results show that, with replacement of silica or  $\text{CaCO}_3$  by HNTs, the cure time ( $t_{90}$ ) and cure rate (CRI) were decreased and increased, respectively. Scanning electron microscopy investigation confirmed that co-incorporation of 5 phr of HNTs with silica would improve the dispersion of silica and enhanced the interactions between fillers and EPDM matrix. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3910–3919, 2009

**Key words:** halloysite nanotubes; ethylene propylene diene monomer; mechanical properties; electron microscopy; composites

## INTRODUCTION

The reinforcement of rubbers is identified as the capability of the fillers to improve the tensile strength, stiffness as well as abrasion and tear resistance of the vulcanizates.<sup>1–3</sup> Previously, various kinds of carbon blacks have been used as reinforcing fillers for rubbers.<sup>4–7</sup> In recent years, several studies have been reported on the replacement of carbon black with light colored, mineral, and natural fillers such as silica,<sup>8,9</sup> calcium carbonate,<sup>10–12</sup> and clay<sup>3,13–15</sup> as a result of the high cost of carbon black and pollution problems. For instance, Rauline<sup>8</sup> designated that tires which were filled with silica, demonstrate various improvements over tires filled by carbon black. Because of the hydrophobic surface characteristics and special particle shapes of carbon black they can disperse easily within the hydrophobic elastomer. In contrast, however, as silica has hydrophilic surface, its dispersion in the rubbery elastomer had encountered difficulty.<sup>8</sup> A number of techniques have been

developed to relieve the dispersion of silica into the rubber compositions, such as wet and dry blending processes<sup>8,9</sup> but all are complex and costly.

When a non-conjugated diene (a third monomer), is added to the copolymerization of ethylene and propylene, the resulting rubber becomes a terpolymer, i.e. ethylene propylene diene terpolymer (EPDM) which can then be vulcanized by sulfur. The particularly high mechanical, dynamic, and electrical properties as well as resistance to heat, aging, and oxidation and having low temperature flexibility as well as the resistance to swelling, makes EPDM the most suitable rubber for automotive sealing systems, electrical applications, building profiles, roof sheeting, and under the hood applications.<sup>1–4</sup>

Halloysite nanotubes (HNTs) are naturally dioctahedral 1 : 1 clay mineral ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ), which has the same chemical composition as kaolinite.<sup>16</sup> The outer surface of halloysite is similar to  $\text{SiO}_2$  whereas the properties of inner side and edges of the tubes could be considered as  $\text{Al}_2\text{O}_3$ .<sup>17,18</sup> The HNTs have typical dimensions of 150 nm – 2  $\mu\text{m}$  long, 20–100 nm outer diameter, and 5–30 nm inner diameter and their most common morphology is hollow tube.<sup>19</sup>

The aim of this work is to study the reinforcing effect of partial replacement of silica or calcium carbonate by HNTs on the tensile, curing,

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**TABLE I**  
**Formulation Used in EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT Composites (phr)**

EPDM/Silica/HNT or EPDM/CaCO <sub>3</sub> /HNT	ZnO	Stearic acid	MBT	TMTD	Sulphur
100/30/0	5	1.5	0.8	1.5	1.5
100/25/5	5	1.5	0.8	1.5	1.5
100/15/15	5	1.5	0.8	1.5	1.5
100/5/25	5	1.5	0.8	1.5	1.5
100/0/30	5	1.5	0.8	1.5	1.5

morphological, and dynamic mechanical properties of EPDM composites.

## EXPERIMENTS

### Materials and mixing procedures

The EPDM, 778Z with ethylene content of 67%, ENB of 4.3%, and ML (1+4) 125°C of 63 MM was purchased from Keltan DSM Elastomers. The HNTs grade of ultrafine were supplied by Imerys Tableware Asia Limited, New Zealand. The elemental composition of HNTs is as follows (wt %): SiO<sub>2</sub>, 49; Al<sub>2</sub>O<sub>3</sub>, 34.8; Fe<sub>2</sub>O<sub>3</sub>, 0.35; TiO<sub>2</sub>, 0.12; Na<sub>2</sub>O, 0.25; MgO, 0.15.<sup>20</sup> After 24 h drying at 80°C in an oven, the density of HNTs was found to be 2.14 g cm<sup>-3</sup>, measured by a Miromeritics, Accupyc 1330 (gas pycnometer). Calcium carbonate (OMYACARB 2T-SA) was obtained from Malaysian Calcium Corporation (M) Sdn Bhd. whereas precipitated Silica (Vulcasil C) as a filler, as well as zinc oxide as an activator for sulfur vulcanization, stearic acid as a dispersing agent, and accelerator activator, tetramethyl thiuram disulfide (TMTD) and 2-mercapto benzothiazole (MBT) as accelerators and sulfur acts as a crosslinking agent between rubber molecules during vulcanisation, were all obtained from Bayer (M) Ltd and used as received. The formulation of the composites and comparison of physical characteristics of fillers are shown in Tables I and II, respectively. The ratio of all vulcanization ingredients and sulfur was chosen due to the standard formulations which used for preparation of the EPDM based products in the rubber industry and reported by various researchers.<sup>1,2,21</sup>

Five different compositions of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT compounds were prepared on a laboratory-sized (160 × 320 mm<sup>2</sup>) two-roll mill; model XK-160. The mixing time of 21 min was kept constant for all compounds. The vulcanization behavior of composites such as cure time (*t*<sub>90</sub>), scorch time (*t*<sub>S2</sub>), maximum torque (*M*<sub>H</sub>), minimum torque (*M*<sub>L</sub>), viscous torque (*S*'), and tan delta were determined at the processing temperature of 150°C using a Monsanto Moving Die Rheometer (MDR 2000). In addition to the curing characteristics, the cure rate index (CRI) of the cured compounds and

difference between *M*<sub>H</sub> and *M*<sub>L</sub> ( $\Delta S$ ) were calculated according to eqs. (1) and (2), respectively:

$$\text{CRI} = 100/(t_{90} - t_{S2}) \quad (1)$$

$$\Delta S = M_H - M_L \quad (2)$$

Compression molded sheets were prepared by curing the compounds in hot press at the temperature of 150°C, based on the *t*<sub>90</sub> obtained in MDR measurements.

