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Carbon Nanotubes Reinforced Natural Rubber Composites

Apinya Krainoi, Jobish Johns, Ekwipoo Kalkornsurapranee and Yeampon Nakaramontri

Abstract

Several advanced methods have been introduced to disperse CNTs in the NR matrix. Various aspects highlighted in this chapter include the mixing processes such as melt mixing and latex mixing methods. As well as, formations of functional groups on the surfaces of CNT using silane coupling agents (i.e., ex-situ and in-situ functionalization). Moreover, hybrid CNT are beneficial to achieve better electrical conductivity of NR/CNT composites. These efforts are aimed to reduce the percolation threshold concentration in the NR composites for application as conducting composites based on electrically insulating rubber matrix. Sensor application is developed based on conducting NR composites. NR composites showed changing of resistivity during elongation termed as piezoresistivity. The most commonly used rubber matrices such as NR, ENR and IR are mixed with a combination of CNT and CB fillers as hybrid filler. The presence of linkages in the ENR composites results in the least loss of conductivity during external strain. It is found that the conductivity becomes stable after 3000 cycles. This is found to be similar to the NR-CNT/CB composite, while a few cycles are needed for IR-CNT/CB owing to the higher filler agglomeration and poor filler-rubber interactions. This is attributed to the polar chemical interactions between ENR and the functional groups on the surfaces of CNT/CB.

Keywords: natural rubber, carbon nanotube, nanocomposites, electrical conductivity, sensor

1. Introduction

Natural rubber (NR) is widely used in various industries owing to its excellent elasticity and mechanical properties. NR has been typically used in many industrial applications including tires, sports articles, sealing materials, medical glove, rubber boots and dairy rubber items [1]. Moreover, application of NR can be more applied by addition of fillers, such as silica, clay, carbon black, and carbon nanotube that is properties of NR can be induced by filler. As NR was converted from insulator material to be used as semi-conductive.

CNT have been widely interested for using as conductive filler in NR composites, due to the sp^2-hybridized carbon molecules throughout its molecular structure. Its carbon–carbon bond angles can be mechanically distorted reversibly, and core electrons can act as free electrons of the carbon atoms on CNT surfaces. Thus, the

special molecular structure of CNT provides it with high mechanical properties, excellent thermal conductivity, and outstanding electrical conductivity [2].

Furthermore, nanocomposite of NR and CNT provided high elasticity material and also sensitivity on electricity due to CNT networks in NR matrix are easy to break under stretching and fast rebuilt under releasing [2]. Therefore, it well proper for application as smart sensors to monitor the applied external stimulus. That is, NR/CNT composites based stretchable strain sensors have been interested to emerging applications, such as human motion detection [3, 4].

However, several works have been researched on human motion detection as adsorbing graphene woven fabrics on polydimethylsiloxane (PDMS) and medical tape composite. The wearable strain sensor could well detect human movements, including hand clenching, pulse, expression change, blink, phonation, and breathing [4]. Additionally, it is observed that the stretchable CNTs/carbon black (CB)/ isoprene rubber (IR) composites could be used to detect human motions and emotional expressions [5]. It was reported that the percolation threshold concentration of composites was significantly increased, while optimal conductivity increased, on adding conductive CB in CNT composites [5]. Furthermore, using CB also improves the sensitivity of electrical resistivity to stress and strain, due to its spherical shape that eases disconnection of conductive particles by strain, while the long cylindrical CNT particles can have sliding contact. This increases potentially the piezoresistive responsiveness, combining excellent conductivity of CNT with strain sensitivity of the electrical pathways on using CNT-CB blended filler [6, 7]. Furthermore, using NR, incorporation of CNT and CB hybrid filler can keep a very stable sensor performance, showing good mechanical properties, when the composites are dynamically elongated several times [6, 8]. Also, NR composites are easy to process, cost-effective, and well-known as hydrophobic biopolymers [9], so that humidity does not effect on an NR sensor.

This review article focuses on the preparation and electrical property of NR/ CNT composites, the methods to improve the dispersion CNT are also mentioned as well as overview of applying NR/CNT composites for motions sensors application.

2. Properties of CNTs

Usually, CNT has extremely high tensile strength compared to other carbon materials. The excellent strength makes CNTs suitable for developing composite material with higher reinforcing efficiency. It was also found that, the incorporation of 0.5 phr MWCNT in NR composite reflected the best properties of increasing 61% of tensile strength and 75% of modulus [10]. Moreover, CNT exhibits excellent electronic properties as the details given in **Table 1** [11, 12].

Properties	SWCNT	MWCNT
Young's modulus (GPa)	100–500	20–95
Tensile strength (GPa)	15–53	11–63
Electrical conductivity (S/cm)	10^2–10^6	10^3–10^5
Electron mobility (cm^2/Vs)	$\sim 10^5$	10^4–10^5
Thermal conductivity (W/m K)	6000	2000

Table 1.
Properties of carbon nanotube.

3. CNTs-based natural rubber composites

3.1 Modified natural rubber-carbon nanotube composites and its properties

Natural rubber (NR) is a well-known biopolymer that consists of isoprene units linked together in *cis*-1,4 configuration. NR has attracted tremendous scientific and industrial interests due to its unique molecular structure with superior and unique properties such as high elasticity, flexibility and some level of biodegradability. However, NR has intrinsically poor aging, weathering, oil resistance, and electrical conductivity that limits the use of NR in some applications. However, the application of NR can be extended by the modification of NR molecules in various forms, such as epoxidized natural rubber (ENR) and maleated natural rubber (MNR). Various properties of NR products (i.e., modulus, viscosity and strength) could be improved by incorporating special types of fillers to form NR composites. Therefore, different types of fillers into NR as an elastomeric matrix, including carbon black, silica, clay, calcium carbonate, carbon fibers or carbon nanotubes, have been widely investigated. CNT filled NR composites were used with various types of natural rubbers, especially unmodified natural rubber (NR), epoxidized natural rubber (ENR) and maleated natural rubber (MNR) [13]. Consequently, after the modification of rubber, the electrical conductivity of composites was found to be enhanced when compared to the unmodified NR-CNT (**Figure 1**). The percolation limit for CNTs in ENR-CNT and MNR-CNT composites is approximately 1 phr, while a value of 4 phr was found for unmodified NR-CNT composite. Lower percolation value of ENR-CNT and MNR-CNT composites than that of the unmodified NR-CNT composite proves the enhanced degree of CNT dispersion in the rubber matrix. It is gained by the occurrence of chemical interaction between the functional groups present in ENR or MNR molecules and the polar groups on CNT surfaces as shown in **Figure 2**. This confirms that, the polar nature of rubber molecules (i.e., ENR and MNR) causes significantly a greater degree of CNT dispersion and consequently the composites reach the percolation limit at smaller CNT concentration. However, for all the composites studied, the maximum electrical conductivities are the same. It means at the CNT concentrations
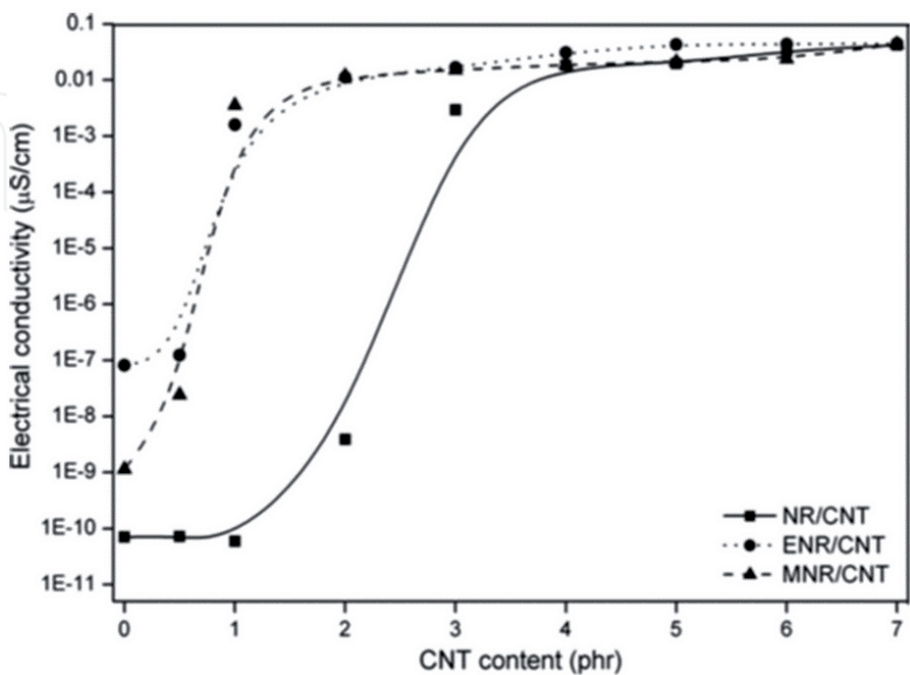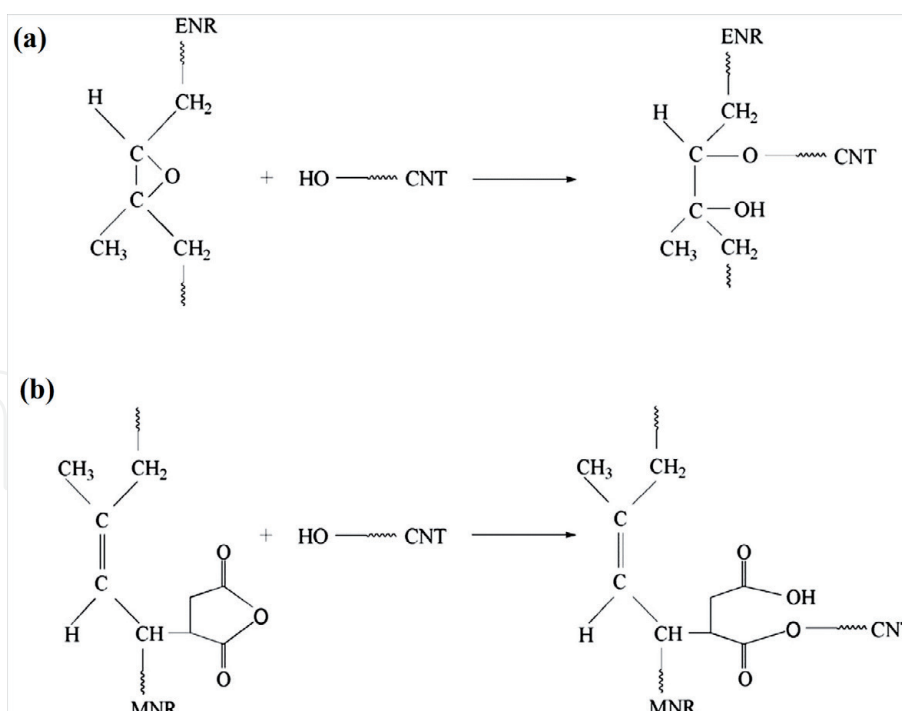

Figure 1.
Electrical conductivity of CNT-filled rubber composites with various CNT contents of 0–7 phr [2].

