Material Characterisation

# Influence of critical carbon nanotube loading on mechanical and electrical properties of epoxidized natural rubber nanocomposites

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## ARTICLE INFO

## ABSTRACT

Nanocomposites based on carbon nanotube (CNT) filled epoxidized natural rubber (ENR) were prepared by melt mixing method with the main aim to elucidate the critical CNT loading that provides optimal mechanical and electrical properties. The reinforcing effect of CNT in ENR matrix was assessed from torque difference ($M_H$-$M_L$) and 100% moduli that increased with CNT loading. Furthermore, dielectric constant and electrical conductivity increased with CNT loading. In addition, the percolation threshold concentration was about 2.3 phr of CNT with the *t*-value of fundamental percolation theory at 1.74. This indicates three dimensional (3D) CNT networks dispersed in the ENR matrix. In addition, the dipole-dipole interactions of ENR and CNT increased the polarization effect that caused formation of conductive material with micro-capacitor characteristics.

## 1. Introduction

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 some unique and superior properties, including high elasticity, flexibility and some level of biodegradability. However, NR has intrinsically poor aging, weathering, oil resistance, and electrical conductivity properties; limiting the use of NR in some applications. However, the applications of NR can be extended by various molecular modifications, such as epoxidized NR (ENR) and maleated NR (MNR), as well as by addition of fillers, including silica, clay, carbon black, and carbon nanotubes (CNT) [1].

CNT have also spurred wide interest in research and industrial applications, 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. Also, CNT has low bulk density, high specific surface area and especially high particle aspect ratio. These facilitate physical interactions of CNT with polymer molecules and hence further enhance its reinforcement efficiency in polymer composites. While the addition of CNT in an NR matrix produces composites with various properties, the CNT has strong tendency

to agglomerate. This is due to Van-der Waals attractions among the CNT particles and the strong hydrogen bonds of polar functional groups on CNT surfaces. The resulting poor dispersion of CNT in rubber matrix may degrade its reinforcing effects and thereby the mechanical properties [2]. It was found that the modulus of a CNT/NR composite increased by up to 12 fold with addition of 10 wt% CNTs, while tensile strength and elongation at break decreased [3]. In addition, different preparation methods of NR nanocomposites influence dispersion of CNT in the NR matrix. There are a variety of preparation methods, including solution mixing [4,5], latex mixing [6,7], and melt mixing [8]. In solution mixing, CNTs and polymer are mixed in a suitable solvent under controlled conditions. The nanocomposite film is eventually cast on a smooth substrate. In some cases, CNT agglomeration was found after solvent evaporation, which drastically reduced the mechanical properties of the composites [4,5]. In latex mixing, the CNT is first dispersed in deionized water before mixing with latex. Then, the mixture is cast on a glass plate or other smooth surface and thereafter dried in a hot air oven. The composites formed by latex mixing showed improved mechanical properties relative to those from solution mixing [9]. However, some CNT agglomerates still exist in the composites, due to the different polarities of CNT and rubber. In melt mixing, the agglomerates are dispersed in the rubber matrix by strong shear forces [6]. Melt mixing remains the most attractive option, because melt processing is typical in the current polymer industry.

CNT agglomeration not only affects mechanical properties of the

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composites, but also electrical performance and dielectric behavior. Typically, CNT in the polymer matrix act as dipoles, which can be considered nano-capacitors that contribute to interfacial polarization by dipole–dipole interactions of polymer and filler. The interfacial polarization causes dielectric constant and electric conductivity to increase with filler loading [10]. However, interfacial polarization is difficult to observe in neat NR or in NR with low conductive filler content. This may be due to the electrically insulating and non-polar nature of NR. Thus, high content of a conductive filler such as CNT is needed to induce interfacial polarization. However, a highly polar NR derivative such as ENR might give composites with higher interfacial polarization. CNT filled ENR composites have strongly increased electrical conductivity, in comparison to CNT filled unmodified NR composites [1]. This might be attributed to improved filler-rubber interactions that help disperse the CNT particles, relative to composites with non-polar NR. Thus, new chemical linkages between the epoxirane rings in ENR molecules and the polar functional groups on CNT surfaces might have formed in CNT filled ENR composites [1].

In the present work, reinforcement efficiency and other related properties of CNT filled ENR vulcanizates were investigated by determining torque difference ($M_H$-$M_L$), modulus, electrical conductivity, dielectric constant and morphological properties. CNT filled ENR composites with various CNT loadings were prepared. Furthermore, the critical CNT loading that allows formation of an "infinite" 3D network by CNT in the ENR matrix was also characterized. Consequently, the real dispersion and network state of CNT in ENR matrix were effectively investigated, and were further assessed in relation to percolation theory and models.

