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Effect of electric field induced alignment and dispersion of functionalized carbon nanotubes on properties of natural rubber

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ABSTRACT

The original equipment and method for orienting multi-walled carbon nanotubes (MWCNTs) in natural rubber (NR) by alternating current (AC) electric field were reported in the present study. MWCNTs with various volume fractions were dispersed in the mixture latex which composed of natural rubber, additives and methylbenzene. The application of AC electric field during nanocomposites curing process was used to induce the formation of aligned conductive nanotube networks between the electrodes. The aligned MWCNTs in the composites have a better orientation performance and dispersion quality than these of random MWCNTs by analyzing TEM and SEM images. The effects of MWCNTs anisotropy on thermal conductivity, dielectric properties, and dynamic mechanical properties of NR were studied. The mean value of thermal conductivity of composites loading with aligned MWCNTs was 8.67% higher than that of composites with random MWCNTs due to the anisotropy of aligned MWCNTs. The compounds with aligned MWCNTs possessed low dielectric constant, loss tangents and conductivity, namely a good insulativity. The compounds loading with aligned MWCNTs had lower loss modulus and better dynamic mechanical properties than those with random MWCNTs. This method can make full use of the high thermal conductivity of MWCNTs axis, and expand the application areas of natural rubber like conducting heat in a certain direction with a high efficiency.

1. Introduction

The tubular structures of Carbon nanotubes (CNTS) are frizzled by graphite sheets. CNTs have become the most potential carbon materials and are called “the super fiber” due to their excellent performances [1]. The tensile strength and the Young’s modulus of MWCNTs are up to 200 GPa and 1 TPa, respectively. The density of MWCNTs is only 1/6 of the steel density [2,3]. Therefore, many matrix materials have been filled in with CNTs to enhance the overall properties of composites [4], such as polymers, ceramics, and metals. MWCNTs are the typical one-dimensional quantum nanomaterials and anisotropic in heat transfer and electric conduction due to the high aspect ratio. The thermal conductivity on axial direction of MWCNTs can reach 6000 $W{\cdot}m^{-1}{\cdot}K^{-1}$[5], while the thermal conductivity on radial direction is far below it. The electric conductivities on axial and radial direction are 1000 S/m and 150 S/m [6–8], respectively. Hence, the axial anisotropy of CNTs should be used sufficiently for the sake of giving full play to structural advantages of CNTs and promoting the properties of composites.

Two main directions for CNT to be aligned are in situ and ex situ methods. The alignment is concurrent in the CNT preparing process by in situ methods [9]. The prepared CNTs are aligned by ex situ methods. The commonly used ex situ orientation methods include mechanical forces [10–12], magnetic fields [13–15], electric fields [16–22], and shear flow [23,24]. However, the approaches mentioned above also have limitations. Mechanical and shear forces can damage the structure of CNTs [25]. Magnetic fields are not suitable for large scale applications as a large magnetic field strength is required (>5T) [25]. In contrast, the electric field alignment seems as the most promising and versatile ex situ technique because it is scalable and suitable for a wide range of applications [26–29].

Many studies reported that CNTs aligned along the plane of the substrate rather than perpendicularly to the substrate through electric field induced alignment, such as CNTs-polymer composites with the anisotropic mechanical and electrical properties [30–33]. In the present study, CNTs were perpendicular to the plane of the substrate to get the nanocomposites with a high thermal conductivity due to the anisotropy of aligned CNTs.

Studies on nanoparticle-epoxy composites showed the forming of oriented filler networks, which were induced in both direct current (DC) and alternating current (AC) fields [32,34,35]. The

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resulting structure of the filler networks was related to the classification of the electric field in which the AC fields generally leads to more homogeneous networks than those in the DC fields. MWCNTs were dispersed in epoxy system and were induced by both AC and DC electric fields for 100 V/cm during nanocomposites curing process [32]. More uniform and more aligned networks can be achieved from AC fields which are compared to the inhomogeneous and branched structures obtained from DC fields. Therefore, the AC electric fields were applied in many literatures, which induced the fine alignment of MWCNTs and SWCNTs [36–38].

The alignment and dispersion of pristine MWCNTs and chemically functionalized MWCNTs within a PMMA matrix induced by an AC electric field were investigated [39]. Dramatic increment in alignment stability and dispersion quality for oxidized MWCNTs as compared to pristine MWCNTs was obtained. Because the reduced length of oxidized MWCNTs and repulsive interaction between the functional groups –OH and –COOH on MWCNTs can result in a better dispersion of oxidized MWCNTs [40]. It indicates that the oxidation of MWCNTs not only prevents agglomeration but also enhances the electric field-induced alignment of MWCNTs in host polymer.