Tensile test was performed on dumb-bell shaped samples which were cut from the molded sheets using a universal tensile testing machine (Instron 3366) at room temperature (25 ± 2°C) and at a cross-head speed of 500 mm/min according to ASTM D 412-51. A minimum of five readings of tensile strength, elongation at break (*E*<sub>b</sub>), and tensile modulus at 100% and 300% of elongation (*M*<sub>100</sub> and *M*<sub>300</sub>) were used to determine the mean values.

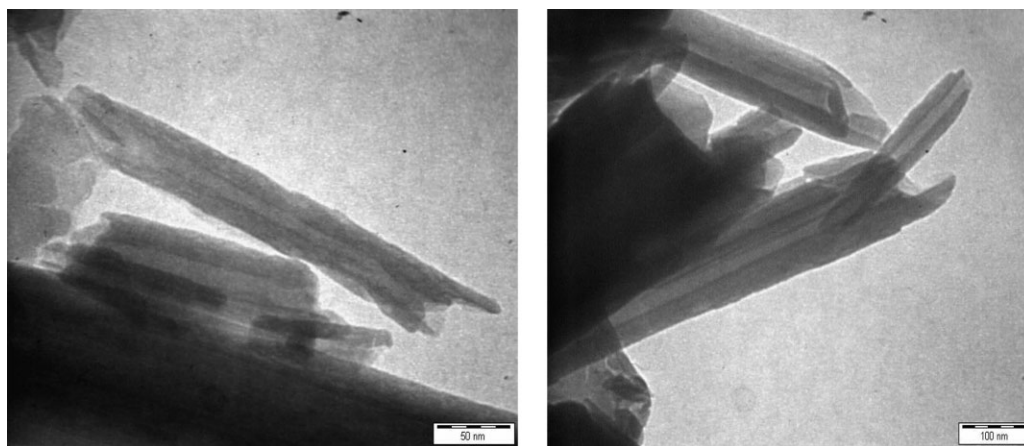
Dynamic mechanical properties were measured by using a dynamic mechanical analyzer (Perkin Elmer DMA7). The samples were subjected to a cyclic tensile strain with force amplitude of 0.1 N at a frequency of 10 Hz. Storage modulus and mechanical loss factor (Tan  $\delta$ ) were determined in the temperature range from -90°C to 60°C at a heating rate of 2°C/min.

The morphologies of tensile fracture surfaces of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT composites were observed under a Supra-35VP field emission scanning electron microscope (SEM). The fracture surfaces of the samples were coated with a thin layer of Pd-Au, to prevent electrostatic charging during evaluation.

Particle size and surface area of HNTs was determined by a dry-powder technique using a laser diffraction particle analyser (Helos Windox5, Sympatec GMBH, Germany). Nanotubular shape of the halloysite was examined by a transmission electron microscopy (Philips CM12). The halloysite was suspended in ethanol and subsequently a droplet was pipette out from suspension and placed on a carbon thin film coated 400 mesh copper grid for 2 min. The dispersed halloysite was then dried and observed by TEM.

**TABLE II**  
**Physical Properties of Halloysite Nanotubes, Silica, and Calcium Carbonate**

Parameter	Halloysite nanotubes (HNTs)	Silica (vulcasil C)	Calcium carbonate
Density (g/cm <sup>3</sup> )	2.1	2.0	2.7
Surface area (m <sup>2</sup> /g)	85.0	50.0	3.6



**Figure 1** TEM micrograph showing the inner diameter and straight form of a HNT.

## RESULTS AND DISCUSSION

### Transmission electron microscopy of halloysite nanotubes

Figure 1 clearly demonstrates that the HNTs have a hollow tubular morphology with extremely straight form which enables them to have good dispersion inside the polymer matrix. As we have reported in our previous work<sup>19</sup> and from Figure 1, there is a hollow space (lumen structure) inside the HNTs with inner diameter from 5 to 30 nm. The HNTs have typical dimensions of 150 nm – 2 μm long, 20–100 nm outer diameter. The volume percentage of this lumen can be as high as 15%.

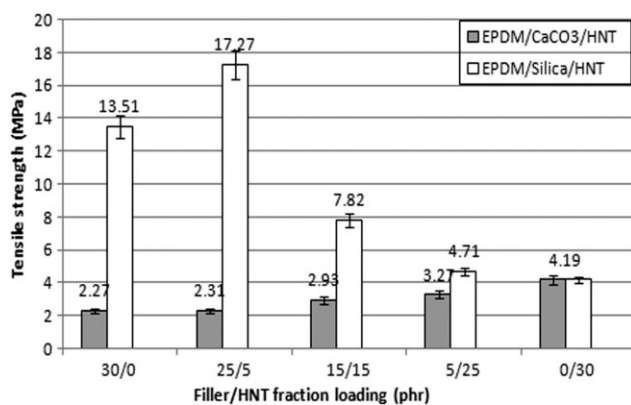
### Curing behavior

The curing characteristics of partially filled EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT compounds are demonstrated in Table III. The optimum cure time ( $t_{90}$ ) significantly decreased in both compounds involving replacement of silica or calcium carbonate by HNTs from 0 to 30 phr loading. The decreasing of  $t_{90}$  for EPDM/Silica/HNT composites is attributed to the high tendency of silica and calcium carbonate to interact with accelerators which led to

