Mechanical, Thermal, Morphology and Barrier Properties of Flexible Film Based on Polyethylene-Ethylene Vinyl Alcohol Blend Reinforced with Graphene Oxide

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Abstract Ethylene-vinyl alcohol (EVOH) copolymers are widely used in the food packaging industry as gas barrier properties to oxygen, organic solvents, and food aromas. EVOH is very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. This work aims to prepare flexible films based on melt-blending high density polyethylene (HDPE) and ethylene-vinyl alcohol (HDPE/EVOH/EVA blend) reinforced with graphene oxide (GO). The HDPE/EVOH/EVA/GO flexible films were prepared by twin-screw extrusion and blown film extrusion processing. The flexible films samples were characterized by tensile tests, TG, DSC and FE-SEM analysis and the correlation between properties was discussed. In addition, the oxygen permeability tests were performed at 23 °C, 0 and 90% relative humidity using an OX-TRAN (MOCON Inc.).

Keywords HDPE/EVOH blend · DSC · TG · Graphene oxide · Tensile tests · DSC

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Introduction

Ethylene vinyl alcohol (EVOH) copolymers has been widely applied in food packing, formed by random sequences of ethylene and vinyl alcohol [1]. It is one of the lowest oxygen permeability reported among polymers, commonly used in packaging, due to their excellent barrier properties to oxygen and organic compounds [2, 3]. EVOH copolymers with 32 mol% ethylene is considered to have the superior gas barrier properties when compared to most of the polymeric materials, it is outstanding barrier to gas, odor, and flavor, EVOH presents good chemical resistance, high transparency, low thermal stability and harmlessness toward health [4, 5]. However, EVOH copolymers are severe hygroscopicity, and consequently your applications seriously limited. Such properties are caused by strong hydrogen bond interactions, both inter and intra-molecular, which reduce the free volume of the polymer chains [6–8]. High density polyethylene (HDPE) that is a thermoplastic resulting from the polymerization of ethylene, and is widely used in various industries due to its mechanical properties, chemical resistance, water impermeability, ease of processing and low cost. HDPE is an inexpensive commodity polymer, but its use in some engineering applications may depend on improving its properties by crosslinking [9].

Blending polymer can be an effective alternative for create new materials with enhanced physical properties and polymer diversification. The small quantity of a barrier material into a low-cost matrix material can lead to a low-cost product with a good improvement in barrier properties, where are prominent in the packaging industry. Environmental concerns have thoughts with EVOH application as a thermoplastic, combining high oil resistance with excellent transparency, superior gas barrier properties and easy processability [10]. Its hydrogen-bonded structure, though beneficial to low permeability, causes moisture absorption, which results in the deterioration of the same property. Thus blending with a hydrophobic polymer, like HDPE, may offset this drawback.

These requirements are met through use of multilayer structures consisting of different polymers, each contributing certain specific functions. Because of the stringent requirement of withstanding the rigors of high temperatures and pressures, relatively few polymers are suitable for retort applications. The most common retortable plastic containers are thermoformed from co-extruded multilayer structures consisting of polyolefins (e.g., polypropylene (PP) and polyethylene (PE)), high density (HD) at the surfaces, with an internal oxygen barrier layer. Relevant work reported by Kamal and coworkers on the PP/EVOH blend compatibilized with PP modified with maleic anhydride (PP-g-MA). The influence of various processing parameters on morphology, permeability and impact strength were examined for extruded films. In another work, Prasad and Jackson reported on the mechanical properties and morphology of melt-blended EVOH in an HDPE matrix using PE-g-MA as a compatibilized [11–13]. Nowadays the high-energy radiation is a powerful technique for the modification of polymers, some authors indicates that in certain blends systems the recombination reaction of different macromolecule free radicals induced by irradiation may occur in the interface area, so complex grafting or cross-linking structures may be formed. New structures can improve interphase bonding, and lead to a significant change in mechanical and thermal properties. According with Goulas et al. the effect of radiation on the properties of multilayer films containing EVOH/HDPE blends can be improved by ionizing radiation [14, 15].

