Natural rubber nanocomposites based on hybrid filler of zinc nanoparticles and carbon nanotubes: Electrical conductivity and other related properties

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Abstract. Hybrid filler of carbon nanotubes (CNT) and zinc oxide (ZnO) nanoparticles were prepared and then mixed with natural rubber (NR). The ZnO nanoparticles were first synthesized by the sol–gel method. The NR-CNT/ZnO nanocomposites were prepared by latex mixing. Various proportions of ZnO in the CNT/ZnO hybrid filler were tested by mixing with NR to eventually form NR-CNT/ZnO nanocomposites. It was found that the optimum ZnO content in CNT/ZnO hybrid filler was about 3 phr. These ZnO contents provided the NR hybrid composite with superior mechanical properties in terms of tensile strength and modulus, together with good electrical conductivity and dielectric properties. In addition, stress relaxation tests revealed stronger filler network formation after incorporation of CNT-ZnO hybrid filler into the NR matrix. It might be due to electrostatic interactions between CNT and ZnO, also contributing to high electrical conductivity and dielectric properties of the NR-CNT/ZnO composites, when compared to a solely CNT filled NR composite. Furthermore, the Payne effect and morphological properties were qualitatively analyzed, indicating that CNT dispersion was finer in the NR-CNT/ZnO composites having about 1 to 3 phr ZnO content in CNT/ZnO. Higher contents of ZnO in CNT/ZnO hybrid filler caused large filler aggregates degrading mechanical and electrical properties.

Keywords: nanocomposites, natural rubber, carbon nanotube, zinc oxide nanoparticles, hybrid filler

1. Introduction

Conductive rubber composites have been widely investigated by incorporating electrically conductive fillers into the insulating rubber matrix. In recent years, a great deal of attention has been paid to a new type of carbon nanofiller, the carbon nanotubes (CNT). It has been well established that a CNT consists of rolled-up graphite sheets built from sp² carbon units. That is, a carbon atom in a CNT structure contains one valence electron, which is capable of moving around the CNT surfaces. This definitely

enhances both thermal and electrical conductivities [1]. Therefore, CNT has been extensively studied in rubber nanocomposites due to their unique structure and properties [2]. Incorporating CNT can cause dramatic changes owing to their ability to form three-dimensional interconnected networks at very low loadings. The high aspect ratio and large specific surface area of CNT facilitate interfacial interactions with the rubber matrix, complementing the remarkable structural, mechanical, and electrical properties [3]. Typically, CNT fillers could transform natural rubber

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(NR) from an electrical insulator to a conductive material with outstanding flexibility, elasticity, and mechanical properties [4].

However, agglomeration of CNT normal in the rubber matrix due to interactions of polar functional groups on CNT surfaces via hydrogen bonds and Van der Waals attraction. It makes it more difficult for CNT networks or conductive paths to form in the insulating rubber matrix, and even the paths formed require electron tunneling between the conductive particles [1]. The agglomeration of CNT may also cause inferior electrical conductivity and mechanical properties of the NR/CNT nanocomposites [5]. This major drawback is still a challenge for developing a new generation of NR/CNT composites. Generally, the main route to improve the dispersion of CNT in the rubber matrix is by reducing their hydrogen bonding and Van der Waals interactions, thereby reducing the agglomeration tendency. Also, surface treatment of CNT to either reducing H-bond or polarity of CNT has been performed [6].

The CNT loadings and its agglomeration play an important role in the properties of NR nanocomposites. It was found that the optimum CNT loading in NR/CNT nanocomposite was about 3 phr [6]. Higher CNT loading caused the formation of CNT agglomerate in NR matrix that caused deterioration of mechanical properties due to the failure points at the CNT agglomeration locations. Therefore, to enhance the electrical conductivity of the NR/CNT nanocomposites, several approaches have been exploited to improve the CNT dispersion in a natural rubber matrix [5]. One prominent attempt was by adding secondary fillers into the composites, generating a new conductive hybrid filler [7]. For instance, secondary fillers are used together with CNT for synergy in reinforcing the NR matrix, such as carbon black (CB) [7, 8], ionic liquid (IL) [5], or silver nanoparticles (AgNP) [9].

Zinc oxide (ZnO) nanoparticles are a kind of inorganic multifunctional filler, which has been extensively used as an additive in rubber compounding [10]. It is noted that the ZnO is a semi-conductive material with remarkable physical and chemical properties, including low toxicity, low cost, high optical activity and stability, high sensitivity to ultraviolet and visible light, together with high thermal and mechanical stability at room temperature [11, 12]. These properties reveal that ZnO is a useful material in

electronics, optics, photonics, room temperature UV lasers, light-emitting diodes, and sensors [13]. Also, it is applicable in photocatalytic degradation of organic pollutants under ultraviolet-visible light [14]. Some studies have decorated CNT surfaces with ZnO nanoparticles, with the main aim of promoting CNT network formation. It was found that the ZnO/ CNT hybrid filler exhibited synergy in photo-inactivation of bacteria [15]. Also, the ZnO/CNT hybrid filler had enhanced recyclability and improved rate capability as anode for lithium-ion batteries (LIBs) [16]. Moreover, the ZnO/MWCNT (Multi-walled carbon nanotubes) hybrid filler has also been used for enhancing various properties of polypropylene nanocomposites [17]. It was found that the ZnO/MWCNT/ PP nanocomposite films showed improved thermal stability, antibacterial, and antifungal properties, fire resistance, and lower combustion toxicity than the neat PP film [17]. In the present work, the NR-CNT/ZnO nanocomposites were prepared via a latex mixing method. The main aim was to gain a fine dispersion of the CNT/ ZnO hybrid filler in the NR matrix for superior mechanical properties and electrical conductivity. Effects of loading level of ZnO in CNT/ZnO hybrid filler on properties of NR-CNT/ZnO nanocomposite were also investigated relative to NR composites filled with solely CNT (NR-CNT composites). The electrical properties, relaxation behavior, bound rubber content, and morphological properties were carefully examined.

2. Experimental

2.1. Materials

High ammonium natural rubber latex (HA) with 60% dry rubber content (DRC) was manufactured by Tha Chang Rubber Co., Ltd (Surat Thani, Thailand). It was used as the rubber matrix. The multiwalled carbon nanotubes (MWCNT), filler grade, NC7000 with 9.5 nm diameter, 1.5 μm length, and 90% purity, were manufactured by Nanocyl S.A. (Sambreville, Belgium). The zinc acetate with 99% purity, the density of 1.94 g/cm³, and molecular weight of 219.49 g/mol was manufactured by Ajax (Sydney, Australia). The curing agents, including sulfur (Ajax Chemical Co., Ltd., Sydney, Australia) and the cure accelerator mercaptobenzothiazole (MBT) (Flexsys Inc., Termoli, Italy) were used as received. The other compounding ingredients were cure activator zinc

oxide (ZnO) (Global Chemical Co. Ltd., Samut Prakarn, Thailand) and stearic acid (Imperial Chemical Co. Ltd., Pathum Thani, Thailand).

2.2. Synthesis of ZnO nanoparticles (ZnO) and the CNT/ZnO hybrid filler

The decoration of ZnO on the CNT surfaces was first performed by the sol-gel process [18]. First, 1.0 g of zinc acetate was dissolved in 5 ml deionized water and 125 ml diethylene glycol. Then, the solution was continuously stirred at 180 °C for 30 min. The solution was then conditioned at room temperature for about 5 h to provide enough time for the formation of ZnO sol. A fixed amount of CNT, about 0.2 g, was then added into the ZnO sol, and it was then sonicated for 1 h for thorough dispersion of the CNT particles. Afterward, the mixture was cooled to room temperature and then centrifuged. After removal of the liquid phase, the product was thoroughly washed with deionized water and then with ethanol several times.