## 2. Experimental

### 2.1. Materials

Epoxidized natural rubber with 25 mol% epoxide (i.e., ENR-25) was used to prepare ENR nanocomposites. The ENR-25 was manufactured by Muang Mai Guthrie Public Company Limited (Surat Thani, Thailand). The multi-wall carbon nanotubes (CNT) with trade name NC7000 had 9.5 nm diameter, 1.5 μm length, and 90% purity, and were manufactured by Nanocyl S.A. (Sambreville, Belgium). Other chemicals used in the rubber formulation were zinc oxide (ZnO), stearic acid, 2,2′-dithiobis (benzothiazole) (MBTs) and sulfur, as summarized in Table 1.

### 2.2. Preparation of ENR/CNT nanocomposites

The CNT filled ENR nanocomposites with various CNT loadings of 1, 2, 3, 4, 5, 6 and 7 phr were prepared on an open two-roll mill with 200 g batch sizes. The process was started by adjusting the nip opening of the mill to approximately 0.5 mm. Then, the rubber compound was prepared according to a formulation shown in Table 1. That is, the ENR

**Table 1**
Compounding formulation of CNT filled ENR compounds and suppliers of the chemical ingredients.

| Chemicals | Suppliers | Contents (phr) |
|---|---|---|
| ENR | Muang Mai Guthrie Public Company Limited, Surat Thani, Thailand | 100 |
| Stearic acid | Imperial Chemical Co. Ltd., Pathum Thani, Thailand | 1 |
| Zinc oxide (ZnO) | Global Chemical Co. Ltd., Samut Prakarn, Thailand | 5 |
| 2,2′-Dithiobis-(benzothiazole) (MBTs) | Flexsys Inc., Termoli, Italy | 1 |
| Sulfur | Ajax Chemical Co. Ltd., Samut Prakarn, Thailand | 2.5 |
| CNT | Nanocyl S.A., Belgium | Varied 0-7 |

was first masticated and then mixed with the activators, zinc oxide and stearic acid, for about 2 min. Then, the CNTs were added into the compound and thereafter mixing was continued for another 5 min. After that, the accelerator (i.e., MBTs) and sulfur were added, and mixing was continued for another 5 min to the total mixing time of 12 min. The compound was then sheeted out through the nip of the two-roll mill, repeating for several cycles in order to improve the dispersion state of CNTs. The cure characteristics of rubber compounds were then determined by a moving die rheometer (MDR) (Monsanto, Ohio, USA) at 160 °C. Rubber vulcanizates were eventually prepared by compression molding (Charoen Tut, Co., Ltd, Samutprakarn, Thailand) at 160 °C, and the respective cure times were based on the MDR test.

## 3. Characterization

### 3.1. Attenuated total reflection fourier transform infrared spectroscopy

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was performed with Thermo Nicolet Avatar 360 FTIR (Thermo Electron Corporation, Thermo Nicolet, Madison, WI, USA). The analysis was carried out over the wavenumber range 4000–400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$.

### 3.2. Thermal analysis

Thermal analysis in terms of thermal resistance of the gum ENR and the CNT filled ENR vulcanizates with various CNT loadings of 1, 2, 3, 4, 5, 6 and 7 phr was carried out with a thermogravimetric analyzer, TGA-SDTA 851 (Mettler Toledo, Zurich, Switzerland). The measurement was performed from 30 °C to 900 °C at 10 °C/min heating rate. In addition, a nitrogen ($N_2$) atmosphere was used in the temperature range from 30 °C to 600 °C, and this was switched to oxygen ($O_2$) atmosphere for the temperature range from 600 °C to 900 °C.

### 3.3. Cure characteristics

Cure characteristics of gum and filled ENR compounds with various CNT loadings were determined using a moving die rheometer (MDR) (Monsanto Co., Ltd., Ohio, USA). The measurements were performed at the fixed 1.66 Hz oscillation frequency with 1 arc degree amplitude at 160 °C.

### 3.4. Tensile properties

Tensile properties of gum and filled ENR composites with various CNT loadings of 1, 2, 3, 4, 5, 6 and 7 phr were investigated using a universal tensile testing machine (Tinius Olsen, Co., Ltd., Honey Crock Lane, UK). The tests were carried out with 500 mm/min$^{-1}$ cross-head speed at room temperature, according to ISO 37. Five specimens were used for each test.

### 3.5. Payne effect

The Payne effect was estimated by relation of storage moduli as a function of strain amplitude measured by a rubber process analyzer (RPA) (Alpha Technologies, Akron, USA). The strain sweep test was performed in the strain ranges of 0–100% with a fixed oscillating frequency of 1 Hz and tested temperature of 100 °C.

### 3.6. Electrical properties

Electrical properties in terms of dielectric constant ($\varepsilon'$) and electrical conductivity ($\sigma$) of gum and CNT filled-ENR vulcanizates with various CNT loadings of 1, 2, 3, 4, 5, 6 and 7 phr were measured at room temperature using an LCR meter (Hioki IM 3533, Hioki E.E. Corporation, Nagano, Japan) and the electrode plates of a dielectric test