Figure 2.
Possible chemical reactions between (A) ENR and CNT, and (B) MNR and CNT [13].

below the percolation threshold the electrical conductivity is dominated by the rubber matrix. Whereas the CNT network plays the dominating role above the percolation limits. This correlates well to Earp *et al*. which indicated a comparable conductivity of the NR composites with and without CNT loading since the CNT was covered by the insulated NR molecules. After the increase of CNT concentration, the percolative CNT are formed and the NR matrix had CNT pathway dispersing throughout the samples. This CNT connection induces and carries well transferring of electron which causes increment of electrical conductivity [14]. This is agreement to Ma *et al*. which found that electrically conducting behavior of composites consisting of conducting fillers and insulating matrices can be applied to explain the percolation theory originating in the materials. It was found that the composite undergoes an insulator-to-conductor transition while the conducting filler content is gradually increased. The critical filler concentration is referred to the percolation threshold where the measured electrical conductivity of the composite had sharply increased for several orders of magnitude relating the formation of continuous electron paths or conducting networks [11]. Moreover, critical CNT loading in matrix effects on the overall properties of CNT filled ENR nanocomposites [2]. On varying the CNT loading from 1 to 7 phr showed the critical loading at 3 phr and significantly improved the electrical conductivity.

3.2 Dispersion technique of carbon nanotubes and their network formations on the properties of natural rubber-carbon nanotube composites

Recently, CNT becomes a promising filler for the NR based composites due to its several unique properties. Perfect molecular structure of CNT with sp^2-hybrided carbon structure causes extremely high mechanical properties, excellent thermal conductivity and outstanding electrical conductivity [11]. In addition, low density, high specific surface area and extremely high aspect ratio make the CNT as an interesting carbon filler same as graphene and other carbon fibers. In the recent years, many researchers have attempted to incorporate CNT into rubber matrix (i.e., natural rubber [15–17] and synthetic rubber [18, 19]) to utilize the intrinsic properties of CNT for enhancing the properties of rubber composites, particularly for the electrical

conductivity. However, the property enhancement is not so easy and still the vigorous investigations are ongoing. The major drawback to use CNTs as the reinforcing filler in NR is their agglomeration, since CNT contains very high aspect ratio and strong Van-der Waals attractions between the particles. Small polar functional groups on the CNT surface are also the reason for their self-association behavior inside NR matrix. Altogether it provides strong filler-filler interaction which causes very poor dispersion of CNTs. Weak physical and chemical interactions among CNT and NR matrix generally lead to poor mechanical properties and electrical conductivity due to the incompatibility between them [20]. Therefore, homogeneous dispersion of CNTs inside the rubber matrix is an important challenge by optimizing the condition for the preparation of rubber-CNT composites. To obtain high conductive CNT-based rubber composites, a proper preparation method has also been widely investigated. Melt blending and latex state mixing processes are the most effective methods in terms of the process ability and properties of nanocomposites by using a two-roll mill and an internal mixer [21]. Shearing force and mixing temperature during rubber operation cause reduction of NR viscosity and therefore the CNT can be easily dispersed and distributed in NR matrix. However, this mixing system had originated much the heat and not environmentally friendly operation owing to dispersion of low density of CNT. Thus, latex-based composites are represented and it showed significantly improved properties than relative to the one preparing from melt mixing. It was found that the lowest percolation threshold concentration of approximately 0.5 phr of CNTs was observed in the latex–CNT composites [22]. Electrical conductivity is one of the properties that can be applied to characterize the quality of filler dispersion in CNT composites. If a continuous filler network of electrically conductive fillers is formed, the material undergoes a sudden transition from insulator to conductor. As a result, the electrical conductivity rises by several orders of magnitude. **Figure 3** shows the effect of filler loading on the electrical conductivity of CNT-filled composites based on NR from ADS and latex. Here, the latex-based composites exhibited a percolation threshold at a CNT concentration lower than 1 phr. This is due to the orientation of nanotubes along a specific path around the rubber particles which resulted in the formation of segregated nanotube network [23, 24] as confirmed by the TEM image (**Figure 4**).
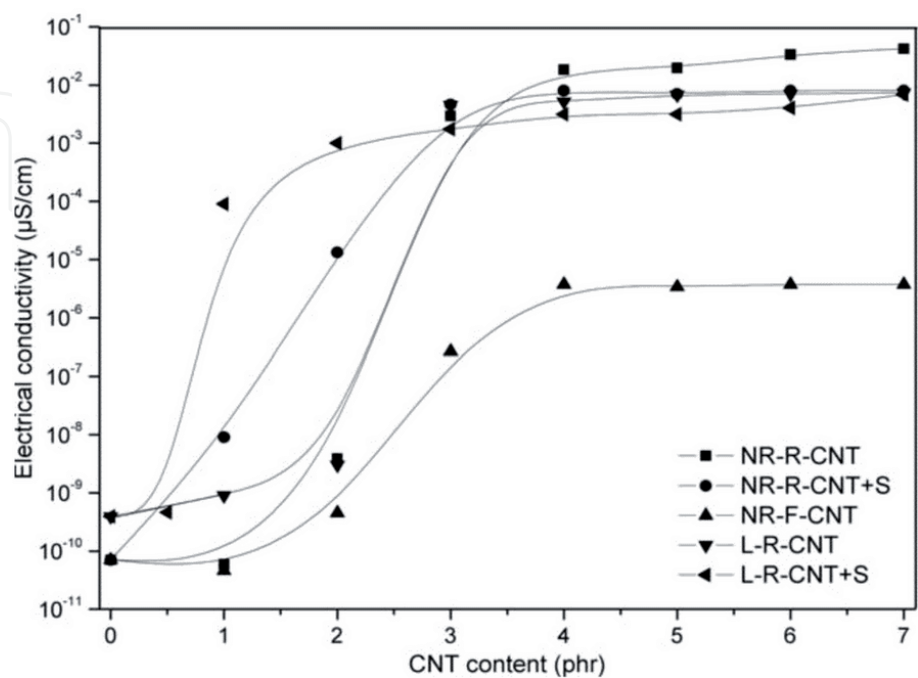

Figure 3.
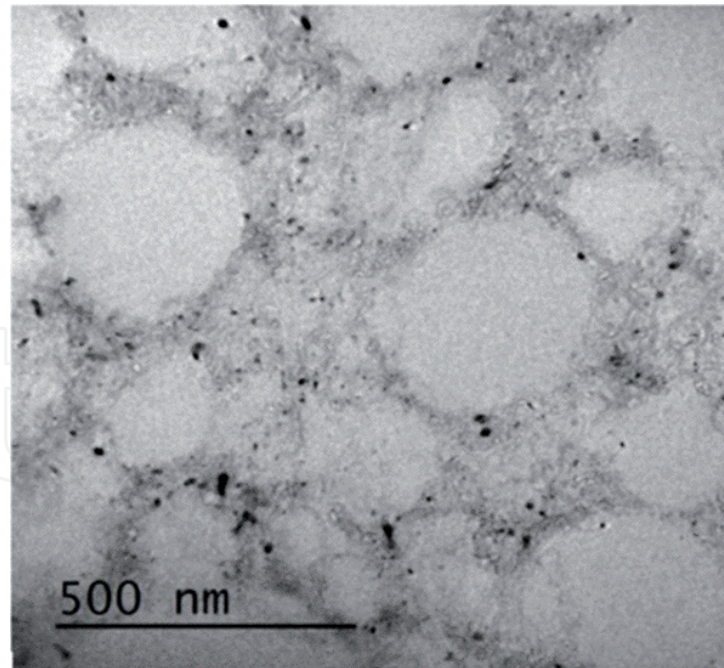*Electrical conductivity of composites as a function of CNT content [22].*

Figure 4.
TEM image of natural rubber composite film containing segregated network of MWCNT [23].

3.3 Functionalization of carbon nanotubes and the properties of natural rubber-carbon nanotube composites

The major drawback of CNT as a reinforcing filler in NR is its agglomeration tendency, since the CNT fibers have very high aspect ratio and strong Van-der Waals attraction between each other. This is due to the lack of polar functional groups on the CNT surfaces which also leads to the self-association behavior in the NR matrix. Generally, the filler-filler interactions are too strong compared to filler-matrix interactions causes very poor dispersion of the filler. The poor physical and chemical bonding between CNT and NR or the incompatible nature generally leads to exhibit poor stability of the composites in terms of their mechanical properties and electrical conductivity [20]. Therefore, attaining a homogeneous dispersion of CNTs in the rubber matrix remains a challenge and addressed by seeking the optimal conditions for the preparation of rubber-CNT composites. To improve the dispersion of CNTs in the NR matrix, a silane coupling agent was applied by expecting that the filler-rubber interactions would be enhanced by reducing the Van-der Waals attractions of CNT particles. The *ex-situ* functionalization of CNTs with silane has been introduced to improve the CNT dispersion in rubber-CNT composites. However, this method is time consuming and more expensive, and might not be appropriate in practical applications. Thus, recent studies have investigated *in-situ* functionalization of CNTs with silane. Similar to rubber-silica composites [25, 26], silane was added directly during the mixing of rubber and silica. The silanization of silica particles can take place during mixing if the mixing conditions are suitable. This alternative process can provide a short processing cycle compared to *ex-situ* silanization. On the other hand, the functional groups on the raw CNTs are readily available and sufficient to react with silane molecules during mixing [22] as similar to the silica-filled composites. Thus, the way of mixing is most important to improve the reinforcing efficiency of CNTs in rubber-CNT composites [27, 28]. CNT filled NR composites were prepared by melt mixing and latex mixing methods. The *in-situ* functionalization of CNTs with a silane coupling agent, namely bis (triethoxysilylpropyl) tetrasulfide (TESPT) was done to improve
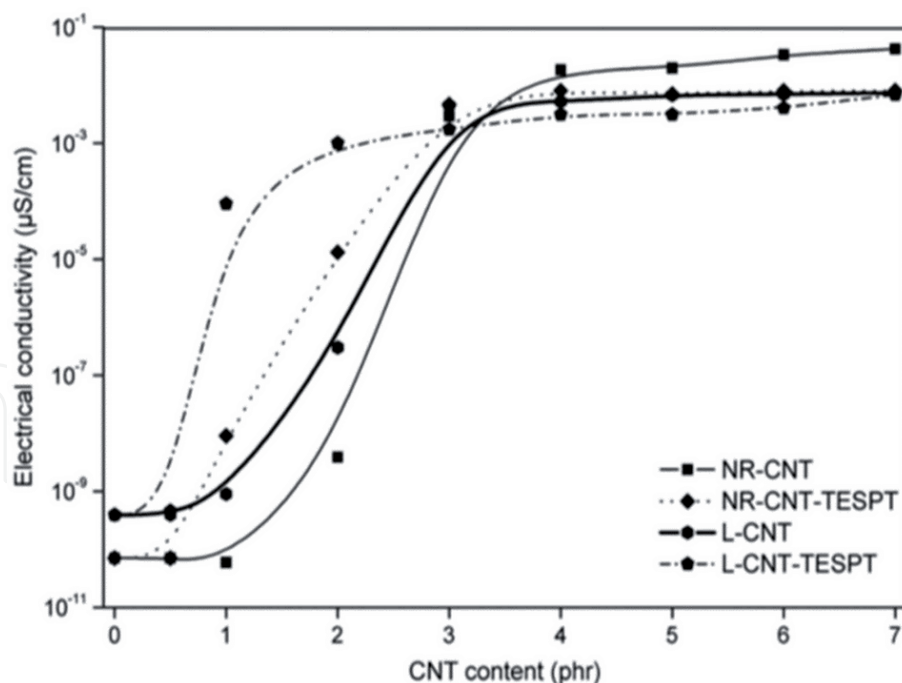
Figure 5.
Variation of electrical conductivity as a function of CNT content for various NR–CNT composites [30].