Packaging scientists are working on developing solutions like to the moisture sensitivity problem. The incorporation of desiccants in the layers surrounding EVOH to reduce the amount of moisture reaching the EVOH layer, blending of EVOH with other materials to improve properties, use of nanocomposites, etc. [16]. The structural uniqueness of graphite can greatly improve the thermal, mechanical, and gas barrier properties of a polymer if the graphite is well dispersed in the polymer matrix. Graphene oxide is a monolayer of carbon atoms, which may be obtained from exfoliation of graphite and is considered an ultrathin, perfect two dimensional (2D) barrier against gas diffusion [17–20]. Recently, graphene oxide (GO), which have been prepared by chemically oxidizing graphite to graphite oxide with strong oxidants and ultrasonic cleavage for graphene oxide nanosheets, has gained significant attention for incorporation in different polymers for improve the gas barrier and mechanical properties. Because GO has a large number of polar groups such as hydroxyl, ether, and carboxylate groups, intercalation of water-soluble polymers in GO is possible. EVOH/GO nanocomposites can present enhanced molecular ordering and the long tortuous pathway for water and gas molecules may explain the good water/oxygen barrier properties in flexible films [21].

This study aims to evaluate morphology, thermal, mechanical and barrier properties of HDPE/EVOH/EVA/GO flexible films compatibilizer by ionizing radiation.

Experimental

Material

- Graphene oxide
- (GO) nanosheets prepared from conventional flake graphite [15, 16];
- Ethylene vinyl alcohol copolymer (EVOH) with 32% mol/ethylene (EVAL™ manufactured by Kuraray Co. Ltd.);
- High density polyethylene (HDPE);
- Ethylene Vinyl Acetate (EVA).

Preparation of HDPE/EVOH/EVA/GO Flexible Films

The HDPE/EVOH/EVA/GO films were processed by twin-screw extrusion and extrusion blown film processing. The HDPE/EVOH/EVA/GO flexible films with addition of 0.1 wt% of GO nanosheets were prepared 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 182/192/197/197/205/205 °C and a screw speed of 30 rpm. The extrudates materials were cooled down for a better dimensional stability, pelletized by a pelletizer, dried again and fed into extrusion blown film, single screw machine (Carnevalli) with 25 mm diameter and flexible film test samples were obtained. The temperature profile used in the blow extrusion process of HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films were 190/195/210/215/215/220 °C and screw speed was 30 rpm (Table 1).

Electron-Beam Irradiation

Part of HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films were submitted to electron-beam irradiation at 150 kGy, using a 1.5 meV electron beam accelerator, at room temperature in presence of air.

Characterization of GO Nanosheets and HDPE/EVOH/EVA/GO Flexible Films

Mechanical tests: Tensile tests were determined using an INSTRON Testing Machine model 5564, according to ASTM D882-91 in order to evaluate the mechanical behavior of the materials studied. Each value obtained represented the average of five samples.

Differential scanning calorimetry (DSC): analyses were carried out using a Mettler Toledo DSC 822e from 25 to 250 °C at a heating rate of 10 °C/min under

Table 1 DSC analysis results of EVA/EVOH/HDPE/GO Nanocomposite Flexible Films

Composites	Melting temperature (T_{m1}, °C)	Melting temperature (T_{m2}, °C)	Melting enthalpy (ΔH_{m1}, Jg^{-1})	Melting enthalpy (ΔH_{m2}, Jg^{-1})
HDPE/EVOH/EVA[a]	132.9	178.1	128.0	14.4
HDPE/EVOH/EVA/GO[b]	131.4	178.3	110.7	12.3
HDPE/EVOH/EVA/GO*[c]	131.4	175.1	97.3	8.0

[a]HDPE/EVOH/EVA (70/20/10 wt%); [b]HDPE/EVOH/EVA/GO (70/20/9.99/0.1 wt%); [c]HDPE/EVOH/EVA/GO (70/20/9.99/0.1 wt%)*150 kGy

nitrogen atmosphere (50 ml/min). DSC analyses of the materials were performed on four samples of the materials. DSC were carried out to obtain melt temperature (T_m) and melting enthalpy (ΔH_m).