reduce the number of active sulfurating agents and higher surface area of HNTs in comparison to calcium carbonate and silica. By partial replacement of silica or calcium carbonate by HNTs the number of sulfurating agents was increased and subsequently the  $t_{90}$  of the vulcanizates decreased. Teh et al.<sup>14</sup> and Younan et al.<sup>22</sup> have reported that the high tendency of silica and calcium carbonate to interact with accelerators would lead to increasing of cure time by addition of silica and calcium carbonate. The scorch time, which is the measure of premature vulcanization, means the number of minutes which takes to 2 dNm rise above  $M_L$ .<sup>2</sup> The scorch time of EPDM compounds was not changed so much with partial replacement of silica by HNTs from 0 to 30 phr loading, but with HNTs replaced of CaCO<sub>3</sub>, the scorch time decreased. A longer scorch time relieved filling of complex molds with uncured rubber compounds and on the other hand a shorter scorch time decreased the shelf life of products. As can be seen in Table III, the minimum torque of EPDM/Silica/HNT composites was decreased with partial replacement of silica by HNTs. The decreasing of  $M_L$  reveals the easier processability of compounds in the presence of HNTs. On the other hand, the increment of  $M_L$  and  $M_H$  of EPDM/CaCO<sub>3</sub>/HNT with

**TABLE III**  
Curing Behaviour of Composites with 100 phr EPDM Content

Composition	Silica/HNT					CaCO <sub>3</sub> /HNT				
	30/0	25/5	15/15	5/25	0/30	30/0	25/5	15/15	5/25	0/30
Fraction	30/0	25/5	15/15	5/25	0/30	30/0	25/5	15/15	5/25	0/30
$t_{90}$ (min)	28.72	28.08	22.23	17.30	14.00	21.82	17.00	14.32	14.02	14.00
$t_{s2}$ (min)	1.24	1.39	1.69	1.68	1.26	7.41	4.15	2.13	1.51	1.26
$M_H$ (dN m)	24.81	22	20.54	18.1	17.61	15.56	16.01	16.3	17.14	17.61
$M_L$ (dN m)	3.53	2.0	0.98	0.68	0.65	0.51	0.55	0.56	0.61	0.65
$\Delta S = M_H - M_L$	21.28	20.0	19.56	17.42	16.96	15.05	15.46	15.74	16.53	16.96
CRI (min <sup>-1</sup> )	3.92	4.03	5.12	6.96	7.92	6.94	7.78	8.2	7.4	7.92
Tand @MH	0.116	0.084	0.041	0.036	0.032	0.055	0.055	0.044	0.038	0.032
$S''@MH$ (dN m)	3.10	2.01	0.89	0.69	0.56	0.86	0.87	0.72	0.66	0.56



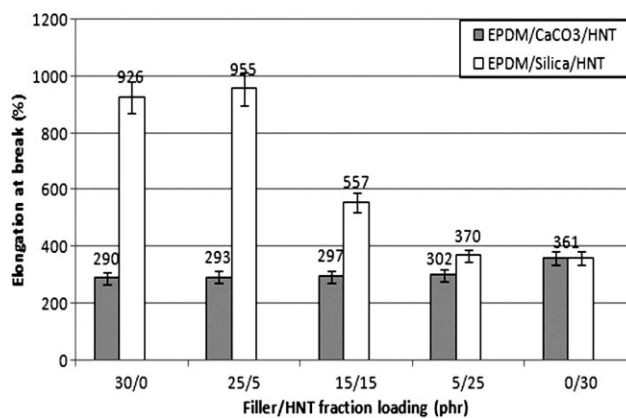
**Figure 2** Comparison of tensile strength of EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT compounds.

increasing of HNTs loading from 0 to 30 phr designates that HNTs have greater reinforcing effect on EPDM in comparison with CaCO<sub>3</sub>. The higher  $M_H$  value of EPDM composite with 30 phr of silica compared to EPDM filled with 30 phr of CaCO<sub>3</sub> is attributed to the higher reinforcing effect of silica over calcium carbonate. The curing rate (CRI) of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT composites was increased with increasing of HNT loading as shown in Table III.

The  $\tan \delta$  ( $\tan \delta @MH$ ) and viscous torque ( $S''@MH$ ) of rubbers are related to the resilience and damping characteristics of compounds, respectively.<sup>23</sup> The lower value of  $\tan \delta$  for cured compound, the greater its resilience.<sup>24</sup> The results show that both  $\tan \delta$  ( $\tan \delta @MH$ ) and viscous torque ( $S''@MH$ ) of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT composites were decreased with partial replacement of silica or calcium carbonate by HNTs. These results show that the addition of HNTs in partial replacement of silica and calcium carbonate would reduce the damping properties and increase the resilience of EPDM composites.

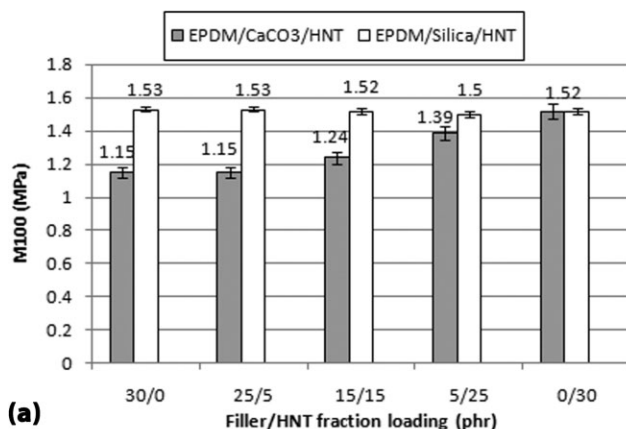
### Tensile properties

The tensile strength and elongation at break ( $E_b$ ) of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT composites are shown in Figures 2 and 3, respectively. It can be seen that the tensile strength and  $E_b$  of EPDM/CaCO<sub>3</sub>/HNT composites increased gradually with replacement of CaCO<sub>3</sub> by HNTs. As reported in our previous studies,<sup>19,25</sup> this enhancement in tensile properties is attributed to the well dispersed HNTs inside the EPDM, intertubular and interfacial interactions between the HNTs and EPDM as well as the intercalation of HNTs by EPDM and other ingredients such as MBT and stearic acid. On the other hand, Figures 2 and 3 also show that the maximum value of tensile strength and  $E_b$  for EPDM/

