

Interdigitated electrodes (IDE) using elastomer functionalized multi-walled carbon nanotube (MWNT) nanocomposites for the detection of oil spills

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Abstract. IDE using elastomer functionalized MWNT nanocomposites was fabricated and applied for the oil sensor. Two types of nanocomposites (i.e., MWNT-grafting-polyisoprene and Si-MWNT/natural rubber) having elastomer content of ~70 wt% were used as a sensing material of oil sensor and the relative electrical resistance response of the sensor to three different kinds of oils (i.e., gasoline, engine oil and pump oil) was investigated. Among three kinds of oils, the response of MWNT-grafting-polyisoprene nanocomposites IDE sensor to gasoline was the most significant. It showed the maximum relative electrical resistance of 18 within 20 min of dropping of 200 μ L gasoline at room temperature for the MWNT-grafting-polyisoprene nanocomposites, which is far superior in sensitivity to the experimental results reported by Ponnammam et al in 2016 [1]. On the other hand, the response of Si-MWNT/natural rubber nanocomposites IDE sensor to gasoline was not appreciable. The elastomer functionalized MWNT nanocomposites prepared by “grafting-from” method, which is MWNT-grafting-polyisoprene in this study, is an excellent candidate material for the detection of oil spills.

1. Introduction

Accidents involving tankers, cargo ships, offshore platforms or drilling rigs and wells result in the release of significant amounts of crude oil and then it leads to the severe environmental disaster caused by soil and marine pollution. Oil spills can be controlled by expensive and time-consuming remedies such as chemical dispersion, combustion, mechanical containment and/or adsorption. However, monitoring oil spills with the help of sensing devices is the first step to ensure regulatory compliance. A lot of researches on oil sensors have been reported based on the measurements of UV fluorescence, IR reflection, ultrasonic, light scattering, electromagnetic absorption, conductivity, capacitance and other properties. These sensor devices have problems such as large size, large energy consumption, low sensitivity and high cost. Therefore, reliable and inexpensive oil sensor operating at room temperature needs to be developed.

There are noted three interesting research reports using electrically conductive elastomer nanocomposites of MWNT [1], polyaniline [2] and graphite [3] for the detection of oil spills. It has been known that carbon nanotube (CNT) based polymer nanocomposites are promising material components for the design of smart chemical sensor. Remarkable features of using CNTs in



nanocomposite materials are the quite low percolation threshold (i.e., < 5 wt%) due to the high aspect ratio greater than 1000 and the appearance of excellent reinforcing effect for electrical, mechanical and thermal properties in nanocomposites. An essential prerequisite condition to maximize the material properties while minimizing the amount of CNTs added is the uniform dispersion of CNTs in the matrix without agglomeration caused by the van der Waals interaction forces between them. It has been known that polymer functionalization of CNT surface is an effective strategy for not only providing uniform dispersion but also suppressing the agglomeration of CNTs in polymer matrix. In this study, two different types of elastomer functionalized MWNT nanocomposites, which are MWNT-grafting-PI (polyisoprene) by “grafting-from” method and Si-MWNT/NR (natural rubber) by “grafting-to” method, were prepared and applied for oil sensor. It is the first experimental study on the IDE sensor using elastomer functionalized MWNT nanocomposites for the detection of oil spills, which has never been reported so far.

2. Experimental

2.1. Preparation of elastomer functionalized MWNT nanocomposites

Figure 1 shows the schematic procedures for the preparation of MWNT-grafting-PI by “grafting-from” method and Si-MWNT/NR by “grafting-to” method. The application of the activators regenerated by electron transfer for atom transfer radical polymerization (ARGET-ATRP) process [4] regarding the “grafting-from” method and the covalent bonding of NR to the silane treated MWNT [5] regarding the “grafting-to” method was made in this study.

