



## MORPHOLOGY, OPTICAL TRANSPARENCY AND OXYGEN BARRIER OF EVOH/GRAPHENE OXIDE FILMS

Angel Ortiz<sup>1</sup>, Meshude Akbulut<sup>2</sup>, Julyana G. Santana<sup>1</sup>, Vijay K. Rangari<sup>3</sup>, Francisco Valenzuela-Díaz<sup>4</sup>, Olgun Güven<sup>2</sup>, Esperidiana Moura<sup>1\*</sup>

<sup>1</sup>Center for Chemical and Environmental Technology, Nuclear and Energy Research Institute, CQMA/IPEN-CNEN/SP, Sao Paulo, Brazil

<sup>2</sup>Hacettepe University, Department of Chemistry, Polymer Chemistry Division, Beytepe, Ankara, Turkey

<sup>3</sup>Department of Materials Science and Engineering, Tuskegee University, Tuskegee, AL, USA

<sup>4</sup>Metallurgical and Materials Engineering Department, Polytechnic School, University of Sao Paulo Sao Paulo, SP, Brazil

\*Corresponding author: eabmoura@ipen.br

**Abstract:** Food packaging materials require high gas and moisture barrier in order to preserve the quality of the products during storage and handling. Polyolefin materials have been widely used due to their water vapor resistance. Ethylene–vinyl alcohol copolymer (EVOH) is used as a gas barrier layer in packaging products that require high gas barrier. However, EVOH is very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. In order to overcome the adverse effects of moisture on EVOH film this paper studies the incorporation of small amount of graphene oxide in EVOH by melt processing and evaluates their effects on morphology, optical transparency and oxygen barrier of EVOH film. The EVOH/Graphene oxide (EVOH/GO) film were processed by twin-screw extrusion and extrusion blown film processing. The films was characterized by XRD, FEG-SEM, and UV/VIS analysis. In addition, the oxygen transmission rate (OTR) were performed at 23 C, 0 % and 90 % relative humidity using an OX-TRAN (MOCON Inc.). According to the results of the optical transparency measured, the EVOH/GO retaining good transparency films for all graphene oxide percentage added. The graphene oxide at only 0.1 wt. % into the EVOH matrix drastically improved the oxygen barrier properties of EVOH/GO flexible film in both, 0 % and 90 % of the relative humidity test conditions.

**Keywords:** EVOH/Graphene oxide film, barrier properties, morphology

### 1. INTRODUCTION

In recent years, there has been a rising demand for packaging that offers both ease of use and high quality food to consumers with busy lifestyles. Currently, the use of plastic (polymer petroleum-derived) in food packaging has increased worldwide according the trend of overall packaging industry. Flexible packaging are widely used for food packaging applications instead of rigid packaging. Flexible plastics are a category of plastics that are thin, light, and easily stretchable. They are also chemically inert and due to the smaller amount of resin required for its manufacturing presents cost effectiveness in comparison with rigid packaging. Because of its characteristics like low weight, durability, easily to be shaped and attractiveness, the brand appeal of the food product packed is broadly highlighted. Therefore,

flexible food packaging should be high gases and vapours barrier properties to protect the food from external environment to prevent the deterioration of food by oxidation of the components, discoloration, loose texture, nutrient loss. In addition to the good barrier properties are yet required good mechanical strength, heat resistance, puncture resistance, chemical resistance, transparency, gloss, and printability.

The various characteristics required for flexible food packaging can be achieved by laminated or co-extruded with metal foil and other different polymers layers with specific functions which depends upon the food and of intended shelf-life [1-4]. Among the polymers used in flexible food packaging, polyethylenes and polypropylenes (homo- and copolymers) are used for contact with the product because of their good chemical resistance and inertness to most foods, good barrier properties to water, and thermoselability. Polyethylene terephthalate (PET) provides very good tensile and yield strength properties as well as being transparent after processing. Polyamides offers good chemical resistance, toughness, and low gas permeability. Ethylene-vinyl alcohol (EVOH) has one of the lowest oxygen permeability reported among polymers used in flexible packaging [3-5].