Thermogravimetric analysis (TG): In this study the TG analyses were made in a Mettler Toledo TGA module "TGA/SDTA851e" from 25 to 500 °C at a heating rate of 10 °C/min under nitrogen atmosphere (50 ml/min).

Field emission scanning electron microscopy (FE-SEM): FE-SEM of irradiated and non-irradiated HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO samples cryofractured under liquid nitrogen were carried out using a JEOL-JSM-6701F, microscope with an accelerating voltage of 1–30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in carbon sputtered samples.

Results and Discussion

DSC analysis results of HDPE/EVOH and HDPE/EVOH/GO flexible films: Fig. 1 shows the DSC analysis results for HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films.

Thermogravimetric analysis (TG) results: Fig. 2 shows the TG thermograms of HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films. As can be seen in Fig. 2, the HDPE/EVOH/EVA/GO showed a great reduction in the onset temperature when compared with HDPE/EVOH/EVA without GO addition.

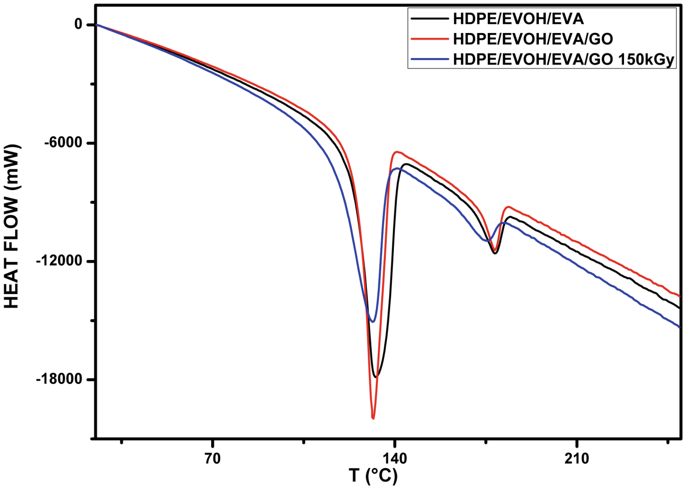

Fig. 1 DSC analysis results for HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films

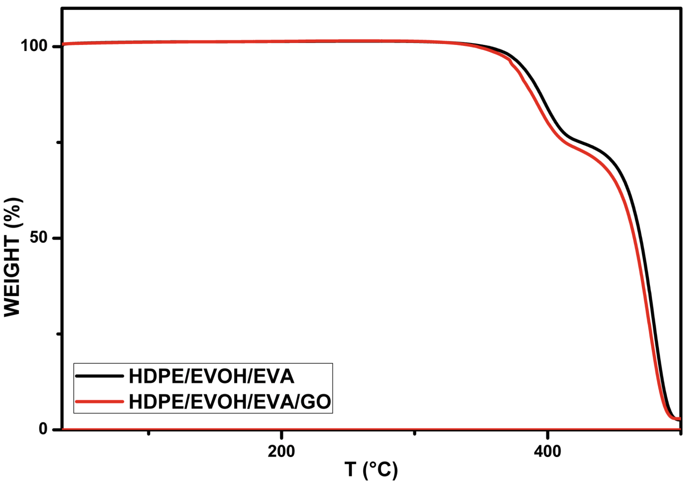

Fig. 2 TG analysis results for HDPE/EVOH and HDPE/EVOH/GO flexible films

Table 2 Decomposition temperature and weight loss of HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films

Flexible films	T_{onset} (°C)	T_{max} (°C)	Weight loss (%)
HDPE/EVOH/EVA	448.56	457.28	97.41
HDPE/EVOH/EVA/GO	363.86	454.97	96.88

The decomposition temperatures and weight loss for HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films are presents in Table 2.