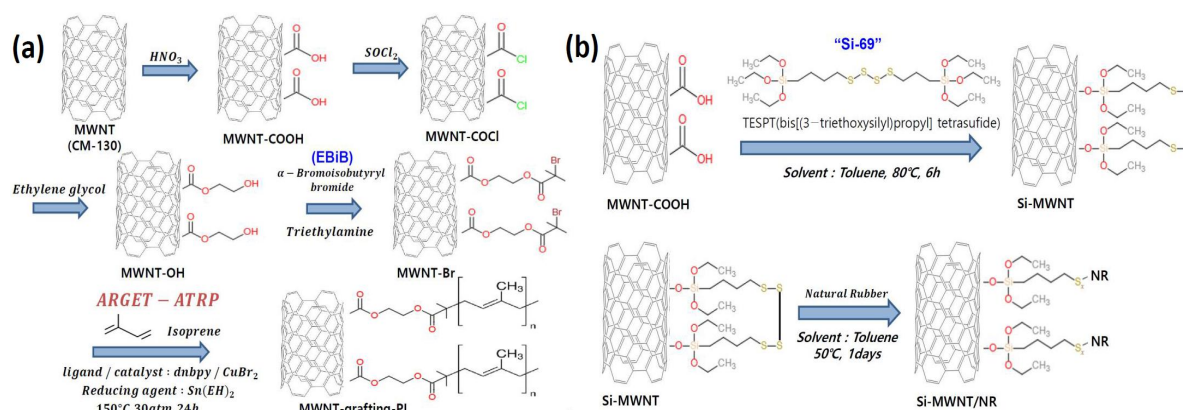


Figure 1. Preparation flow of elastomer functionalized MWNT nanocomposites: (a) “grafting-from” method and (b) “grafting-to” method.

It was tried the preparation of PI functionalized MWNT nanocomposites (MWNT-grafting-PI) having a maximum content of PI in order to promote the sufficient swelling of PI when being contacted with oil. Characterization of nanocomposites was carried out by the application of thermogravimetric analyser (TGA) and vibrational viscometer, and also the C-Br content of MWNT-Br sample was estimated by the application of specific peak area analysis tool (e.g., “Origin-Polygon Area”) regarding the corresponding X-ray photoelectron spectroscopy (XPS) spectrum.

2.2. Fabrication of IDE device and its application for oil sensor

A fabrication flow of IDE device and the working principle of oil sensor are schematically shown in figure 2. Pattern deposition on the glass substrate was carried by using indium as a metal source and the fabricated IDE pattern showed the electrode width of 300~350 μm and the electrode spacing of 250~270 μm . It was investigated the response of elastomer functionalized MWNT nanocomposites IDE sensor to three different kinds of oils, which are automotive fuel (i.e., gasoline), automotive engine oil (i.e., 5W30) and rotary pump oil (MR-100, Moresco). The electrical resistance measurements were performed with the electrometer (Keithley 6517B) in two electrode mode.

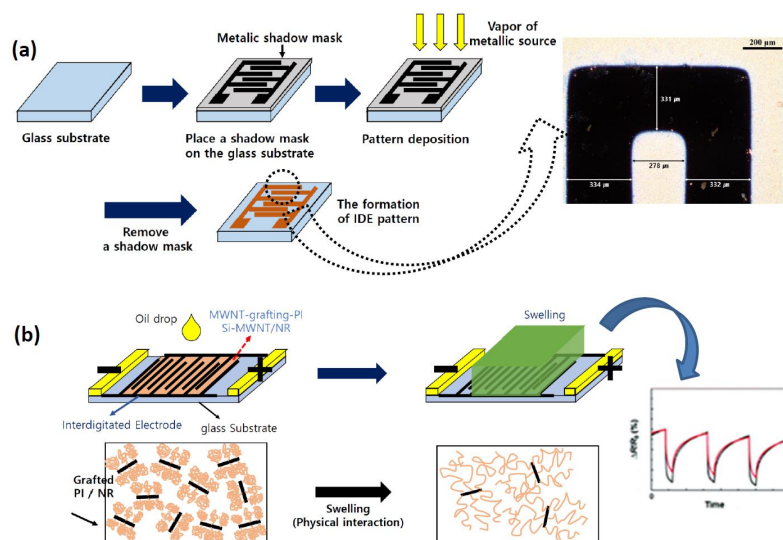


Figure 2. (a) Fabrication flow of IDE device and (b) working principle of IDE oil sensor using elastomer functionalized MWNT nanocomposites.

3. Results and discussion

Figure 3 shows how to control the elastomer (i.e., PI) content in MWNT-grafting-PI nanocomposites by using the combined analysis of TGA, viscometer and XPS.