In this work, the NR-CNT/ZnO nanocomposite was prepared by a latex mixing method. Therefore, an aqueous dispersion of the hybrid filler is needed, and the CNT/ZnO hybrid filler in 0.5 wt% sodium dodecyl sulfate (SDS) surfactant was dispersed in water. The CNT/ZnO dispersion was thoroughly mixed with sonication (OMNI Ruptor 4000, Georgia, USA) for about 10 min at room temperature. The pH of the dispersion was then adjusted to 11, with 3 wt% sodium hydroxide solution. In this work, the quantity of CNT was fixed at 3 phr because it was the percolation threshold concentration of NR filled CNT [6], but the content of ZnO was varied at 1, 3, 5 or 7 phr. The CNT/ZnO hybrid filler dispersions with various contents of ZnO were then added into the NR latex (10% DRC) with continuous mechanical stirring at a rotor speed of 300 rpm for about 30 min. The latex mixture was then cast to glass molds and eventually dried in a hot air oven at 60 °C for 24 h to obtain the NR-CNT/ZnO nanocomposite films.

2.3. Compounding of NR-CNT/ZnO nanocomposites

The NR-CNT/ZnO compounds were prepared by dry mixing with other chemical ingredients, including stearic acid and zinc oxide activators, MBT accelerator, and sulfur curing agent, per formulation and mixing schedule shown in Table 1. The mixing was performed in an internal mixer (Brabender® GmbH & Co. KG, Duisburg, Germany) with a mixing

Table 1. Compounding formulations and mixing schedule for NR-CNT and NR-CNT/ZnO compounds.

Compound	Content [phr]	Mixing time [min]
NR	100	7
CNT ₃ /ZnO	0, 1, 3, 5, 7	
Stearic acid	3	1
Zinc oxide (ZnO)	5	1
Mercaptobenzothiazole (MBT)	0.6	1
Sulfur	2.5	2

chamber capacity of 70 cm³ at 60 °C and a rotor speed of 60 rpm with a total mixing time of 12 min. Besides, cure characteristics of the rubber compounds were analyzed using a moving die rheometer (MDR 2000) (Alpha Technologies, Ohio, USA) at 145 °C. Vulcanized samples were then prepared by compression molding, with model PR1D-W400 L450PM (Charon Tut Co., LTD., Samut Prakarn, Thailand), at 145 °C using the respective cure time (*i.e.*, t_{c90}) for each sample from the MDR tests. To investigate the influences of ZnO content in ZnO/CNT hybrid filler on properties of NR nanocomposites, the fixed CNT loading at 3 phr was used with various loadings of ZnO (1, 3, 5, or 7 phr) to prepare the NR/CNT-ZnO nanocomposites.

2.4. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), with Perkin-Elmer Spectrometer, Spectrum Two (Perkin Elmer, CA), was used to analyze the gum NR and the NR-CNT/ZnO composite films. The analysis was performed over the wide wavenumber range from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

2.5. X-ray diffraction (XRD)

The X-ray diffraction (XRD) pattern of the ZnO nanostructure was recorded with Empyrean X-ray diffractometer (PANalytical B.V., Almelo, The Netherlands) with Cu-K α radiation ($k = 0.1542$ nm).

2.6. Morphological properties

Morphological properties of CNT/ZnO hybrid filler were characterized by TEM imaging (Jeol JEM 2010, Jeol Ltd., Tokyo, Japan) with an accelerating voltage of 200 kV. The samples were first dispersed in deionized water before spotting on the sample grid for TEM imaging. Furthermore, the morphological

properties of the NR-CNT/ZnO composites were also characterized by using scanning electron microscopy (SEM) (FEI-Quanta 400, Thermo Fisher Scientific, Brno, Czech Republic) and field emission scanning electron microscopy (FESEM) (Apreo, Thermo Fisher Scientific, Brno, Czech Republic). The samples were first cryogenically fractured in liquid nitrogen to create fresh cross-sectional surfaces. Then, the samples were sputter-coated with a thin layer of gold under vacuum before imaging by SEM or FESEM. In this study, the dispersion of filler in NR-CNT/ZnO composites was characterized by fluorescence stereo microscopy (Leica M205 FCA, Heerbrugg, Switzerland). The samples were initially fast cut with a razor blade in order to create a smooth sample surface for examining.

2.7. Temperature scanning stress relaxation (TSSR)

The stress relaxation measurements were performed using a TSSR meter (Brabender® GmbH & Co. KG, Duisburg, Germany). Dumbbell shaped specimens (type 5A, ISO 527). The vulcanized samples were prepared and placed in the sample holder in the test chamber of the TSSR meter. The sample was then conditioned at 23 °C and 50% strain for 2 h to allow the isothermal short-time relaxations [19]. The non-isothermal test was then carried out by increasing test temperature from 23 to 220 °C at a constant heating rate of 2 °C/min (v). The relaxation spectrum ($H(T)$) was automatically calculated based on the relation of relaxation modulus ($E(T)$) and temperature (T) [19] as shown by Equation (1):

$$H(T) = -T \left[\frac{dE(T)}{dT} \right]_{v = \text{const}} \quad (1)$$

2.8. Bound rubber contents

Bound rubber contents of the NR composites were analyzed by dissolving the soluble parts of the unvulcanized rubber compounds in a solvent. The NR compounds were initially immersed in toluene and conditioned to the equilibrium state for at least 72 h, and the toluene was renewed every 24 h. The samples were later separated from the solvent and then dried at 105 °C for at least 24 h. In the same manner, the NR compounds were immersed in toluene for at least 72 h at room temperature either in the normal state or in an ammonia atmosphere with the renewal of toluene every 24 h. Then, the solvent was separated,

and the samples were dried at 105 °C for 24 h and eventually weighted. It is noted that the ammonia was used to cleave the physical linkages between rubber molecules and filler surfaces. The bound rubber content was then determined as shown by Equations (2) [20]:

$$\text{Bound rubber content [\%]} = \frac{W_{fg} - W_f}{W_p} \quad (2)$$

where W_f and W_p are the weights of filler and rubber in the specimens, respectively. W_{fg} is the weight of filler with bound rubber absorbed on it after toluene extraction.

2.9. Payne effect

The Payne effect was determined by measuring the storage modulus as a function of strain amplitude with a rubber process analyzer (RPA) (Alpha Technologies, Akron, USA). The Payne effect is typically used to indicate the state of filler dispersion. The test was performed by measuring the storage shear modulus (G') of each filled un-vulcanized rubber compound under shear deformation with a strain amplitude range of 0.56–100% at a fixed 1 Hz oscillation frequency and 100 °C. The Payne effect was quantified by the difference of storage moduli at very low strain ($G'_{0.56}$) and at very high strain (G'_{100}).

2.10. Electrical properties

Electrical properties of gum and NR-CNT/ZnO vulcanizates were measured at room temperature using an LCR meter (Hioki IM 3533, Hioki E.E. Corporation, Nagano, Japan). A sample with ~2 mm thickness was first placed between the plates, and then the test was performed over the frequency range from 1 to 10⁵ Hz. The electrical conductivity (σ), and dielectric constant (ϵ') were calculated by using Equation (3) and (4), respectively [21]:

$$\sigma = \frac{1}{\rho} = \frac{d}{(R_p)A} \quad (3)$$

$$\epsilon' = \frac{C_p(A)}{A(\epsilon_0)} \quad (4)$$

where d and A refer to the sample thickness and the area of an electrode, respectively. The factor ρ is the volume resistivity, the reciprocal of conductivity, and R_p is resistance. The parameter C_p is the parallel capacitance, and ϵ_0 is the dielectric constant of the free space, which is $8.854 \cdot 10^{-12}$ F/m.