the interactions between CNT surfaces and rubber molecules. **Figure 5** shows the effect of CNT loading on the electrical conductivity of rubber–CNT composites with and without TESPT prepared by melt mixing and latex mixing processes. The lowest percolation threshold was observed in the composites prepared by latex mixing with *in-situ* functionalization. This is due to the chemical interactions of CNT surfaces, silane, and NR molecules (**Figure 6**) that improved the CNT dispersion and reduced the electrical percolation threshold. As a result, percolation thresholds were observed at approximately 2 and 1 phr of CNTs in NR–CNT–TESPT and L–CNT–TESPT composites, respectively. In addition, it was obtained the same trend as NR and ENR vulcanizates reinforced with CNT, CCB and CNT/CCB hybrid filler that decreasing of physically bound rubber absorption with addition of TESPT are showed, while the chemically bound amount had significantly increased. It was also found that superior conductive material with low dielectric constant of NR and ENR vulcanizates with CNT and CCB hybrid filler are received after the addition of TESPT [29].

In addition, composites of CNT and ENR were also prepared with in-situ functionalization of CNT with two alternative silane coupling agents such as bis(triethoxysilylpropyl) tetrasulfide (TESPT) and 3-aminopropyltriethoxysilane (APTES). The reactions of ENR molecules with the functional groups present on the CNT surfaces and also with the silane molecules were schematically shown in **Figures** 7 and **8**.

Composites of ENR–CNT and ENR–CNT–TESPT were successfully prepared with a very low electrical percolation threshold at 1 phr CNT content as showed in **Figure 9**. Furthermore, the highest electrical conductivity was achieved in the ENR–CNT–TESPT composite, due to its higher cross-link density and near-optimal CNT dispersion. Moreover, the morphological study of ENR–CNT and ENR–CNT–TESPT composites was used to confirm the fine dispersion of CNTs in the ENR matrix with loosely agglomerated CNTs. Consequently, the composites of ENR–CNT and ENR–CNT–TESPT exhibited improved tensile properties with higher cross-link density and electrical conductivity than the baseline of pristine ENR.
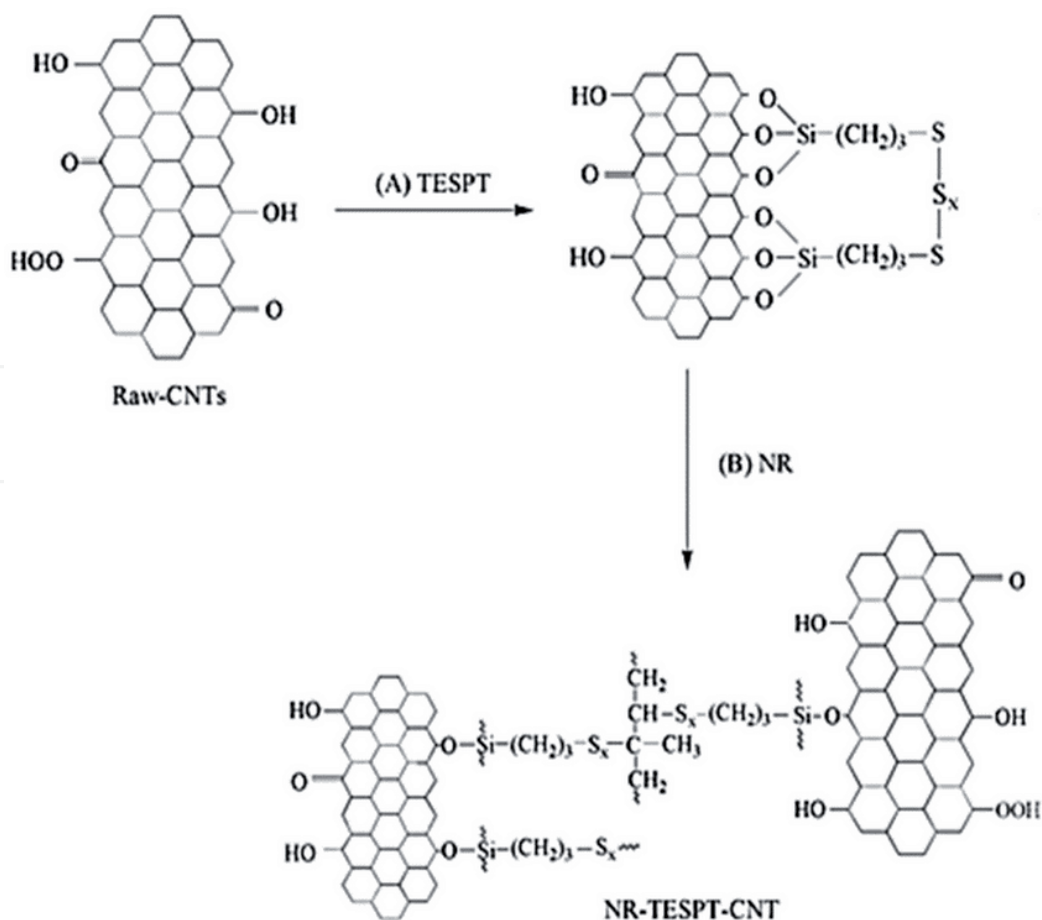
Figure 6.
Chemical reactions of functional groups on CNT surfaces and TESPT molecules (A), and silanized CNTs and NR molecules (B) [30].
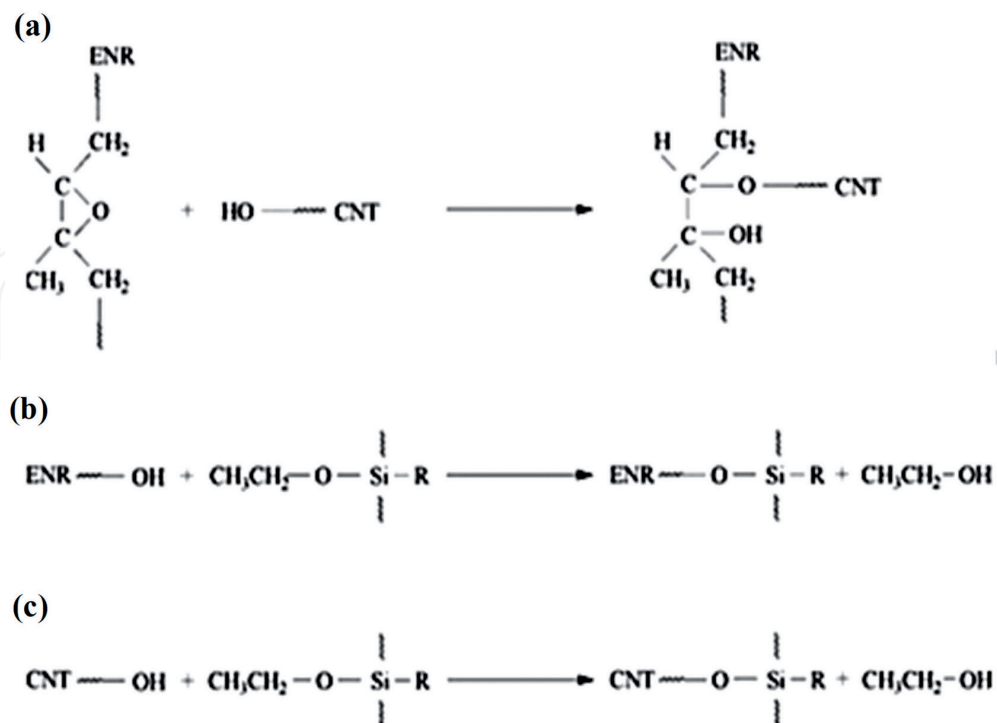

