Moisture Barrier Composites Made of Non-Oxidized Graphene Flakes

Jungmo Kim, Sung Ho Song, Hyeon-Gyun Im, Gabin Yoon, Dongju Lee, Chanyong Choi, Jin Kim, Byeong-Soo Bae, Kisuk Kang, and Seokwoo Jeon*

With the phenomenal rise of flexible electronics, the demand for flexible encapsulation layers with high-performance is growing rapidly. Consequently, researchers have developed various strategies to effectively block oxygen and moisture, while providing the flexibility required for the targeted applications. The most widely used approaches are multiple stacking of alternating inorganic and organic layers, and fabricating polymer composites with impermeable fillers. While the multiple-stacked layers exhibit the best barrier properties, the expensive cost, low processability, and the degradation due to defect formation limit their application. On the contrary, polymer composites are cost-effective, easy to produce, and suitable for long-term use. Despite the advantages, the low barrier performances of the composites need significant improvement. Efforts to solve this issue, especially by using fillers with high aspect ratios (i.e., clays, cellulose platelet), have been successful for blocking oxygen, but have been less successful in blocking moisture.

Recently, graphene flake (GF) has been studied as a promising candidate for the filler material owing to its extremely high aspect ratio and perfect molecular impermeability even to helium. Because of their easy production in large quantity, initial researches focused mostly on the incorporation of graphene oxide (GO) or reduced graphene oxide (RGO) flakes into the polymer matrices (i.e., polyurethane, EVOH, polyimide, etc.). Unfortunately, those composites show only limited enhancement of moisture barrier properties, recording water vapor transmission rate (WVTR) of 1.3 g m⁻² day⁻¹ at best. The reason for this could be the innate defects of GO and RGO, bonded with hydrophilic functional groups, which act as permeation paths for the H₂O molecules in both in-plane and transplanar directions. Therefore, low defect GFs with minimal oxidation can be a solution to fully utilize the potential of the GFs as the filler material in the barrier composites.

In this work, we demonstrate improved moisture barrier property of polyethylene (PE) composite, approaching the theoretical value, by incorporating non-oxidized graphene flakes (NOGFs) synthesized through a facile and simple method. To date, NOGFs have been produced through several approaches: exfoliation from pristine graphite, unzipping of carbon nanotubes, and exfoliation from the graphite intercalation compounds. However, their applicability is often limited due to small flake sizes, usually in sub-micrometer level, and poor dispersion in the target solvents without proper functionalization. In the recent method, the fabrication of NOGFs in micrometer scale (over 1 µm in size) and their functionalization were simultaneously achieved by introducing solvothermal intercalation of an organic solvent, quinoline. Partial intercalation of quinoline molecules promoted exfoliation efficiency by lowering the interlayer binding energy of graphite by 30 meV, calculated from density functional theory (DFT)-based simulations. Compared to NOGFs produced solely from sonication, the produced NOGFs had increased average size while exhibiting high crystallinity and extremely low oxidation, comparable to that of source graphite. Moreover, the conjugated nature of quinoline resulted in stable non-covalent functionalization of the NOGFs whose zeta potential is ~20 mV, large enough for uniform dispersion with increased hydrophobicity in the matrix polymer.

The low defect NOGFs with minimal oxidation and high hydrophobicity are ideal as nanofillers for moisture barrier composite. The WVTR of PE–NOGF composite film with a 1 wt% loading compared to the pristine PE film and the PE–GO composite film of similar loading showed a reduction of the WVTR of 58% and 37.5%, respectively. The measured WVTR value of PE–NOGF was 1.2 × 10⁻¹ g m⁻² day⁻¹, which is an order of magnitude lower than the previously reported value for polymer–graphene composites. The superior material property of NOGFs, interestingly, made the PE–NOGF composite match the theoretical performance.
predicted by the Cussler model,[31] which could not be achieved when GO was used. These results shed light on the future potential of NOGFs as filler materials in the encapsulation layers of flexible electronics.