In this study, the effects of electric fields on alignments and dispersions of functionalized MWCNTs in AC fields with 130 V/cm using new electric field orienting device were studied. The alignment quality and dispersion level of MWCNTs with different contents in natural rubber matrix were investigated.

Table 1
The composition of composites.

Ingredients	phr[a]
NR	100
Sulfur	3
Zinc oxide	5
Accelerator ZDC	1
Stearic acid	2
Antioxidant RD	1
Ethylxanthic acid potassium salt	1
MWCNTs GT-600	Variate[b]

[a] Per hundred of natural rubber in quality.
[b] The amount of the MWCNTs was determined by the volume fraction, which was calculated by the Eq. (1).

2. Materials and experimental details

2.1. Materials

MWCNTs of GT-600 manufactured by the way of catalytic chemical vapor deposition (CCVD) with purity >95%, diameter 50–60 nm, length 2–8 μm were provided by Dazhan Nanomaterial Limited Company. Natural rubber was purchased from Hainan Natural Rubber Group. All other chemicals were used as an analytical grade and without further purification.

2.2 The formula of the CNTs/NR composite

$$\frac{M_{filler}}{\rho_{filler}} = \left(\frac{M_{filler}}{\rho_{filler}} + \frac{M_{NR}}{\rho_{NR}} + V_{add}\right) \times C\%, C \in (0, 0.5, 1, 2, 4, 6) \tag{1}$$

Here, M_{filler} and ρ_{filler} are the mass and density of MWCNTs, V_{add} is the total volume of all the additives used in the Table 1. C is the volume fraction of CNTs in NR.

2.3 Preparation of the CNTs/NR composite

Firstly, the MWCNTs were chemically functionalized. In the process, a mixture of concentrated acid ($v(HNO_3)$:$v(H_2SO_4)$ = 1:3) was prepared. Then, CNTs were added into the acid and the blending was stirred by ultrasonic cleaning equipment for 1 h. Afterwards, CNTs were filtered out and rinsed continuously with deionized water till they were chemically neutral.

CNTs/NR composites were prepared in the following steps. 10 g NR, divided into small particles, was dissolved in 200 mL methylbenzene for 48 h. And then the rubber latex was obtained by mechanical agitation for 24 h. The desired weight fraction of functionalized CNTs was blended with 50 mL methylbenzene by ultrasonic for 30 min. The additives was dispersed in 50 mL methylbenzene using ultra-sonication for 30 min at 50 °C, so that some additives can be dissolved in methylbenzene. Three kinds

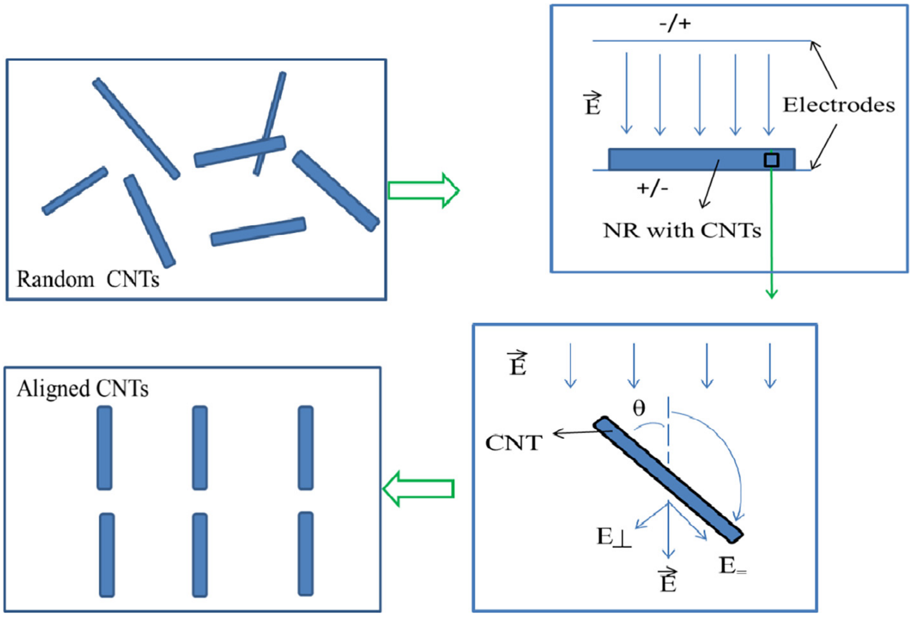

Fig. 1. The diagram of the mechanism of CNTs induced by electric field.