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A Review of Natural Rubber Nanocomposites Based on Carbon Nanotubes

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The original form of Natural Rubber (NR) has limited usage despite its excellent elasticity and reversible deformability. Further improvement of its undesired properties, i.e. *low hardness, durability and tear resistance will allow for application of NR on a broader scale. Traditional reinforcing materials such as carbon black have indicated improvement in NR-based composites. However, the increasing range of newly emerging applications comprising polymeric composites motivates researchers to focus on developing NR-based composites with better physical properties. Many nanoscale fillers have been widely researched to attain extraordinary properties in NR based products. Among the different nanostructures, carbon nanotubes (CNTs) have been widely examined for NR modification.Addition of a tiny amount of well-dispersed CNTs to NR allows for significant improvements in physical properties of NR. Preparing nanocomposites comprising CNTs and other types of fillers also demonstrates enhancement of NR properties. Besides improvements in mechanical properties, the presence of CNTs considerably improves other properties of NR, such as thermal stability as well as electrical and thermal conductivity. However, owing to interactions between individual CNTs as well as CNTs and other components (NR or other fillers), property improvement varies depending on the type of fillers and their ratio in NR. This review summarises the reported processing conditions and property improvements in NR reinforced with CNTs as a solefiller or with other additive fillers. This paper will help to better understand the status of research on developing an NR/CNT nanocomposite and discover challenges and obstacles that need to be resolved.*

Keywords: Natural rubber; carbon nanotubes; composite; polymer; filler

Rubber is broadly used in different fields for industrial and societal applications due to its excellent elasticity and reversible deformability as well as water and heat resistance properties. Two types of rubber in common use are that of natural and synthetic rubbers. Natural rubber (NR) is a polymer of isoprene obtained from latex which is extracted from special tropical trees, while synthetic rubber (SR) originates from petrochemical feedstocks resulting from polymerisation of several monomers such as isoprene, chloroprene, isobutylene and 1,3-butadiene. Natural rubber has limited applications and SR serves as a substitute for NR when improved mechanical properties are in demand. However, SR consumption of is presently being reduced in view of environmental concerns and the increasing price of energy. However, NR in its original or unmodified form has limited potential for some applications because of its relatively poor properties such as low modulus, hardness, durability and tear resistance. If NR is proposed to fulfil market expectations, its undesired physical properties need to be improved. In this respect, NR is cured using chemical additives. Of late, nanofillers including carbon nanotubes (CNTs) have evoked much interest for improving NR-

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based products. This manuscript, after a brief description on NR and its characteristics, will present detailed information on preparing CNT-based nanocomposites and will specifically focus on the achievements and challenges regarding fabrication of NR/CNT nanocomposites.

Natural Rubber

Commercial NR, derived from *Hevea brasiliensis*, consists of a combination of poly(*cis*-1,4-isoprene) [poly(2-methyl-1,3-butadiene)] and a small percentage (up to 5% of dry mass) of biological elements, such as proteins, fatty acids and resins, and also inorganic materials (*Figure 1*). The natural rubber originating from gutta-percha is composed of *trans*-1,4-polyisoprene. These two types of NR have similar, but not identical, properties[1].

Natural rubber, like other elastomers, is elastic, flexible and waterproof. It exhibits higher tack and tensile strength compared to SR. Natural rubber also has some other excellent properties including strain induced crystallisation, antivirus permeation and biodegradability. However, raw NR cannot meet the requirements of many applications because of its undesirable properties including low durability, tensile strength, tear resistance, initial modulus and heat build-up. Apart from these weaknesses, NR may be soft or brittle depending on the weather or temperature conditions. Accordingly, raw NR is generally cured to make it suitable for practical applications. In rubber technology, vulcanisation is applied where the long chains of rubber molecules are crosslinked using an additive known as a vulcanisation or crosslinking agent[2]. Vulcanisation of rubber shortens each free section of its chain that causes the chains to tighten rapidly for a given length of strain. Consequently, its elastic force constant increases and makes the rubber harder and less extensible. The properties of vulcanised NR, such as quantity and the type of crosslinks formed during vulcanisation are governed by the nature of the crosslinked network and the process conditions utilised[3]. Vulcanised rubbers possesses low hysteresis, excellent dynamic properties and fatigue resistance as well as high resistance to heat, light and the ageing process[4]. Although vulcanised NR has brought about significant improvements in NR-based products, its application is still limited to tyres, some sport products, sealing materials and dairy rubber items[1,5]. Therefore, further improvement in mechanical properties of NR has been an important task for many industries. Reinforcing elements like carbon black[6,7], calcium carbonate[8,9,10], modified montmorillonite[11], silica[12,13] and starch[14] have been examined for NR reinforcement. However, high amounts of these fillers are required to strengthen the rubber and the reinforcement is less effective. If such conventional fillers are replaced by nanoscale ones, the physical properties of NR can be effectively improved with addition of lesser amounts of fillers[15-19]. Nanofillers, due to their extraordinary properties endow the