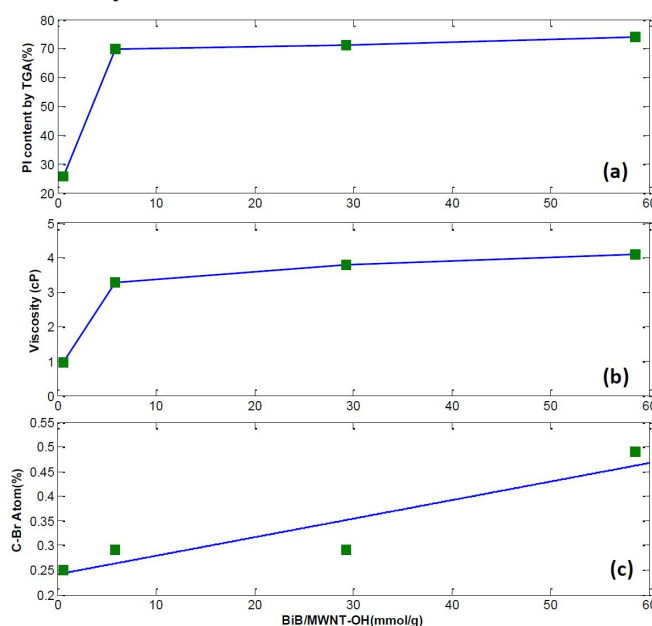


Figure 3. Variation of PI content by (a) TGA and (b) viscosity regarding MWNT-grafting-PI nanocomposites and also (c) C-Br Atom% of MWNT-Br depending on the BiB content based on the weight of MWNT-OH sample.

The MWNT-Br intermediate is used as an initiator and it reacts with isoprene, and then it leads to the preparation of MWNT-grafting-PI nanocomposites by the application of ARGET-ATRP process ("grafting-from" method). The MWNT-Br intermediate is prepared by the reaction of MWNT-OH intermediate with α -bromoisobutyryl bromide (BiB), and therefore the amount of C-Br bonds present in MWNT-Br can be controlled by the variation of the ratio of BiB to MWNT-OH, which is

[BiB]/[MWNT-OH] (mmol/g). The Br element covalently bonded to MWNT is used as a polymerization site of isoprene and thus it can be made a theoretical anticipation of the higher C-Br atom(%) value the larger polymerization yield. Figure 3-(c) shows a linear dependence of C-Br atom(%) value on the increase of [BiB]/[MWNT-OH]. However, both the PI content by TGA (figure 3-(a)) and the viscosity value by viscometer (figure 3-(b)) show a plateau state above 5.86 of [BiB]/[MWNT-OH]. In the experimental condition of this study, the PI functionalized MWNT nanocomposites (MWNT-grafting-PI) having more than 70 wt% of PI content were successfully prepared.

The preparation of NR functionalized MWNT nanocomposites (Si-MWNT/NR) was made by the application of “grafting-to” method and the NR content was adjusted to ~70 wt% using the TGA analysis based on the residual weight percent at a specified temperature. The quantitative estimation of elastomer content in the nanocomposites prepared in this study was made using TGA thermograms of MWNT-grafting-PI and Si-MWNT/NR shown in figure 4.

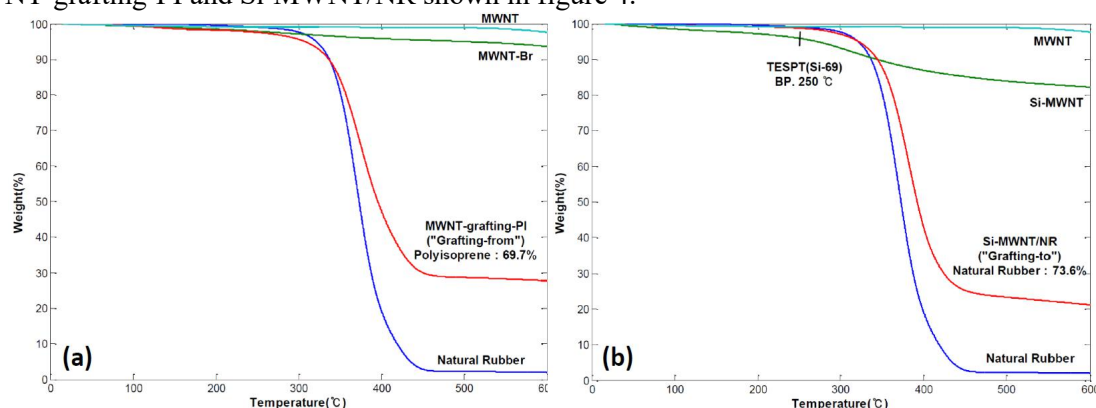


Figure 4. TGA thermograms of (a) MWNT-grafting-PI and (b) Si-MWNT/NR.

