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Effects of the functionalized graphene oxide on the oxygen barrier and mechanical properties of layer-by-layer assembled films

Seon-Guk Kim [a, d], Nam-Ho You [a], Wonki Lee [a], Jun Yeon Hwang [a], Myung Jong Kim [a, b], David Hui [c], Bon-Cheol Ku [a, b, **], Joong Hee Lee [d, e, *]

[a] Institute of Advanced Composites Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bondong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea
[b] University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 305-350, Republic of Korea
[c] Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA
[d] Department of BIN Convergence Technology, Chonbuk National University, Baekje-daero 567, Duckjin-Gu, Jeonju, Jeollabuk-do 561-756, Republic of Korea
[e] Department of Polymer-Nano Science and Technology, Chonbuk National University, Baekje-daero 567, Duckjin-Gu, Jeonju, Jeollabuk-do 561-756, Republic of Korea

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A B S T R A C T

An effective method to fabricate high-performance oxygen gas barrier films by alternately stacking negatively charged graphene oxide (GO) and positively charged aminno-ethyl-functionalized GO (AEGO) on PET substrates was suggested. The GO was prepared by the Hummer's method using natural graphite powder and the AEGO was synthesized by a carbodiimide reaction of the GO. High resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the introduction of functional groups of GO and AEGO. GO/AEGO/GO layers on a PET film were formed through spray coating method. The gas barrier and mechanical properties of the film were examined. One layer of GO/AEGO/GO stacked film coated on a PET substrate showed an oxygen permeability of 0.01 cc/m^2 day atm, which is 10^3 times lower than that of pure PET. The results corresponding to tensile strength and modulus of the film revealed an increase of approximately 61 and 41% compared to those of pure PET, respectively.

1. Introduction

Graphene has a honeycomb lattice structure of *sp*^{2}-bonded carbon atoms and is one of carbon allotropes consisting of a two-dimensional sheet of carbon atoms with a thickness of 0.3–0.34 nm [1–3]. Chemical vapor deposition (CVD), and chemical exfoliation using natural graphite are considered as the main routes to produce graphene [4–10]. Its large surface area and excellent mechanical, thermal and electrical properties compared to other nanomaterials such as clay, carbon nanotubes (CNTs), and graphite have attracted much of interests in polymer composites [8]. Accordingly, there have been lots of attempts to develop polymeric composites or surface coating using graphene [5,6]. Graphene can be served as a gas barrier filler while it is planar direction as a result of deposition on substrates due to its high aspect ratio and planar structure. It forms a 'tortuous path' for gas permeation and thus will increase the gas path length, leading to enhanced gas barrier properties [7–10].

A great number of research works has shown the superior functionality of graphene-based hybrid composites compared to the individual components [11–13]. Therefore, in order to design novel functional materials to be applicable in various fields such as sensors, supercapacitors, solar cells, lithium ion batteries, electrodes, drug carriers, gas barriers, field-effect transistors, graphene-based composites are highly desired.

However, the main problem with many graphene-based composites has been their highly disordered structure, which causes some difficulties in reproducing their performance as well as studying the effect of each component on a specified device

* Corresponding author. Department of BIN Convergence Technology, Chonbuk National University, Baekje-daero 567, Duckjin-Gu, Jeonju, Jeollabuk-do 561-756, Republic of Korea. Tel.: +82 63 270 2342; fax: +82 63 270 2341.

** Corresponding author. Institute of Advanced Composites Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bondong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea. Tel.: +82 63 219 8132; fax: +82 63 219 8139.

E-mail addresses: cnt@kist.re.kr (B.-C. Ku), jhl@chonbuk.ac.kr (J.H. Lee).

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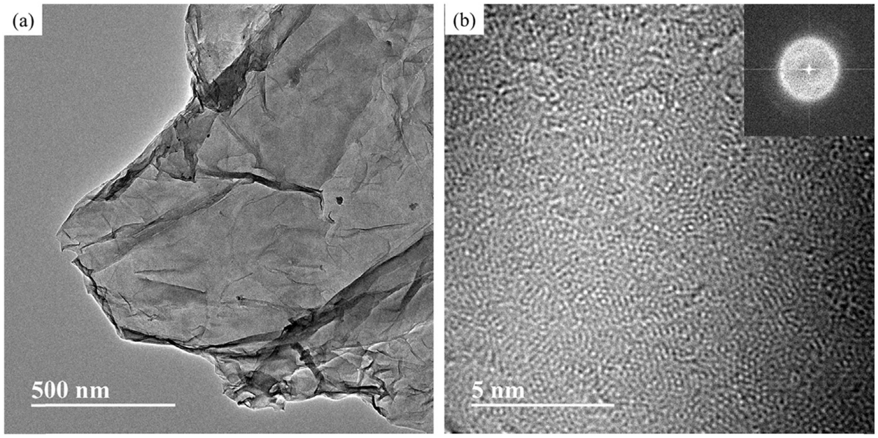