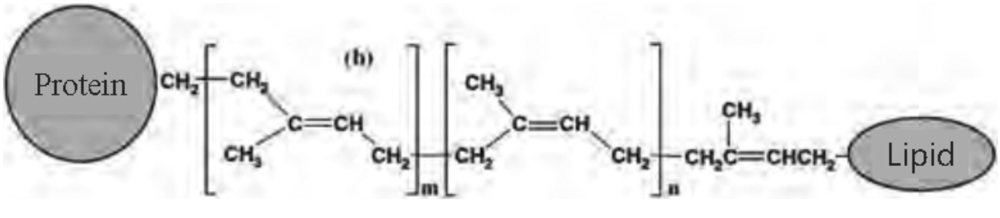

*Figure 1. Microstructure of NR ,poly(*cis-*1,4-isoprene), derived from* Hevea brasiliensis*[1].*

nanocomposites unique properties. Among different types of nanofillers, Carbon Nanotubes (CNTs) have attracted a great attention in composite technology including NR. In the following discussion, the focus will be on CNTs characteristics, CNT-based nanocomposites preparation prior to recent advances and state of the art for NR/CNT representation.

CNTs Characteristics

CNT consists of a rolled graphene, a hexagonal sp^2 carbon layer, which forms cylinders with diameters of nanometre sizes and lengths of up to several millimetres (*Figure 2*). The combination of its dimension, structure and topology translates into a range of extraordinary properties (like high conductivity, excellent strength and stiffness, chemical specificity) attributing to the uniqueness of CNT [20, 21]. The elastic modulus and Young's modulus of CNTs were predicted to be at least one TPa (1000 GPa)[21] and 270 – 950 GPa[22], respectively. Tensile strength of individual CNTs could come close to a few 100 GPa[23], while its break strength was reported to be as high as 200 GPa[24]. Interestingly, although CNTs have high stiffness, they are very flexible and can sustain large strains under compression. Unlike carbon fibres, which fracture easily while under compression, the kink-like ridges in CNTs allow the structure to relax elastically[25]. Carbon nanotubes, like other nanoparticles, possess a large surface area, which is an attractive characteristic for mechanical and chemical applications.

It is worth mentioning here that CNTs are nowadays produced with significantly different morphologies and impurity levels. These two parameters are likely to affect the effective properties of the nanocomposite. Further, CNTs morphology, in particular their aspect ratio, is one of the most influential parameters on the mechanical properties of the nanocomposite.

NR/CNT Nanocomposites

Natural rubber, like other elastomers, exhibits low Young's modulus, weak electrical and thermal conductivity. Incorporation of CNTs into NR not only improves its mechanical strength but also its electrical and thermal properties[3, 15, 26-29, 30-31, 35-57]. Early examples of the use of CNTs for the reinforcement of NR were reported by Fakhru'l-Razi *et al.*[37]. Preparation of the nanocomposites was carried out using a solvent casting method in which toluene was

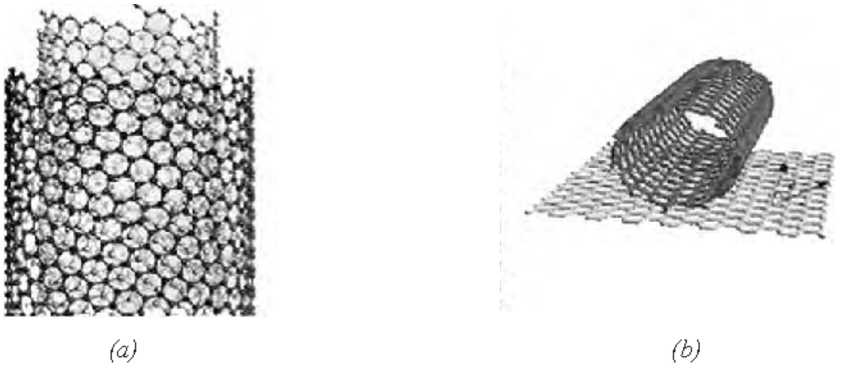

Figure 2. (a) Synthesis of SWCNTs from a graphitic sheet; (b) Computer generated image of multiwalled carbon nanotubes[20].

used as a solvent. They studied the effects of different percentage of CNT loadings on the nanocomposites behaviour and indicated that by increasing the amount of CNTs, the rubber the material becomes stronger and tougher but at the same time more brittle[37]. In their study, the highest strain value obtained for the nanocomposite was at 1 wt% of the CNTs. The composite at this percentage was more ductile and more elastic compared to other percentages of CNTs. In accordance with their results, other researchers presented significant improvement in the mechanical properties (strength, elasticity, toughness, and durability) of NR[3,15, 27-29, 31, 33, 38, 43-,45-47, 50-51].