It was made the investigation of response of elastomer functionalized MWNT nanocomposites IDE sensor to the exposure of a specified amount of oil drop and the experimental results are shown in figure 5.

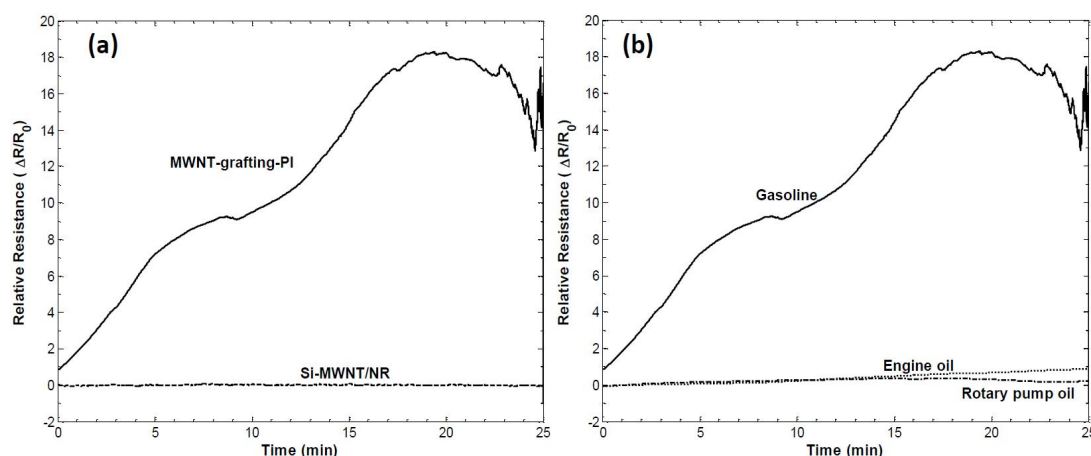


Figure 5. Response of (a) elastomer functionalized MWNT nanocomposites IDE sensor to gasoline and (b) that of MWNT-grafting-PI nanocomposites IDE sensor to three different kinds of oils.

Two types of composites showed quite different sensor responses in figure 5-(a). The relative electrical resistance, which is defined by the equation of $\Delta R(=R-R_0)/R_0$ in this study, for the PI functionalized MWNT nanocomposites (MWNT-grafting-PI) steadily increased with the oil exposure time and reached the maximum level of ~18 at 19 min of oil dropping of 200 μ L gasoline. Ponnamm

et al [1] reported the response of relative electrical resistance for the MWNT-filled NR composites prepared by a solution mixing of MWNT and chloroform to hydraulic oil, in which the maximum relative electrical resistance value was less than 1.3 at 15 min. The relative electrical resistance response for the NR functionalized MWNT nanocomposites (Si-MWNT/NR) was marginal showing less than 0.03. It reveals that the elastomer functionalized MWNT nanocomposites prepared by the “grafting-from” method provide far superior sensor sensitivity in detecting oil spills to the nanocomposites prepared by the “grafting-to” method, which could be ascribed to the relatively uniform dispersion and distribution of MWNTs in elastomer (polyisoprene).

Figure 5-(b) shows the relative electrical resistance response of MWNT-grafting-PI IDE sensor to three different kinds of oils. It is noted that the sensitivity to gasoline is the most noticeable among them and therefore the MWNT-grafting-PI IDE sensor represents the excellent sensor selectivity in detecting gasoline.

4. Conclusions

It is certainly feasible developing a reliable and inexpensive oil sensor operating at room temperature to prevent a catastrophic disaster caused by the oil spills involved in marine accidents. A practical strategy suggested in this study is the utilization of the elastomer functionalized MWNT nanocomposites as a sensing material for the detection of oil spills along with IDE device, and also the nanocomposites need to be prepared by “grafting-from” approach in order to obtain the uniform dispersion and distribution of MWNT in elastomer. How to maximize the PI content in PI functionalized MWNT nanocomposites (MWNT-grafting-PI) was proposed and the estimated content of PI was 69.7 wt% based on the TGA thermogram. The MWNT-grafting-PI nanocomposites IDE sensor showed not only the quite significant relative electrical resistance response to gasoline but also the outstanding sensor selectivity for gasoline among three different kinds of oils.

Acknowledgement

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