



# Antioxidant sustained release from carbon nanotubes for preparation of highly aging resistant rubber



Ye Fu<sup>a,b,c</sup>, Chun Yang<sup>a,b</sup>, Yuri M. Lvov<sup>c</sup>, Liqun Zhang<sup>a,b,\*</sup>, Wencai Wang<sup>a,b,\*</sup>

<sup>a</sup>Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing 100029, China

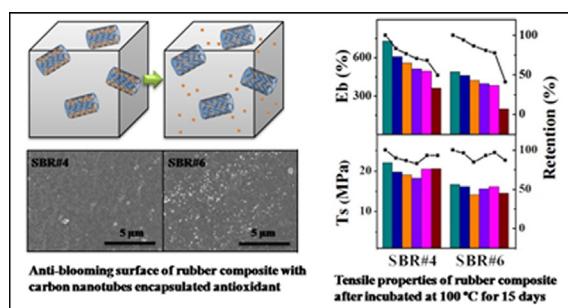
<sup>b</sup>State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

<sup>c</sup>Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71270, United States

## HIGHLIGHTS

- A method to load antioxidant into carbon nanotubes for sustained release is proposed.
- The sustained release of antioxidant from carbon nanotubes extends its action time.
- The antioxidant amount in the rubber composite is enlarged without causing blooming.
- The thermal-oxidative & ozone aging resistance of SBR/CNTs is improved.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 29 March 2017

Received in revised form 24 May 2017

Accepted 25 June 2017

Available online 27 June 2017

### Keywords:

Aging resistant  
Sustained release  
Carbon nanotubes  
Elastomer  
Antistatic

## ABSTRACT

In this work, a novel strategy to avoid the blooming of antioxidants and improve the aging-resistance of styrene-butadiene rubber (SBR) was proposed by using carbon nanotubes (CNTs) loaded with antioxidant N-(1, 3-dimethyl) butyl-N'-phenyl-p-phenylenediamine (4020) as filler. The sustained release of antioxidant from carbon nanotubes extends its action time. The amount of antioxidant in the rubber composites allows for a concentration of 2.0 wt.% without causing blooming by encapsulating antioxidant into carbon nanotubes. The aging resistance of SBR/CNTs composites was studied by comparing the mechanical properties before and after thermal-oxidative and ozone aging. A fifteen-day thermal-oxidative aging test at 100 °C shows preservation of mechanical properties and a twenty-four-hour ozone aging test shows no cracks. Furthermore, due to the present of thermal and electrical conductive carbon nanotubes, the rubber composites emerge thermal conductivity of 0.303 W/m·K and electrical conductivity of  $4.74 \times 10^7 \Omega\text{-cm}$  which can be extended for many potential applications, such as long service life tires and antistatic conveyor belts. This loading and sustained release approach can be extended to antimicrobial, antifouling, and other application.

© 2017 Published by Elsevier B.V.

## 1. Introduction

Physicochemical and mechanical properties of the elastomer materials always progressive deteriorate due to the combined effect of internal and external factors of aging, which leads to the

main manifestations of cracks, getting sticky, hardening, chalking, discoloration and finally lose its value in application [1]. The more common aging are thermal-oxidative aging and ozone aging. In order to slow down the aging, antioxidants are added into the rubber composites [2–6]. However, antioxidants often diffuse toward

\* Corresponding authors at: Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing 100029, China.

E-mail addresses: [zhanglq@mail.buct.edu.cn](mailto:zhanglq@mail.buct.edu.cn) (L. Zhang), [wangw@mail.buct.edu.cn](mailto:wangw@mail.buct.edu.cn) (W. Wang).

the surface of rubber products through the elastomer cross-linked networks in a phenomenon called “blooming”, which results in microdefects, getting loss of antioxidant protection, and contamination of environment [7]. Macromolecular rubber additives and micro-capsule technology have been studied for the anti-blooming in recent researches [8–12]. However, the application of these methods is restricted by the complex preparation process and high costs.

Carbon nanotubes are nanoscale diameter seamless tubular material wrapped by one or up to dozens of layers of the graphite sheet according to certain helix angle [13]. The excellent mechanical property carbon nanotubes, which also have good electrical conductivity, thermal conductivity are a kind of ideal polymeric reinforcing materials [14–18]. Therefore, the carbon nanotubes play an important role in many different areas, such as battery electrode materials, field emission cathode material for flat panel displays and the oxygen storage adsorbent material with maximum capacity, etc. [19–23]. The electrical and thermal conductive property can be given to rubber composite by doping carbon nanotubes into rubber matrix. The thermal conductive elastomer composite can conduct out the heat in time thus to slow down the thermal-oxidative aging process [24–25]. Inspired with our previous work on antioxidant encapsulation with halloysite as nanocontainer, carbon nanotubes are expected to perform the same function on sustained release [26–28]. Many studies on loading metal nanoparticles into carbon nanotubes are reported [29–32]. However, the sustained release of antioxidant from carbon nanotubes to prepare the anti-blooming aging resistant elastomer composites has not been published.