The drop in loss tangent of the nanocomposites also proved the effect of CNTs on the thermal stability of a nanocomposite and its ability to disperse the heat[28]. In other words, the loss angle of NR is bigger than that of the NR/CNT nanocomposites, meaning that NR is able to absorb more energy than NR/CNT nanocomposites under an acute strain environment. The increase in absorbed energy increases possibility of thermal degradation and thus weakening of mechanical properties of a substance[28]. Better heat dispersion and thus better thermal stability of NR/CNT nanocomposites suggest that this nanocomposite can be used in distortional and rolling conditions.

CNTs, which are conductive fillers, make the nanocomposite electrically conductive and therefore develop its area of applications. Conductive rubber nanocomposites have different applications in developing flexible electronic devices, nanoelectronic devices, electrical protection of buildings, substations and power systems. For instance, NR/CNT nanocomposites with improved thermal and mechanical properties can be used in the fabrication of seals for probing and excavating deep oil resources[42]. The electrical conductivity of nanocomposites is accredited to the formation of percolation pathways among the CNTs in the matrices. At a particular concentration of CNTs, commonly referred to as the percolation threshold, a sudden increase in the composite conductivity was observed[30,31].

Thomas *et al.*[31] studied the effects of incorporating CNTs into NR on electrical properties of nanocomposites. It was indicated that the dielectric constant increases with respect to the filler loading for both pristine and functionalised CNTs. However, the effect was less pronounced in the case of functionalised CNTs. Functionalisation caused improvement in dispersion of CNTs in the NR matrix corroborated by the increase in electrical resistivity. In contrary, Bhattacharyya *et al.*[27] presented dielectric measurements at room temperature and their data revealed a low percolation threshold (<1 wt%) associated with the formation of an interconnected nanotube network. Many other researchers also tried to reduce the percolation threshold of CNTs. For example, Nakaramontri *et al.* [47] have observed a very low electrical percolation threshold, namely 1 phr CNTs content, in the ENR–CNT and the ENR–CNT–TESPT composites.

George *et al.*[52] have covalently functionalised MWCNTs by using a mixture of sulfuric acid and nitric acid and then prepared NR/MWCNTs composite by latex blending an aqueous dispersion of MWCNTs in NR. They found that the oxidised CNTs adhered around NR latex spheres resulting in a network of segregated CNTs. This individual CNTs produced a very low electrical percolation threshold (0.086 vol%), high electrical conductivity and dielectric constant with distribution of nanotubes at the boundaries between the polymer grains.

Table 1 summarises the result of several studies to indicate that the effect of CNT on the mechanical properties of NR-based compounds will be more pronounced if functionalised CNT is used. However, the level of enhancement obtained is different, depending on the type and amount of CNTs used as well as the procedure applied for nanocomposites fabrication. These three factors will be further discussed in the following paragraphs.

The versatile physicochemical features of CNTs are limited by their scarce solubilisation in both aqueous and organic solvents. Despite pristine CNTs having a π-conjugative structure with a highly hydrophobic surface, their dispersion into polymeric matrices is difficult due to a high molecular weight and their tendency to entangle and form 3D networks through persistent van der Waals interactions[29-33,37,40]. Since effective reinforcement of a polymer relies on the efficient dispersion of sufficient amounts of CNT in the matrix, recent studies have attempted to overcome this problem. Functionalisation of CNTs, which is chemical manipulation of CNTs, provide strong CNTs–matrix interfacial adhesion, enhances their dispersion in the solvent and polymer matrices and ultimately improves the mechanical and electrical properties of the composite[15, 27-29, 31, 41, 44, 48-56]. Up to now, the main approaches for CNTs functionalisation can be grouped into two main categories, depending on whether the moieties are attached to the tips or sidewalls of CNTs: (a) the covalent attachment of chemical groups, through reactions on the conjugated skeleton of CNTs, and (b) the noncovalent adsorption or wrapping of various functional molecules onto the tubes.