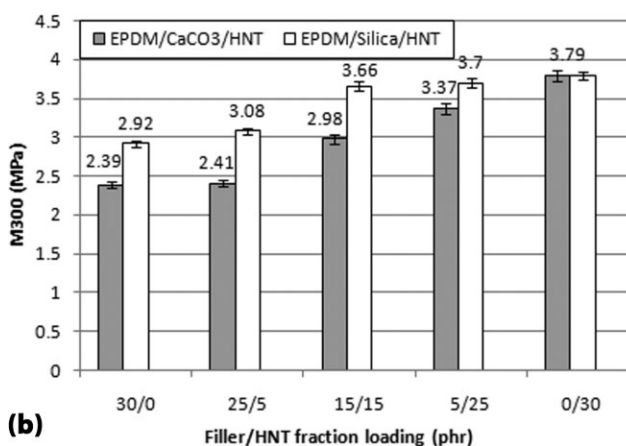


**Figure 3** Comparison of elongation at break of EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT compounds.

Silica/HNT compounds was obtained at 5 phr of HNT loading. The mixing of 5 phr of HNT and 25 phr of silica could make a synergistic effect on reinforcement of EPDM matrix. Adding 5 phr of HNT helped to improve dispersion of silica inside the EPDM because of special charge distribution,



(a)



(b)

**Figure 4** Comparison of tensile modulus of EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT compounds; (a) M100, (b) M300.

unusual crystal shape, and good dispersion of HNTs inside the EPDM and nanotubular shapes of the HNTs. As also stated by Yu et al.<sup>26</sup> mixing two materials with different shapes may enhance the reinforcement effect of the composite because of synergistic effect and new reinforcement mechanism.

Figure 4(a,b) shows the effect of partial replacement of silica or calcium carbonate by HNTs on the M100 and M300 (tensile modulus at 100% and 300% strains respectively) as a function of filler loading. It can be seen that the M100 and M300 of EPDM/CaCO<sub>3</sub>/HNT composites increased with increasing of the HNT loading. The increasing of M100 and M300 is because of the increasing in stiffness of the composites. The stiffness of composites was enhanced due to the smaller particle size, nanotubular shapes of HNTs and their ability to have a good dispersion inside the EPDM in comparison to calcium carbonate. Similarly Figure 4(b) also revealed that the M300 of EPDM/Silica/HNT composites were enhanced with increasing of HNT loading as substitution of silica while the M100 remain unchanged. The results of M100 and M300 of the EPDM/Silica/HNT composites after replacement of silica by HNTs indicated that the higher the HNT loads the higher stiffness of the composite at higher strains. Basically, rubbers deform elastically by uncoiling of long and convoluted molecules.<sup>27</sup> It has been reported in our previous works<sup>19,25</sup> that the HNTs have nanotubular shapes with the average length dimensions between 150 nm to 2  $\mu$ m. Due to nanotubular shapes and charge distribution of hydroxyl groups on the edges and inner of the tubules,<sup>28</sup> the length and quantity of the crosslinked rubber chains were increased in comparison to silica. The increase in quantities of crosslinked chains is responsible for increasing of stiffness at low strains while the increase in length of crosslinked chains would enhance the stiffness of composites at higher strains. As mentioned before the volume percentage of the lumen structure of the HNTs is higher than 15%. EPDM and other ingredients could fill the lumen structure, entrapped at the edge of the tubes and especially intercalated inside the basal spacing of HNT planes which helps EPDM to act as part of a filler rather than as part of a deformable matrix. Medalia<sup>29</sup> has also proposed that in a carbon black-rubber system the rubber which fills the void space within each aggregate is occluded and shielded from deformation. Fröhlich et al.<sup>30</sup> have also reported that this occluded rubber inside the filler increased the effective volume of the filler enormously and can enhance the high strain modulus remarkably.

The increment of tensile strength,  $E_b$ , M100, and M300 with replacement of CaCO<sub>3</sub> by HNTs from 0 to 30 phr loading and improvement of tensile

