Composites Science and Technology 121 (2015) 41–48

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Electrical properties and piezoresistive evaluation of polyurethane-based composites with carbon nano-materials

H. Souri [a], I.W. Nam [b], H.K. Lee [b, *]

[a] Carbon Convergence Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, San 101, Eunha-ri, Bongdoung-eup, Wanju-gun, Jeollabuk-do, 565-905, South Korea
[b] Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon, 305-701, South Korea

ARTICLE INFO

Article history:
Received 2 August 2015
Received in revised form
30 October 2015
Accepted 2 November 2015
Available online 10 November 2015

Keywords:
Carbon nanotubes
Expanded graphite
Graphite nanoplatelet
Three-roll milling process
Electrical characteristics
Piezoresistivity
Polyurethane
Composite

ABSTRACT

The present study assesses the applicability of carbon materials-embedded polyurethane (PU) composites characterized by high piezoresistive capability, as a traffic loading sensor. PU composites incorporating multi-wall carbon nanotubes (MWNTs), expanded graphite (EG), and a hybrid of MWNTs and graphite nanoplatelets (GNPs) were fabricated and their electrical conductivities were measured in an effort to determine the most suitable filler type for the piezoresistive sensor and its optimum content ratio. The best electrical characteristics were achieved by the MWNT/PU composites as exhibiting the percolation threshold at 5 wt.% of MWNT and the maximum electrical conductivity of 0.33 S/m at 7 wt.%. Accordingly, the MWNT/PU composites were prepared as a piezoresistive sensor, and its sensing capabilities and durability were examined by three different tests, i.e., lab-scale loading, vehicular loading, and cyclic wheel loading tests. The composite with MWNT 5 wt.% showed the best sensing capability in terms of the electrical resistance change rate obtained from the lab-scale and vehicular loading tests. In addition, the cyclic wheel loading test demonstrated that the 5 wt.% MWNT-embedded PU composite was durable during 2000 cycles of the wheel loading.

1. Introduction

Fabrication of polymer-based composites is considered as a critical area of current nanotechnology and composite science due to their multi-functionalities and remarkable mechanical, electrical, and thermal properties as well as other useful attributes [1]. In particular, the use of polymer-based composites embedded with micro/nano-scaled carbonic materials has attracted the interest of researchers owing to their diverse applications in the automotive, aerospace, construction, and electronic industries [2,3]. In recent decades, the demands for lower percolation threshold of conductive composites have motivated researchers to employ highly conductive carbonic fillers [2]. In particular, the addition of CNTs to polymeric matrices not only provides composites with high electrical conductivity, but also alters the electrical resistance under applied load/strain, a phenomenon known as piezoresistivity [4,5].

In the past few years, the electrical conductivity of composites has been extensively researched and the percolation threshold obtained from less than 1.0 wt.% to over 10.0 wt.% of filler loading. For instance, Chen et al. (2001) prepared a EG/Polymethyl methacrylate (PMMA) composite by the *in-situ* polymerization method, which showed the percolation threshold at 3.5 wt.% of EG loading [6]. Jiang et al. (2005) reported maximum electrical conductivity of 10 S/m at 7.4 wt.% of multi-walled CNTs (MWNTs) and 0.3 wt.% as the percolation threshold for MWNT/polyimide (PI) composites prepared by an *in-situ* polymerization method [7]. Moreover, Yu and Li (2008) obtained the percolation threshold of a GNP/polyvinyl alcohol (PVA) composite made by solution casting method at 4 wt.% of GNP loading whereas the peak value of electrical conductivity was 10^{-5} S/m at 7 wt.% of GNP content [8]. McNally et al. (2005) fabricated a polyethylene (PE) matrix containing 10 wt.% of MWNTs using melt blending method which showed maximum conductivity as high as 10^{-3} S/m and the percolation threshold at 7.5 wt.% [9]. Furthermore, She et al. (2007) manufactured a PE composite incorporating modified EG which showed the percolation threshold at 5.7 wt.% of EG loading and the maximum electrical conductivity value of the composites was as high as 10^{-1} S/m at 8 wt.% [10].

* Corresponding author.
E-mail address: leeh@kaist.ac.kr (H.K. Lee).

http://dx.doi.org/10.1016/j.compscitech.2015.11.003
0266-3538/

Recently, CNT-embedded polymer composites have been frequently used as piezoresistive sensors since CNT exhibited promising merits such as low percolation threshold, notable piezoresistive characteristics, and so forth [11,12]. For instance, Kang et al. (2009) reported that 0.05 wt.% of single-wall CNTs (SWNTs) addition in a PI matrix showed a 2% electrical resistance change under tensile stress of 16 MPa, while the electrical resistance of a 10 wt.% MWNT/PI system changed up to 0.35% under the same loading conditions [13]. Also, Wichmann et al. (2009) studied the piezoresistive response of epoxy-based composites with MWNTs and CB under a tensile load and reported the electrical resistance change rate from 7 to 12% as the MWNT loading was increased from 0.1 to 0.5 wt.% [14].

However, few studies in the literature focused on comparison of electrical properties of composites incorporating various carbon fillers and determination of the percolation threshold of the composites to ascertain the optimum filler content leading to the maximum electrical resistance change rate of piezoresistive sensors [15]. There also exists a lack of research in the literature in which three-roll milling machine technique, which is fast, simple, and compatible with standard industrial techniques, was used to fabricate MWNT/PU composites as well as EG and hybrid of MWNT and GNP embedded PU composites. In addition, experimental studies to examine the piezoresistive response of MWNT/PU composites subjected to external loads and their applicability as traffic loading sensors were scarce.