2.11. Dynamic mechanical analysis

Dynamic mechanical thermal analysis (DMTA) was carried out using Perkin Elmer DMA 8000 (Perkin Elmer Inc., Waltham, USA) in tension mode. The samples were scanned over the temperature range from -100 to 100°C with a heating rate of $3^\circ\text{C}/\text{min}$ and fixed deformation frequency of 1 Hz .

2.12. Mechanical properties

Tensile properties of the gum NR vulcanizate together with NR-CNT/ZnO composites were investigated using a universal tensile testing machine (Tinius Olsen, Co., Ltd., Honey Crock Lane, UK). It is noted that the dumbbell-shaped specimens were prepared from compression-molded sheets. The tests were carried out with an extension rate (or cross-head speed) of $200\text{ mm}/\text{min}$ at room temperature, according to ISO 37, Type 1A.

3. Results and discussion

3.1. Characterization of ZnO and CNT/ZnO hybrid filler by XRD and TEM

Figure 1 shows the XRD patterns of ZnO nanoparticles, CNT and CNT/ZnO hybrid. The XRD peaks for ZnO nanostructure are seen at $2\theta = 31.73, 34.40, 36.21, 47.49, 56.52, 62.83, 66.30, 67.87, 69.01, 72.56, 76.88, \text{ and } 81.36^\circ$. These correspond respectively, to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and (104) crystal planes of ZnO with hexagonal structure [13, 22, 24]. The crystallite size (D) of the ZnO nanoparticles was then estimated from Scherrer's Equation (5) [23].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

Figure 1. XRD patterns of ZnO nanoparticles, CNT and CNT/ZnO hybrid filler.

where D is the crystallite size, 0.9 is the shape factor, λ is the X-ray wavelength, β is the full width at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

It was found that the crystallite size (D) of ZnO nanoparticles calculated based on the maximum peak (101), together with Equation (5), was approximately 8.50 nm . This proves the nano-scale of ZnO particles. It is also seen in Figure 1, that the XRD pattern for CNT shows a peak at $2\theta = 26^\circ$. This relates to the (002) plane in the graphite structure of CNT [15, 24]. Furthermore, the XRD pattern of the CNT/ZnO hybrid composite has a combination of the peaks for CNT and ZnO. The crystallite size (D) of ZnO nanoparticles decorated on CNT surfaces (*i.e.*, CNT/ZnO) was also calculated based on the maximum peak (101) together with Equation (5) was approximately 5.49 nm .

Figure 2. Transmission electron micrographs (TEM) of zinc oxide decorations on CNT surfaces to form CNT/ZnO hybrid nanoparticles at magnifications: (a) $150\,000\times$, and (b) $250\,000\times$.

Figure 3. A proposed reaction mechanism for the decoration of CNT bundle surfaces with ZnO nanoparticles.

Figure 2 shows the TEM micrographs of CNT/ZnO hybrid filler. It is clear that the decoration of ZnO on CNT surfaces to form the hybrid filler was successful, as clearly seen in Figures 2a and 2b. The ZnO particles adhere to the CNT bundle surfaces. This is clearer in the TEM micrograph of CNT/ZnO hybrid filler with the higher 200 000 $\times$ magnification (Figure 2b). Therefore, ZnO nanoparticles and CNT bundle surfaces were clearly in contact. This might be due to interactions between functional groups, *i.e.*, hydroxyl ($-\text{OH}$) and carboxyl groups ($-\text{COOH}$), with negative charges on CNT surfaces and the positive charges of zinc ions (Zn^{2+}) in ZnO, as proposed in Figure 3. The ZnO with a hexagonal structure has an electrical double layer generated by Zn^{2+} on the surfaces of ZnO particles [25], while the surfaces of CNT have hydroxyl and carboxyl functional groups with negative charges that are capable of attracting Zn^{2+} in the ZnO nanoparticles, together with metal co-ordination linkages [26, 27]. Furthermore, the size of ZnO nanoparticles estimated from the TEM image in Figure 2b is approximately 8 to 14 nm, which matches well the 8.5 nm particle size estimated from XRD pattern.

3.2. ATR-FTIR

ATR-FTIR spectra of gum NR, NR-CNT₃, and NR-CNT₃/ZnO₃ composites are shown in Figure 4. Also,

the assignments of the FT-IR absorption peaks are listed in Table 2. The absorption peaks of gum NR are seen at the wavenumbers 1663 and 1546 cm^{-1} , which are assigned to C=C stretching and N-H bending vibrations of mono-substituted amide II in NR [28], respectively. Additionally, the absorption peak at 841 cm^{-1} is assigned to C-H out-of-plane bending vibrations. Furthermore, the absorption peaks at 1455 and 1375 cm^{-1} indicate $-\text{C}-\text{H}$ scissoring and $-\text{CH}_3$ bending vibrations in NR, respectively. It is also seen in Figure 4 that the FTIR spectrum of NR-CNT₃

Figure 4. ATR-FTIR spectra of gum NR, and NR-CNT₃ and NR-CNT₃/ZnO₃ composites.

Table 2. Peak assignments for gum NR, NR-CNT₃ and NR-CNT₃/ZnO₃ nanocomposite films in the FTIR spectra of Figure 4.

Wavenumber [cm ⁻¹]	Assignment
2963	–CH ₃ stretching vibration
2914	–CH ₂ stretching vibration
2852	–CH ₂ stretching vibration
1663	C=C stretching vibration
1546	N–H bending vibration of amide
1593	C=O stretching vibration
1445	–CH ₂ bending vibration
1375	–CH ₃ bending vibration
1221	C–O stretching vibration
1080	C–O stretching vibration
1018	C–O stretching vibration
997	C–H out-of-plane bend
841	=C–H out of plane bending
632	C–H bending vibration
428	Zn–O stretching vibration

composite demonstrated a new absorption peak at wavenumber 1593 cm⁻¹, which indicates C=O stretching vibrations in CNT [29, 30]. Additionally, the peak at wavenumber 1018, 1080, and 1221 cm⁻¹ are assigned to C–O stretching vibrations [31], which indicates the presence of functional groups on CNT surfaces. Also, FTIR peaks at 1018 and 1221 cm⁻¹ were observed. They are assigned to C–N stretching vibrations of functional groups on CNT surfaces [31]. It is noted that CNT should not have the C–N linkages in the structure, but this is possible to be the impurities in the CNT that did not exist in the FTIR spectrum of gum NR in Figure 4.

It is also clearly seen in Figure 4 that the FTIR spectrum of NR-CNT₃/ZnO₃ film exhibits a new absorption peak at 428 cm⁻¹, which is characteristic of zinc-oxygen stretching vibrations [13]. Moreover, the peaks at 1658 and 3396 cm⁻¹ are assigned to O–H bending and stretching vibrations. The FTIR spectrum of NR-CNT₃/ZnO₃ shows a lower peak intensity of the functional groups on CNT surface at 1593 cm⁻¹. Also, the absorption peaks at 1221, 1080, and 1018 cm⁻¹ in NR/CNT₃ spectrum were slightly shifted to 1218, 1077, and 1016 cm⁻¹ in the NR-CNT₃/ZnO₃ spectrum, respectively. This might be due to the influence of the hybridization of CNT and ZnO particles, as indicated in the TEM micrographs (Figure 2) and the proposed reaction mechanisms in Figure 3.