The overall schematic diagram showing the fabrication of PE–NOGF composite is laid out in Figure 1. When the mixture of quinoline and graphite is heated in the solvo-thermal vessel, the internal pressure is heightened due to the increased vapor pressure, leading to the partial intercalation of quinoline molecules into the interlayers of the immersed graphite (Figure 1a, 1b). The X-ray diffraction (XRD) data in the inset of Figure 1c show the rise of additional peaks at 2θ values of 12.3°, 19.5°, and 21.3°. These peaks correspond to the increased interlayer distances due to the intercalation and partial distortions of the layered structure.[32] A comparison with the XRD data of quinoline–graphite mixtures indicates that the additional peaks are induced only after the solvothermal reaction. The calculation results from DFT simulations show that the intercalation of quinoline molecules lowers the interlayer binding energy by 30 meV (Figure 1c, simulation details are provided in the Supporting Information). In theory, the binding force scales roughly to \(d^{-6}\), where \(d\) is the interlayer distance, thus the interlayer energy should decrease over 50 meV. It is predicted that the charge transfer interaction between the quinoline molecule and the graphene layers reduces the effect of interlayer expansion. However, the generated Columbic force is weak enough to be overcome, and thus the partial intercalation aids the exfoliation of the graphene layers by promoting the function of the quinoline molecules as the “molecular wedge.”[33,34] Figure 1d shows the quinoline–NOGF solution and the scheme of the exfoliated NOGFs after sonication (30 min). It should be noted that the intercalation of quinoline itself does not fully exfoliate the GFs from graphite, and that a brief sonication process is required for the exfoliation. The atomic force microscopy (AFM) analysis for the sample before sonication (Figure S1, Supporting Information) proves that only thick graphitic flakes with thickness of over 15 nm were produced before the sonication step. One of the major advantages of this process is that the exfoliated NOGFs are noncovalently functionalized in situ by the quinoline molecules. This enables the functionalized NOGF to be re-dispersed in other organic solvents without aggregation (Figure 1e). The re-dispersed NOGFs were fabricated into the PE–NOGF composite film through solution-mixing with PE, followed by hot-pressing (135 °C under 50 kg cm\(^{-2}\)). The measured dimension of the PE–NOGF film was approximately 5 cm × 5 cm × 100 µm (Figure 1f). (See details in Experimental section and Supporting Information).

The morphology and the structural properties of the produced NOGFs were analyzed. Figure 2a is a representative AFM topography image of a NOGF. The flake shows the lateral size of 4 µm and the height of 1.7 nm, which corresponds to the height of a tri-layer graphene.[35–37] The AFM images of NOGFs with different number of layers are shown in Figure S3 (Supporting Information). The distribution of the number of layers verifies that over 75% of the produced flakes are less than 10 layers thick (Figure 2b), and over 50% of the flakes show a lateral size over 1 µm (Figure S4, Supporting Information). In comparison, the majority of the GFs
produced without the solvothermal process have sizes below 500 nm, validating the effectiveness of the solvothermal process. The transmission electron microscopy (TEM) image in Figure 2c also shows that monolayer NOGF with the lateral size up to 10 µm was produced. The flake was verified as monolayer through observing the fringe pattern at the edge of the flake via high-resolution TEM (Figure S5, Supporting Information). Moreover, the hexagonal pattern from the FFT data in Figure 2c (inset) shows that the crystallinity of the NOGF is not degraded after the treatment, which complies with the Raman mapping in Figure 2d. The mapping data were fitted to show $I_D/I_G$ ratio, which is regarded as the defect ratio of graphene. The $I_D/I_G$ ratio at the basal plane of NOGF showed the maximum of only 0.1, which is significantly lower than that of GO (Figure 2e). The small rise of the D peak is mostly due to the effects from the edges of residual quinoline molecules and the small flakes stacked on the top of the NOGFs. The extremely low defect ratio correlates to the low oxidation content of the NOGFs. The extremely low defect ratio correlates to the low oxidation content of the NOGFs. The result shows blue shifts in G peak and 2D peak, and down-shift in 2D peak, which is regarded as the evidence of p-doping in GFs by non-covalent functionalization. The same shifts are observed when the mechanically exfoliated GFs are functionalized with quinoline (Figure S7, Supporting Information), which again proves the existence of charge interaction between the non-covalently bonded quinoline molecules and the graphene. The UV–vis spectroscopy result in Figure 3b further confirms the functionalization by showing the $\pi-\pi^*$ excitation peak of quinoline at 314 nm in Q-NOGF, and, the characteristic peak of the asymmetrical C=N=C bonding (near 1560 cm$^{-1}$) for quinoline is detected in the Fourier-transform infrared (FT-IR) spectroscopic analysis of Q-NOGFs (Figure S8, Supporting Information). The thermogravimetric analysis (TGA) data in Figure 3c show that the weight loss of the Q-NOGF is approximately 11.4 wt% in the region of quinoline sublimation, which is deduced by comparing the weight loss plot with that of the pristine graphene. The region starts after the sharp drop at 100 °C, which corresponds to the vaporization of the captured moisture in the sample, and ends near 600 °C, where the decomposition of GFs begins. The main role of the functionalization is to prevent the aggregation of NOGFs in various organic solvents through formation of negative charges on the surface of the NOGFs. Figure 3d shows that Q-NOGFs exhibit moderate zeta potential near $-20$ mV in both acetone and methanol, thus leading to a stable dispersion. Another important role of quinoline functionalization is increased hydrophobicity. The contact angle measured from the functionalized NOGF film is 114.8°, which is significantly larger than that of the GO film (Figure 3e, f). Moreover, the surface energy calculated from the contact angle of NOGF film is $42.2 \text{ mJ m}^{-2}$, which coincides with the surface energy of quinoline.
The high hydrophobicity from the functionalization of NOGF improves moisture barrier property through inhibition of in-plane diffusion of H₂O molecules on the NOGFs, and the decrease in the local solubility of moisture in the polymer matrix. It should be noted that the lowered local solubility is related to the hindrance effect, rather than to the overall solubility of the composite, since a sole addition of quinoline in PE matrix did not show any significant effect on the moisture barrier performance.