In this study, the electrical properties and the percolation threshold of MWNTs, EG, and a hybrid of MWNT and GNP-embedded polyurethane (PU) composites fabricated with a three-roll milling process were investigated. Subsequently, the piezoresistive characteristic of the MWNT/PU composites, which showed a low percolation threshold, was studied through lab-scale loading tests. In the specimen fabrication, PU was adopted as the matrix material due to its excellent properties such as abrasion resistance, UV durability, high hardness and impact resistance, etc., which make this material an excellent choice to be used in a wide range of civil engineering applications such as coating on pipelines, roofs and floors, and suitable choices for fabricating sensors [16–18]. Subsequently, the piezoresistive characteristic of the MWNT/PU composites, which showed low percolation threshold, was studied through lab-scale loading tests.

2. Specimen preparation

In the present study, chemical vapor deposition (CVD) growth MWNTs were purchased of Hyosung Inc. (M1111). The purity and diameter of the MWNTs were 96.6% and 12.29 ± 2.18 nm, respectively. Acid washed graphite flakes were provided by Asbury Carbons Inc. (Item number 3772) as the source material to produce EG and GNPs. PU consisted of PF-359 and E-145 and was supplied from Kangnam Hwasung Chemical Co. Ltd. Toluene was used as a solvent for the two-component PU in an effort to make low viscous composite mixtures.

In order to produce EG, the acid-washed graphite flakes were heated to 1050 °C for 30 s with the aid of a furnace [19]. To obtain GNPs, EG was ultrasonicated in acetone using a high power bath-type sonicator for 8 h [19]. Subsequently, the GNPs were filtered by a filter paper and dried at room temperature. All experiments were conducted at room temperature.

A variety of conductive filler contents were employed in order to investigate the electrical conductivity behavior of various types of composites. The MWNT ratios ranged from 4 to 8 wt.% of the total amount of two components of PU whereas the EG ratios were from 3 to 7 wt.%. Moreover, in the case of the hybrid of MWNT and GNP embedded PU composites, the weight fraction of each filler ranged from 2 to 5 wt.% of the total PU. The ratio of toluene was approximately 5 wt.% of the total PU. On the other hand, MWNT loadings of 5, 6, and 7 wt.% of the total PU were chosen to fabricate the piezoresistive sensors (Table S1, Supplementary information).

The specimen preparation can be explained as follows: a specified amount of each component of PU was measured and poured into a steel bowl. Afterwards, the carbon nano-materials including MWNT, EG, and a hybrid of MWNT/GNP were measured according to the mix proportions in Table S1. These were thoroughly mixed with the mixture of the two components of PU for 2 min. In this stage, toluene was added to the mixture in order to reduce the viscosity of the mixture. It is noteworthy to say that the viscosity of the mixture has to be low so that it will be feasible to use a three-roll milling machine to manufacture the composites. After the mixture was pre-mixed, the three-roll milling machine (EXAKT80S, EXAKT Technologies Inc., Germany) was used to achieve a better dispersion quality of MWNT, EG, and hybrid of MWNT/GNP in the fabricated composites (Fig. S1 (a)) [20]. The mixture was poured into the three-roll milling machine where the parallel rollers rotated at a rate of 200 rpm [20]. Note that the gap size between the rollers was 5 μm for the MWNT/PU composites, but it was increased for other types of composites due to the size of carbon materials used. This mixing process was performed five times for each batch [20]. During this process, the fillers within premixed mixtures could be more dispersed with the aid of the shear force applied by the rotating rollers. A schematic illustration of this process is shown in Fig. S1 (b). In the middle of the process, toluene was mostly eliminated from the mixture. Afterwards, the final mixture was poured into a 2.5 × 2.5 × 2.5 cm^3 plastic mold to shape the cubic specimens.

Silver paste was applied to two surface sides facing each other in the specimen as electrodes when the DC conductivity of the composites was examined. Two copper electrodes coated with silver paste with a size of 1 cm in width, 3.5 cm in length, and 0.5 mm in depth were embedded with a spacing of 8 mm in the MWNT/PU composite specimens to evaluate their piezoresistivity (Fig. S2). Due to the use of fast curing PU, all specimens were removed from the mold after a day of curing at room temperature.

3. Test methods

3.1. Electrical conductivity

The direct contact method was chosen to measure the DC resistance of the composites. In this method, the two probes of a digital multi-meter (Agilent Technologies 34410A) were brought into contact with two opposite sides of the specimen, where each side was coated with silver paste in order to make better contact. All measurements were conducted at room temperature.

The DC conductivity σ (S/m) of the composites was calculated by Ohm's law by plugging the obtained resistance values into the following equation [21,22]:

$$\sigma = \frac{1}{\rho} = \frac{1}{R}\frac{L}{A} \tag{1}$$

where ρ (ohm·m), R, L, and A denote the DC resistivity, DC resistance, the distance of the two opposite sides of the specimen, and the cross sectional area of composite specimen, respectively [21,22].

3.2. Piezoresistivity

In the present study, the DC resistance change of the composite specimens under compressive loading was measured using a two-