Figure 7.
Possible chemical reactions among (a) oxirane ring of ENR and functional groups of CNT, (b) hydroxyl groups of ENR and ethoxy groups of silanes, and (c) hydroxyl groups of CNT and ethoxy groups of silane molecules [9].
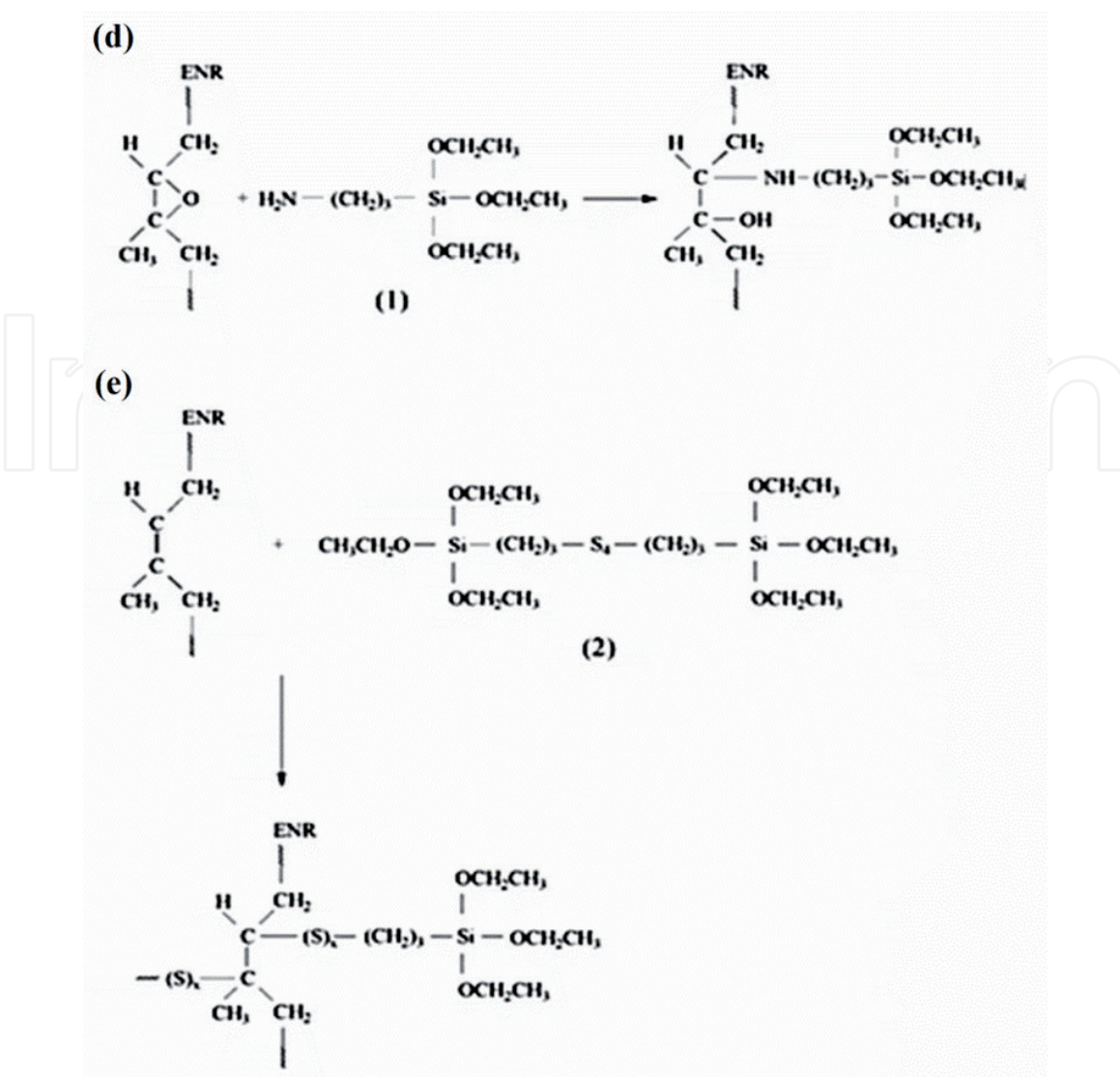
(d)

(e)

Figure 8.
Possible chemical reactions among (d) oxirane ring of ENR and amino group of APTES and (e) double bond of ENR and sulfur of TESPT molecules, where (1) and (2) are the molecular structures of APTES and TESPT [9].

3.4 Hybrid carbon nanotubes filled natural rubber composites

Several attempts have been made to disperse the CNTs in NR matrix by avoiding its re-agglomeration. To overcome this limitation, the addition of secondary fillers was introduced into the composites by generating new conductive hybrid filler pathways [32, 33]. An improved conductivity was achieved by adding carbon black (CB) into the CNT polymer composites [34–37]. Electrical conductivity of the composites was found to be slightly increased with CB concentration when the CNT content lies below its percolation threshold. However, no significant increase in the electrical conductivity occurred above the percolation threshold concentration. This might be due to the agglomeration of CB connected to CNT surfaces, which impedes the conductivity of hybrid ternary composites [35]. Thus, the CB can bridge CNT encapsulates and contribute new electron pathways only with highly homogeneous distribution of both the fillers. In this regard, the extremely high viscosity of NR is essential to enhance the conductivity by enabling good dispersion of fillers during mixing. No prior studies have been reported on the NR vulcanizates to assess the electrical conductivity with the dual fillers CB and CNT. A hybrid epoxy-based nanocomposite was developed by reinforcing CNT and CB. It was found that, the gaps between carbon nanotubes were
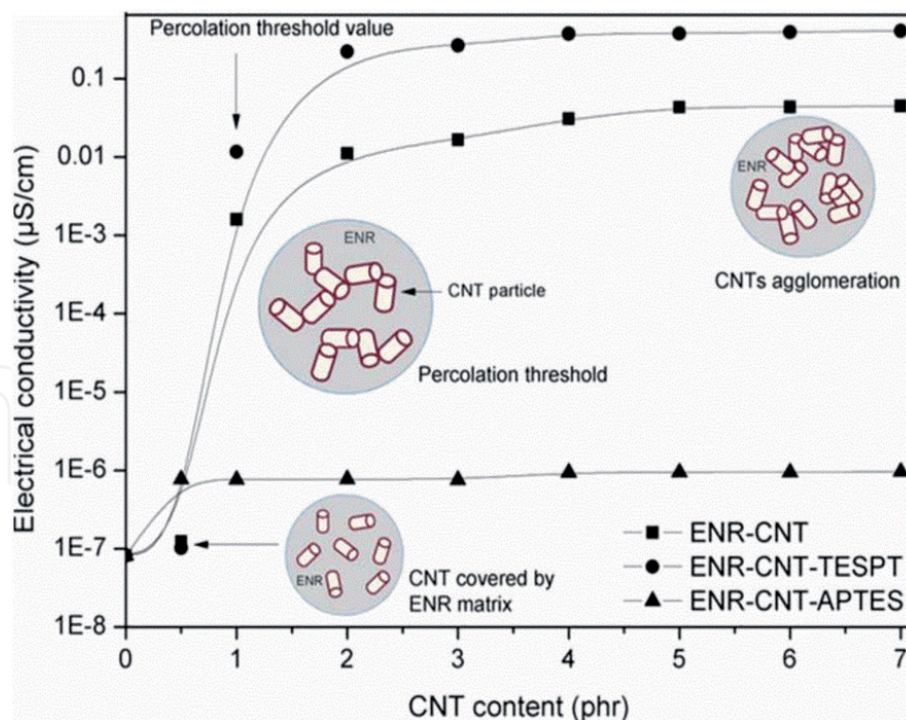
Figure 9.
Electrical conductivity of ENR–CNT, ENR–CNT–TESPT, and ENR–CNT–APTES composites prepared by in-situ functionalization with various CNTs contents of 0–7 phr [31].

connected by the CB nanoparticles, causing the formation of conducting networks [32, 34] as shown in **Figure 10**. The same behavior was observed in the hybrid of expanded graphite (EG)-CNT filled cyanate ester (CE) [38], graphene nanoplatelets (GNPs)-CNT/epoxy composites, titania nanoparticles (TiO$_2$)-CNT/epoxy composites [39] and hybrid of Ag nanoparticles (Ag-NPs)-CNT [40].

3.4.1 Hybrid composites of carbon nanotubes and conductive carbon black reinforced natural rubber

Filled NR vulcanizates were prepared by incorporating carbon-based fillers, namely carbon nanotubes (CNT), conductive carbon black (CCB), and CNT/CCB hybrid filler [41]. Reinforcement of CNT and CCB was carefully done by using a two-roll mill. The main aim was to generate an optimal state of filler dispersion in the NR matrix, in which CCB particles/aggregates bridge the CNT encapsulates. It improved the optimum electrical conductivity of NR composites by enabling electron tunneling and it is appropriate to provide fillers in the NR matrix. It was expected that, the achievable conductivity would synergistically be better than those of rubber composites with solely CNT or CCB. The variation of conductivity (at f = 1 Hz) with the filler volume fraction according to the Voet model is shown in **Figure 11**. It is seen that, the increment in conductivity appears in different steps for the NR vulcanizates filled with CCB (4 steps), CNT (3 steps), and CNT/CCB hybrid filler (2 steps). As already stated, there is no percolation threshold observed in case of CCB filler in NR vulcanizate, even though increasing the CCB loading up to 15 phr. In **Figure 11**, the NR vulcanizate filled with CNT/CCB hybrid filler showed only two step increments in conductivity. It is also clear that the filled NR vulcanizate had linear conductivity in between 1to10 phr of CCB in the CNT/CCB hybrid filler and saturates at 15 phr of CCB owing to the strong agglomeration. This means that