The covalent approaches include chemical modification methods which involve the introduction of various chemical moieties on CNTs' surface *via* chemical or electrochemical reactions[27-28,31,34,35,52-61]. The covalent functionalisation of CNTs typically involves a reaction, including sidewall oxidation, fluorination, amidation halogenations, hydrogenation, cycloadditions, radical additions, nucleophilic addition, alkylation, Billups reaction[58] , Prato reaction[59], nitrene reaction[60], Bingel reaction[61], *etc*. In these methods, CNTs are covalently connected to chemical species such as oxygen, fluorine and nitrogen or organic agents (biomolecules). The functional groups on the surface of CNTs, such as carboxyl, carbonyl, hydroxyl and amino groups, can not only improve their dispersion in solvents or polymers, but also act as reactive sites for further chemical modification.

The disadvantage of covalent functionalisation approach is that it converts the sp^2 carbon atoms to sp^3 carbon atoms, and therefore, the electrical properties of the CNTs are changed.

The other method is non-covalent functionalisation, which is mainly based on weak interactions, such as van der Waals forces, π-π stacking and hydrophobic interactions, between CNTs and modifier molecules. The type of interaction between the stabilising agent and the polymer matrix depends on the functional group on the CNT and the polymer matrix. Modifier molecules are organic molecules that range from low molecular weight molecules to polymers. Surfactants, *e.g.* sodium dodecyl sulfate and sodium dodecylbenzene sulfonate, are commonly used modifier molecules,[27-28,31,34, 35, 52-55]. They change the properties of CNTs by adsorbing onto the surface of CNTs or wrapping CNTs. Noncovalent functionalisation is of great interest since it offers attaching functional groups between the CNTs and polymeric

TABLE 1. MECHANICAL PROPERTIES OF NR AND ITS NANOCOMPOSITES

Sample	Amount of filler	Hardness	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)	Ref.
NR	–	–	14.9	0.5 (at 100%)	1332	31
NR/P-CNT[a]	1 phr	–	19.4	0.7 (at 100%)	1271	
NR/P-CNT	5 phr		18.0	1.0 (at 100%)	978	
NR/P-CNT	10 phr		15.4	1.1 (at 100%)	727	
NR/m-CNT[b]	1 phr	–	16.3	0.7 (at 100%)	1278	
NR/m-CNT	5 phr		19.2	1.2 (at 100%)	1140	
NR/m-CNT	10 phr		15.6	1.5	773	
NR	–	–	21.7	1.65 (at 100%) 3.46 (at 200%) 6.03 (at 300%)	593	51
NR/P-CNT	n	–	20.0	2.22 (at 100%) 4.63 (at 200%) 8.12 (at 300%)	481	
NR/m-CNT	n	–	26.2	2.11 (at 100%) 4.35 (at 200%) 7.53 (at 300%)	559	
NR	n	–	19.0	0.6 (at 100%) 1.0 (at 300%) 1.5 (at 500%)	930	28
NR/P-CNT	1%	–	24.9	0.7 (at 100%) 1.2 (at 300%) 1.9 (at 500%)	932	
NR/m-CNT	1%	–	30.0	0.8 (at 100%) 1.3 (at 300%) 2.3 (at 500%)	962	
NR	–	62.5 (J/m^3)	15.0	0.53	1332	44
NR/P-CNT	1 phr	77.7 (J/m^3)	18.5	0.65	1316	
NR/P-CNT	5 phr	60 (J/m^3)	17.8	1.02	948	
NR/P-CNT	10 phr	48.3 (J/m^3)	15.4	1.12	727	
NR/m-CNT	1 phr	60.3 (J/m^3)	18.9	0.67	926	
NR/m-CNT	5 phr	57.1 (J/m^3)	18.7	0.98	714	
NR/m-CNT	10 phr	31.7 (J/m^3)	15.1	1.26	569	

Sample	Amount of filler	Hardness	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)	Ref.
NR	–	41*	7.1	1.8 (at 300%)	690	36
NR/P-CNT	25 phr	54	19.4	7.5 (at 300%)	505	
NR/B-CNT[c]	25 phr	62	25.5	12.3 (at 300%)	490	
NR/CB[d]	25 phr	54	23.5	9.6 (at 300%)	480	
NR	–	49			–	57
NR/CNT	0.1%	55	–		–	
NR/CNT	0.3%	59	–		–	
NR/CNT	0.5%	63	–		–	
NR/CNT	1%	72	–		130	
NR	–	–	–	0.58 (at 100%)	–	56
NR/CNT	0.5 phr	–	–	0.82 (at 100%)	–	
NR/CNT	1 phr	–	–	0.96 (at 100%)	–	
NR/CNT	3 phr	–	–	2. 28 (at 100%)	–	
NR/CNT	5 phr	–	–	3.28 (at 100%)	–	
NR/CNT	10 phr	–	–	4.7 (at 100%)	–	
NR	–	34.8 ±0.22*	21.0 ±0.49	1.06 (at 300%)	1691 ±10	52
NR/CNT	0.05%	35.5 ±0.87	23.0 ±0.35	1.24 (at 300%)	1638 ±41	
NR/CNT	0.1%	42.5 ±1.08	28.2 ±0.58	1.32 (at 300%)	1660 ±40	
NR/CNT	0.3%	43.4 ±1.18	30.4 ±0.47	1.74 (at 300%)	1550 ±38	
NR/CNT	0.5%	55.4 ±1.02	33.9 ±0.62	1.88 (at 300%)	1480 ±63	
NR/CNT	1%	30.3 ±0.56	23.3 ±0.81	1.21 (at 300%)	1485 ±86	

