



New insight on the interfacial interaction between multiwalled carbon nanotubes and elastomers



Nanying Ning^{a, c}, Dongliang Cheng^a, Jianhua Yang^a, Li Liu^{a, c}, Ming Tian^{a, b, c},
Youping Wu^{a, c}, Wencai Wang^{a, c}, Liqun Zhang^{a, b, c}, Yonglai Lu^{a, c, *}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

^b Beijing Advanced Innovation Center for Soft Matter Science and Engineering, No. 15 Bei-San-Huan East Road, ChaoYang District, Beijing 100029, China

^c Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

We studied the effect of the microstructure of multiwalled carbon nanotubes (MWCNTs) on interfacial interaction in seven kinds of MWCNT/natural rubber (NR) composites. Unexpectedly, the degree of defects (I_D/I_G) of MWCNTs was found to play a key role in the interfacial interaction of MWCNT/NR composites. The content of bound rubber (BR) of the composites almost linearly increased with the increase in the I_D/I_G of MWCNTs. Then we studied the interfacial interaction between MWCNTs with high degree of defects and NR. Interestingly, the BR of the composites consisted of loosely adsorbed BR (LBR) and tight BR (TBR). TBR occupied about half of the total BR, and cannot be removed by extraction in hot toluene for 48 h. Meanwhile, the mobilities of macromolecules in TBR were more restricted than those in LBR. We discussed in depth the molecular origin of the interfacial interaction between defected MWCNTs and NR, and then proposed that LBR was topologically confined by the steps-like structure of defected MWCNTs whereas TBR was principally chemically bonded to MWCNTs. This study provided new insight on the interfacial interaction between MWCNTs and NR and thus provides guidance for the preparation of high-performance elastomer composites with strong interfacial interaction.

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1. Introduction

Carbon nanotubes (CNTs) have been considered as excellent candidates in substituting conventional fillers such as carbon black (CB) in elastomer composites, and thus have attracted considerable attention because of their large aspect ratio, low density, high flexibility and strength, excellent conductivity, and good thermal conductivity [1–3]. For example, reports showed that conductive CNTs/elastomer composite combines high elasticity and sealability of elastomers and the high electrical conductivity of CNTs, and thus can be applied in electromagnetic interference (EMI) shielding elastomers, sensors, and electrostatic charge dissipation [3–5]. In addition, CNTs were introduced into elastomers to largely improve the thermal conductivity of tire tread, and consequently increase heat dissipation in tires [6,7]. Furthermore, a number of previous studies reported that CNTs can not only act as good reinforcing

agents but also as nanosping that can adjust the viscoelasticity, reduce the hysteresis loss of elastomers, and thus reduce fuel consumption in the field of automobile tire industry [2,8].

A key factor to obtain high-performance CNTs/elastomer composites is the interfacial interaction between CNTs and elastomers. Until now, many studies have been focusing on the interaction between raw CNTs and elastomers [9,10]. Interestingly, different conclusions on interfacial interaction were reported even for the same CNTs/elastomer system. Some studies reported that the interfacial interaction between CNTs and elastomer is strong. For example, Wang et al. [11] observed the obvious NR interfacial regions around the CNTs by using the nanomechanical mapping technique of an atomic force microscopy. Le et al. [12] reported that NR molecules can wet CNTs surface effectively through cation- π linkage, indicating a good interfacial interaction between CNTs and NR. In addition, Lopez-Manchado et al. [13] reported a strong interaction between single-walled carbon nanotubes (SWCNTs) and NR by using a dynamic mechanical analysis. However, other studies reported a weak interfacial interaction between CNTs and elastomer. For instance, Bokobza et al. [14] observed no obvious

* Corresponding author. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China.

E-mail address: luyonglai@mail.buct.edu.cn (Y. Lu).

shift on Raman peaks when the CNTs/elastomer composites were subjected to an extensional strain, indicating a weak interfacial interaction. Nah et al. [15] also reported that interfacial interactions between CNTs and NR were weak in comparison with the relatively strong adhesion between rubber and CB by testing the BR, Payne effect and Mullins effect as well as scanning electron microscope (SEM) observation. These reports motivated us to ask the following two questions. Why they draw different conclusions on the interfacial interaction between raw CNTs and elastomers? What is the molecular origin of interfacial interaction between CNTs and elastomers?

In this study, we selected seven kinds of MWCNTs and characterized the microstructure of these MWCNTs using Raman spectroscopy (RS) and X-ray photoelectron spectroscopy (XPS). Some of these MWCNTs have the same content of oxygen-containing functional groups, diameter, and purity but different degree of defects (I_D/I_G). Other MWCNTs possess the same degree of defects (I_D/I_G), diameter, and purity but different content of oxygen-containing functional groups. Then, we studied the effect of microstructure of MWCNTs on the interfacial interaction between MWCNTs and NR by testing the BR and mechanical properties of the MWCNT/NR composites. Unexpectedly, the results showed that the degree of defects of MWCNTs plays a key role in the interfacial interaction of MWCNT/NR composites, whereas the number of oxygen-containing functional groups has no obvious effect on their interfacial interaction. Therefore, we studied in depth the interfacial interaction between MWCNTs with high degree of defects and NR by using Fourier transform infrared spectroscopy (FTIR), RS, BR test, and low-field solid nuclear magnetic resonance (LFSNMR). Based on the experimental results and fundamental chemistry principles, we proposed the molecular origin of interfacial interaction between defected MWCNTs and NR. This study aims to provide guidance for the preparation of high-performance elastomer composites with strong interfacial interaction. To the best of our knowledge, such a kind of study has not ever been reported yet.