Ethylene-vinyl alcohol (EVOH) copolymers are a family of resins with excellent gas-barrier properties. The permeability of EVOH depends on the copolymerization ratio of ethylene and vinyl alcohol. EVOH copolymers with 25–45 mol % ethylene are considered to have the superior gas barrier properties compared to most of the polymeric materials. EVOH is widely used in the food packaging industry as gas-barrier materials for foods that are sensitive to certain levels of oxygen or carbon dioxide due to their outstanding gas barrier properties to oxygen and organic compounds. For certain foods such as soups or juices in which any change in taste must be prevented, EVOH resins are ideal for flavor barrier, because EVOH has a low absorption rate of odor and flavor, and EVOH resins have almost no odor. Furthermore, the excellent resistance of EVOH to oils and organic solvents makes EVOH suitable for packaging edible oils, oily foods such as potato chips, mineral oils, organic solvents and agricultural chemicals [6, 7]. EVOH presents a considerable chemical resistance, high transparency and easy processability on a wide range of conventional co-extrusion processing equipment. However, EVOH are very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. Besides the increase in the permeability values of EVOH due to water absorption at high relative humidity conditions, their thermal and mechanical properties are also affected [8-10]. It has been reported that to overcome the sensitive to moisture and improve its physical properties the EVOH can be reinforced with nanofillers such as clay and graphene. The inclusion of impermeable lamellar fillers, such as clay and graphene, with sufficient aspect ratio can significantly enhanced the gas barrier properties of polymer, because of high aspect ratio of these nanofillers the gas diffusing molecules follow longer and more tortuous pathways to pass through the nanocomposite film [5, 11-15].

Graphene, a monolayer carbon atoms arranged in a hexagonal lattice is a material consisting of an extremely thin layer of graphite with high aspect ratio and two-dimensional structure and stable under ambient conditions. Graphene has more and more attracted attention because exhibits remarkable and unusual gas impermeable characteristic, high optical transmittance, thermal conductivity, chemical stability, excellent mechanical and electrical properties. Chemical modification of graphene oxide (GO), which is exfoliated from graphite oxide contains a range of reactive oxygen functional groups [14-16]. One of the most promising applications of GO is in nanocomposites based on polar polymer matrix. Due to the increased interfacial adhesion between GO and polar polymer matrix a highly exfoliated structure and homogeneous dispersion can be easily achieved achieve [15-17]. Due to its gas barrier performance as well as thermal and mechanical properties GO have been incorporated into various thermoplastic polymers such as polyurethane, poly(methyl methacrylate), polyethylene, polystyrene, poly(vinyl alcohol), polyethylene terephthalate, poly(ethylene vinyl alcohol), poly(lactic acid) [16-20].

This paper studies the incorporation of small amount of graphene oxide in EVOH by melt processing and evaluates their effects on morphology, optical transparency and oxygen barrier of EVOH film.



## 2. EXPERIMENTAL

### 2.1. Material

In this work were used the materials: graphite flakes from Quimesp Química Ltda (Sao Paulo, Brazil); sulfuric acid ( $H_2SO_4$ , 98 %); phosphoric acid ( $H_3PO_4$ , 85 %); potassium permanganate ( $KMnO_4$ , 99.9 %); hydrogen chloride (HCl, 37 %); hydrogen peroxide ( $H_2O_2$ , 30 %); ethylene vinyl alcohol copolymer (EVOH) with 32% mol/ethylene (EVAL<sup>TM</sup> manufactured by Kuraray Co. Ltd.).

### 2.2. Preparation of graphene oxide (GO) nanosheets

Graphene oxide (GO) was prepared from purified conventional flake graphite employing the method used by Huang et al. (simplified Hummer's method) [21]. Synthesis of GO was carried out by mixing  $H_2SO_4:H_3PO_4$  (320:80 mL), graphite flakes and  $KMnO_4$  (18 g) in a magnetic stirrer. After this process, the synthesis product was poured into a  $H_2O_2$  solution (400 ml of distilled water and 20 ml of  $H_2O_2$ ). Then GO obtained was washed with a 1 M HCl aqueous solution and repeatedly with deionized water until a pH of 4–5 was achieved. Then the GO (in water solution) was irradiated with a high intensity ultrasonic (20 kHz, and 450W/cm<sup>2</sup>) for 10 minutes and centrifuged at 3900 rpm for 5 minutes in order to a highly exfoliated GO nanosheets is achieved. The GO gel was dried at 90 C for 24 h in air atmosphere. Finally, the product was grind and sieved using a sieve with a 90  $\mu$ m mesh size. The detailed GO nanosheets preparation method can be seen in Ruiz, et al. [22].

### 2.3. Preparation of EVOH/GO flexible films

The EVOH/GO films were processed by twin-screw extrusion and extrusion blown film processing. The incorporation of 0.1 to 0.5 wt. % of GO nanosheets in EVOH resin was carried out by melting extrusion process, using a twin-screw extruder Haake Rheomex P332 with 16 mm and L/D = 25 rate from Thermo Scientific. The temperature profile was of 182/ 192/ 197/197/ 205/ 205C °C and a screw speed of 30 rpm. The extrudates coming out of the extruder were cooled down for a better dimensional stability, pelletized by a pelletizer, dried again and fed into extrusion blown film, single screw machine with 25 mm diameter, Carnevalli, and flexible film test samples were obtained. The temperature profile used in the blow extrusion process of the EVOH films was 190/ 195/ 210/ 215/ 215/ 220 °C and screw speed was 30 rpm.