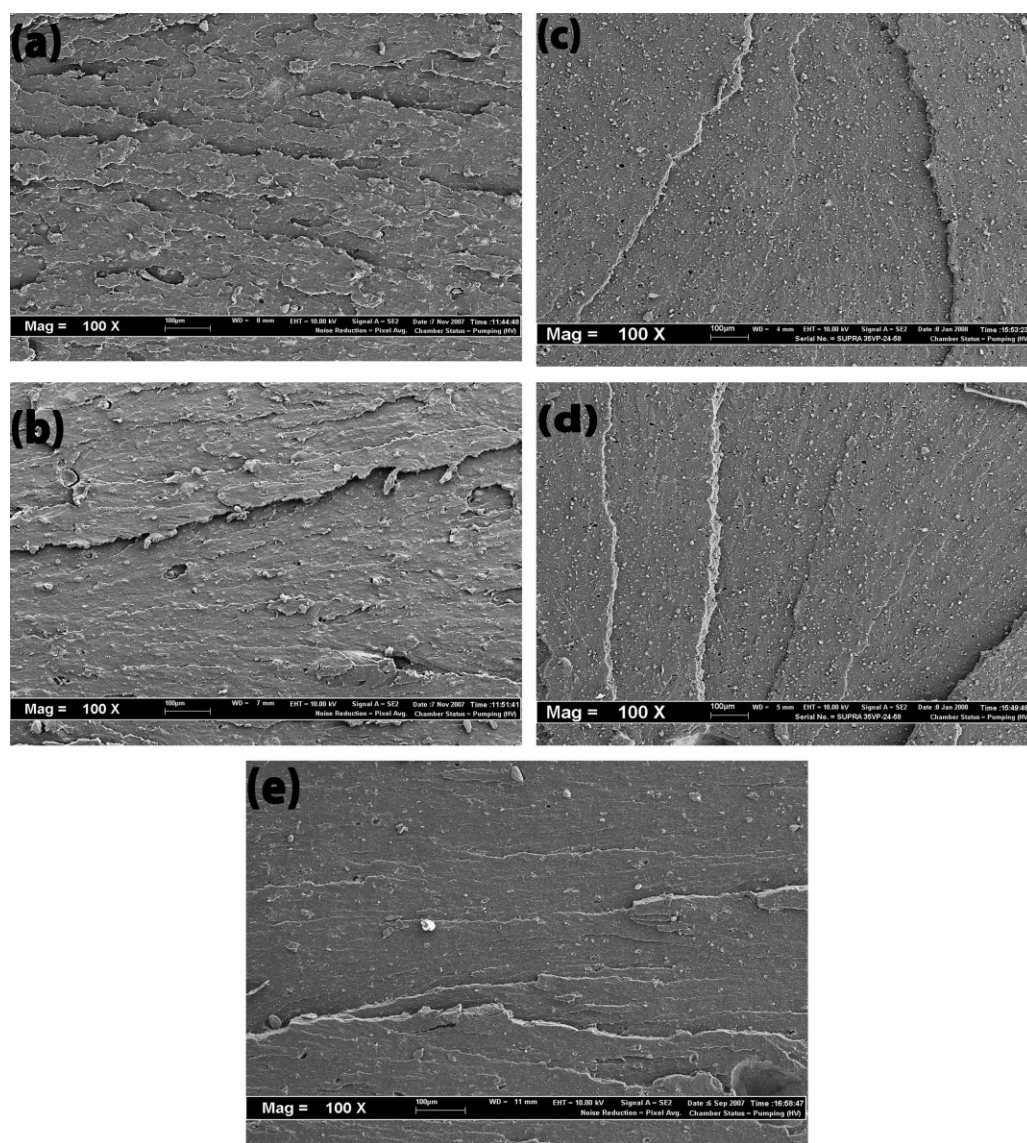
strength and  $E_b$  of EPDM/Silica/HNT composites after combining of 5 phr of HNT with 25 phr of silica can confirmed that the HNTs have more effective reinforcing effect than calcium carbonate and can be used as a co-filler to increase the dispersion of silica into the EPDM matrix.

### Scanning electron microscopy

SEM micrographs of EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT composites are shown in Figure 5. Figure 5(a–d) shows the tensile fractured surfaces of EPDM/Silica/HNT and EPDM/CaCO<sub>3</sub>/HNT composites with 0 and 5 phr loading of HNTs, respectively whereas Figure 5(e) belongs to the EPDM/HNT composite with 30 phr of HNT without silica or calcium carbonate. Careful analysis of the micrographs in Figure 5 (c, d, and e) revealed that the roughness of the fracture surfaces of EPDM/CaCO<sub>3</sub>/HNT composites is increased from 100/30/0 to 100/0/30. The comparison of the micrographs in Figure 5(a, b, and e) revealed that the roughness and matrix tearing of EPDM/Silica/HNT composites with 5 phr of HNT is higher than those in Figure 5(a,e). The more matrix tearing and rougher fractured surface requires higher energy to cause failure, which results in higher tensile strength and  $E_b$ . This is in good agreement with the tensile properties obtained whereby the EPDM/Silica/HNT composite with 5 phr of HNT has the highest tensile strength and  $E_b$  when compared with the other composites.

Figure 6 (a–c,g) show the fracture surfaces of the various EPDM/Silica/HNT composites at higher magnification (1500X). Figure 6(b) (100/25/5) clearly shows a strong interaction between the EPDM, silica and HNTs in comparison to the other micrographs [Fig. 6(a,c, and g)]. As it can be seen in Figure 6(b), combining 5 phr of HNTs with 25 phr of silica showed an increase in the interaction between matrix and fillers by creation of a more homogeneous dispersion of silica (with less agglomeration) on the fracture surface of the composites. In addition to well dispersed fillers inside the matrix in Figure 6(b), a high plastic flow and more torn matrix are observed compared to [Fig. 6 (a,c, and g)] which indicates bearing more stress before failure.

Figure 6 (d–g) demonstrates the fracture surface of EPDM/CaCO<sub>3</sub>/HNT composites with 0, 5, 25 and 30 Phr of HNT loading, respectively, at the higher magnification (1500 $\times$ ). There are many voids with same size of CaCO<sub>3</sub> particles on the fracture surface of EPDM/CaCO<sub>3</sub>/HNT composites with 30 and 25 phr of CaCO<sub>3</sub>. This is attributed to the low interface adhesion between CaCO<sub>3</sub> and EPDM as well as the non-reinforcing character of CaCO<sub>3</sub>. Most of the voids disappeared with replacement of CaCO<sub>3</sub> by higher amounts of HNTs.



**Figure 5** SEM micrographs for EPDM/Silica/HNT composites; (a) 100/30/0 and (b) 100/25/5; and for EPDM/CaCO<sub>3</sub>/HNT composites; (c) 100/30/0, (d) 100/25/5; and for EPDM/HNT composite (e) 100/30. (All fractions are in phr).