3.3. Morphological properties

FESEM and fluorescence stereo-microscopy were used to evaluate the morphological properties of NR-CNT and NR-CNT/ZnO composites. Figure 5 shows FESEM micrographs of gum NR, NR-CNT, NR-CNT₃/ZnO₃, and NR-CNT₃/ZnO₅ composites. The gum NR (Figure 5a) shows a smooth surface with some small white spots of ZnO. Furthermore, it is clear that NR-CNT composites (Figure 5b and 5e) had CNT agglomerates. This indicates filler-filler interactions among CNT bundles dominating over filler-matrix interactions between NR and CNT. This may degrade the mechanical strength of NR-CNT composites. However, upon the decoration of CNT surfaces with 3 phr of ZnO, the filler dispersion in NR-CNT₃/ZnO₃ nanocomposites (Figures 5c and 5f) seems finer than in the NR-CNT composites (Figures 5b and 5e). This might be attributed to the formation of infinite CNT-ZnO hybrid filler networks in the NR matrix (Figures 2a and 2b). However, large filler agglomerates are seen again upon increasing ZnO content to 5 phr in the NR-CNT₃/ZnO₅ composites (Figures 5d and 5g). This confirms that more than 3 phr of ZnO in the CNT/ZnO hybrid produced larger filler agglomerates. The FESEM micrographs in Figure 5 correlate well to the fluorescence stereo microscopic images, seen in Figure 6. That is, the gum NR vulcanizate showed a large white agglomerate of ZnO activator (Figure 6a). Also, the NR-CNT composite displayed strong CNT agglomeration with the agglomerate of ZnO activator (Figure 6b), whereas the NR-CNT₃/ZnO₁ (Figure 6c) and NR-CNT₃/ZnO₃ (Figure 6d) composites display better filler dispersion. Furthermore, clearly adding more than 3 phr ZnO into the CNT/ZnO hybrid filler gave larger filler agglomerates shown in Figures 6e and 6f. These characteristics of morphological properties agree with the proposed model in Figure 7. Large CNT agglomerates are formed in the NR-CNT composite because of Van der Waals forces and hydrogen bonding among CNT particles. This typically provides degraded mechanical and other related properties to an NR-CNT composite. However, the NR-CNT/ZnO hybrid composites with the optimum amounts of ZnO (about 1 and 3 phr) gave a finer distribution of CNT in the NR matrix. This might be attributed to the hybrid filler connecting to networks in the NR matrix by chemical interactions between the functional groups

Figure 5. FESEM micrographs of (a) gum NR: 100 000 $\times$, (b) NR-CNT: 100 000 $\times$, (c) NR- CNT₃/ZnO₃: 100 000 $\times$, (d) NR- CNT₃/ZnO₅: 100 000 $\times$, (e) NR-CNT: 250 000 $\times$, (f) NR-CNT₃/ZnO₃: 250 000 $\times$, and (g) NR-CNT₃/ZnO₅: 250 000 $\times$.

on CNT surfaces with the positively charged zinc ions, as described in Figure 3. In the NR composites with CNT/ZnO hybrid filler that has more than 3 phr ZnO (Figures 6e and 6f), strong agglomeration is

clear. This is because the fixed 3 phr of CNT consumes ZnO to form hybrid filler for about 3 phr, while a higher ZnO loading leaves excess ZnO in the system. Therefore, the strong and large filler

Figure 6. Fluorescence stereo micrographs of (a) gum NR, (b) NR-CNT, (c) NR-CNT₃/ZnO₁, (d) NR-CNT₃/ZnO₃, (e) NR-CNT₃/ZnO₅, and (f) NR-CNT₃/ZnO₇ nanocomposites.

Figure 7. A proposed model for dispersion of CNT and CNT/ZnO hybrid filler in NR matrix.

agglomerates formed in the NR matrix, seen in the FESEM micrographs of Figures 5d and 5g and the fluorescence stereo micrographs in Figures 6e and 6f. Thus, it can be concluded that the optimum ZnO loading in the NR-CNT/ZnO composites is below about 3 phr.

3.4. Temperature scanning stress relaxation (TSSR) and bound rubber content

The mechano-thermal relaxation behaviors of the NR gum vulcanizate, NR-CNT, NR-CNT/ZnO hybrid composites were characterized by the TSSR technique, as shown in Figure 8, revealing the dependence of relaxation modulus on temperature for all sample types. Also, the relaxation modulus-temperature curves in the temperature range 23–30 °C are affected by the entropy effects. Other parts of the relaxation modulus-temperature curve indicate physically bound rubber (30–90 °C), sulfur crosslinks (90–160 °C), and rubber or polymer chain degradation (160–220 °C) [32]. In Figure 8a, it is seen that the incorporation of CNT and CNT/ZnO hybrid fillers in the NR matrix gave significantly higher initial relaxation modulus than that of the gum NR vulcanizate, which indicates reinforcement effect of the

fillers. Furthermore, CNT/ZnO hybrid filler with below 3 phr ZnO content (*i.e.*, CNT₃/ZnO₁ and CNT₃/ZnO₃) gave higher initial modulus and curve below 100 °C temperatures than those of the NR-CNT composite. This may be due to the finer dispersion together with more network formation with the CNT-ZnO hybrid fillers, which promote reinforcement of the NR matrix (Figures 5c and 5f together with Figures 6c and 6d). However, with over 3 phr loading of ZnO in CNT/ZnO hybrid filler, strong filler agglomeration occurred (Figures 5d and 5g as well as Figures 6d and 6f). Therefore, the relaxation modulus became lesser than that for NR-CNT composite. This relates to the proposed model for the dispersion of CNT and CNT/ZnO hybrid filler in the NR matrix, shown in Figure 7. Also, this was confirmed by the FESEM and fluorescent stereo micrographs in Figures 5 and 6, respectively. Therefore, the CNT₃/ZnO₃ has a near-optimal weight ratio of CNT/ZnO to create a hybrid filler that bridges networks of CNT and ZnO in the NR matrix. In Figure 8a, it is also seen that the relaxation modulus of gum NR is almost constant for 50–130 °C, while the relaxation moduli of NR-CNT and NR-CNT/ZnO clearly decreased with temperature. This was caused

Figure 8. Stress relaxation versus temperature (a), and the relaxation spectra (b) for the gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

by the physical desorption of bound rubber in the NR-CNT and NR-CNT/ZnO composites, which relaxes the filler–rubber interactions. Furthermore, decreasing moduli are seen in the temperature range from 120 to 220 °C in all cases. This might be due to thermo-oxidative chain scission of rubber molecules, together with the breakdown of sulfidic crosslinks in the rubber vulcanizates.

The rubber–filler interactions can be assessed from the bound rubber contents in the rubber vulcanizates, which in turn could be estimated from the relaxation spectra ($H(T)$), as shown in Figure 8b. That is, the relaxation peaks appearing from 50 to 80 °C indicate desorption of physically bound rubber. It is clear that CNT₃/ZnO₃ showed a much larger peak height and peak area than those of the NR-CNT composite. This might be due to the better filler dispersion of CNT₃/ZnO₃ than of CNT in the NR matrix. Also, the proper ratio of CNT₃/ZnO₃ improved filler dispersion and distribution. This affected the initial relaxation, the large peak height, and peak area, together with the highest bound rubber content in the swelling test, as shown in Figure 9. In Figure 8, it is also seen that the NR filled with CNT₃/ZnO₁ shows lesser initial modulus, peak height, and peak area, and bound rubber content (Figure 9) than the CNT₃/ZnO₃ filled NR composite. However, the NR filled with CNT₃/ZnO₁ had higher properties than several other cases, including NR-CNT, NR-CNT₃/ZnO₅, and NR-CNT₃/ZnO₇ composites. This corresponds to the fluorescence stereo-micrographs in Figure 6, where the NR-CNT₃/ZnO₁ composite showed some finely dispersed filler with a small number of aggregates. Nevertheless, CNT-ZnO hybrid filler with higher than 3 phr ZnO content gave less bound rubber as indicated by

Figure 9. Bound rubber contents determined by swelling method for the gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

the lower peak height and peak area in the relaxation spectrum ($H(T)$) (Figure 8b) and also by the bound rubber content in Figure 9. This might be due to the CNT₃/ZnO₅ and CNT₃/ZnO₇ filled NR composites having less physically bound rubber than CNT₃/ZnO₁ and CNT₃/ZnO₃ and the one with CNT filler.