Fig. 1. (a) TEM image of AEGO sheets, and (b) higher magnification of aberration corrected-TEM image in the multi-layer AEGO; the inset shows the Fast Fourier Transform.

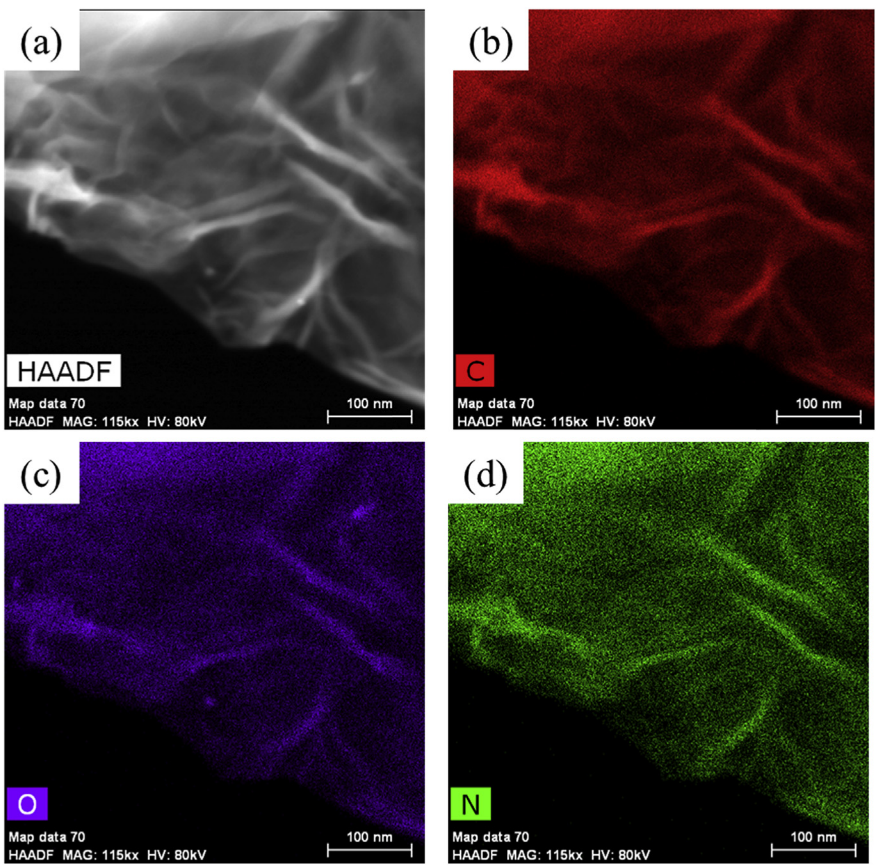

Fig. 2. (a) Scanning transmission electron microscopy (STEM) image of the high angle annular dark field (HAADF) detector in a ROI. EDX quantification mapping images of AEGO sheets (b) C–K edge atomic counts, (c) O–K edge atomic counts and (d) N–K edge atomic counts.

Table 1
The EDX quantification data table of K-factor method.

Atomic-% (norm.)	Area (counts)	C–K	N–K	O–K
ROI	260,608	90.2	3.86	5.94

characteristic. Among the techniques for fabricating films by polymer–graphene combination, layer-by-layer (LbL) assembly method is widely used in industries, due to being simple and advantageous in fabricating multi-layered high strength thin films [14]. The thickness of the layer of LbL assembly can also be adjusted at nanometer level by using various types of intermolecular attractions including electrostatic interactions, hydrogen bonds and covalent bonds [15–18]. Furthermore, LbL method can be used to fabricate very stable multilayer thin films regardless of substrate size and morphology. However, the thickness, and gas permeability of the fabricated films are sensitive to the fabrication process factors such as filler concentration, temperature, pH value of the solution, and deposition time in the LbL process [17–21].