Field Emission Scanning Electron Microscopy (FE-SEM) analysis results: FE-SEM micrographs of cryofractured surfaces of irradiated and non-irradiated HDPE/EVOH/EVA blend and HDPE/EVOH/EVA/GO nanocomposite were studied to understand the failure mechanisms and also study possible interaction between different components after electron-beam irradiation. FE-SEM micrographs of HDPE/EVOH/EVA blend and its composite are showed in Fig. 3. The micrographs of irradiated Blend and nanocomposite showed better compatibilization between the different components when compared with non-irradiated samples.

Tensile tests results: Table 3 presents the results of tensile tests of the HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films. The results presented shows the average values calculated from the data obtained in tests for five test specimens.

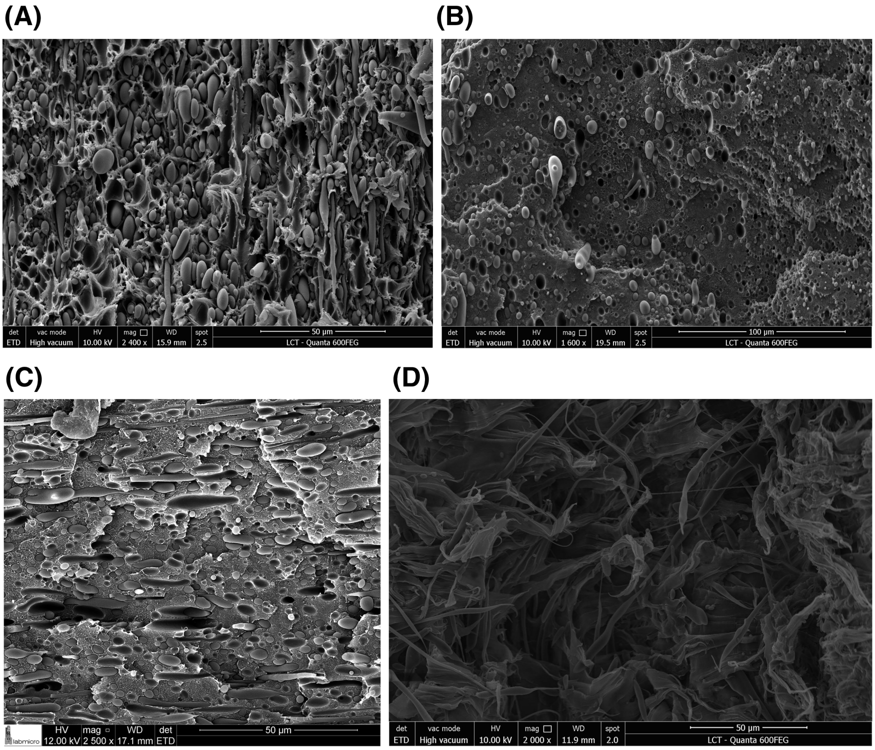

Fig. 3 **a** HDPE/EVOH/EVA blend (2400×), **b** HDPE/EVOH/EVA blend at 150 kGy (1600×), **c** HDPE/EVOH/EVA/GO nanocomposite (2500×), **d** HDPE/EVOH/EVA/GO nanocomposite at 150 kGy (2000×)

Table 3 Tensile test results of the HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO flexible films

Flexible films	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (GPa)
HDPE/EVOH/EVA[a]	9.2 ± 0.2	120 ± 10.6	0.54 ± 0.04
HDPE/EVOH/EVA*[b]	10.8 ± 0.5	127 ± 9.3	0.65 ± 0.03
HDPE/EVOH/EVA/GO[c]	13.6 ± 0.2	121 ± 10.4	0.76 ± 0.04
HDPE/EVOH/EVA/GO*[d]	14.3 ± 0.7	122 ± 9.8	0.81 ± 0.06

[a]HDPE/EVOH/EVA; [b]HDPE/EVOH/EVA* irradiated at 150 kGy; [c]HDPE/EVOH/EVA/GO; [d]HDPE/EVOH/EVA/GO* irradiated at 150 kGy

Conclusions

The results showed that the incorporation of GO nanosheets led to an important increase in Tensile strength at break and Young's modulus without an important variation in Elongation at break properties. The FE-SEM micrographs of irradiated

HDPE/EVOH/EVA and HDPE/EVOH/EVA/GO nanocomposite showed better compatibilization between the different components when compared with non-irradiated samples.

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References

1. Franco-Urquiza E et al (2010) Influence of processing on the ethylene-vinyl alcohol (EVOH) properties: application of the successive self-nucleation and annealing (SSA) technique. Express polym Lett 4(3):153–160
2. Mokwena KK, Tang J (2012) Ethylene vinyl alcohol: a review of barrier properties for packaging shelf stable foods. Food Sci Nutr 52:640–650
3. Ramakrishnan S (1991) Well-defined ethylene-vinyl alcohol copolymers via hydroboration: control of composition and distribution of the hydroxyl groups on the polymer backbone. J Macromol 24:3753–3759
4. Lagaron JM, Giménez E, Saura JJ (2001) Degradation of high barrier ethylene–vinyl alcohol copolymer under mild thermal-oxidative conditions studied by thermal analysis and infrared spectroscopy. J Polym Int 50:635–642
5. Lima JA, Felisberti MI (2008) Poly(ethylene-co-vinyl alcohol) and poly(methyl methacrylate) blends: phase behavior and morphology. J Eur Polym 44:1140–1148
6. Aucejo S, Marco C, Gavara R (1999) Water effect on the morphology of EVOH copolymers. J Appl Polym Sci 74:1201–1206
7. Cabedo L et al (2006) 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. Polym Test 25:860–867
8. Kucukpinar E, Doruker P (2004) Effect of absorbed water on oxygen transport in EVOH matrices. A molecular dynamics study. Polymer 45:3555–3564
9. Canevarolo Jr SV (2006) Ciência dos Polímeros. Artliber Ed Ltda 2
10. Samios CK, Kalfoglou NK (1998) Compatibilization of poly(ethylene-co-vinyl alcohol) (EVOH) and EVOH/HDPE blends with ionomers. Structure and properties. Elsevier Science Ltd. Polymer 39(16):3863–3870
11. Kamal MR, Garmabi H, Hozhabr S, Arghyris L (1995) The development of laminar morphology during extrusion of polymer blends. Polym Eng Sci 35(1):41–51
12. Walling N, Kamal MR (1995) Adv Polym Technol 5:269
13. Prasad A, Jackson P (1996) Polym Mater Sci Eng 75:281
14. Goulas AE, Riganakos KA, Kontominas MG (2003) Effect of ionizing radiation on physicochemical and mechanical properties of commercial multilayer coextruded flexible plastics packaging materials. Radiat Phys Chem 68:865–867
15. Elmaghor F, Zhang LY, Li HQ (2002) China Synth Rubber Ind 25:175
16. Mokwena KK, Tang J (2012) Ethylene vinyl alcohol: a review of barrier properties for packaging shelf stable foods. Crit Rev Food Sci Nutr 52:640–650
17. Yang J et al (2013) Thermal reduced graphene based poly(ethylene vinyl alcohol) nanocomposites: enhanced mechanical properties, gas barrier, water resistance, and thermal stability. Ind Eng Chem Res 52:16745–16754
18. Hummers, JWS (1957) Preparation of graphitic acid. US Patent 2798878
19. Geim AK, Novoselov KS (2007) The rise of graphite. Nat Mater 6:183–191

20. Du J, Cheng H-M (2012) The fabrication, properties, and uses of graphene/polymer composites. Macromol Chem Phys 213(10–11):1060–1077
21. Kim D, Kwon H, Seo J (2014) EVOH nanocomposite films with enhanced barrier properties under high humidity conditions. Polym Compos 35:644–654