3.5. Payne effect

In order to assess filler networks or filler–filler interactions in the NR composites in terms of strain-induced breakdown, the dynamic properties were examined by plotting storage modulus against a wide range of strains. Figure 10 shows the storage modulus (G') as a function of strain amplitude for the gum NR vulcanizate, NR-CNT, and different types of NR-CNT/ZnO composites containing various ZnO fractions in CNT/ZnO hybrid filler. Furthermore,

Figure 10. Storage modulus as a function of strain amplitude for the gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

Table 3 shows storage moduli at the low strain ($G'_{0.56}$) and the high strain regimes (G'_{100}), as well as storage modulus difference ($\Delta G'$) for the gum NR vulcanizate and NR-CNT/ZnO composites. In Figure 10, an almost linear viscoelastic behavior is seen for most strain amplitudes tested, but a slight drop in storage modulus at high strain is seen for the gum NR vulcanizate. This might be due to the disentanglement of natural rubber molecules under the influence of stress. However, large drops in storage moduli are seen with increasing strain amplitude for all the filled NR composites. These are due to the breakdown of filler–filler networks under shear in the dynamic test, known as the Payne effect [33]. It is noted that the level of Payne effect or filler–filler interactions is commonly quantified as the difference between storage moduli at very low strain ($G'_{0.56}$) and at very high strain (G'_{100}). In this work, the Payne effect is given in terms of $G'_{0.56} - G'_{100}$, indicated by ($\Delta G'$) in Table 3. A high Payne effect or a strong decrease in storage modulus indicates large filler agglomerates. This is how strong CNT agglomeration in the NR-CNT composites can be demonstrated [34].

Table 3. Storage modulus at very low strain ($G'_{0.56}$) and at very high strain (G'_{100}), and their difference ($\Delta G'$) for gum NR un-vulcanizate, NR-CNT and NR-CNT/ZnO nanocomposites.

Compound	G'_0 [MPa]	G'_{100} [MPa]	$\Delta G'$ [MPa]
Gum NR	0.11	0.09	0.02
NR-CNT ₃	0.24	0.11	0.13
NR -CNT ₃ /ZnO ₁	0.17	0.09	0.08
NR-CNT ₃ /ZnO ₃	0.19	0.10	0.09
NR-CNT ₃ /ZnO ₅	0.24	0.07	0.17
NR-CNT ₃ /ZnO ₇	0.23	0.05	0.18

Furthermore, the lowest Payne effect or the least filler–filler interactions were observed for NR-CNT₃/ZnO₁ ($\Delta G' = 0.08$) and NR-CNT₃/ZnO₃ ($\Delta G' = 0.09$) composites. They have smaller drops in storage moduli with strain amplitude in Figure 10. The NR-CNT composite had a larger Payne effect ($\Delta G' = 0.13$) with a larger drop of modulus (Figure 10) in comparison to these cases. The larger Payne effect of CNT filled natural rubber relates to strong filler networks from filler–filler interactions [35]. Moreover, the nanocomposites with CNT/ZnO hybrid filler having over 3 phr of ZnO, namely NR-CNT₃/ZnO₅ ($\Delta G' = 0.17$) and NR-CNT₃/ZnO₇ ($\Delta G' = 0.18$), showed larger Payne effects than the NR-CNT composite, indicating stronger filler–filler interactions with over 3 phr ZnO content. Therefore, a higher Payne effect was observed in NR-CNT and NR-CNT/ZnO composites with higher loading levels of ZnO in CNT/ZnO than 3 phr. This might be attributed to the ZnO at 3 phr in the CNT/ZnO hybrid filler being a proper ratio giving finer filler dispersion with stronger filler–rubber networks in the NR matrix. This also leads to lesser filler–filler interactions but stronger filler–polymer attractions, promoting dispersion and distribution of CNT/ZnO hybrid filler in the NR matrix. However, with ZnO contents over 3 phr, a greater Payne effect was found. This might be due to stronger ZnO and CNT agglomerates contributing to stronger average filler–filler interactions or Payne effect. Therefore, the dispersion of CNT and ZnO hybrid filler in the NR matrix was significantly enhanced in the NR-CNT₃/ZnO₃ case, achieving larger values in relaxation spectrum (Figure 8), larger bound rubber content (Figures 8 and 9) and lesser Payne effect (Figure 10) than the other composites tested.

3.6. Electrical conductivity

The electrical properties of the NR vulcanizates were examined to confirm the formation of filler pathways with CNT-to-CNT, ZnO-to-ZnO, and CNT-to-ZnO connections, to enable electric currents in the NR matrix. Figure 11 shows electrical conductivity as a function of frequency for the gum NR vulcanizate, NR-CNT, and the various types of NR-CNT/ZnO composites. It can be seen that electrical conductivity linearly increased with frequency and that CNT filler strongly increased electrical conductivity from that of the NR gum vulcanizate. Moreover, a further increase in electrical conductivity was observed after the incorporation of various types of CNT/ZnO hybrid

Figure 11. Electrical conductivity as a function of frequency for the gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

filler, and the highest electrical conductivity at a given frequency was for the NR-CNT₃/ZnO₃ composite. This might be a synergistic effect of intrinsic high electrical conductivities of CNT and ZnO, forming filler networks that enable the movement of electrons throughout the rubber matrix. In addition, the electrical conductivity of NR-CNT/ZnO nanocomposites is clearly higher for the composite with finer filler dispersion and distribution, *i.e.*, NR-CNT₃/ZnO₃ (Figures 5–7) with high bound rubber content (Figures 8 and 9). Due to that, pathways of CNT and ZnO were formed, connecting electric currents throughout the NR matrix, as demonstrated in Figure 7.

In order to evaluate the critical ZnO content in CNT/ZnO hybrid filler that is optimal for formation of an infinite conductive network in the NR matrix, percolation theory was applied [36]. That is, the optimal conductivity ($\omega_{\max}$) observed at a critical filler concentration in the rubber matrix was recognized as the percolation threshold concentration (ϕ_c) [37]. Figure 12 shows the relationship of the electrical conductivity of the NR-CNT/ZnO hybrid composite with various ZnO content in the CNT/ZnO hybrid filler. Also, the electrical conductivities of gum NR vulcanizate and NR-CNT composite are included in Figure 12 for comparison. It is confirmed that the NR-CNT/ZnO hybrid composites had higher conductivity than did the gum NR vulcanizate and the NR-CNT composite (Figure 11). Additionally, a sudden increase in the electrical conductivity was observed with 1 phr loading of ZnO. Furthermore, increasing the ZnO content in CNT/ZnO hybrid filler to 3 phr caused a marginal increase in the electrical conductivity. However, on increasing ZnO content

Figure 12. Electrical conductivity of NR-CNT vulcanizate and NR-CNT/ZnO nanocomposites with different ZnO loadings in CNT/ZnO hybrid filler.

in CNT-ZnO beyond 3 phr, electrical conductivity remained almost constant. This indicates the formation of infinite conductive filler networks in NR matrix after the addition of 1 phr ZnO into the CNT-ZnO hybrid composite. This allows the free movement of electrons throughout the rubber matrix. It is noted that the maximum gradient of the curve is taken as the percolation threshold concentration, which is as low as 0.25 phr of ZnO in this case. This confirms that the CNT/ZnO hybrid filler improved the electrical conductivity of NR from solely CNT filled NR-CNT composite.