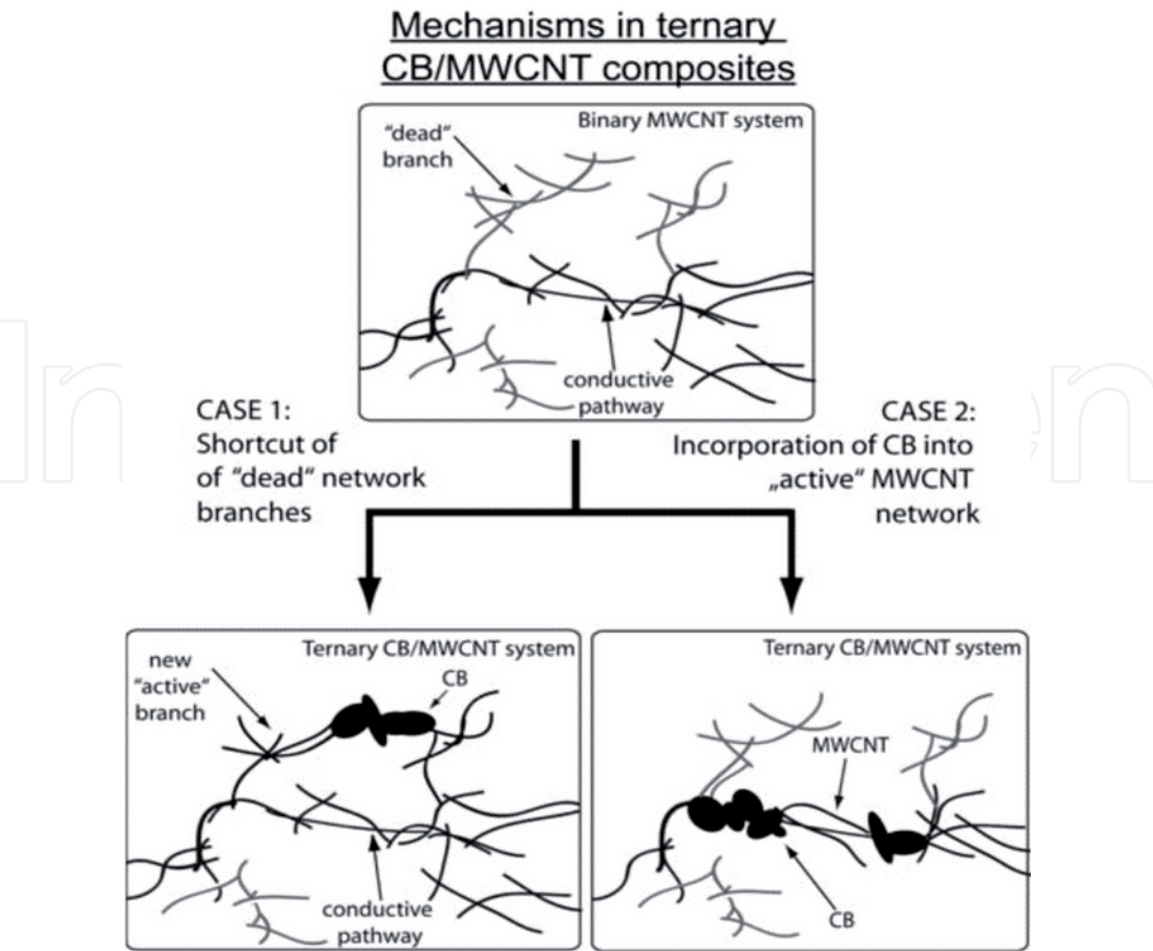**Figure 10.**
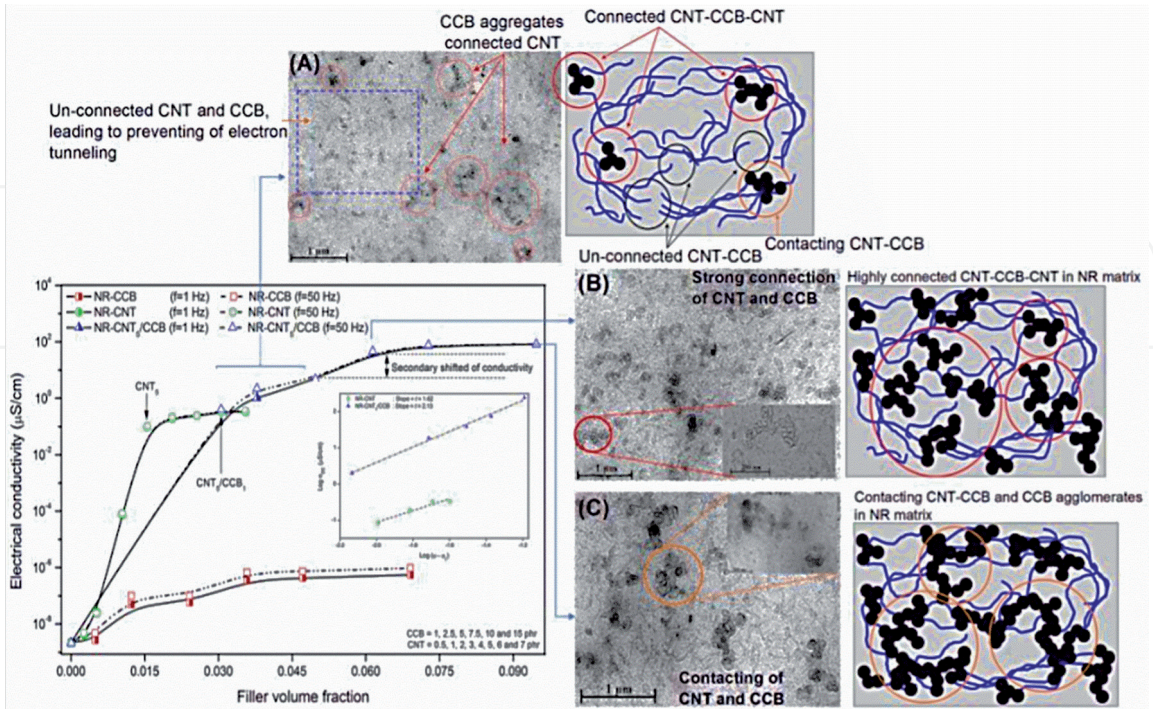*Principles of conductive pathway formation in ternary CB/MWCNT systems [32].*

Figure 11.
Electrical conductivity of the NR vulcanizates filled with CCB, CNT, and CNT/CCB hybrid filler at various filler loadings [41].

NR vulcanizate filled with 5 phr CNT is an Ohmic conductor in between 1to10 phr of added CCB. It confirms the synergistic effect of CNT and CCB fillers in the NR vulcanizates, that improved and extended the conductivity of the NR composites by enhancing the electron tunneling and reducing the gaps between CNT encapsulates.

3.4.2 Hybrid carbon nanotubes and silver nanoparticle in natural rubber composites

The conductive NR composite with CNT-decorated AgNP (**Figure 12**) was prepared via the latex mixing method to get homogenous dispersion of the filler [42]. The decoration of CNT surfaces with AgNP significantly enhanced the electrical conductivity and lowered the percolation threshold concentration of NR composites when compared to the composites with plain CNT filler.

The percolation threshold concentrations of CNT and CNT-AgNP filled NR composites (**Figure 13**) are found to be 3.64 and 2.92 phr respectively. The combination of AgNP with CNT hybrid filler caused decreasing the percolation concentration and significantly increasing the optimal conductivity of the NR composites. This is due to the network formation of CNT-AgNP in the NR matrix favors the flow of electrons as compared to the NR filled with solely CNT. Therefore, better movement of the electrons by tunneling throughout the NR matrix was encountered. The degree of network formation of fillers in rubber matrix can be estimated by the t values. In **Figure 13(b)** and (**c**), the t values of CNT and CNT-AgNP filled NR vulcanizates are noticed as 2.34 and 1.86, respectively. This clarifies that the CNT-AgNP filled NR vulcanizates are fully three-dimensional networks of fillers in the NR matrix, whereas the CNT filled NR vulcanizates showed stronger CNT agglomeration as indicated by higher t value. It also confirms the bridging of AgNP with end-to-end of CNT in the NR matrix which usually improves significantly the electrical conductivity and the percolation threshold of the composite.

3.4.3 Hybrid carbon nanotubes and ionic liquid in natural rubber composites

To enhance the electrical conductivity of the rubber composites, several methodologies have been exploited by improving the CNT dispersion in rubber
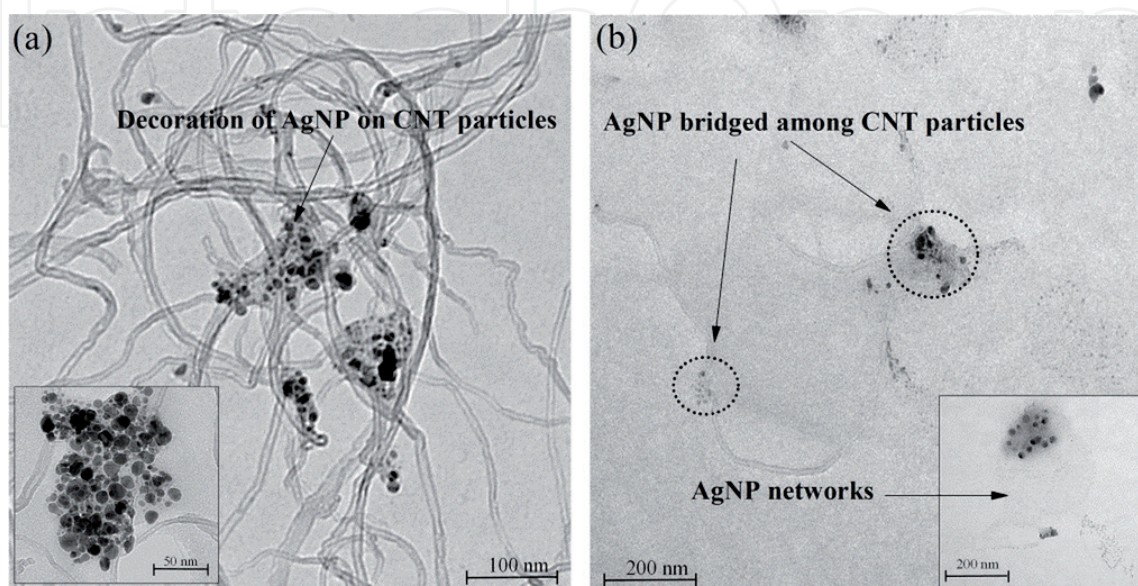