[a] P-CNT stands for pure CNT

[b] m-CNT stands for modified CNT or functionalised CNT

[c] B-CNT stands for ball-milled CNT

[d] CB stands for carbon black

[n] was not reported

*Shore A

**Tear strength (Mpa)

matrix without affecting the electronic network of the tubes. Modifier molecules such as surfactants are the disadvantage of non-covalent functionalisation in some cases. Covalent functionalisation can overcome this limitation due to the excellent stability of covalent bonds. However, it may reduce their length, decrease their diameter and alter their electronic property. Therefore, it is a crucial issue in research to develop a convenient, economical and mild covalent functionalisation route of CNTs. Different methods for functionalisation of CNTs are schematically presented in *Figure 3*.

The loading amount of CNTs is another factor that remarkably influences the degree of enhancement. Tarawneh, *et al.*[41] prepared NR/CNT nanocomposites with different amounts of CNT loadings and studied their thermal properties. From the results obtained, higher thermal conductivity, thermal diffusivity and specific heat were achieved for nanocomposites containing CNTs compared to the NR. However, any sample with CNTs content higher than 3 wt% indicated inferior thermal properties compared to NR. TEM observation confirmed when the CNTs content is less than 3%; there is a good dispersion of CNTs in the NR matrix, which is important for enhancing thermal properties of the nanocomposites. Pristine CNTs easily aggregate due to their high surface energy by lots of pp electron interactions among the tubes[15]. The amount of CNTs in a matrix should not go beyond the point where aggregation of CNTs begins [26,32]. A small amount of CNTs added in the NR matrix results in having a large number of nanotubes in the system because of their small diameter.

Besides the amount of CNTs, the method of their dispersion in the matrix is important

CNT: Carbon nanotube

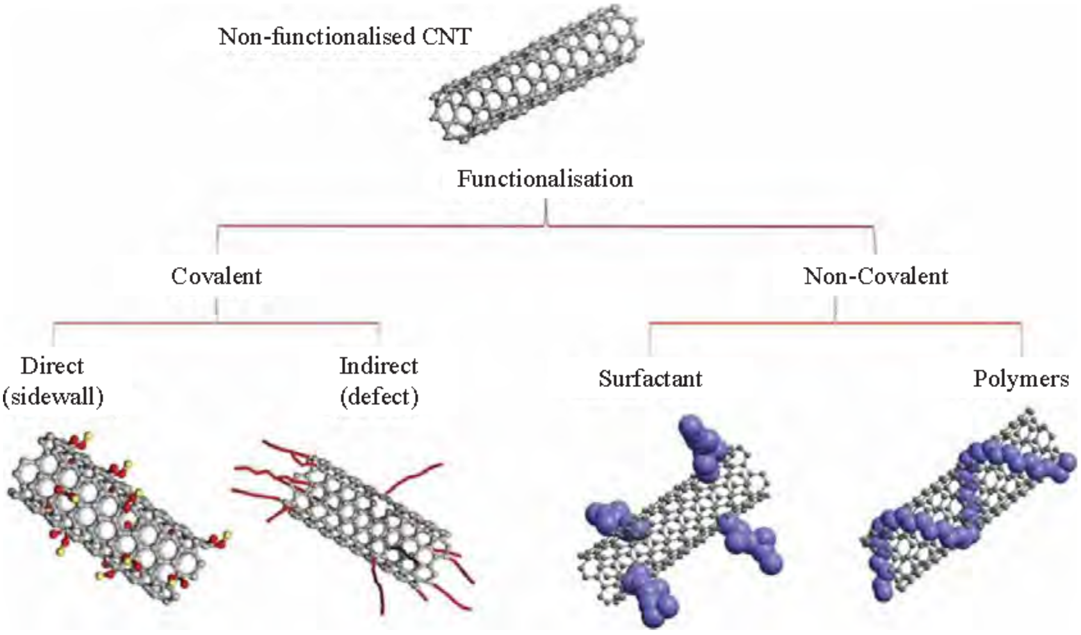

Figure 3. Different methods for functionalisation of CNTs[62].