Dielectric constant of a material is defined as the ratio of electric permeability of the material and electric permeability of free space (*i.e.*, vacuum), and it can be measured by appeal to a simplified capacitor model [38]. Figure 13 shows the dielectric constants of the NR-CNT and the NR-CNT/ZnO hybrid composites as functions of frequency. Clearly, the gum NR vulcanizate had a frequency-independent dielectric constant. However, all the composites had a slightly decreasing dielectric constant. This may be due to the orientation polarization of polar functional groups in the composites, which becomes more difficult as frequency increases. Furthermore, CNT filler increased the dielectric constant from that of the gum NR vulcanizate. The abrupt increase in the dielectric constant was observed from the incorporation of the CNT/ZnO hybrid fillers, due to the conductive nature of CNT and the finer filler networks of CNT and ZnO. Therefore, the NR-CNT/ZnO was able to hold more electric charges for long periods of time, and/or to hold comparatively large quantities of charge. This might be attributed to the charges that can easily move via

Figure 13. Dielectric constant as a function of frequency for NR-CNT and various types of NR-CNT/ZnO nanocomposites with different ZnO loadings in CNT/ZnO hybrid filler.

the filler pathways and propagate in the NR matrix, to increase conductivity with a high total surface charge reorientation in the surface of CNT/ZnO hybrid filler networks. This can be explained by the formation of bridges between CNT and ZnO particles, which increased the remaining electron charges collected at the end of a CNT. Therefore, the electron charges in NR-CNT/ZnO hybrid composites can easily flow throughout the NR matrix due to significantly more bound rubber (Figures 8 and 9), higher electrical conductivity (Figure 11) and dielectric constant (Figure 13), but very low percolation threshold concentration (Figure 12). Furthermore, it is noted that superior electrical conductivity, together with high dielectric constant, was found in NR-CNT/ZnO hybrid composites. This could enable making smart materials, for example, for actuators, where high conductivity and high dielectric properties are needed.

3.7. Dynamic mechanical analysis

Figure 14 shows the storage modulus (G') and the loss tangent ($\tan \delta$) as functions of temperature for gum NR vulcanizate together with NR-CNT, and

Figure 14. Storage modulus and $\tan \delta$ as functions of temperature for gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

NR-CNT/ZnO composites. Also, Table 4 shows the glass transition temperatures (T_g), $\tan \delta_{60}$, and $\tan \delta_{\max}$ for the materials tested in Figure 14. The NR-CNT and NR-CNT/ZnO composites gave larger storage moduli in the glassy region (glass transition) and rubbery region than the gum NR vulcanizate. This is attributed to polymer–filler and filler–filler interactions together with hydrodynamic effects of the fillers (*i.e.*, CNT and CNT-ZnO hybrid). Also, the formation of CNT and ZnO networks in the NR matrix might be another reason for the higher storage moduli. Furthermore, immediate drops in storage moduli are seen in all samples at the glass transition region, from which the maximum point of decreasing gradient indicates the glass transition temperature (T_g). This could also be identified at the peak location in the $\tan \delta$ curve. In Figure 14, it can be seen that single T_g s are seen for all the samples tested, and these are listed in Table 4. It is clear that the T_g s of NR-CNT composite and NR-CNT/ZnO hybrid composites are shifted towards higher temperatures from that of the gum NR vulcanizate. This might indicate that the CNT and CNT-ZnO networks in the NR matrix restricted NR chain mobility.

Table 4. Glass transition temperature (T_g), $\tan \delta_{60}$, $\tan \delta_{\max}$ and crosslink density based on TSSR tests for gum NR vulcanizate together with NR-CNT and different types of NR-CNT/ZnO nanocomposites.

Compounds	T_g [°C]	$\tan \delta_{60}$ °C	$\tan \delta_{\max}$ [°C]	Crosslink density [mol/m ³]
Gum NR	−55.72	0.05	1.98	68.25
NR-CNT ₃	−50.43	0.06	1.73	84.14
NR -CNT ₃ /ZnO ₁	−49.17	0.03	1.83	96.56
NR-CNT ₃ /ZnO ₃	−46.24	0.03	1.86	113.84
NR-CNT ₃ /ZnO ₅	−49.84	0.03	1.77	73.22
NR-CNT ₃ /ZnO ₇	−48.80	0.05	1.44	67.58

In Table 4, it is seen that increased loading of ZnO in CNT/ZnO composite induced an increase in T_g until 3 phr ZnO level, where the highest T_g occurred. Increasing the loading of ZnO past 3 phr decreased T_g . This can be explained in terms of good filler-filler interactions favoring the formation of CNT/ZnO networks, creating strong interactions between the filler particles and the polymer matrix. Thus, the NR molecular mobility or flexibility was restricted by the formed CNT/ZnO networks, and hence the highest T_g was found in the CNT/ZnO composite containing 3 phr of ZnO. However, ZnO at more than 3 phr gave a lower T_g . This might be because stronger ZnO agglomeration increased the free volume in the NR matrix that enabled the NR molecular chains to move freely [39]. Also, the glass transition temperature (T_g) related to the crosslink density of materials, as shown in Table 4. In this work, the apparent crosslink density was estimated from the maximum slopes at the initial parts of the relaxation modulus-temperature curves in Figure 8a, by applying Equations (6) and (7) [19, 40]:

$$v_e = \frac{k}{R(\lambda - \lambda^{-2})} \quad (6)$$

$$v_e = \frac{\rho}{M_c} \quad (7)$$

where v_e is the apparent crosslink density [mol/m^3], R is the universal gas constant, k is the nominal strain ratio, k is the temperature coefficient of stress (the derivative of mechanical stress with respect to temperature), ρ is the mass density, and M_c is defined as the average molar mass of the elastically active network chains, respectively.

In Table 4, it is confirmed that the highest T_g was found in the CNT/ZnO composite containing 3 phr of ZnO (*i.e.*, NR-CNT₃/ZnO₃) with the highest crosslink density. Also, the NR-CNT/ZnO with ZnO at more than 3 phr gave a lower T_g . This matches well the $\tan \delta_{\max}$ in Table 4 where the gum NR gave the highest $\tan \delta_{\max}$ while incorporating CNT or CNT/ZnO caused reduced $\tan \delta_{\max}$. This indicates that the NR-CNT and NR/CNT-ZnO vulcanizates had less damping than did the gum NR vulcanizates. Besides, the $\tan \delta$ at 60 °C is also depicted in Table 4. It is an important index for high-performance rubber associated with rolling resistance [41]. It can be seen that the NR-CNT composites exhibited higher $\tan \delta$ at 60 °C than does the gum NR vulcanizate. However,

incorporation of CNT/ZnO hybrid fillers tended to decrease $\tan \delta$ at 60 °C. This suggests decreased rolling resistance, energy conservation, and environmental benefits from these hybrid composite materials.