2. Experiment

See [supporting information](#).

3. Results and discussion

3.1. Influence of MWCNTs microstructure on interfacial interactions

We selected seven kinds of MWCNTs to study the effect of MWCNTs structure on the interfacial interaction between MWCNTs and NR. Among these MWCNTs, three are graphitized MWCNTs (G-MWCNTs) (Chengdu Organic Chemicals Co., Ltd.) with much less defects than that of the other four kinds of not graphitized MWCNTs (NG-MWCNTs). These G-MWCNTs have almost the same diameter and purity (see [Table S1](#) in supporting information) but different composition of oxygen-containing functional groups (see [Table S2](#) in supporting information). The non-functionalized G-MWCNTs and the G-MWCNTs functionalized by hydroxyl (OH) and carboxyl (COOH) were named as GM3, GMH3 and GMC3, respectively. Among the four kinds of ungraphitized MWCNTs, one of them (industrialized MWCNTs, IM3) was provided by Chengdu Organic Chemicals Co., Ltd, whereas the other three (trade marked as F9000, F9011, F7000) were purchased from Beijing Cnano Technology Co., Ltd. F9000 and F9011 have the same diameter and purity but different content of oxygen-containing functional groups, whereas F7000 and IM3 have the similar diameter and purity but different content of oxygen-containing (see [Tables S1 and S2](#) in supporting information).

The MWCNTs were first characterized using RS and XPS to test

the defects and the content of oxygen. The results are shown in [Fig. 1](#) and [Table S2](#) in supporting information, respectively. From [Fig. 1](#), we observe two strong peaks at about 1350 and 1587 cm^{-1} for the four ungraphitized MWCNTs, representing the D peak and the G peak of MWCNTs, respectively. For the three graphitized MWCNTs, the weak peak is at about 1354 cm^{-1} whereas the strong peak is at about 1582 cm^{-1} . As reported in previous studies [16], the D peak represents a disordered structure, which arises from the multiple phonon scattering caused by defects or amorphous carbon, whereas the G peak represents the carbon atoms of MWCNTs having a complete hexagonal structure (sp^2 hybridization). The ratio of the I_D/I_G can be used to evaluate the defects of the MWCNTs and the results are summarized in [Fig. 1](#). As expected, the value of I_D/I_G of G-MWCNTs is much smaller (0.11–0.21) than that of the NG-MWCNTs (1.00–1.15), demonstrating that G-MWCNTs have much less defects than that of the NG-MWCNTs. In addition, the value of I_D/I_G of GM3 is smaller than that of GMH3 and GMC3, indicating that GM3 has the lowest degree of defects. On the other hand, we obtained the TEM images of F9000 and GM3 (see [Figure S1](#) in supporting information) as an example to represent the different degree of defects for MWCNTs with different I_D/I_G . Clearly, F9000 with larger I_D/I_G shows much more defects than that of GM3.

The content of oxygen-containing functional groups (including hydroxyl groups, carboxyl groups, and carbonyl groups) of the MWCNTs was characterized using XPS, and the results are summarized in [Table S2](#) in supporting information. Among the four NG-MWCNTs, F7000 has the highest content for oxygen-containing functional groups, whereas F9000 has the lowest. In addition, F9011 and IM3, F9000 and GM3, GMC3 and GMH3 show almost the same content of oxygen-containing functional groups, which are approximately 4.9%, 4.0%, and 3.1%, respectively. Therefore, we can study the effect of defects of MWCNTs on the interfacial interaction of MWCNT/NR composites by comparing the composites with two different MWCNTs but the same content of oxygen-containing functional groups.

Measurement of the content of BR (see [section 2.3](#) in supporting information), a widely used method of studying the filler-rubber interaction, was used in this study to evaluate the interface interaction between MWCNTs and NR; and the results are shown in [Fig. 2](#). The content of BR versus the I_D/I_G of the MWCNTs is shown in [Fig. 3\(a\)](#), presenting the effect of defects of MWCNTs on the interfacial interaction between MWCNTs and NR. Interestingly, the

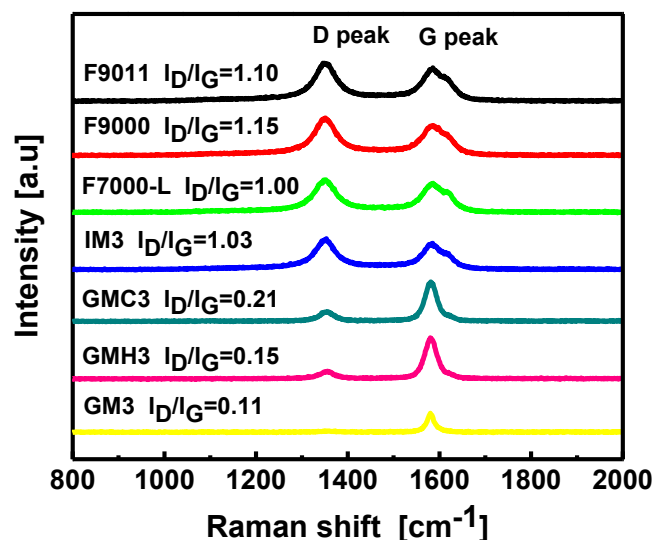


Fig. 1. RS of various MWCNTs with different I_D/I_G .

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