Figure 4 shows the analysis results for structural characterization and moisture barrier properties assessment of the fabricated PE–NOGF film. As can be seen in the Figure 4a, the fabricated PE–NOGF film maintains the intrinsic flexibility of PE, showing no mechanical deformation after bending with a bending radius below 1 mm. Next, linear relationship found in the UV–vis absorption data of the fabricated PE–NOGF films with different NOGF loading confirms that the uniform dispersion state was preserved within the NOGF loading level tested in this paper (Figure 4b). This was once again verified by analyzing the fracture surface of PE–NOGF composite film via SEM (Figure 4c). It can be seen that the well-dispersed NOGFs are protruding out of the fracture surface. Finally, the moisture barrier performances of the fabricated composite films were tested. Figure 4d,e are the WVTR and the relative permeability of pure PE, PE–GO, and PE–NOGF films at different loading levels. The lowest WVTR value is measured for the PE–NOGF films at 1 wt% loading; recording 1.2 × 10⁻¹ g m⁻² day⁻¹, which is the lowest value reported for a polymer–graphene composite (Figure S10, Supporting Information). The PE–NOGF film shows 58% enhancement in the barrier performance compared to the pure PE film, which is 37.5% of enhancement compared to the PE–GO film. The size distribution of the GO flakes was controlled to match that of NOGFs in order to clearly see the effect of the defects on the WVTR by unifying the aspect ratios of NOGF and GO flakes (Figure S11, Supporting Information). It is also interesting to note that the relative permeability of PE–NOGF film shows close resemblance to the values predicted by the Cussler model (see calculation details in the Supporting Information) while PE–GO film shows large deviation. (Figure 4f) The possible reason for this deviation is the existence of hydrophilic defects in GO. The key assumption in the Cussler model is that the filler materials are perfectly impermeable and have no interaction with the permeating species. The NOGFs used in this research complies with the assumptions due to their extremely low defect ratio, and strong hydrophobicity. On the other hand, GO flakes have numerous defects, which provide fast trans-planar channels of water molecule through the defects even smaller than 1 nm. The GO and RGO flakes also possess various functional groups inducing hydrophilicity on the flake surface for easy diffusion of H₂O that greatly increase chances to arrive at the penetrable channels.

In conclusion, we demonstrated an approach to maximize the potential of GFs as the nanofiller in polymer moisture barrier composites by utilizing NOGFs. The NOGFs were produced through exfoliation from a partial graphite intercalation compound formed by solvothermal intercalation of quinoline. The decreased interlayer binding energy aided the exfoliation of NOGFs resulting in the increased average lateral size from nanometer-scale to micrometer-scale, with extremely low defect ratios and oxygen contents. The NOGFs were also non-covalently functionalized in situ, enabling the stable dispersion in various organic solvents, and allowing the strong hydrophobicity. As the result, NOGFs were uniformly dispersed in the PE–NOGF composite films, and led to the enhanced moisture barrier property, which...
showed the lowest WVTR yet reported for polymer–graphene composite, meeting the theoretical value. The strong possibility of further enhancement through improving the aspect ratio and the alignment of the NOGFs in the polymer matrix positions the NOGFs to be a strong candidate for the nanofillers in the encapsulation layers of flexible electronics.

**Experimental Section**

*Fabrication of Non-Oxidized Graphene Flakes:* Graphite powder (Bay Carbon) was immersed in quinoline (Sigma–Aldrich), and transferred to an autoclave vessel (Parr) for solvothermal reaction at 300 °C for 12 h. The produced partial intercalation compound solution was sonicated for 30 min to obtain NOGF solution. The solution was centrifuged at 3000 rpm for 30 min to remove the partially un-exfoliated GFs. For comparison, GO was synthesized using Hummer’s method,[42] followed by exfoliation in ethanol.