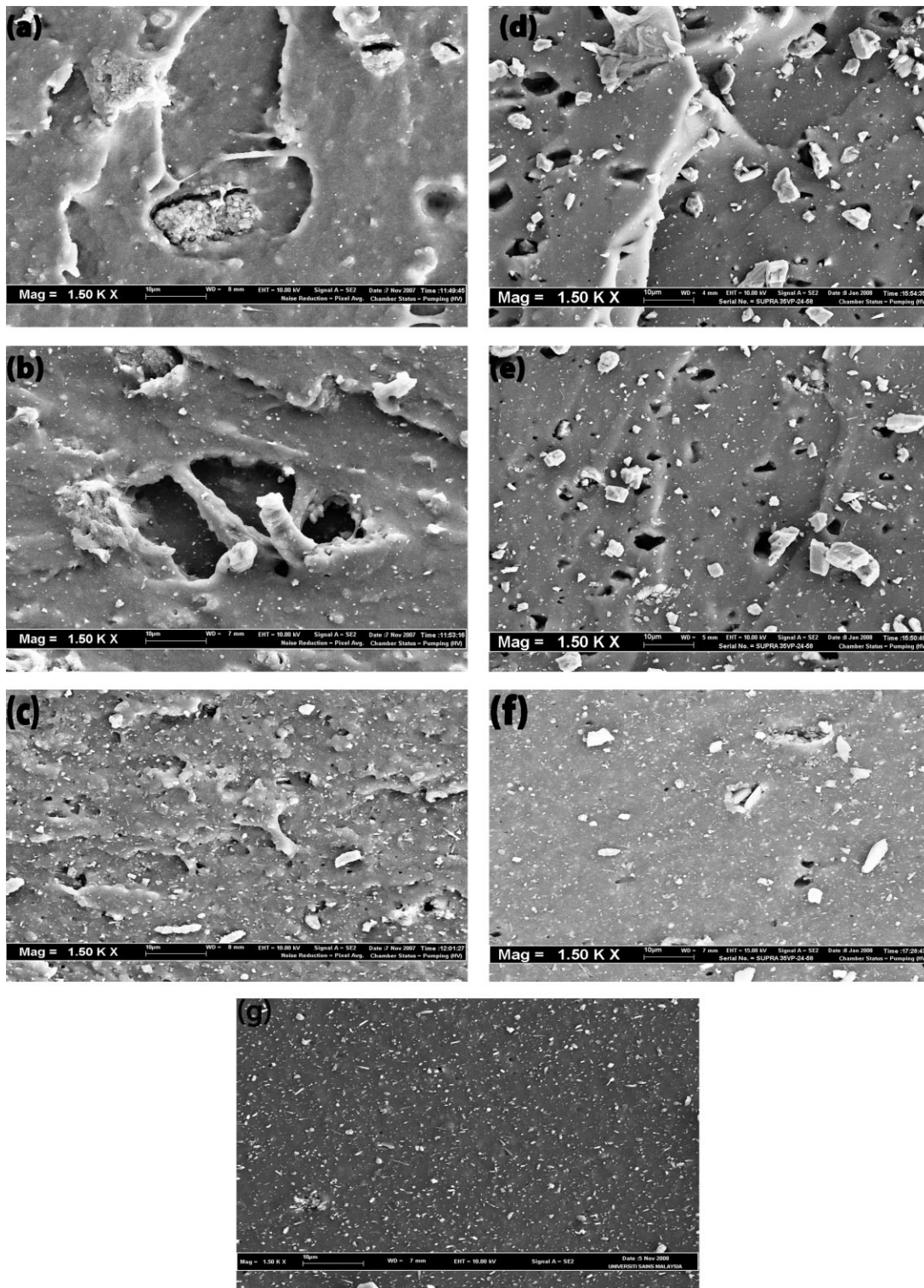
The micrographs clearly confirm the higher tensile properties of EPDM/Silica/HNT with 5 phr of HNT [Figs. 5(b) and 6(b)], and hence, further confirm the improved tensile properties of EPDM/CaCO<sub>3</sub>/HNT composites from 0 to 30 phr of HNT loading.

#### Dynamic mechanical analysis

Figure 7(a,b) represents the temperature dependence of the storage modulus ( $E'$ ) of the EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT composites, respectively. From Figure 7(a) it is obvious that the  $E'$  of EPDM/CaCO<sub>3</sub>/HNT composite is increased by replacement of CaCO<sub>3</sub> by HNTs. This finding is in good agreement with M100 and M300 results mentioned earlier in this article (section 3.3) which revealed an increasing in the stiffness of the compo-

sites by adding HNTs. However, the EPDM/CaCO<sub>3</sub>/HNT composite with 25 phr of HNT has the highest storage modulus among the other composites in the glassy region. This happened because the coexistence of two different kinds of fillers with different shapes and dimensions may produce a new filler structure which would respond more effectively to the periodic forces.

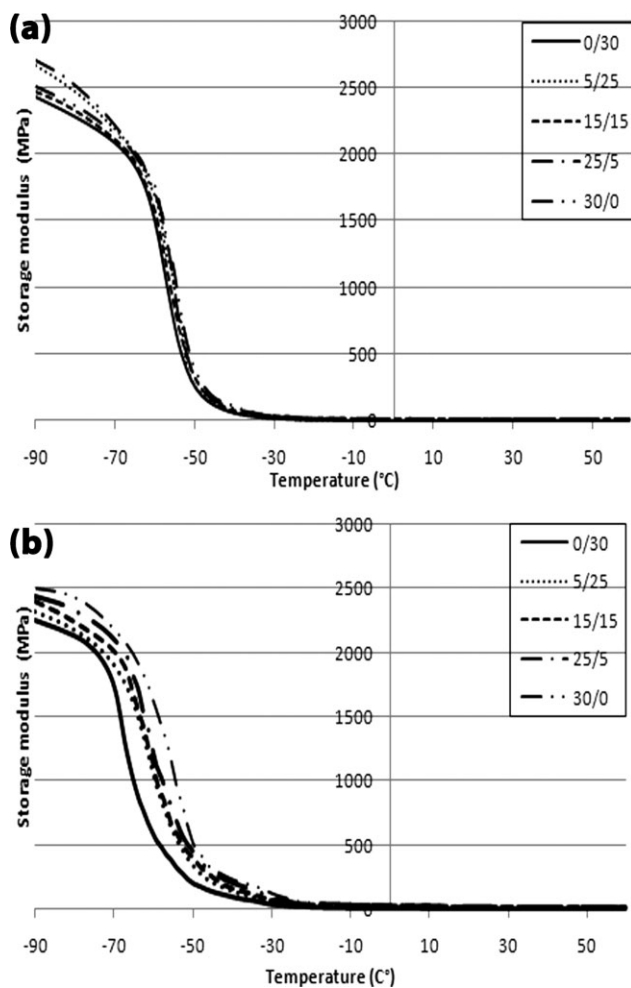
Similarly Figure 7(b) shows the storage modulus of EPDM/Silica/HNT composites is continuously increased with replacement of silica by HNTs from 0 to 30 phr loading. It is well known that stiffness or modulus of filled rubber compounds affected by particle size or specific surface area, the structure or the degree of the irregularity and the surface activity of the filler.<sup>30</sup> As EPDM does not have any polar group in its backbone structure<sup>1-3</sup> the enhancing of



**Figure 6** SEM micrographs for EPDM/Silica/HNT composites; (a) 100/30/0 and (b) 100/25/5, (c) 100/5/25, for EPDM/CaCO<sub>3</sub>/HNT composites; (d) 100/30/0, (e) 100/25/5, (f) 100/5/25, and for EPDM/HNT composite (g) 100/30. (All fractions are in phr).

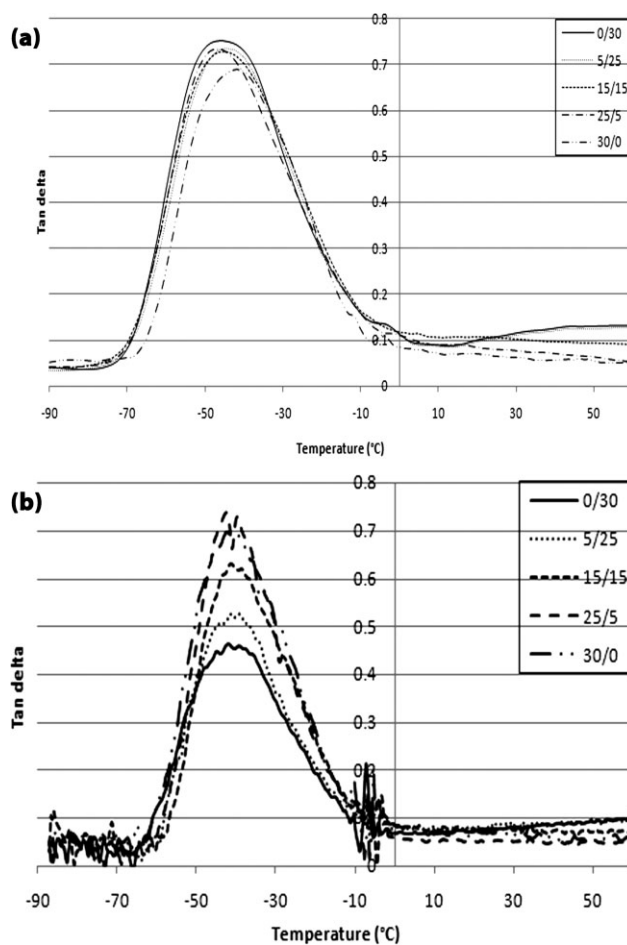
the stiffness of the composites by adding the HNTs from 0 to 30 phr loading, may be attributed to the higher surface area of HNTs compared to silica and CaCO<sub>3</sub>.

The relationship between  $\tan \delta$  and temperature as a function of HNT/CaCO<sub>3</sub> or HNT/Silica fraction loading are presented in Figure 8(a,b). It can be observed that the peak of  $\tan \delta$  of EPDM/CaCO<sub>3</sub>/



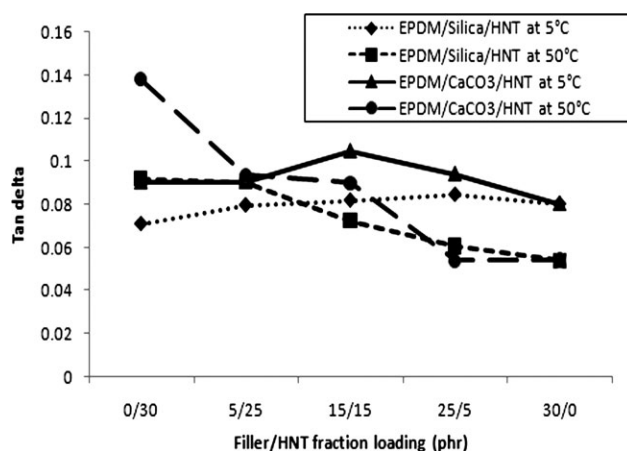
**Figure 7** Storage modulus ( $E'$ ) as a function of temperature at different fractions loading of HNT/filler for (a) EPDM/CaCO<sub>3</sub>/HNT and (b) EPDM/Silica/HNT composites.

