Graphene-based coatings on polymer films for gas barrier applications

Z. Y. Xia¹, M. Christian², S. Ligi³, M. Minelli⁴, V. Morandi², F. Doghieri⁴, V. Palermo¹ and D. Pierleoni^{4*}

¹ Institute of Organic Synthesis and Photoreactivity (ISOF), National Research Council of Italy (CNR), Bologna, Italy.

² Institute for Microelectronics and Microsystems (IMM), National Research Council of Italy (CNR),

Bologna, Italy.

³GNext sas, Bologna, Italy.

^{4*} Department of Civil, Chemical, Environmental and Material Engineering (DICAM),

Alma Mater Studiorum - University of Bologna, Bologna, Italy. E-mail:davide.pierleoni4@unibo.it (D.Pierleoni)

The peculiar 2D shape confers to graphene and its derivatives unique properties, such as the capability to block small penetrant molecules [1]. This makes graphene suitable for a series of applications, among others as a protective coating and a barrier to gas permeation.

The industrial exploitation of graphene properties for gas barrier applications requires its combination with e.g. conventional polymers. Indeed graphene or GO platelets are often dispersed in polymer matrixes to decrease gas permeability [2,3], or employed as a graphene-based coating on the polymer surface, fabricating laminated structures [4-7].

In this work, soluble graphene derivatives prepared by different methods are employed to fabricate thin barrier coatings on different commercial polymer films (PET, Nylon, PP, PVC and PLA). The coating process was performed using a combination of solution processing, filtering, drying and transfer onto the polymer film surface [Figure 1], using different graphene sources, both aqueous and organic solvent solutions, and two different transfer techniques. Performances to gas barrier were evaluated using a lab-made closed volume manometric apparatus, as Oxygen Transfer Rate (OTR) [8,9] of coated films.

Excellent results were obtained using DMF solutions of electrochemically exfoliated graphene oxide – EGO – (C/O ratio 8.2) [10], which formed stable and resistant coatings on any substrate investigated. The coating showed a continuous and completely crack-free surface, as acquired through a Scanning Electron Microscopy (SEM) analysis [Figure 2]. No individual flakes of graphene or agglomerates are clearly observable, and the layer is formed by several thin graphene sheets stacked together.

References

- [1] R. R. Nair et al., Science, 335 (2012) 442.
- [2] T. Kuilla et al., Prog. Polym. Sci., 35 (2010) 1350.
- [3] H. Kim et al., Macromolecules, 43 (2010) 6515.
- [4] J.-T. Chen et al., Carbon, 75 (2014) 443.
- [5] F. Guo et al., Environ. Sci. Technol., 46 (2012) 7717.
- [6] K.-H. Lee et al., Carbon, 83 (2015) 40.
- [7] Y. Su et al., Nat Commun, 5 (2014).
- [8] M. Minelli et al., Europ. Polym. J., 44 (2008) 2581.
- [9] ASTM Standard D 1434, 1982 (2009), www.astm.org.
- [10] Z.Y. Xia et al., Carbon, 84 (2015) 254.
- [11] O. C. Compton et al., Adv. Mater., 22 (2010) 4759.
- [12] This research was supported by European Union Seventh Framework Programme under grant agreement n°604391 Graphene Flagship, Operative Program FESR 2007-2013 of Regione Emilia-Romagna – Attività I.1.1 & CIRI-MAM (Università di Bologna)

The laminated materials were able to enhance the barrier properties, as the OTR is significantly lowered [Figure 3]. A remarkable 74% decrease of OTR is obtained for the most performing sample (onto PET substrate) using a very limited amount of EGO (approximately 0.2 % vol.), for a very effective exploitation of graphene properties [11].

Results demonstrate convincingly that this coating process is a robust and versatile approach, suitable to fabricate graphene-based polymer coating making use of different transfer processes, raw materials and substrates. [12]



Figure 1. Fabrication of graphene-coated samples, in 4 steps: a) dilution of graphene dispersion, b) graphene deposition on a nylon filter by vacuum filtration, c) roll-to-roll or press transfer procedure, d) peel-off of the nylon filter from the graphene coated polymer.



Figure 2. SEM images of PET+EGO coating: coating surface (plane view, up) and cross section (transverse view, down)



Figure 3. OTR of the different samples tested. Samples PET0, PLA0, PP0 and PVC0 (patterned bars) are the reference samples, processed like the others but without any coating. Error bars are ~1% in all samples