and bundles of CNTs in the matrix can be dispersed applying a suitable method, like physical mixing, or ultrasonication. Researchers have attempted to develop novel procedures for NR/CNT composites with enhanced properties. For instance, Peng *et al.*[28] adopted a self-assembly process combining latex compounding technique to prepare NR/CNT composites. In this technique, the CNTs were first functionalised, and then assembled with poly (diallyldimethylammonium chloride) and latex particles. Using this procedure, the self-aggregation of pristine CNTs was suppressed and thus the interfacial adhesion between CNTs and latex particles was improved leading to enhancement in properties and performance of the nanocomposites comparedto NR reinforced with pristine CNTs. In another work, Nakaramontri *et al.*[48] prepared various composites of CNTs and epoxidised NR (ENR) by a melt mixing method with two alternative silane coupling agents and without a silane coupling agent. They observed, due to its high crosslink density, the highest electrical conductivity was achieved in the ENR–CNT composite with bis(triethoxysilylpropyl) tetrasulfide (TESPT). In a different approach, Junkong *et al.*[54] first prepared a mixture of MWCNTs in ethanol and a non-ionic surfactant. Then they used various amounts of this mixture to prepare MWCNTs-filled NR as well as MWCNTs/CB-filled NR vulcanisates with a two-roll mill. The results showed that adding CB enhanced the dispersion of MWCNTs in the matrix andthe edge-cut tensile strength increases with increasing MWCNTs loading. Nakaramontri, *et al.*[55] also fabricated NR/CNT composites using two alternative methods; the melt and latex mixing processes with *in situ* functionalisation of CNTs by TESPT. They concluded that latex mixing in combination with *in situ* functionalisation of CNTs by TESPT improved the CNTs dispersion in the matrix and hence indeed enhanced the properties of nanocomposites such as initial relaxation modulus, electrical properties, tensile strength, crosslink density and torque difference. Torque difference is a measure of the shear dynamic modulus, which indirectly relates to the crosslink density of the nanocomposites.

Despite consensus in improvement of most properties in NR-based compounds containing CNT, there is an obvious inconsistency in the effect of CNT on the glass transition temperature (T_g) of the NR-based compounds. *Table 2* summarises the values reported for T_g of NR and its composites containing CNT. Abdullatif *et al*, 2011[44] reported a small shifting of 1 – 3°C in T_g of compounds when either pristine or modified CNTs were added to NR. Their results are in accordance with some other researchers, who did not observe significant changes in the T_g of NR-based compounds containing CNTs[15,36]. Contrary to their finding, Peng *et al.*[28], observed that NR-based compounds reinforced with acid-modified CNTs have a significantly higher T_g than both NR itself and the compound with pristine CNT. Another research group[41] also observed such an increase when a hybrid filler (nanoclay and CNTs) were added to NR. Recently, in another research[47], addition of CNT and modified montmorillonite on the T_g of NR were compared and a significant decrease of $T_g$was observed when CNTs were used. All these observations infer the degree invariation of T_g depends on the type of filler and its content in the compound.

The glass transition temperature of a compound is important because the reinforcing mechanism of a polymeric matrix is related to the viscoelastic behaviour of the matrix, *i.e.* glassy and rubbery[27]. In the rubbery state of a polymeric matrix, reinforcement is originally "hydrodynamical" as the entropy effects dominate the elasticity rather than the elemental bond stiffness. The movement of NR molecular chains in the nanocomposite