### 2.4. Characterization of GO nanosheets and EVOH/GO flexible films

**X Rays Diffraction (XRD):** XRD patterns of graphite, GO nanosheet and EVOH/GO flexible films were recorded on a Simens - D5000 diffractometer operated at 40 kV and 40 mA, with  $CuK\alpha$  radiation ( $\lambda = 15.4 \text{ \AA}$ ).

**Oxygen transmission rate (OTR):** were carried out based on ASTM D 3985 – 81, using an OX-TRAN 2/20 (Mocon Inc.) at test conditions of 23°C, 0 and 90 % relative humidity.

**UV/VIS:** UV/VIS spectra were obtained using a Shimadzu UV1601PC spectrophotometer.

**Field Emission Scanning Electron Microscopy (FE-SEM):** FE-SEM of cryofractured samples under liquid nitrogen were carried out using a JEOL-JSM-6701 F, microscope with an accelerating voltage of 1-30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in carbon sputtered samples.

### 3. RESULTS AND DISCUSSION

#### 3.1. X rays diffraction (XRD) analysis results:

XRD analysis results of graphite and graphene oxide nanosheets: the XRD patterns of graphite and graphene oxide nanosheets (GO) are presented in Figure 1.

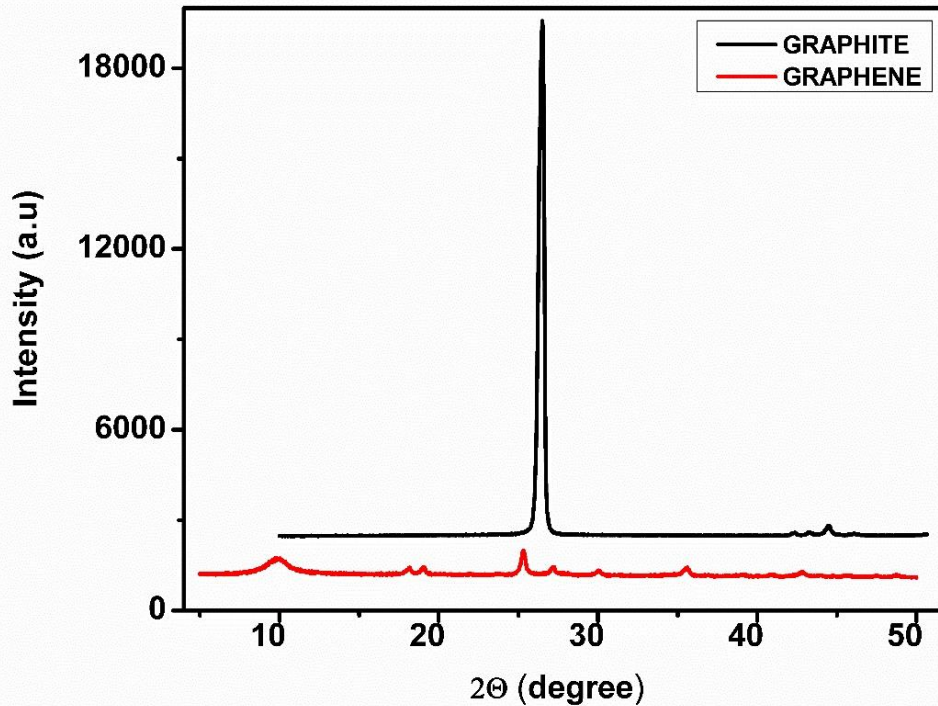


Figure 1. XRD diffraction patterns for the graphite and graphene oxide nanosheets (GO).

XRD spectra of graphite shows a sharp reflection peak at  $2\theta = 26.5^\circ$  while in XRD spectra of GO this graphite peak has been greatly reduced, and new distinct diffraction peaks at  $2\theta = 10^\circ$ ;  $18.4^\circ$  and  $18.9^\circ$ , corresponds to graphene oxide appeared (Fig. 1).

The large reduced of a peak at  $2\theta = 26.5^\circ$  observed suggests that graphite was almost completely converted into graphene oxide. The interlayer spacing “d” values for graphite powder and GO calculated according to the Bragg law (1) was about 0.34 nm for graphite powder and around 0.47 ( $2\theta = 18.9^\circ$ ), 0.48 ( $2\theta = 18.4^\circ$ ) and 0.88 nm ( $2\theta = 10^\circ$ ) for GO nanosheets. The presence of interlayer basal spacing “d” 0.47 and 0.48 nm may be due to the presence of residual oxygen and hydrogen and can indicate that the graphene oxide was not completely reduced [23]. Nevertheless, the results suggest that the interlayer spacing of graphite flakes was increased for GO due to the introduction of oxide functional groups to the basal plane via chemical oxidation reaction.