3.8. Mechanical properties

The tensile properties of gum NR, NR-CNT, and NR-CNT/ZnO were investigated, and the stress-strain behaviors are shown in Figure 15. It is seen that Young's modulus (initial slope), 100% modulus, and tensile strength were higher for NR-CNT, NR-CNT₃/ZnO₁, and NR-CNT₃/ZnO₃ composites than for the gum NR vulcanizate. This is due to the reinforcing efficiencies of CNT and NR-CNT/ZnO hybrid fillers with ZnO contents of 1 and 3 phr. Furthermore, increasing the loading level of ZnO in CNT/ZnO hybrid filler increased Young's modulus, 100% modulus, and tensile strength until 3 phr ZnO loading, where the highest value is seen. Incorporation of more than 3 phr of ZnO in CNT/ZnO decreased these properties. This is attributed to the formation of CNT/ZnO networks with strong interactions between the filler particles and the polymer matrix, particularly at 3 phr ZnO loading. Whilst higher ZnO loading in CNT/ZnO hybrid filler caused excess ZnO nanoparticles in the system. Therefore, strong and large ZnO agglomerates were formed in combination to the free micro-ZnO activator in NR matrix, which caused decreasing of Young's modulus, 100% modulus, and tensile strength (Figure 15). This matches well the filler dispersion (Figures 5 and 6), relaxation modulus (Figure 8), and bound rubber content (Figures 8 and 9). Furthermore, lesser elongations at break are seen for NR-CNT and NR-CNT/ZnO composites than for

Figure 15. Stress-strain curves of the gum NR vulcanizate, NR-CNT and different types of NR-CNT/ZnO nanocomposites.

the NR vulcanizate. The reduction of extension ability of the composites could be due to the rigid natures of CNT and CNT-ZnO hybrid fillers.

4. Conclusions

ZnO nanoparticles were successfully decorated on CNT surfaces to form a hybrid filler that eagerly networked in an NR matrix. The interactions between carbonyl and hydroxyl groups on CNT surfaces and Zn ions were observed in FTIR peaks of the functional groups of CNT and ZnO, and in TEM micrographs. The CNT/ZnO hybrid filler at low contents of ZnO from 1 to 3 phr improved key properties of the NR-CNT/ZnO composites, namely initial stress, bound rubber content, storage modulus, electrical conductivity, and dielectric properties. The finer dispersion and distribution of CNT and ZnO fillers in the NR matrix with CNT/ZnO network formation and stronger filler-rubber interactions induced the mentioned properties. The dispersion of the fillers was clearly visualized by FESEM and fluorescence stereomicrographs, indicating finer filler dispersion in NR-CNT₃/ZnO₃ than in NR-CNT composite. Increased bound rubber along with T_g shift to a higher temperature, were observed for the NR-CNT₃/ZnO₃ composite.

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References

- [1] Nakaramontri Y., Nakason C., Kummerlöwe C., Vennemann N.: Influence of modified natural rubber on properties of natural rubber-carbon nanotube composites. *Rubber Chemistry and Technology*, **88**, 199–218 (2015).
<https://doi.org/10.5254/rct.14.85949>
- [2] Sharika T., Abraham J., Arif M., George S. C., Kalarikkal N., Thomas S.: Excellent electromagnetic shield derived from MWCNT reinforced NR/PP blend nanocomposites with tailored microstructural properties. *Composites Part B: Engineering*, **173**, 106798/1–106798/13 (2019).
<https://doi.org/10.1016/j.compositesb.2019.05.009>
- [3] Grossiord N., Loos J., Regev O., Koning C. E.: Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites. *Chemistry of Materials*, **18**, 1089–1099 (2006).
<https://doi.org/10.1021/cm051881h>
- [4] Jose T., Moni G., Salini S., Raju A. J., George J. J., George S. C.: Multifunctional multi-walled carbon nanotube reinforced natural rubber nanocomposites. *Industrial Crops and Products*, **105**, 63–73 (2017).
<https://doi.org/10.1016/j.indcrop.2017.04.047>
- [5] Krainoi A., Kummerlöwe C., Nakaramontri Y., Wisunthorn S., Vennemann N., Pichaiyut S., Kiatkamjornwong S., Nakason C.: Influence of carbon nanotube and ionic liquid on properties of natural rubber nanocomposites. *Express Polymer Letters*, **13**, 327–348 (2019).
<https://doi.org/10.3144/expresspolymlett.2019.28>
- [6] Nakaramontri Y., Kummerlöwe C., Nakason C., Vennemann N.: The effect of surface functionalization of carbon nanotubes on properties of natural rubber/carbon nanotube composites. *Polymer Composites*, **36**, 2113–2122 (2015).
<https://doi.org/10.1002/pc.23122>
- [7] Nakaramontri Y., Pichaiyut S., Wisunthorn S., Nakason C.: Hybrid carbon nanotubes and conductive carbon black in natural rubber composites to enhance electrical conductivity by reducing gaps separating carbon nanotube encapsulates. *European Polymer Journal*, **90**, 467–484 (2017).
<https://doi.org/10.1016/j.eurpolymj.2017.03.029>
- [8] Guo H., Jerrams S., Xu Z., Zhou Y., Jiang L., Zhang L., Liu L., Wen S.: Enhanced fatigue and durability of carbon black/natural rubber composites reinforced with graphene oxide and carbon nanotubes. *Engineering Fracture Mechanics*, **223**, 106764/1–106764/12 (2020).
<https://doi.org/10.1016/j.engfractmech.2019.106764>
- [9] Krainoi A., Kummerlöwe C., Nakaramontri Y., Wisunthorn S., Vennemann N., Pichaiyut S., Kiatkamjornwong S., Nakason C.: Novel natural rubber composites based on silver nanoparticles and carbon nanotubes hybrid filler. *Polymer Composites*, **41**, 443–458 (2020).
<https://doi.org/10.1002/pc.25378>
- [10] Panampilly B., Thomas S.: Nano ZnO as cure activator and reinforcing filler in natural rubber. *Polymer Engineering and Science*, **53**, 1337–1346 (2013).
<https://doi.org/10.1002/pen.23383>
- [11] Padmavathy N., Vijayaraghavan R.: Enhanced bioactivity of ZnO nanoparticles – An antimicrobial study. *Science and Technology of Advanced Materials*, **9**, 035004/1–035004/8 (2008).
<https://doi.org/10.1088/1468-6996/9/3/035004>
- [12] Fan Z., Lu J. G.: Zinc oxide nanostructures: Synthesis and properties. *Journal of Nanoscience and Nanotechnology*, **5**, 1561–1573 (2005).
<https://doi.org/10.1166/jnn.2005.182>

- [13] Largani S. H., Pasha M. A.: The effect of concentration ratio and type of functional group on synthesis of CNT–ZnO hybrid nanomaterial by an *in situ* sol–gel process. *International Nano Letters*, **7**, 25–33 (2017).
<https://doi.org/10.1007/s40089-016-0197-4>
- [14] Kołodziejczak-Radzimska A., Markiewicz E., Jesionowski T.: Structural characterisation of ZnO particles obtained by the emulsion precipitation method. *Journal of Nanomaterials*, **2012**, 656353/1–656353/9 (2012).
<https://doi.org/10.1155/2012/656353>
- [15] Akhavan O., Azimirad R., Safa S.: Functionalized carbon nanotubes in ZnO thin films for photoinactivation of bacteria. *Materials Chemistry and Physics*, **130**, 598–602 (2011).
<https://doi.org/10.1016/j.matchemphys.2011.07.030>
- [16] Li H., Liu Z., Yang S., Zhao Y., Feng Y., Bakenov Z., Zhang C., Yin F.: Facile synthesis of ZnO nanoparticles on nitrogen-doped carbon nanotubes as high-performance anode material for lithium-ion batteries. *Materials*, **10**, 1102/1–1102/10 (2017).
<https://doi.org/10.3390/ma10101102>
- [17] Upasani P., Sreekumar T. V., Gaikar V. G., Jha N.: Preparation of ZnO/MWCNT/PP composite film and its application as multifunctional protective film. *Polymer Composites*, **39**, 157–170 (2018).
<https://doi.org/10.1002/pc.23916>
- [18] Chaudhary D., Singh S., Vankar V. D., Khare N.: ZnO nanoparticles decorated multi-walled carbon nanotubes for enhanced photocatalytic and photoelectrochemical water splitting. *Journal of Photochemistry and Photobiology A: Chemistry*, **351**, 154–161 (2018).
<https://doi.org/10.1016/j.jphotochem.2017.10.018>
- [19] Vennemann N., Böckamp K., Bröker D.: Crosslink density of peroxide cured TPV. *Macromolecular Symposia*, **245–246**, 641–650 (2006).
<https://doi.org/10.1002/masy.200651391>
- [20] Wolff S., Wang M.-J., Tan E.-H.: Filler-elastomer interactions. Part VII. Study on bound rubber. *Rubber Chemistry and Technology*, **66**, 163–177 (1993).
<https://doi.org/10.5254/1.3538304>
- [21] Guggilla P., Batra A. K., Edwards M. E.: Electrical characterization of LiTaO₃:P(VDF–TrFE) composites. *Journal of Materials Science*, **44**, 5469–5474 (2007).
<https://doi.org/10.1007/s10853-009-3753-8>
- [22] Samadi M., Shivaee H. A., Zanetti M., Pourjavadi A., Moshfegh A.: Visible light photocatalytic activity of novel MWCNT-doped ZnO electrospun nanofibers. *Journal of Molecular Catalysis A: Chemical*, **359**, 42–48 (2012).
<https://doi.org/10.1016/j.molcata.2012.03.019>
- [23] Kumar S., Chaudhary D., Dhawan P. K., Yadav R. R., Khare N.: Bi₂Te₃-MWCNT nanocomposite: An efficient thermoelectric material. *Ceramic International*, **43**, 14976–14982 (2017).
<https://doi.org/10.1016/j.ceramint.2017.08.017>
- [24] Zhu L.-P., Liao G.-H., Huang W.-Y., Ma L.-L., Yan Y., Yu Y., Fu S.-Y.: Preparation, characterization and photocatalytic properties of ZnO-coated multi-walled carbon nanotubes. *Materials Science and Engineering: B*, **163**, 194–198 (2009).
<https://doi.org/10.1016/j.mseb.2009.05.021>
- [25] Yu Y., Huang W.-Y., Li J.-L., Ma L.-L.: Preparation and photocatalytic property of ZnO/MWCNTs composites. in ‘Solid state chemistry research trends’ (ed.: Buckley R. W.) Nova Science, New York, 1–22 (2007).
- [26] Yu Y., Ma L.-L., Huang W.-Y., Li J.-L., Wong P.-K., Yu J. C.: Coating MWNTs with Cu₂O of different morphology by a polyol process. *Journal of Solid State Chemistry*, **178**, 1488–1494 (2005).
<https://doi.org/10.1016/j.jssc.2005.02.016>
- [27] Jia B., Gao L., Sun J.: Self-assembly of magnetite beads along multiwalled carbon nanotubes *via* a simple hydrothermal process. *Carbon*, **45**, 1476–1481 (2007).
<https://doi.org/10.1016/j.carbon.2007.03.025>
- [28] Junkong P., Cornish K., Ikeda Y.: Characteristics of mechanical properties of sulphur cross-linked guayule and dandelion natural rubbers. *The Royal Society of Chemistry*, **7**, 50739–50752 (2017).
<https://doi.org/10.1039/C7RA08554K>
- [29] Wang L., Qi T., Hu M., Zhang S., Xu P., Qi D., Wu S., Xiao H.: Inhibiting mercury re-emission and enhancing magnesia recovery by cobalt-loaded carbon nanotubes in a novel magnesia desulfurization process. *Environmental Science and Technology*, **51**, 11346–11353 (2017).
<https://doi.org/10.1021/acs.est.7b03364>
- [30] Gómez S., Rendtorff N. M., Aglietti E. F., Sakka Y., Suárez G.: Surface modification of multiwall carbon nanotubes by sulfonitric treatment. *Applied Surface Science*, **379**, 264–269 (2016).
<https://doi.org/10.1016/j.apsusc.2016.04.065>
- [31] Coates J.: Interpretation of infrared spectra, A practical approach. in ‘Encyclopedia of analytical chemistry’ (ed.: Meyers R. A.) Wiley, New York, 10815–10837 (2006).
<https://doi.org/10.1002/9780470027318.a5606>
- [32] Vennemann N., Schwarze C., Kummerlöwe C.: Determination of crosslink density and network structure of NR vulcanizates by means of TSSR. *Advanced Materials Research*, **844**, 482–485 (2014).
<https://doi.org/10.4028/www.scientific.net/AMR.844.482>
- [33] Payne A. R.: Effect of dispersion on the dynamic properties of filler loaded rubbers. *Journal of Applied Polymer Science*, **9**, 2273–2284 (1965).
<https://doi.org/10.1002/app.1965.070090619>
- [34] Subramaniam K., Das A., Stöckelhuber K. W., Heinrich G.: Elastomer composites based on carbon nanotubes and ionic liquid. *Rubber Chemistry and Technology*, **86**, 367–400 (2013).
<https://doi.org/10.5254/rct.13.86984>

- [35] Fröhlich J., Niedermeier W., Luginsland H-D.: The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. *Composites Part A: Applied Science and Manufacturing*, **36**, 449–460 (2005).
<https://doi.org/10.1016/j.compositesa.2004.10.004>
- [36] Bokobza L.: Enhanced electrical and mechanical properties of multiwall carbon nanotube rubber composites. *Polymer Advanced and Technology*, **23**, 1543–1549 (2012).
<https://doi.org/10.1002/pat.3027>
- [37] Bokobza L.: Multiwall carbon nanotube elastomeric composites: A review. *Polymer*, **48**, 4907–4920 (2007).
<https://doi.org/10.1016/j.polymer.2007.06.046>
- [38] Brebels J., Manca J. V., Lutsen L., Vanderzande D., Maes W.: High dielectric constant conjugated materials for organic photovoltaics. *Journal of Materials Chemistry A*, **5**, 24037–24050 (2017).
<https://doi.org/10.1039/C7TA06808E>
- [39] Salaeh S., Boiteux G., Cassagnau P., Nakason C.: Flexible 0–3 ceramic-polymer composites of barium titanate and epoxidized natural rubber. *International Journal of Applied Ceramic Technology*, **12**, 106–115 (2015).
<https://doi.org/10.1111/ijac.12129>
- [40] Matchawet S., Kaesaman A., Vennemann N., Kumerlöwe C., Nakason C.: Effects of imidazolium ionic liquid on cure characteristics, electrical conductivity and other related properties of epoxidized natural rubber vulcanizates. *European Polymer Journal*, **87**, 344–359 (2017).
<https://doi.org/10.1016/j.eurpolymj.2016.12.037>
- [41] Lin Y., Chen Y., Zeng Z., Zhu J., Wei Y., Li F., Liu L.: Effect of ZnO nanoparticles doped graphene on static and dynamic mechanical properties of natural rubber composites. *Composites Part A: Applied Science and Manufacturing*, **70**, 35–44 (2015).
<https://doi.org/10.1016/j.compositesa.2014.12.008>