TABLE 2. GLASS TRANSITION TEMPERATURES OF NR-BASED COMPOUNDS

Type of compound	**Amount of filler**	**Method of characterisation**	**T_g (°C)**	**Ref.**
NR	–	DSC	-61.72	44
NR p-CNTs	1 phr		-61.9	
NR p-CNTs	5 phr		-61.7	
NR p-CNTs	10 phr		-62.1	
NR m-CNTs	1 phr		-61.8	
NR m-CNTs	5 phr		-61.7	
NR m-CNTs	10 phr		-62.1	
NR	–	DSC	-65.85	36
NR p-CNTs	25 phr		-64.08	
NR b-CNTs[2]	25 phr		-63.56	
NR	–	DMA	-69	28
NR p-CNTs	1%		n	
NR m-CNTs	1%		-55	
TPNR[3]		DMA	-51	41
TPNR Nanoclay			-48	
TPNR CNT			-45	
TPNR Nanocaly-CNT			-43	
NR	–	DMA	-46.8	47
NR CNT	2 phr		-47.8	
NR Nanoclay-CNT	4 – 2 phr		-49.1	
NR Nanoclay-CNT	20 – 2 phr		-47.6	
NR	–	DSC	-68.48	57
NR/CNT	0.1%		-69.83	
NR/CNT	0.3%		-70.12	
NR/CNT	0.5%		-71.18	
NR/CNT	1%		-72.12	
NR	–	DSC	-60	31
NR/P-CNT[a]	1 phr		-57	
NR/P-CNT	5 phr		-56	
NR/P-CNT	10 phr		-54	
NR/m-CNT[b]	1 phr		-58	
NR/m-CNT	5 phr		-57	
NR/m-CNT	10 phr		-55	

DMA: Dynamic mechanical analysis
DSC: Differential scanning calorimetry

is restricted when strong interfacial adhesion between the NR matrix and CNTs exists. The graphitic nature of CNT's surface is not energetically favoured to absorb the NR molecular chains and it will be worse with aggregated CNTs present in the matrix. Proper surface modification accompanied with good dispersion of CNTs will enhance this interaction. Besides these issues, it seems addition of a proper filler like nanoclay can also improve the NR-CNT interaction. Consequently, apart from the type of NR-CNT interaction, the crosslink density will also influence the thermo-physical behaviour of the compound and thus its T_g.

The differences in T_g reported by various researchers is due to complexity of the glass transition process that involves a number of factors, including heating rate, ageing history, morphology, molecular weight, which affect this process. Accordingly, measurement of T_g requires particular considerations. As mentioned in *Table 2*, researchers applied both DSC and DMA to determine the T_g of compounds. However, these results are not comparable quantities because the two devices are sensitive to different units of molecular motion and the information delivered by the two techniques is different from a fundamental viewpoint.

Cataldo *et al.*[45] studied the effects of addition of MWCNTs on the viscoelastic behaviour NR compound filled with 50 phr carbon black at 100°C. According to their results, addition of MWCNTs from 2.5 to 15 phr significantly increases the viscosity of the compounds. Such an increase was attributed to the strong anisotropy in the shape of the nanotubes and thus the Enstein-Guth equation (*Equation 1*) was used to obtain the shape factor for MWCNTs. The Enstein-Guth equation describes viscosity of a polymer matrix loaded with a filler[64].

$$\eta_f = \eta_u(1 + 0.67f\Phi + 1.62f^2\Phi^2) \quad \text{...1}$$

where where η_f is the viscosity at a given temperature after the addition of the filler; η_u is the viscosity of the pure rubber matrix; Φ is the volume fraction of the filler and f is the filler shape factor.

The shape factor is defined as the ratio between the main and secondary axis of the particles.

Using the Enstein-Guth equation, they showed that in the case of using CNTs the anisotropy factor (or shape factor) reaches the value of 52.5, while this factor is only 6 for reinforcing with carbon black[64]. Accordingly, they proved that the reinforcing effect imparted by CNTs to the NR/CNT nanocomposite is due to the hydrodynamic effect exerted by the large anisotropic factor of the CNTs molecular threads.

In a different study, a magnetorheological elastomer (MRE) was prepared by adding pristine and functionalised (carboxylated and hydroxylated) MWCNT to the NR[65,66]. Its rheological properties was investigated under a different magnetic field. The storage modulus and loss factor of MRE with functionalised MWCNTs exhibited a noticeable increment in MR performance compared to pristine CNT parallel with the frequencies increment[65]. It was also indicated that when a higher content of carboxylated CNT (up to 1.0 wt%) was added, the MRE exhibits a higher MR effect of up to 17.5%[66].

Wang *et al.*[48] investigated heterogeneity of NR/CNT composites to understand the mechanisms through which enhanced mechanical properties are achieved. A "cellular structure" model in NR/CNT composites was proposed and the formation of a cellular structure was assigned as responsible for improving mechanical properties of the nanocomposite. According to this model, when the CNTs loading is low, the CNTs and the mechanical interfacial regions linked to the CNTs are dispersed in the NR matrix individually and homogeneously. However, the mechanical property of such a composite is not improved considerably because no interaction exists among CNTs. By increasing the CNTs loading, both CNTs and mechanical interfacial regions connect to each other and form a three-dimensional structure. These three-dimensional interconnections among the CNTs and mechanical interfacial regions were named a "cellular structure". Consequently, when the loading amount of CNTs is high enough, the cellular structure

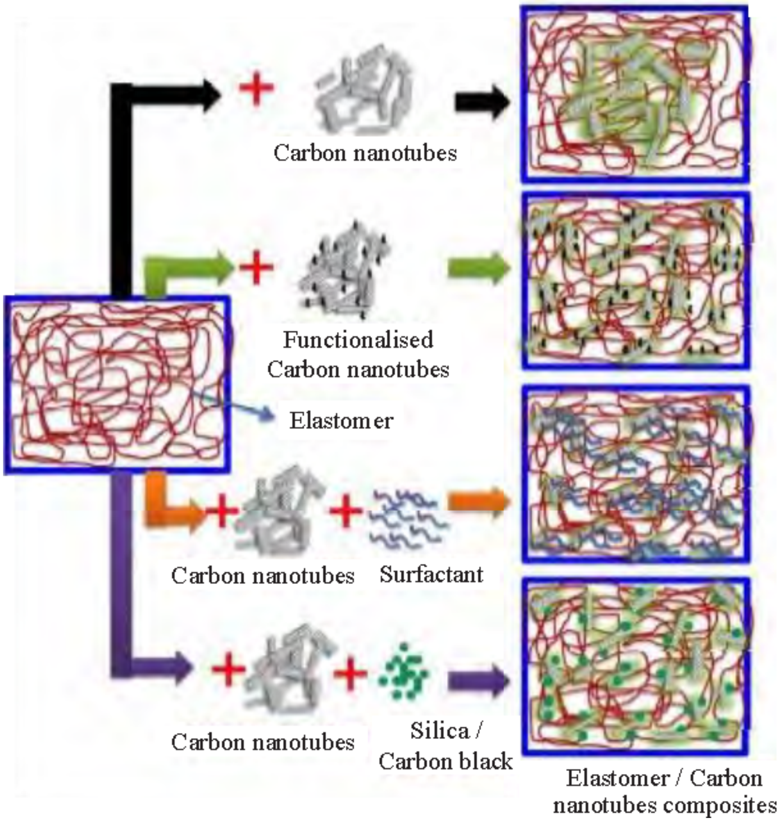

Figure 4. A schematic representation for CNT/elastomer composites[63].

forms and improvement in the mechanical properties of the nanocomposite is significant. *Figure 4* illustrates different nanocomposites containing CNTs.

As mentioned before, CNTs are classified according to their wall numbers; single wall and multiwalled CNTs. Comparing these two, MWCNTs have been predominantly used as a filler due to their lower cost, better availability and easier dispersability[41]. A nanocomposites comprising MWCNTs with other filler types have been reported by some[35,41,44-47]. However, the results in terms of mechanical and thermal properties improvement will be different depending on the types of fillers and their ratios in NR. Another issue which most researchers did not consider in their researches is the degree of NR vulcanisation. Zhao and co-researchers[3] indicated that the mechanical response of the NR compounds was changed as a function of the amount of sulfur used for crosslinking.

CONCLUSION

Despite having excellent elasticity and reversible deformability, unmodified forms of natural rubber (NR) has limited usage owing to its undesired properties such as hardness, durability and tear resistance. Traditional reinforcing materials are used to improve these properties, however, they cannot provided enhanced properties such as electrical, thermal and heat conductivity apart of reinforcement. Emergence of nanofillers has recently evoked much interest in property enhancement of polymeric materials including NR. Compared to the pure polymer or composites comprising conventional fillers, nanocomposites possess superior mechanical, thermal, optical, magnetic and electromagnetic properties. Among different nanostructures, the extraordinary properties of carbon nano-tubes (CNTs) have promoted research into the fabrication of CNTs-based nanocomposites. Researchers proved that only dispersed isolated nanotubes that form a network structure can transfer stress and thus mechanically strengthen the composites. However, dispersion of CNTs into the polymeric matrix and interface adhesion between them are problematic due to their scarce solubilisation in the matrices. These issues become more challenging in rubbers because of the high viscosity of elastomeric materials. It was indicated that the homogenous dispersion of CNTs is a function of the loading amount of CNTs, the interfacial interaction between the matrix and CNTs, as well as method of dispersion. The NR-CNT interaction is important as it influences the characteristics of the final integrated system. Improvement effects of incorporating CNTs to NR matrix are more pronounced if functionalised CNTs are applied. Due to the high price of CNTs, nanocomposites comprising hybrid fillers can be a more practical option. Preparing nanocomposites comprising CNTs with other types of fillers also showed good enhancement of NR properties. However, the results in terms of properties improvement are different depending on the types of fillers, their ratio in NR and the cure system used. In this regard, the effect of cure system and magnetic behaviour of CNT would be an advantage to explore.

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