Figure 12.
Transmission electron microscopy (TEM) images of CNT decorated with silver nanoparticle (CNT-AgNP) [42].
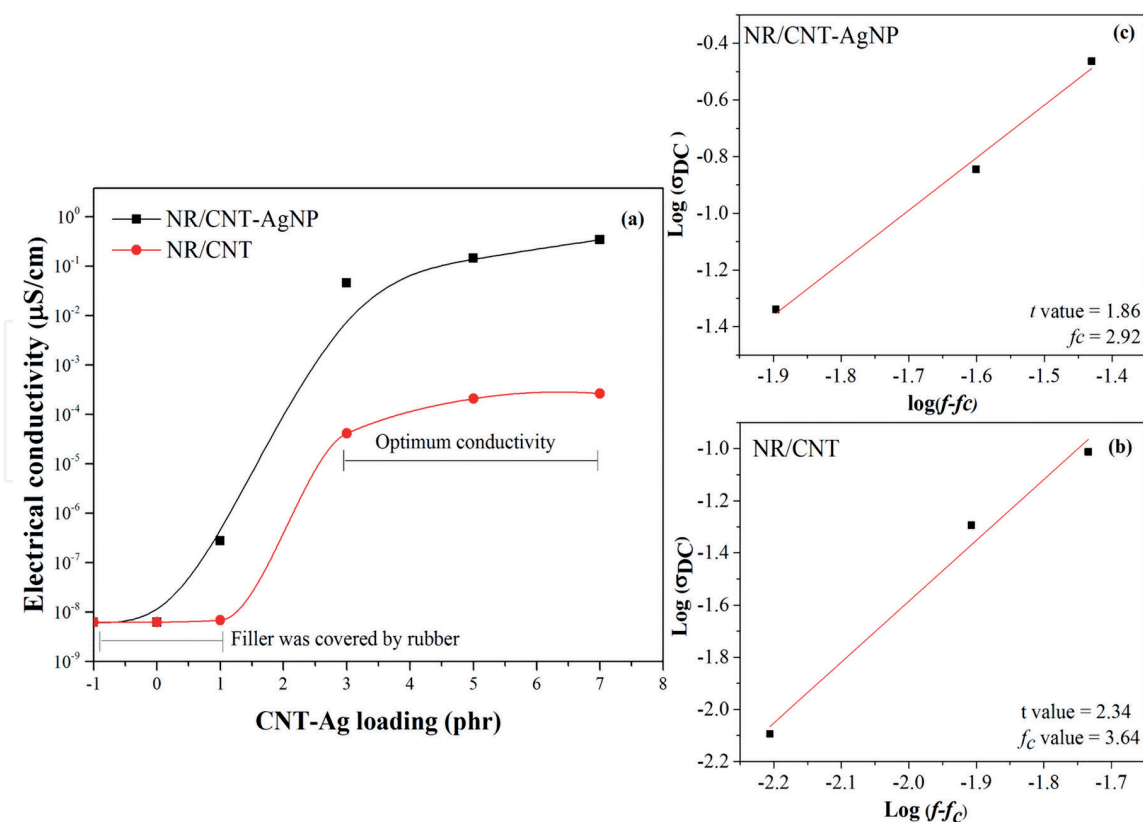
Figure 13.
Electrical conductivity of CNT and CNT-AgNP filled NR vulcanizates with various CNT and CNT-AgNP loadings (a), Plots of log σ_{dc} and log (f-f_c) of CNT filled NR vulcanizates (b) and CNT-Ag filled NR vulcanizates (c) [42].

matrix. One prominent approach is the use of CNT mixed with an ionic liquid (IL) [43]. Typically, the IL molecules have hydrophilic and hydrophobic parts of the inorganic and organic salts in their molecules. It is noted that the hydrophobic part has the ability of interacting with CNT surfaces through cation- ð interaction [44]. Also, some ionic liquids contain -C=C- in the alkyl chain, and this could interact with diene rubbers *via* sulfur bridges in case of sulfur vulcanization system [45]. Therefore, IL forms bridge CNT surfaces with the rubber matrix [45]. The imidazolium ionic liquid has been widely used in various types of polymer matrix [46–49]. It was found that the imidazolium groups play an important role in improving the ionic conductivity of acrylonitrile butadiene rubber (NBR) [48]. Furthermore, NBR/SiO$_2$ in combination with imidazolium ionic liquid exhibited good elastomeric properties, high tensile strength, and high electrical conductivity [49]. In addition, CNT filled NR composites improved the conductivity by the addition of an ionic liquid (IL) 1-butyl-3-methyl imidazolium bis (trifluoromethylsulphonyl)mide (BMI) [50]. **Figure 14** clearly shows the addition of IL in to NR slightly increased the electrical conductivity, but the loading level of IL (BMI) does not significantly affect the conductivity of NR vulcanize. This might be attributed to the encapsulated IL (BMI) by the insulating NR as the imidazolium IL could be more compatible with the hydrophobic rubber matrix [46]. This leads to reduce the electrical conductivity of the NR/IL vulcanizate with no noticeable percolation threshold. On the other hand, the composites of NR/CNT and NR/CNT-IL showed percolation threshold concentrations at 3.64 and 2.92 phr, respectively. Therefore, the NR/CNT-IL composite exhibited comparatively higher electrical conductivity with lower percolation threshold than the composite of NR/CNT. This might be due to the synergy of plasticizing by IL (BMI), contributed to good dispersion of CNT. It forms three-dimensional networks in the NR matrix
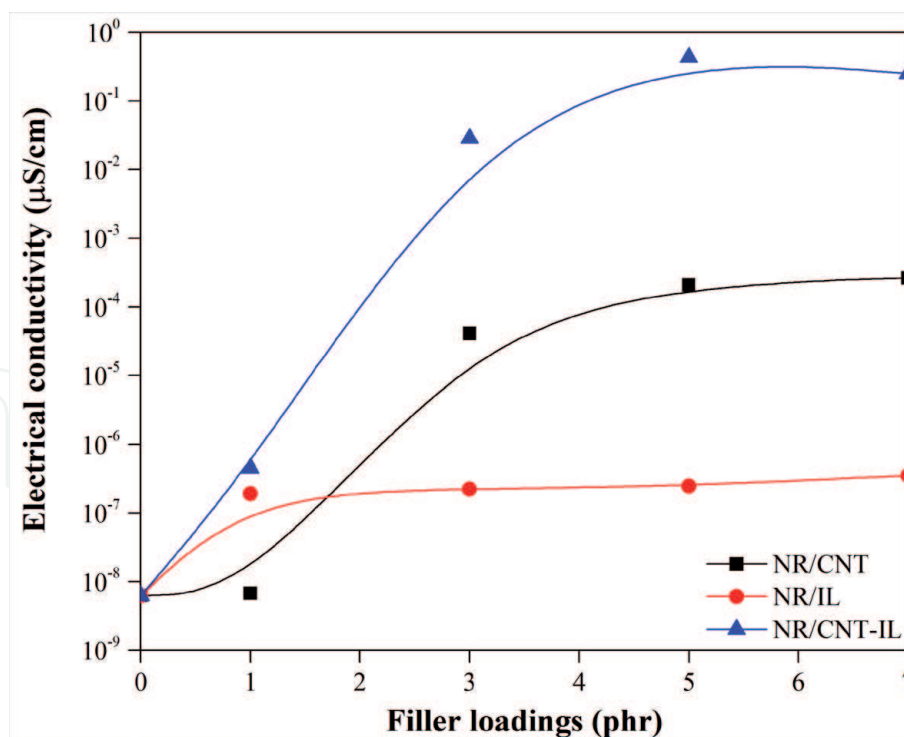
Figure 14.
Electrical conductivity of NR/CNT, NR/IL and NR/CNT-IL vulcanizates with various filler loadings [50].

assisted by the physical interactions of CNT particles. Therefore, the plasticizing effect and physical interactions facilitated CNT network formation and reduced the agglomeration of CNT.

4. Piezoresistive carbon-based composites for sensor applications

Conductive composites based on electrically insulating rubber matrix have attracted both scientific research and industrial interest for several years [11]. The two main parts in such composites are (i) the insulating rubber matrix and (ii) the conducting filler. The filler needs to form conductive pathways in the matrix for carrying electrons, thereby making the composite a semiconductor or a conductor [19]. Such filler pathways are perturbed by breakage and re-arrangement inside the matrix during deformation [33]. This change in resistivity during elongation is known as piezoresistivity and it can be used in motion detector applications [51]. Hence, the sensitivity of a composite sensor is affected by the type of rubber matrix and the type of fillers such as carbon black (CB), carbon fibre, graphene, graphite, and carbon nanotubes (CNT) [34, 35, 52, 53]. The CNT filled composites can serve in sensor applications due to its excellent electrical conductivity, which responds to various external stimuli such as temperature, organic solvents, vapour, strain, and damage [6]. Incorporation of CNT and CB hybrid filler in NR exhibits a very stable sensor performance along with good mechanical properties when the composites are dynamically elongated several times [6, 8]. Therefore, three alternative rubber matrices such as NR, epoxidized-NR (ENR) and isoprene rubber (IR) have been tested to clarify the effectiveness of the rubber matrix in a strain sensor containing CNT and CB as a hybrid filler. An appropriate ratio of CNT:CB was fixed at 1:1.5to form the filler networks throughout the matrix. Melt blending was selected as the mixing method to prepare the composites with the help of an internal mixer and a two-roll mill by optimizing the state of dispersion of fillers in the rubber matrix. Furthermore, the piezoresistivity (strain sensitivity

of electrical resistance) was investigated in terms of the relative change in resistance, $\Delta R/R_0$ (ΔR is the change in resistance with strain, and R_0 is the initial resistance of the composite) [6, 54]. The measurement was performed with the help of an instrumental setup as showed in **Figure 15**.

To assess the effects of long term deformations on the composites, dynamic cyclic tensile testing at 50% strain for 50, 100, 500, 1000, 3000, 5000 and 10000 cycles was performed with an extension speed of 200 mm/min. Here, the resistance of the composites after each run was noticed. **Figure 16** shows the electrical conductivity as a function of cycle count for NR, ENR and IR composites with CNT/CB hybrid filler. The conductivity of these composites was found to be decreased with cycle count. The linkages in ENR composites exhibited the least loss of conductivity. It was found that the conductivity becomes stable after 3000 cycles (from 15.4 µS/cm to 0.044 µS/cm at 3,000 rounds). This is similar to the composites of NR-CNT/CB, while a few cycles were needed for IR-CNT/CB owing to the higher filler agglomeration and poor filler-rubber interactions. This is attributed to the polar chemical interactions between ENR and the functional groups on the surfaces of CNT/CB. Furthermore, the non-rubber components in NR and ENR matrices improved the filler dispersion as seen in the TEM images of **Figure 16**. It can be seen that, the dispersion of CNT/CB particles/clusters was homogeneous in the ENR matrix, whereas poor CNT/CB dispersion with strong filler-filler agglomeration was exhibited in the IR matrix as expected.