In this study, the styrene-butadiene rubber (SBR) composite was prepared by filling 6.3 wt.% of antioxidant N-(1, 3-dimethyl) butyl-N'-phenyl-p-phenylenediamine (4020) loaded inside of carbon nanotubes into the rubber. The release kinetics of antioxidant from carbon nanotubes in water, cyclohexane, and rubber matrix was analyzed. The aging resistance of SBR-carbon nanotubes composites was studied by comparing the mechanical properties before and after thermal-oxidative and ozone aging. The volume resistivity and thermal conductivity of SBR composite was measured to indicate the anti-static and thermal conductive performance of this material.

## 2. Experimental

### 2.1. Materials

Carbon nanotubes with outer diameter of 30–60 nm, inner diameter of 20–50 nm and length of 1–10  $\mu\text{m}$  were supplied by Chengdu Organic Chemicals Co., Ltd., Sichuan Province, China. Sulfuric acid (98%) and nitrate (68%) were analytical reagent grade obtained from Beijing Chemical Plant, Beijing, China. Styrene-butadiene rubber (SBR), with trademark SBR1502 (styrene content is 23.5 wt.%), was manufactured by Jilin Chemical Industry Company, China. Zinc oxide (ZnO) was analytical grade from Sigma-Aldrich, USA. Antioxidant N-(1, 3-dimethyl) butyl-N'-phenyl-p-phenylenediamine (4020) was purchased from SINOPEC Nanjing Chemical Industries Co., Ltd. Other rubber additives, including stearic acid, carbon black (CB) N330, sulfur, 2-Mercaptobenzothiazole, diphenyl guanidine, and tetramethyl thiuram disulfide were industrial grade and used without further purification.

### 2.2. Preparation of antioxidant 4020 loaded carbon nanotubes

The length of pristine carbon nanotubes was truncated into about 1  $\mu\text{m}$  by the ball grinding mill process. Then the milled car-

bon nanotubes were immersed in concentrated sulfuric acid and nitric acid solution (volume ratio 3:1) by ultrasonic for 2 h. After washing to neutral with deionized water, carbon nanotubes were dried in a vacuum oven. The carbon nanotubes were dispersed in antioxidant acetone solution (50 g/L) with mass ratio of 1:1. After 2 h ultrasonic treatment at 100 W, the mixed solution were centrifuged and rinsed with deionized water to remove any unloaded antioxidant followed with drying at 50  $^{\circ}\text{C}$  in a vacuum oven. The obtained samples were denoted as CNTs-4020.

### 2.3. Preparation of the SBR/CNTs composites

SBR and carbon nanotubes were compounded according to the formulations tabulated in Table 1 with rubber additives using a two-roll mill at room temperature. The compound was pressured to a 1-mm-thickness sheet at 150  $^{\circ}\text{C} \times T_{90}$  and then cut into specimens.

### 2.4. Characterization

The morphology of the samples was investigated by scanning electron microscopy (SEM) using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). The SEM measurements were performed at an accelerating voltage of 20 kV after sputtering the sample surface with a thin layer of gold.

Transmission electron microscopy (TEM) images were recorded on a FEI Taicnai G2 20 STWIN TEM at 200 kV. The ultrathin section specimens of SBR/CNTs for TEM observation were cut with a diamond knife on Cro-Ultramicrotome (Leica EM UC6, Germany). HR-TEM was performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV.

Raman spectrometer was took place on an inVia Reflex Raman (Renishaw, England). The experiments were carried out with excitation wavelengths 514 nm from a He-Ne laser at power of 4.7 mW.

Thermogravimetric analysis (TGA) of antioxidant loaded carbon nanotubes was performed on a TGA-60A (Shimadzu, Japan) from 30  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$  with a steady nitrogen flow (50 mL/min).

Fourier transform infrared spectroscopy (FTIR) spectra were obtained by using a TENSOR 27 spectrometer (Bruker, Germany) under ambient conditions. The test samples were prepared by dispersing in KBr uniformly and pressing the powder into pellets.

Ultraviolet visible spectrophotometry (UV-vis) was carried with an Agilent 8453 Spectrophotometer (Agilent Technology, USA). The UV-vis was used to analyze kinetics of antioxidant release from carbon nanotubes. The release in water and cyclohexane was conducted by stirring 50 mg of antioxidant loaded carbon nanotubes in 1 mL of DI water or cyclohexane. At each reading, the supernatant was removed by centrifugation and fresh solvent was added. The antioxidant release process in rubber matrix was studied by immersing 0.5 g rubber in 5 ml acetone solution. At each set period of time, the solvent was removed and the fresh acetone solution was added. The collected solvent was analyzed by UV-Vis spectroscopy at 330 nm for the amount of antioxidant 4020.

The vulcanization characteristics of the SBR compounds were determined at 150  $^{\circ}\text{C}$  by a rotorless rheometer MR-C3 (RAD Co., Ltd., Beijing, China).

Tensile tests were performed on a tensile apparatus (CMT4104, Shenzhen SANS Testing Machine Co., Ltd., China) at 25  $^{\circ}\text{C}$  according to Chinese Standard GB/T528-2009 with the crosshead speed of 200 mm/min. For each sample, five measurements from different specimens were averaged.

The volume resistivity of SBR/CNTs was measured by an EST121 digital ultrahigh resistance meter (Beijing Altek Hui Technology Co., Ltd., Beijing, China). Different applied voltages were used on

Download English Version:

<https://daneshyari.com/en/article/6465361>

Download Persian Version:

<https://daneshyari.com/article/6465361>

[Daneshyari.com](https://daneshyari.com)