XRD analysis results of neat EVOH and EVOH/GO films: figure 2 shows the XRD patterns in the  $2\theta$  range of  $5^\circ$  to  $30^\circ$  for neat EVOH and EVOH/GO flexible films.

As can be seen in Fig.2, for XRD patterns of neat EVOH and EVOH/GO the EVOH characteristic peak at  $20.3^\circ$  [14, 24] was observed. In the case of the EVOH/GO, the GO characteristic peaks at  $10.6^\circ$  -  $10.9^\circ$  were also observed for films with 0.1; 0.3 and 0.5 wt. % of GO nanosheets addition, but with weak intensity which increased in intensity with increasing GO nanosheets content.

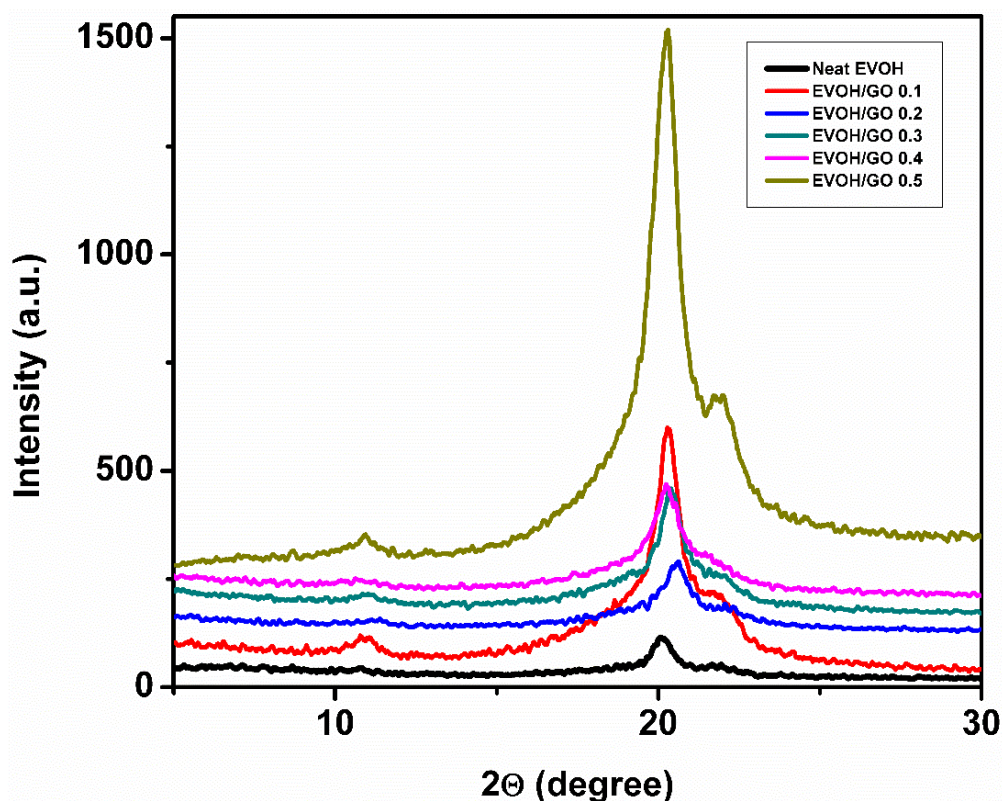


Figure 2. XRD diffraction patterns for the neat EVOH and EVOH/GO flexible films

These XRD diffraction patterns results provides clear evidence that for films with 0.1; 0.3 and 0.5 wt. % of GO nanosheets content some GO with stacked layers remained but a large part of GO nanosheets are intercalated or exfoliated by EVOH chain molecules.

### 3.2. Oxygen transmission rate (OTR) analysis results of neat EVOH and EVOH/GO films

Table 1 presents the oxygen transmission rate (OTR) of neat EVOH and EVOH/GO flexible films results measured at 23 °C and two different relative humidity test conditions (0 and 90 %).

As can be seen in Table I, with an incorporation of 0.1 to 0.4 wt. % of GO nanosheets in EVOH, the oxygen barrier properties of the EVOH/GO nanocomposite films, at 0 % relative humidity test conditions were drastically improved, up to five orders of magnitude relative, when compared with neat EVOH flexible films.

For EVOH/GO flexible film with 0.1; 0.2 and 0.5 wt. % of GO nanosheets content, the factor of increase of OTR in the relative humidity test conditions of the 90 %, was smaller than for neat EVOH film. On the other hand, EVOH/GO flexible films with 0.1 wt. % of GO nanosheets incorporation presented better oxygen barrier properties in both, 0 and 90 % relative humidity test conditions.

Table 1 - Oxygen transmission rate (OTR) results of neat EVOH and EVOH/GO flexible films

Material	Thickness ( $\mu\text{m}$ )	23 °C Relative Humidity (RH) Conditions		OTR Factor of Increase (%)
		0 (%)	90 (%)	
Neat EVOH	40 $\pm$ 2	0.52 cc/m <sup>2</sup> .dia	2.44 cc/m <sup>2</sup> .dia	4.7
EVOH/GO (0.1 wt. % GO)	40 $\pm$ 1.5	0.10 cc/m <sup>2</sup> .dia	0.14 cc/m <sup>2</sup> .dia	1.4
EVOH/GO (0.2 wt. % GO)	30 $\pm$ 1.7	0.48 cc/m <sup>2</sup> .dia	1.8 cc/m <sup>2</sup> .dia	3.8
EVOH/GO (0.3 wt. % GO)	35 $\pm$ 1.3	0.38 cc/m <sup>2</sup> .dia	2.06 cc/m <sup>2</sup> .dia	5.4
EVOH/GO (0.4 wt. % GO)	35 $\pm$ 1.6	0.38 cc/m <sup>2</sup> .dia	3.0 cc/m <sup>2</sup> .dia	7.9
EVOH/GO (0.5 wt. % GO)	30 $\pm$ 1.8	0.62 cc/m <sup>2</sup> .dia	2.58 cc/m <sup>2</sup> .dia	4.2

### 3.3. UV/VIS analysis results of neat EVOH and EVOH/GO films

Figure 3 shows the UV-VIS transmittance spectra for the neat EVOH and EVOH/GO flexible films. It is possible to see that addition of 0.1 – 0.4 wt. % GO nanosheet led to a decrease in % transmittance at low wavelengths (195-350 nm) and to a very slight decrease at higher wavelengths (350 - 750 nm). It is clear that, at wavelengths within the UV range, there is a reduction in light transmission with increase of GO nanosheets addition that is very marked in the spectral region between 195 and 350 nm for 0.4 wt. % of GO nanosheets; interestingly this suggests that the UV barrier has improved due to GO nanosheets incorporation.

The high optical transparency is a significant requirement for the application of food packaging film, because it can allow the visual identification of the condition of foods inside the film, such as freshness or spoilage. In this study, therefore, the effect of graphene nanosheets incorporation on the variation of optical transparency of the EVOH/GO flexible films was examined due to the possibility of its application as oxygen barrier layer in multilayer food packaging structure. It can be seen in Fig. 3 only the 0.2 wt. % of GO nanosheets led to a slight reduction in the UV-VIS light transmittance in the all wavelength range.

The neat EVOH and EVOH/GO flexible films, except for 0.2 % of GO nanosheets incorporation, presented a transparency with light transmittance of around 87 % in the entire visible light region. With the incorporation of 0.2 wt. % of GO nanosheets in the EVOH matrix, the light transmittance slightly reduced, ranging from 84% to 86 % in the visible light region. This result suggests that the incorporation of a small number of graphene nanosheets up to 0.5 wt% can yield nanocomposite film with a good transparency to be utilized as food packaging films.

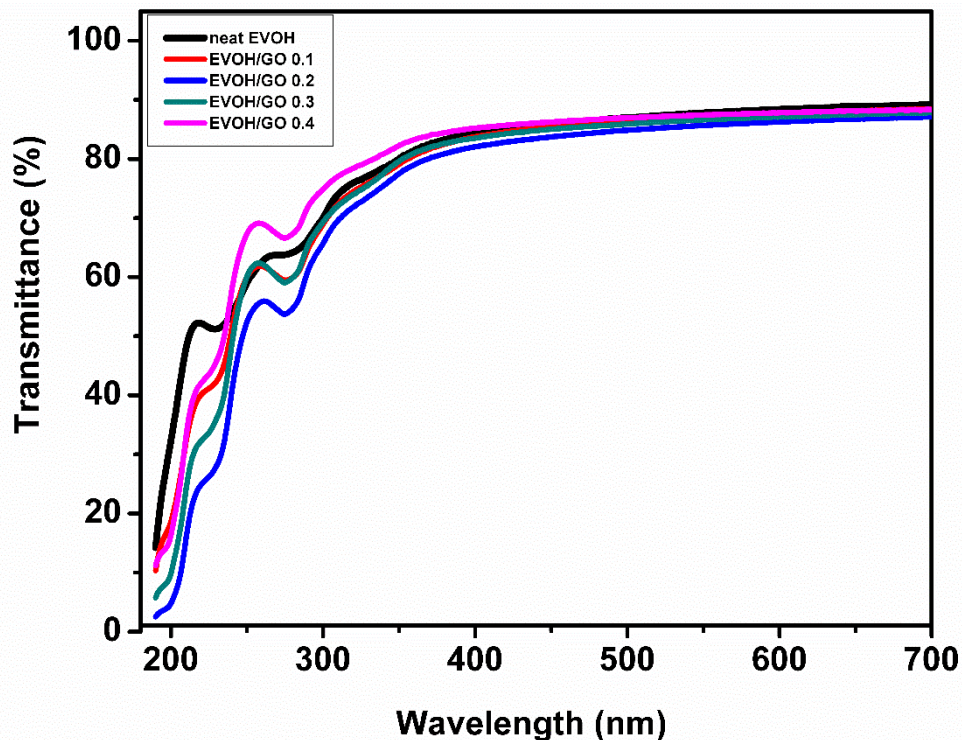


Figure 3. UV-VIS transmittance spectra for the neat EVOH and EVOH/GO flexible films

### 3.4. FE-SEM analysis results of neat EVOH and EVOH/GO films

FE-SEM micrographs of cryofractured surfaces of the neat EVOH and EVOH/GO flexible films were studied to understand the failure mechanisms and also study possible interaction between GO nanoosheets and EVOH resin.

FE-SEM micrographs of neat EVOH and EVOH/GO flexible films in 1000 X, 5000 X and 10000X of magnifications are showed in Figure 4. Figure (4a) shows micrographs of neat EVOH; (4b) shows micrographs EVOH/GO with 0.1 wt. % GO; (4c) shows micrographs EVOH/GO with 0.2 wt.% GO; (4d) shows micrographs EVOH/GO with 0.3 wt.% and (4e) shows micrographs EVOH/GO with 0.4 wt.% GO.

As can be seen in Fig. (4b) GO nanoosheets was homogeneously dispersed without any aggregation in the EVOH matrix. However, when 0.2 wt. % of GO nanoosheets are addition in EVOH matrix, Fig. (4c) the arrangement of GO in EVOH became increasingly irregular and there was some GO agglomeration. It is clear from Fig.(4c) that in this case GO are multilayered structures consisting of many single layers of graphite. It can be seen in Fig. (4d) a homogeneous distribution of GO nanoosheets and in Fig. (4e) some large aggregates of GO and holes are visible in surface of EVOH matrix.

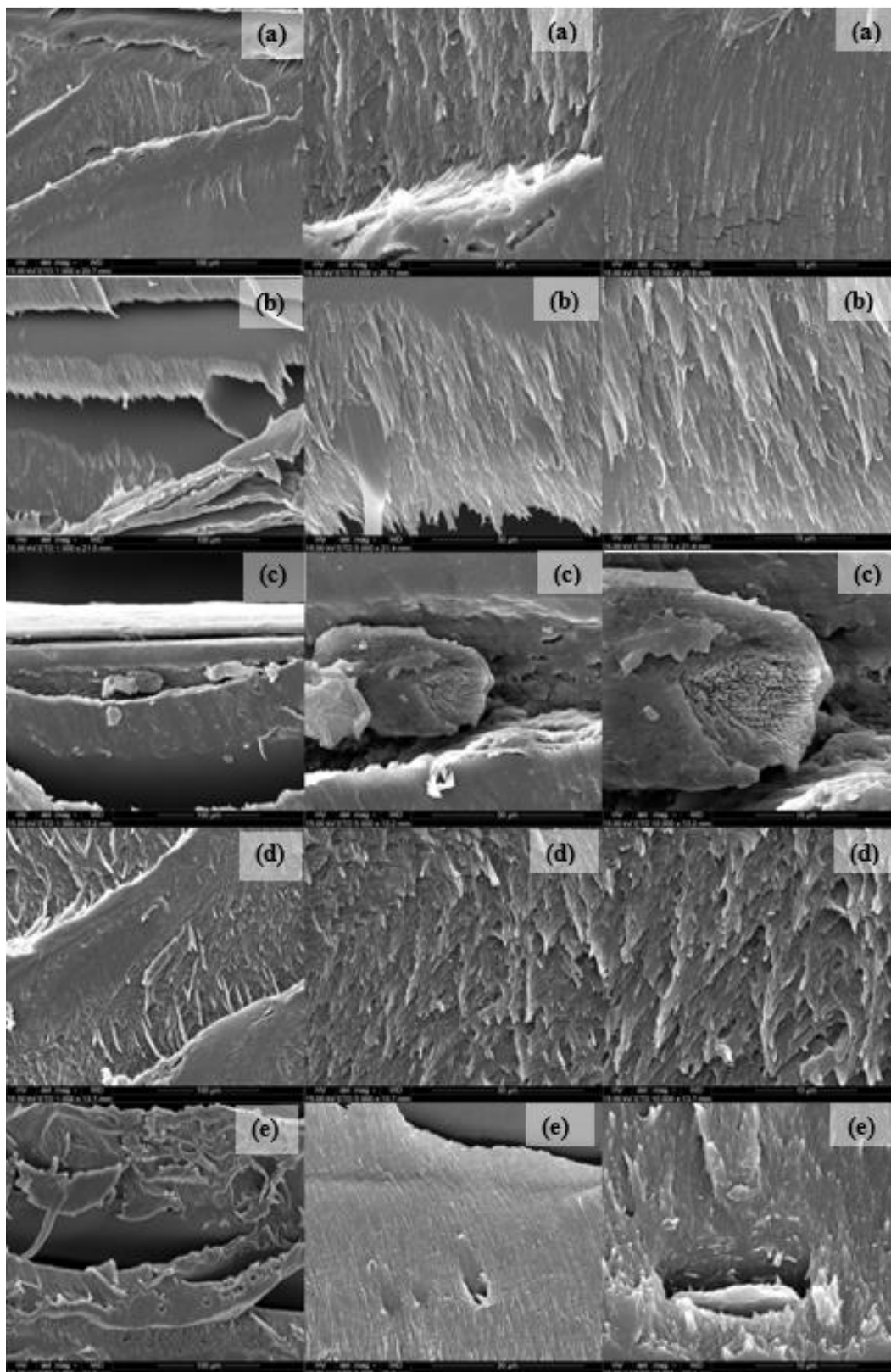


Figure 4. FE-SEM micrographs of cryofractured surfaces of neat EVOH and EVOH/GO flexible films: (4a) neat EVOH in 1000 X, 5000 X and 10000 X magnifications respectively; (4b) EVOH/GO (0.1 % GO) in 1000 X, 5000 X and 10000 X magnifications respectively; (4c) EVOH/GO (0.2 t.% GO) in 1000 X, 5000 X and 10000 X magnifications respectively; (4d) EVOH/GO (0.3 % GO) in 1000 X, 5000 X and 10000 X magnifications respectively and (4e) EVOH/GO (0.4 % GO) in 1000 X, 5000 X and 10000 X magnifications respectively.



#### 4. CONCLUSIONS

Results showed that the incorporation of GO nanosheets in EVOH matrix led to obtaining of EVOH/GO flexible films with the same transparency with light transmittance in the entire visible light of EVOH flexible films, but with better oxygen barrier. Based on this result, it can be concluded that the extent of exfoliation and dispersion state for the graphene oxide nanosheet in the EVOH matrix is a significant factor for producing high-performance composite film based on EVOH resin for food packaging application. However, the methodology used to produce graphene oxide nanosheets is still a limiting factor for large production of EVOH/GO composite films.

#### ACKNOWLEDGEMENTS

The authors wish to thank Intermarketing Brasil and Kuraray Group to provide for raw materials, IPEN/CNEN-SP and IAEA for financial support through IAEA-CRP # 17760 RO.

#### REFERENCES

- [1] Coles, R.; McDowell, D.; Kirwan, M. J. *Food Packaging Technology*, 2003, Blackwell Publishing Ltd., Oxford, UK. ISBN 1-84127-221-3.
- [2] Raheem, D. Application of plastics and paper as food packaging materials? An overview. *Emir. J. Food Agric.* 2013; v. 25, issue 3, p.177-188, doi: 10.9755/ejfa.v25i3.11509.
- [3] Marsh, K., and Bugusu, B. *Food Packaging—Roles, Materials, and Environmental Issues*. Vol. 72, Nr. 3, 2007—*JOURNAL OF FOOD SCIENCE R39*
- [4] Mokwena, K.K.; Tang, J. Ethylene Vinyl Alcohol: A Review of Barrier Properties for Packaging Shelf Stable Foods. *Critical Reviews in Food Science and Nutrition*, 2012, v. 52, p.640–650 doi: 10.1080/10408398.2010.504903
- [5] Cui, Y.; Kundalwal, S.I.; Kumar, S. Gas barrier performance of graphene/polymer nanocomposites. *Carbon* 2016, v. 98, p.313-333..
- [6] Cabedo, L.; Lagaro, J.M.; Cavaa, D.; Saurab, J.J.; Gimenez, E. “The effect of ethylene content on the interaction between ethylene-vinyl alcohol copolymers and water - II: Influence of water sorption on the mechanical properties of EVOH copolymers”, *Polymer Testing*, 2006, v. 25, p.860–867.
- [7] Kucukpinar, E.; Doruker, P., “Effect of absorbed water on oxygen transport in EVOH matrices. A molecular dynamics study”, *Polymer*, 2004, v.45, p.3555–3564.
- [8] Lasagabáster, A.; Abad, M.J.; Barral, L.; Ares, A.; Bouza, R. Application of FTIR spectroscopy to determine transport properties and water–polymer interactions in polypropylene (PP)/poly(ethylene-co-vinyl alcohol) (EVOH) blend films: Effect of poly(ethylene-co-vinyl alcohol) content and water activity. *Polymer*, 2009, v. 50, p. 2981-2989.
- [9] Kim, K.B., Sung, W.M., Park, H.J., Lee, Y.H., Han, S.H., “Hydrophobic properties of ethylene–vinyl alcohol copolymer treated with plasma source ion implantation”, *J. Appl. Polym. Sci.* **92** (4) (2004) 2069–2075.
- [10] Mokwena, K. K.; Tang, J.; Dunne, C. P.; Yang ,T.C.S.; Chow, E. “Oxygen transmission of multilayer EVOH films after microwave sterilization”, *Journal of Food Engineering* **92** (2009) 291–296.
- [11] Arora, A.; Padua, G.W. Review: Nanocomposites in Food Packaging. *Journal of Food Science*, 2010, v. 75, p.43-49.

- [12] Bumbudsanpharoke, N.; Ko, S. Nano-Food Packaging: An Overview of Market, Migration Research, and Safety Regulations. *Journal of Food Science*, 2015, v. 80, p.910-923.
- [13] Kim, D.; Kwon, H.; Seo, J. EVOH nanocomposite films with enhanced barrier properties under high humidity conditions. *Polymer Composites*, 2014, p.644-654
- [14] Kim, S.W.; Choi, H.M. Enhancement of thermal, mechanical, and barrier properties of ethylene vinyl alcohol copolymer by incorporation of graphene nanosheets: effect of functionalization of graphene oxide. *High Performance Polymers*, 2015, v. 27, issue 6, p.694–704.
- [15] Yang, J.; Bai, L.; Feng, G.; Yang, X.; Lv, M.; Hu, C. Z. H.; Wang, X. Thermal Reduced Graphene Based Poly(ethylene vinyl alcohol) Nanocomposites: Enhanced Mechanical Properties, Gas Barrier, Water Resistance, and Thermal Stability. *Ind. Eng. Chem. Res.*, 2013, v. 52, p.16745–16754.
- [16] Yoo, B., Shin, H., Yoon, H. and Park, H. Graphene and graphene oxide and their uses in barrier polymers. *J. Appl. Polym. Sci.*, 2014, v 131, 39628, doi: 10.1002/app.39628
- [17] Kim, H. M.; Lee, H.S. Water and oxygen permeation through transparent ethylene vinyl alcohol/(graphene oxide) membranes. *Carbon Letters*, 2014, v.15, No. 1, p.50-56.
- [18] Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-based composites. *Chem. Soc. Rev.*, 2012, v. 41, p. 666-686.
- [19] Kim, I. H.; Jeong, Y. G. Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. *J. Polym. Sci., Part B: Polym. Phys.*, 2010, v. 48, p.850–858.
- [20] Al-Jabareen, A.; Al-Bustami, H.; Harel, H.; Marom, G. Improving the oxygen barrier properties of polyethylene terephthalate by graphite nanoplatelets. *J. Appl. Polym. Sci.*, 2012, v.128, 1534-1539.
- [21] N. Huang et al., “Simple room-temperature preparation of high-yield large-area graphene oxide,” *International Journal of Nanomedicine*, 2011, v. 6, p. 3443-3448.
- [22] Jesus, G.-R., Lourdes, Y.-L., Sueli, V., da Silva-Valenzuela, M. d. G., Moura, E. and Valenzuela-Díaz, F. (2016) Effects of Graphene Oxide Addition on Mechanical and Thermal Properties of Evoh Films, in *Characterization of Minerals, Metals, and Materials 2016* (eds S. J. Ikhmayies, B. Li, J. S. Carpenter, J.-Y. Hwang, S. N. Monteiro, J. Li, D. Firrao, M. Zhang, Z. Peng, J. P. Escobedo-Díaz and C. Bai), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9781119263722.ch84
- [23] Meng, L.Y.; Park, S.J. Preparation and characterization of reduced graphene nanosheets via pre-exfoliation of graphite flakes. *Bull. Korean Chem. Soc.* 2012, v. 33, n<sup>o</sup> 1, p. 209-214, doi.org/10.5012/bkcs.2012.33.1.209
- [24] Kim, D.; Kwon, H.; Seo, J. EVOH nanocomposite films with enhanced barrier properties under high humidity conditions. *Polymer Composites*, 2014, p. 644-654.