Moreover, NR-CNT/CB composite (CNT/CB 0.5/9 phr) was developed for sensor [6], it was embedded in gloves to understand its efficiency and to get a visual idea about the function of the sensors as shown in **Figure 17**.
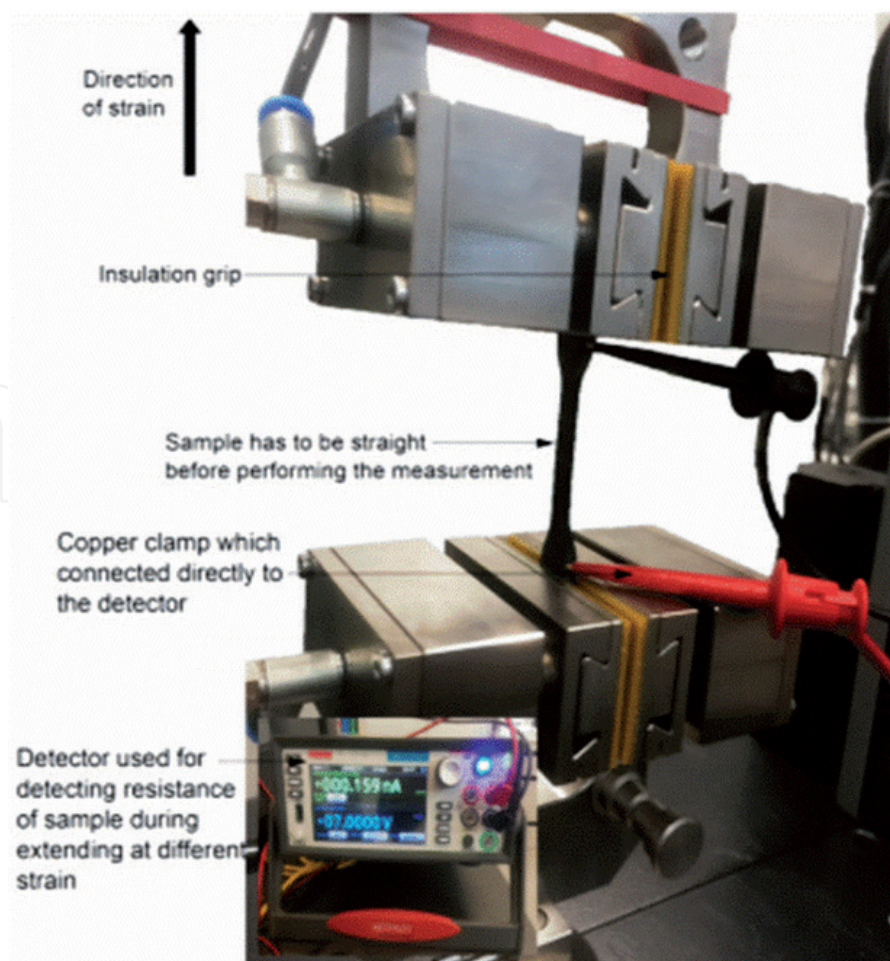

Figure 15.
Instrumental setup for measuring electrical conductivity and resistivity during mechanical tensile strain [6].
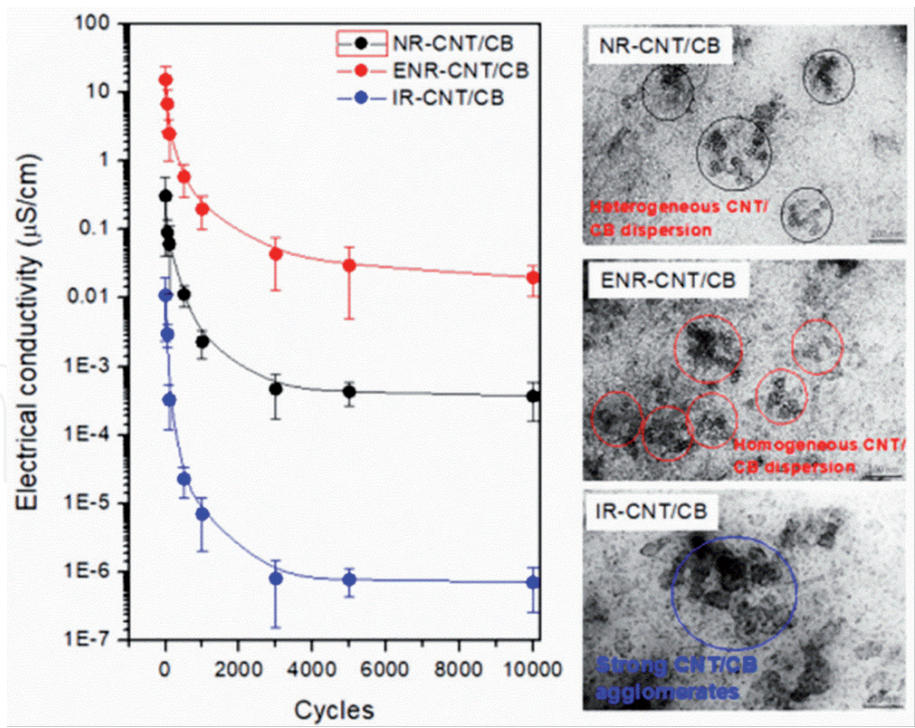
Figure 16.
Electrical conductivity of NR, ENR and IR composites with 5 phr of CNT/CB hybrid filler compared after 0, 50, 100, 300, 500, 1000, 3000, 5000 and 10000 cycles of extensional strain, together with TEM images at the same magnification of 50 kx [6].
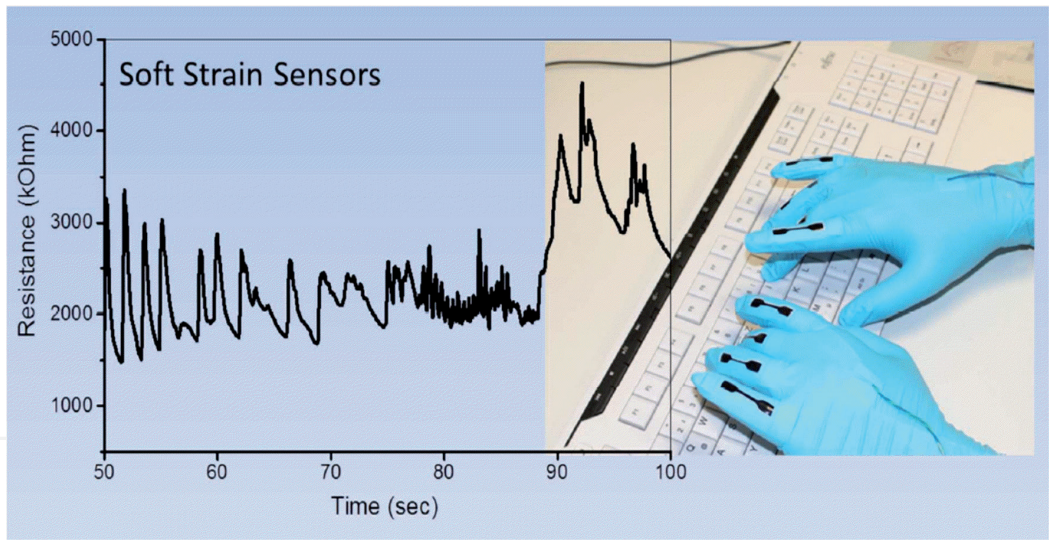

Figure 17.
Detection of finger motion and type of the motion by embodiment of conducting elastomer composite (CNT/CB 0.5/9 phr) on latex gloves. Typing the complex stretching and bending motion of sample is directly reflected in the resistance plot [6].

5. Conclusion

Carbon nanotubes (CNT) have been widely used as the reinforcing and conductive filler in NR. However, the dispersion of CNT in NR matrix is limited and always an important factor to enhance the property of NR composites. In order to obtain a conductive NR material with high quality by the formation of strong CNT networks in an insulating NR matrix is needed. The CNT networks act as electrically conducting pathways to provide electrical conductivity, but the CNT typically has a high aspect ratio and strong Van-der Waals forces that give rise to a strong agglomeration

tendency. It is very difficult to form the conductive paths with in the insulating rubber matrix and this path formation between the conducting particles is a challenge to achieve proper electron tunneling.

This chapter reports several advanced methods to disperse CNTs in the NR matrix. Various aspects highlighted in this chapter include the mixing processes such as melt mixing and latex mixing methods. In addition, formations of functional groups on the surfaces of CNT using silane coupling agents (i.e., ex-situ and in-situ functionalization) as well as using a hybrid CNT are beneficial to achieve better electrical conductivity. These efforts are aimed to reduce the percolation threshold concentration in the NR composites. As mentioned in this review, latex mixing technique exhibits the formation of segregated nanotube network, which enhances the electrical conductivity of the composites. In addition, the improved interaction between CNT and NR matrix by using silane coupling agent enhances the uniformity of dispersion of CNT. It leads to reduce the percolation threshold concentration compared to the composites of NR/CNT without silane coupling agent. Moreover, the addition of secondary fillers into the composites generates new conductive hybrid filler pathways. Comparatively better conductivity is achieved by the addition of CB or AgNP or IL into the CNT polymer composites.

However, conducting composites based on electrically insulating rubber matrix have been developed for sensor applications. Change in resistivity during elongation termed as piezoresistivity can be used in sensor applications. The most commonly used rubber matrices such as NR, ENR and IR are mixed with a combination of CNT and CB fillers as a hybrid filler. The presence of linkages in the ENR composites results in the least loss of conductivity during external strain. It is found that the conductivity becomes stable after 3000 cycles. This is found to be similar to the NR-CNT/CB composite, while a few cycles are needed for IR-CNT/CB owing to the higher filler agglomeration and poor filler-rubber interactions. This is attributed to the polar chemical interactions between ENR and the functional groups on the surfaces of CNT/CB. Furthermore, the non-rubber components in NR and ENR matrices improved the filler dispersion. Finally, it can be concluded that the composite of ENR and CNT/CB are beneficial in sensor applications particularly in case of health monitoring, motion detectors, and other related products because of its cost-effectiveness and ease of processing.

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References

[1] Le H, Abhijeet S, Ilisch S, Klehm J, Henning S, Beiner M, et al. The role of linked phospholipids in the rubber-filler interaction in carbon nanotube (CNT) filled natural rubber (NR) composites. Polymer. 2014;55(18):4738-4747.

[2] Krainoi A, Kummerlöwe C, Nakaramontri Y, Vennemann N, Pichaiyut S, Wisunthorn S, et al. Influence of critical carbon nanotube loading on mechanical and electrical properties of epoxidized natural rubber nanocomposites. Polymer Testing. 2018;66:122-136.

[3] Yamada T, Hayamizu Y, Yamamoto Y, Yomogida Y, Izadi-Najafabadi A, Futaba DN, et al. A stretchable carbon nanotube strain sensor for human-motion detection. Nature nanotechnology. 2011;6(5):296.

[4] Wang Y, Wang L, Yang T, Li X, Zang X, Zhu M, et al. Wearable and highly sensitive graphene strain sensors for human motion monitoring. Advanced Functional Materials. 2014;24(29):4666-4670.

[5] Chen J, Li H, Yu Q, Hu Y, Cui X, Zhu Y, et al. Strain sensing behaviors of stretchable conductive polymer composites loaded with different dimensional conductive fillers. Composites Science and Technology. 2018;168:388-396.

[6] Natarajan TS, Eshwaran SB, Stöckelhuber KW, Wießner S, Pötschke P, Heinrich G, et al. Strong strain sensing performance of natural rubber nanocomposites. ACS applied materials & interfaces. 2017;9(5):4860-4872.