*Characterization of Non-Oxidized Graphene Flakes:* TEM analysis was performed with G2 F30 (Tecnai) at acceleration voltage of 300 keV. Raman spectroscopy and AFM analysis were performed with Senterra system (Bruker) coupled with a customized AFM module. XPS was performed with Sigma Probe system (Thermo VG Scientific) with AlKα radiation source, and the contact angle measurement was performed with Pheonix 300(SEO). UV–vis spectroscopy and FT-IR spectroscopy were, respectively, carried out with UV-3101PC spectrometer (Shimadzu) and FT-IR-4100 type-A FT-IR spectrometer (Jasco). TGA was performed with TG 209 F3 (Netzsch-Gerätebau GmbH) under Ar atmosphere. Zeta potentials of the NOGFs dispersed in acetone, methanol, and ethanol were analyzed with ELS-Z2 (Otsukael).

*Fabrication of Polyethylene–Graphene Composite Film:* The NOGF powder, after washing with methanol, was dispersed in methanol, and then mixed with xylene. Next, the solution was mixed with PE (LLDPE, melt index: 1.0 g/10 min at 190 °C; Sigma–Aldrich) under 140 °C for 12 h. The mixture was then poured into ethanol for coagulation into fibrous form. The obtained fiber was dried and shredded for hot-pressing in a customized mold at 135 °C under 50 kg cm^{-2} of pressure. PE–GO composite was fabricated in the same procedure.

*Evaluation of Polyethylene–Graphene Composite Film:* The fracture surface of PE–NOGF composite film was observed with SEM (S-4800, Hitachi) with a field-emission source at 10 keV. The WVTR of the film (thickness 100 µm) was assessed by using AQUATRAN Model 1 (MOCON) following ASTM protocol F1249. (See further details regarding sample preparation and measurements in Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by the Center for Advanced Soft-Electronics funded by the Ministry of Science, ICT, and Future Planning as Global Frontier (CASE-2013M3A6A5073173), and nanomaterial technology development program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, and Future Planning (2012M3A7B4049807). This work was also supported by the GRC project of KAIST Institute for the NanoCen-
communications

...and funded by LG Display Co., Ltd. The authors give special
thanks to Dr. Dongchin Lee, Dr. Sunghee Cho, and Dr. Jong-Hyun
Park for helpful discussions.

M. Hall, E. Mast, C. Bonham, W. Bennett, M. B. Sullivan, Displays


J. E. Mark, Polymer 2013, 54, 3605.


2010, 10, 4970.

Z. Yan, Z. W. Peng, C. Hwang, G. D. Ruan, E. L. G. Samuel,
P. M. Sudeep, Z. Konya, R. Vajtai, P. M. Ajayan, J. M. Tour, ACS Nano
2013, 7, 10380.


379.


2014, 131, 39628.

1371.

J. M. Parpia, H. G. Craighead, P. L. McEuen, Nano Lett. 2008, 8,
2458.


1015.

G. A. D. Briggs, T. Miyamoto, A. Kano, Y. Tsukahara, M. Yanaka,


[19] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Y. Sun, S. De,
I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun’ko, J. J. Boland,
P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, H. Hutchison,

C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich,
P. May, P. Puczkarshi, I. Ahmed, M. Moebius, H. Petterson,
E. Long, J. Coelho, S. E. Obrien, E. K. McGuire, B. M. Sanchez,
G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing,

458, 877.

[22] D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda,

3504.

[24] C. J. Shih, A. Vijayaraghavan, R. Krishnan, R. Sharma, J. H. Han,
M. H. Ham, Z. Jin, S. C. Lin, G. L. C. Paulus, N. F. Reuel, Q. H. Wang,

2011, 133, 8888.

S. Jeon, Small 2011, 7, 864.

[27] K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Sang,


[29] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim,
6156.


[32] H. Zabel, S. A. Solin, Graphite Intercalation Compounds I: Struc-


[34] X. H. An, T. J. Simmons, R. Shah, C. Wolfe, K. M. Lewis,
M. Washington, S. K. Nayak, S. Talapatra, S. Kar, Nano Lett. 2010,
10, 4295.

[35] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang,
S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306,
666.

F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth,

[37] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, E. D. Williams,

[38] X. C. Dong, D. L. Fu, W. J. Fang, Y. M. Shi, P. Chen, L. J. Li,
Small 2009, 5, 1422.

49, 3660.

1988, 38, 161.

[41] R. R. Nair, H. A. Wu, P. N. Jayaram, I. V. Grigorieva, A. K. Geim,
Science 2012, 335, 442.


Received: December 8, 2014
Revised: February 6, 2015
Published online: