Synthetic Metals 242 (2018) 23–28

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

The effect of crystalline defects and geometry factors of multi-walled carbon nanotubes on electrical conductivity of silver-nitrile butadiene rubber composites

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ARTICLE INFO

Keywords:
Carbon nanotubes
Conductivity
Crystalline defect
Geometry factor
Flexible composites

ABSTRACT

It is important to construct effective electrical network to achieve high electrical conductivity of soft polymer matrix composites. We previously employed one-dimensional multi-walled carbon nanotubes (MWNTs) decorated with silver nanoparticles (nAg-MWNTs) and micron-sized silver flakes in a nitrile butadiene rubber matrix to develop highly conductive flexible adhesive (CFA) films. However, the effect of intrinsic physical properties of MWNTs on the conductivity of CFA was not explored in detail. Here we investigated the influence of crystalline defects and geometry factors of MWNTs on the electrical conductivity of CFA films. The nAg-MWNTs were synthesized using five different MWNTs. The electrical conductivity of the CFA films decreased significantly with an increase in Raman D- to G-mode ratio demonstrating the crystallinity effect. There was the tube diameter dependence. The conductivity increased as the diameter of MWNTs decreased. The dispersion was also a determining factor. The strongly entangled structure of MWNTs originated from the initial synthesis process caused aggregation of tubes in the polymer matrix resulting in a low conductivity of CFA film. However, the tube length dependence was not obvious in the investigated range (5–20 μm). It was possible that all the tubes were long enough not to differentiate the length effect on percolation. These findings may provide a guideline for selection of MWNTs to achieve high conductivity of flexible composites.

1. Introduction

Flexible electronic devices have attracted considerable interest in recent years, and several breakthroughs have been achieved in the development of flexible electronic components including transistors [1–3], batteries [4], touch panel displays [5], and sensors [6]. For integrating devices into a specific operating system, flexible electrical interconnects with high electrical conductivity are necessary. In this regard, silver particles have been actively investigated as conductive fillers because of their high electrical conductivity and oxidation resistance [7–9]. Recently, one-dimensional multi-walled carbon nanotube (MWNT)-based conductive fillers were embedded with Ag particles inside a polymer matrix to simultaneously achieve the high electrical conductivity and the flexible mechanical properties [10–14]. The synergetic effect of Ag particles and one-dimensional carbon nanotube fillers has been also investigated in other types of polymer systems [15]. The thermal conductivity and thermal stability were improved by the three-phase blend of carbon nanotubes, conductive polymer, and silver nanoparticles incorporated into polycarbonate nanocomposites [15].

We previously investigated novel conductive flexible adhesive (CFA) films composed of a flexible nitrile butadiene rubber (NBR) matrix, micron-sized Ag flakes, and MWNTs decorated with Ag nanoparticles on the sidewalls of the nanotubes (nAg-MWNTs) [10,11,13,14]. The electrical conductivity of the CFA films dramatically increased with a small addition of nAg-MWNTs, because of the formation of electrical networks and improved contact interfaces between micron-sized Ag flakes due to the presence of pre-attached Ag nanoparticles on the nanotubes [11]. This conductive filler strategy has also been effectively applied for stretchable polyvinylidenefluoride [12] or rigid epoxy matrices [9,16]. However, the effect of various intrinsic physical properties of MWNT, which is the backbone of 1-dimensional electrical network, on the electrical conductivity of soft polymer-matrix composites was unexplored in detail.

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https://doi.org/10.1016/j.synthmet.2018.04.008
Received 25 February 2018; Received in revised form 15 April 2018; Accepted 25 April 2018
0379-6779/

Here we report the influence of crystalline defects and geometry factors of MWNTs on the electrical conductivity of CFA films. The nAg-MWNTs were synthesized using five different MWNTs. The CFA film was then synthesized using nAg-MWNTs, micron-sized Ag flakes, and NBR matrix, following a previously published protocol [10,11,13,14], and the electrical conductivity was characterized. The concentration of each component was identical for comparison. The Raman intensity ratio of D to G-band (I_D/I_G) indicates the crystalline quality of MWNTs since G-band (~1580 cm^{-1}) corresponds to the graphitic sp^2 carbon bonds and D-band (~1350 cm^{-1}) corresponds to sp^3 or disordered sp^2 carbon bonds [17–19]. The crystalline defects of the MWNTs were first evaluated based on the I_D/I_G value, which was found to vary from 0.23 to 1.12. The electrical conductivity of the CFA films significantly decreased with an increase in the I_D/I_G value of the MWNTs. In addition, the strongly entangled structure of the MWNTs significantly reduced the electrical conductivity of the CFA films owing to poor dispersion properties. The parameters, such as average diameter (5–12.5 nm), length (5–15 μm), and aspect ratio (667–2727) of the MWNTs were also varied to investigate the effect of geometric factors of the MWNTs on the conductivity.

2. Methods

2.1. Synthesis of nAg-MWNTs

The nAg-MWNTs were prepared following a previously published method [9–14,16]. As shown in Fig. 1(a), 200 mL of AgNO$_3$ in ethanol (Kojundo Chemical Laboratory Co., Ltd.; AGH07XB; 0.02 mol L^{-1}) was mixed with 2.4 mL of benzyl mercaptan in ethanol (Sigma-Aldrich Corporation; B25401; 0.1 mol L^{-1}) by stirring for 48 h to synthesize Ag nanoparticles (3–5 nm) functionalized with phenyl groups. The phenyl groups enable uniform dispersion and self-assembly of the Ag nanoparticles on the MWNTs through π-π interactions [9–14,16]. In the next step, 100 mg of MWNTs were added in 500 mL of ethanol and ultrasonicated for 20 min (560 W). The major focus of this work was to investigate the effect of crystalline defects and geometry factors of MWNTs on the electrical conductivity of nanocomposites. Five different MWNTs were investigated which were commercially obtained from three different manufacturers (Nanosolution TMC 220-05 batch-1 (MWNT-1), Hanwha Nanotech CMP-330F (MWNT-2), Nanosolution TMC 220-05 batch-2 (MWNT-3), Hanwha Nanotech CM95 (MWNT-4), and Sigma Aldrich 724,769 (MWNT-5)). Note that the nAg-MWNTs in our previous works were synthesized using only MWNT-1 or another different type (Hanwha Nanotech CMP-310F) which is not manufactured anymore [9–14,16]. The MWNT specimens were designated as MWNT-1–5 following an increasing order of the average I_D/I_G value after ultrasonication, as shown in Table 1, and the corresponding Raman spectra of the specimens are shown in Fig. 2. The MWNTs and the Ag nanoparticle suspension were mixed together and bath-sonicated at 200 W for 4 h. The nAg-MWNTs were finally obtained by vacuum filtration (Millipore; 0.2 μm PTFE membrane) followed by ethanol rinsing and vacuum drying for 24 h at room temperature [9–14,16]. The relative weight percentage between Ag nanoparticles and MWNTs was 35:65 [11,14].

Table 1
Properties of five different MWNTs.

Sample	Diameter (nm)	Length (μm)	I_D/I_G (raw)	I_D/I_G (after sonication)
MWNT-1	4–6	5–20	0.22	0.23
MWNT-2	4–7	10–20	0.17	0.24
MWNT-3	4–6	5–20	0.26	0.29
MWNT-4	10–15	10–20	0.78	0.87
MWNT-5	6–9	5	1.08	1.12

2.2. Synthesis of CFA films

The CFA films were synthesized following a previously published

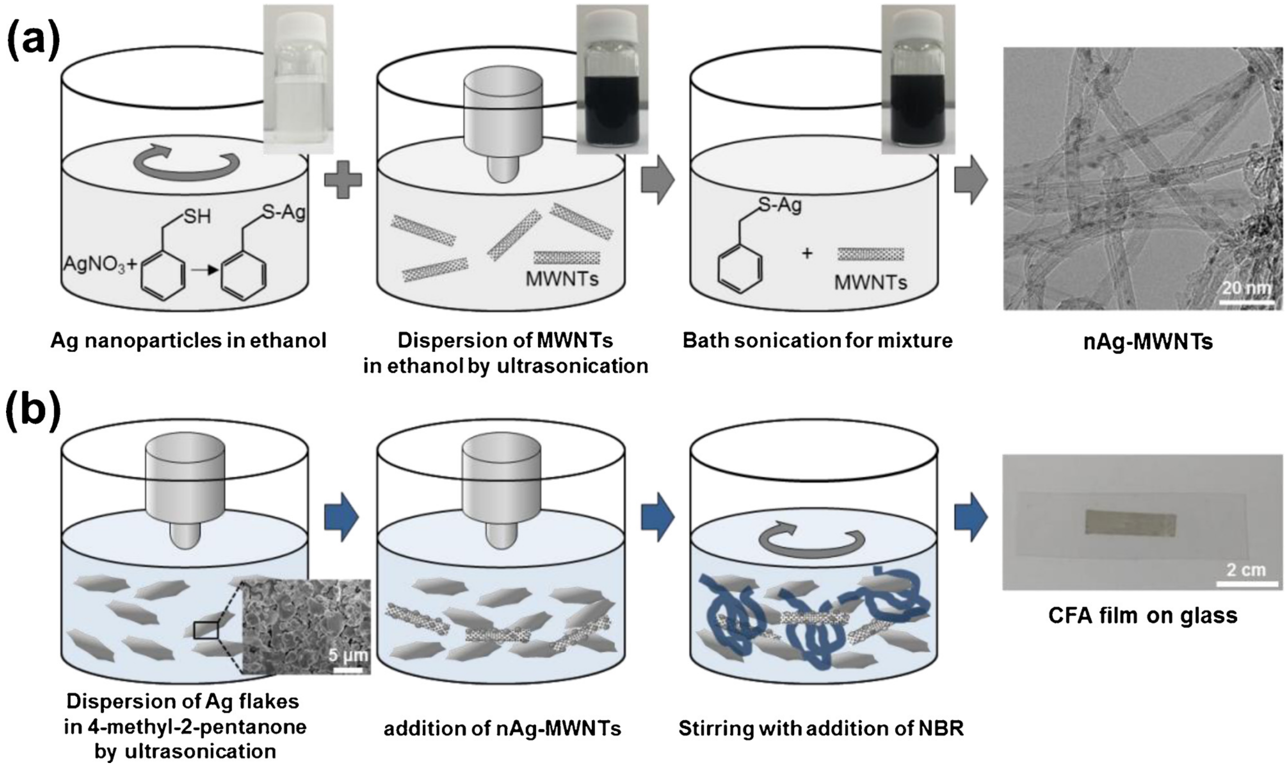

Fig. 1. The nAg-MWNTs and CFA films were synthesized following a previously published protocol [9–14,16]. (a) Schematic of the synthesis process of nAg-MWNTs. Optical images of the specimen are also shown. The HRTEM image of the nAg-MWNTs is shown on the right. (b) Schematic of the synthesis process of CFA films. The inset shows an SEM image of micron-sized Ag flakes. The photograph of the CFA film prepared on the glass substrate is shown on the right.