[7] Zhang XW, Pan Y, Zheng Q, Yi XS. Piezoresistance of conductor filled insulator composites. Polymer international. 2001;50(2):229-236.

[8] Zhao J, Dai K, Liu C, Zheng G, Wang B, Liu C, et al. A comparison between strain sensing behaviors of carbon black/polypropylene and carbon nanotubes/polypropylene electrically conductive composites. Composites Part A: Applied Science and Manufacturing. 2013;48:129-136.

[9] Nakaramontri Y, Nakason C, Kummerloewe C, Vennemann N. Effects of in-situ functionalization of carbon nanotubes with bis (triethoxysilylpropyl) tetrasulfide (TESPT) and 3-amino-propyltriethoxysilane (APTES) on properties of epoxidized natural rubber–carbon nanotube composites. Polymer Engineering & Science. 2015;55(11):2500-2510.

[10] George N, Chandra J, Mathiazhagan A, Joseph R. High performance natural rubber composites with conductive segregated network of multiwalled carbon nanotubes. Composites Science and Technology. 2015;116:33-40.

[11] Ma P-C, Siddiqui NA, Marom G, Kim J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. Composites Part A: Applied Science and Manufacturing. 2010;41(10):1345-1367.

[12] Sun X, Sun H, Li H, Peng H. Developing polymer composite materials: carbon nanotubes or graphene? Advanced Materials. 2013;25(37):5153-5176.

[13] 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. 2015;88(2):199-218.

[14] Earp B, Simpson J, Phillips J, Grbovic D, Vidmar S, McCarthy J, et al. Electrically Conductive CNT Composites at Loadings below Theoretical Percolation Values. Nanomaterials. 2019;9(4):491.

[15] Sui G, Zhong W, Yang X, Zhao S. Processing and material characteristics of a carbon-nanotube-reinforced natural rubber. Macromolecular Materials and Engineering. 2007;292(9):1020-1026.

[16] Nah C, Lim JY, Cho BH, Hong CK, Gent AN. Reinforcing rubber with carbon nanotubes. Journal of applied polymer science. 2010;118(3):1574-1581.

[17] Atieh MA, Girun N, Ahmadun FlR, Guan C, Mahdi E, Baik D. Multi-wall carbon nanotubes/natural rubber nanocomposite. AzoNano–Online Journal of Nanotechnology. 2005;1:1-11.

[18] Bokobza L, Belin C. Effect of strain on the properties of a styrene–butadiene rubber filled with multiwall carbon nanotubes. Journal of applied polymer science. 2007;105(4):2054-2061.

[19] Bokobza L. Multiwall carbon nanotube elastomeric composites: A review. Polymer. 2007;48(17):4907-4920.

[20] Peng Z, Feng C, Luo Y, Li Y, Kong L. Self-assembled natural rubber/multi-walled carbon nanotube composites using latex compounding techniques. Carbon. 2010;48(15):4497-4503.

[21] Subramaniam K, Das A, Stöckelhuber KW, Heinrich G. Elastomer composites based on carbon nanotubes and ionic liquid. Rubber Chemistry and Technology. 2013;86(3):367-400.

[22] 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. 2015;36(11):2113-2122.

[23] George N, Varghese GA, Joseph R. Improved mechanical and barrier properties of Natural rubber-Multiwalled carbon nanotube composites with segregated network structure. Materials Today: Proceedings. 2019;9:13-20.

[24] Krainoi A, Kummerlöwe C, Nakaramontri Y, Wisunthorn S, Vennemann N, Pichaiyut S, et al. Novel natural rubber composites based on silver nanoparticles and carbon nanotubes hybrid filler. Polymer Composites. 2020;41(2):443-458.

[25] Kaewsakul W, Sahakaro K, Dierkes WK, Noordermeer JW. Optimization of mixing conditions for silica-reinforced natural rubber tire tread compounds. Rubber chemistry and technology. 2012;85(2):277-294.

[26] Sengloyluan K, Sahakaro K, Dierkes WK, Noordermeer JW. Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber. European polymer journal. 2014;51:69-79.

[27] Bhattacharyya S, Sinturel C, Bahloul O, Saboungi M-L, Thomas S, Salvetat J-P. Improving reinforcement of natural rubber by networking of activated carbon nanotubes. Carbon. 2008;46(7):1037-1045.

[28] Moniruzzaman M, Winey KI. Polymer nanocomposites containing carbon nanotubes. Macromolecules. 2006;39(16):5194-5205.

[29] Nakaramontri Y, Kummerlöwe C, Vennemann N, Wisunthorn S, Pichaiyut S, Nakason C. Effect of bis (triethoxysilylpropyl) tetrasulfide (TESPT) on properties of carbon nanotubes and conductive carbon black hybrid filler filled natural rubber nanocomposites. Express Polymer Letters. 2018;12(10):867-884.

[30] Nakaramontri Y, Nakason C, Kummerlöwe C, Vennemann N. Enhancement of electrical conductivity and filler dispersion of carbon nanotube filled natural rubber composites by latex mixing and in situ silanization.

Rubber Chemistry and Technology. 2016;89(2):272-291.

[31] Nakaramontri Y, Nakason C, Kummerlöwe C, Vennemann N. Enhancement of electrical conductivity and other related properties of epoxidized natural rubber/carbon nanotube composites by optimizing concentration of 3-aminopropyltriethoxy silane. Polymer Engineering & Science. 2017;57(4):381-391.

[32] Sumfleth J, Adroher XC, Schulte K. Synergistic effects in network formation and electrical properties of hybrid epoxy nanocomposites containing multi-wall carbon nanotubes and carbon black. Journal of materials science. 2009;44(12):3241-3247.

[33] Li C, Thostenson ET, Chou T-W. Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube–based composites. Applied Physics Letters. 2007;91(22):223114.

[34] Ma P-C, Liu M-Y, Zhang H, Wang S-Q, Wang R, Wang K, et al. Enhanced electrical conductivity of nanocomposites containing hybrid fillers of carbon nanotubes and carbon black. ACS applied materials & interfaces. 2009;1(5):1090-1096.

[35] Zhang S, Lin L, Deng H, Gao X, Bilotti E, Peijs T, et al. Synergistic effect in conductive networks constructed with carbon nanofillers in different dimensions. Express Polym Lett. 2012;6(2):159-168.

[36] Lee J-H, Kim SK, Kim NH. Effects of the addition of multi-walled carbon nanotubes on the positive temperature coefficient characteristics of carbon-black-filled high-density polyethylene nanocomposites. Scripta Materialia. 2006;55(12):1119-1122.

[37] Dang Z-M, Shehzad K, Zha J-W, Mujahid A, Hussain T, Nie J, et al. Complementary percolation characteristics of carbon fillers based electrically percolative thermoplastic elastomer composites. Composites science and technology. 2011;72(1):28-35.

[38] Zhang X, Liang G, Chang J, Gu A, Yuan L, Zhang W. The origin of the electric and dielectric behavior of expanded graphite–carbon nanotube/cyanate ester composites with very high dielectric constant and low dielectric loss. Carbon. 2012;50(14):4995-5007.

[39] Sumfleth J, de Almeida Prado LA, Sriyai M, Schulte K. Titania-doped multi-walled carbon nanotubes epoxy composites: Enhanced dispersion and synergistic effects in multiphase nanocomposites. Polymer. 2008;49(23):5105-5112.

[40] Ma PC, Tang BZ, Kim J-K. Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites. Carbon. 2008;46(11):1497-1505.

[41] 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. 2017;90:467-484.

[42] Krainoi A, Kummerlöwe C, Vennemann N, Nakaramontri Y, Pichaiyut S, Nakason C. Effect of carbon nanotubes decorated with silver nanoparticles as hybrid filler on properties of natural rubber nanocomposites. Journal of Applied Polymer Science. 2019;136(13):47281.

[43] Deng F, Ito M, Noguchi T, Wang L, Ueki H, Niihara K-i, et al. Elucidation of the reinforcing mechanism in carbon nanotube/rubber nanocomposites. ACS nano. 2011;5(5):3858-3866.

[44] Fukushima T, Kosaka A, Yamamoto Y, Aimiya T, Notazawa S,

Takigawa T, et al. Dramatic effect of dispersed carbon nanotubes on the mechanical and electroconductive properties of polymers derived from ionic liquids. Small. 2006;2(4):554-560.

[45] Das A, Stöckelhuber KW, Jurk R, Fritzsche J, Klüppel M, Heinrich G. Coupling activity of ionic liquids between diene elastomers and multi-walled carbon nanotubes. Carbon. 2009;47(14):3313-3321.

[46] Subramaniam K, Das A, Simon F, Heinrich G. Networking of ionic liquid modified CNTs in SSBR. European Polymer Journal. 2013;49(2):345-352.

[47] Subramaniam K, Das A, Steinhauser D, Klüppel M, Heinrich G. Effect of ionic liquid on dielectric, mechanical and dynamic mechanical properties of multi-walled carbon nanotubes/polychloroprene rubber composites. European polymer journal. 2011;47(12):2234-2243.

[48] Marwanta E, Mizumo T, Nakamura N, Ohno H. Improved ionic conductivity of nitrile rubber/ionic liquid composites. Polymer. 2005;46(11):3795-3800.

[49] Marzec A, Laskowska A, Boiteux G, Zaborski M, Gain O, Serghei A. The impact of imidazolium ionic liquids on the properties of nitrile rubber composites. European Polymer Journal. 2014;53:139-146.

[50] Krainoi A, Nakaramontri Y, Wisunthorn S, Pichaiyut S, Nakason C, Kummerlöwe C, et al. Influence of carbon nanotube and ionic liquid on properties of natural rubber nanocomposites. Express Polymer Letters. 2019;13(4).

[51] Shui X, Chung D. A piezoresistive carbon filament polymer-matrix composite strain sensor. Smart materials and structures. 1996;5(2):243.

[52] Kim K-S, Rhee K-Y, Lee K-H, Byun J-H, Park S-J. Rheological behaviors and mechanical properties of graphite nanoplate/carbon nanotube-filled epoxy nanocomposites. Journal of industrial and engineering chemistry. 2010;16(4):572-576.

[53] Wang J, Zhang K, Cheng Z, Lavorgna M, Xia H. Graphene/carbon black/natural rubber composites prepared by a wet compounding and latex mixing process. Plastics, Rubber and Composites. 2018;47(9):398-412.

[54] Melnykowycz M, Koll B, Scharf D, Clemens F. Comparison of piezoresistive monofilament polymer sensors. Sensors. 2014;14(1):1278-1294.