HNT and EPDM/Silica/HNT composites decreased and increased respectively with increasing of HNT loading. The  $\tan \delta_{\max}$  value of the EPDM/Silica/HNT composite with 30 phr of silica is the lowest because the presence of 30 phr loading of silica decreased the free volume of the compound. Reducing the free volume of the compound around  $T_g$  have led to the decreasing movement of the rubber segments. Although the specific surface area of the HNTs is higher than silica (Vulcasil C) however, as reported by Leblanc,<sup>31</sup> the reinforcement of rubber by fillers is readily obtained with sizes smaller than 100 nm but particle structure appears as a more decisive factor. The quite complicated tri-dimensional structure of silica which involved several elementary particles of appropriate size helped the silica to have a higher reinforcing effect than HNTs at low temperatures and low strains. On the other hand, as demonstrated in Figure 9, the  $\tan \delta$  of the composites at 5°C and 50°C are increased and decreased, respectively by increasing of the HNT



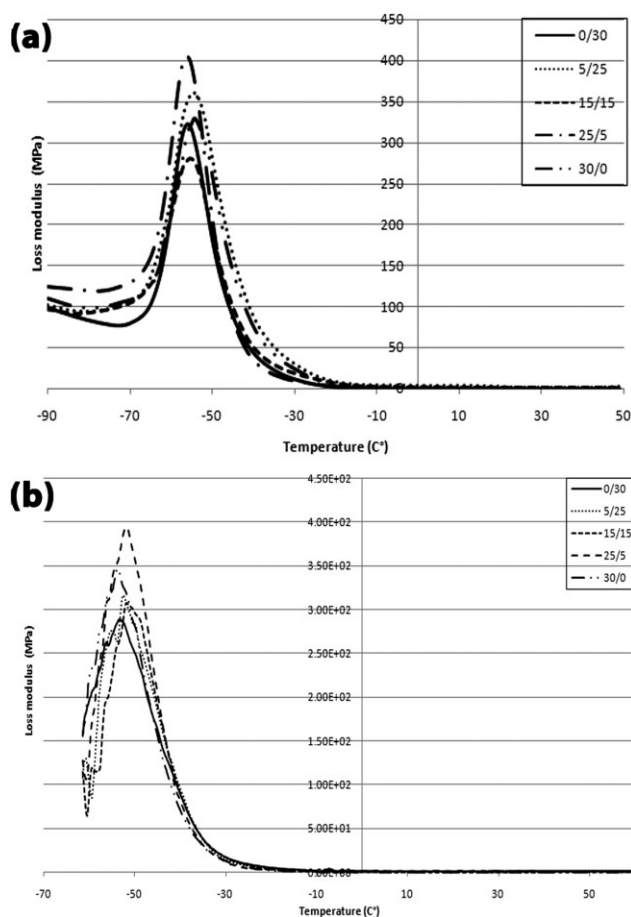
**Figure 8**  $\tan \delta$  as a function of temperature at different fractions loading of HNT/filler for (a) EPDM/CaCO<sub>3</sub>/HNT and (b) EPDM/Silica/HNT composites.

loading from 0 to 30 phr loading. The decreasing of  $\tan \delta$  at 50°C is due to the presence of a lumen structure inside the HNTs. By increasing the temperature, the entrapment of rubber segments at the



**Figure 9** Dependence of  $\tan \delta$  of the EPDM/CaCO<sub>3</sub>/HNT and EPDM/Silica/HNT composites at 5 and 50°C on silica/HNT or CaCO<sub>3</sub>/HNT fraction loading.





**Figure 10** Loss modulus ( $E''$ ) as a function of temperature at different fractions loading of HNT/filler for (a) EPDM/ $\text{CaCO}_3$ /HNT and (b) EPDM/Silica/HNT composites.

edge and inside the tubes of HNTs does not allow them to move easily in comparison to silica. As reported by Donnet,<sup>32</sup> Han et al.,<sup>33</sup> and Rattanasom et al.,<sup>34</sup> a high performance tire should give a low  $\tan \delta$  value at temperature between 50–80°C to reduce rolling resistance and saving energy, while a high  $\tan \delta$  value at low temperature (0–10°C) is necessary to obtain high wet grip.

Figure 10(a,b) shows the loss modulus of the EPDM/ $\text{CaCO}_3$ /HNT and EPDM/Silica/HNT composites respectively. Loss modulus ( $E''$ ) is a measure of energy dissipated as heat during cyclic deformation which can be represented as:

$$E''/E' = \tan \delta \quad (3)$$

An elastic material likes to return back the most energy (high storage modulus ( $E'$ )) and lose the less energy (Low loss modulus ( $E''$ )).

## CONCLUSIONS

The partial substitution of HNTs with silica and calcium carbonate into EPDM were investigated. The

results show that combining 5 phr of HNTs with 25 phr of silica into the EPDM matrix obtained the optimum values of tensile properties of the EPDM/Silica/HNT composites. This revealed that HNTs can be used as a co-filler with silica to achieve better dispersion of silica inside the EPDM, hence higher tensile strength and  $E_b$ . However, the tensile properties of EPDM/ $\text{CaCO}_3$ /HNT composites continuously increase with increasing of HNT from 0 to 30 phr loading. The curing properties show that the  $t_{90}$  and damping characteristics of the composites decreased with replacement of silica or  $\text{CaCO}_3$  by HNTs. Morphological studies by SEM indicate that better dispersion of HNTs inside the EPDM matrix and nanotubular shapes of HNTs in comparison to  $\text{CaCO}_3$ , are responsible for enhancement of mechanical properties of EPDM/ $\text{CaCO}_3$ /HNT composites with increasing of HNT loading from 0 to 30 phr. Dynamic mechanical analysis shows an increasing in storage modulus of the composites while the  $\tan \delta$  at 50°C would reduced with the addition of HNTs.

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