



PREPARATION OF EVOH/GRAPHENE OXIDE BY BLOWN FILM EXTRUSION – CORRELATION BETWEEN FILM PROPERTIES AND GRAPHENE OXIDE ADDITION

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Abstract: This study reports the preparation of EVOH films reinforced with graphene oxide by twin-screw extrusion and blown film extrusion processing. The preparation of EVOH/Graphene oxide (EVOH/GO) films was carried out in two steps: EVOH with Graphene oxide powder (0-0.5 wt. %) was fed into a co-rotating twin-screw extruder, then the EVOH/GO nanocomposite was transformed into thin films using an extrusion blown film, single screw machine with 25 mm diameter and specimens test samples were obtained. The purpose of this study was to evaluate the correlation between mechanical properties and thermal stability of EVOH/GO films and the amount of graphene oxide added to the EVOH matrix. Tensile tests were conducted using an INSTRON Testing Machine. DSC and TG analysis were used for investigate the thermal stability of EVOH/Graphene oxide films. DSC analysis results showed that melting temperature (T_m), melting enthalpy (ΔH_m) and consequently the degree of crystallinity (X_c) of neat EVOH increased with the incorporation of the 0.1 and 0.5 wt. % of GO. TG of the composites showed a great difference in weight loss and in the onset degradation temperature when compared with the neat EVOH. The more important change was observed for EVOH/GO with 0.2 wt. % GO content that presented an increase of the onset degradation temperature. A significant enhancement of the tensile strength at break of EVOH/GO flexible film without important effects on the elongation at break were also observed, except for EVOH/GO with 0.2 wt. % GO content that presented an important increase in both, tensile strength and elongation at break. It can be concluded that the addition of GO is an effective means to improve the EVOH flexible films properties and led to the obtaining of packaging materials with superior properties suitable for several industrial applications.

Keywords: Graphene, EVOH/Graphene, DSC, TG, Tensile Test.

1. INTRODUCTION

Ethylene Vinyl Alcohol Copolymers (EVOH) are semi crystalline materials regardless of vinyl alcohol content. They are prepared commercially by transesterification (saponification) of Ethylene-vinyl acetate copolymers (EVA) [1]. It has one of the lowest oxygen permeability reported among polymers, commonly used in packaging is the most important polymer with excellent barrier properties and have found extensive applications in food packaging [2, 3]. EVOH copolymers with 25-45 mol % ethylene are considered to have the superior gas barrier properties compared to most of the polymeric materials. So EVOH is widely used in various fields, such as food packaging and gasoline tanks, 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 also ideal for flavor barrier, because EVOH has a low absorption rate of odor and flavor, and EVOH resins have almost no odor. In addition to excellent gas barrier properties to oxygen, organic solvents and food aromas EVOH presents good chemical resistance, high transparency, show thermal stability and harmlessness toward health [4, 5]. However, EVOH are very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. 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]. In order to overcome the water absorption in high humidity conditions and improve the physical properties of EVOH, some authors suggested a melt-blending process for preparation of EVOH reinforced with nanofiller, such as graphene [9-12].

Graphene 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 [13,14]. 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.

The aim of this study is to evaluate the correlation between mechanical properties and thermal stability of EVOH/GO films and the amount of graphene oxide added to the EVOH matrix.

2. EXPERIMENTAL

2.1. 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.).

2.2. Preparation of EVOH/GO flexible films

The EVOH/GO films were processed by twin-screw extrusion and extrusion blown film processing. The EVOH/GO flexible films with addition of 0.1 to 0.5 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 (Carnevali) with 25 mm diameter and flexible film test samples were obtained. The temperature profile used in the blow extrusion process of the neat EVOH and EVOH/GO flexible films were 190/ 195/ 210/ 215/ 215/ 220 °C and screw speed was 30 rpm.

2.3. Characterization of GO nanosheets and EVOH/GO flexible films

Mechanical tests: Tensile tests were determined using an INSTRON Testing Machine model 5564, according to ASTM D 882-91 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 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), and crystallinity percentage variation X_C (%) of neat EVOH and EVOH/GO flexible films. The X_C is directly related to melting enthalpy (ΔH_m) and was determined from the following equation:

$$X_C = (\Delta H_m / \Delta H_m^0 (1 - W_f)) \times 100 \% \quad [1]$$

Where:

ΔH_m = melting enthalpy of sample

ΔH_m^0 = melting enthalpy of EVOH assuming 100 % crystallinity = 169.2 J/g

W_f = mass fraction of the GO in the flexible films

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).

3. RESULTS AND DISCUSSION

3.1. Mechanical test results of neat EVOH and EVOH/GO flexible films:

Table 1 presents the mechanical test results of neat EVOH and EVOH/GO flexible films. The results presented in Table 1 shows the average values calculated from the data obtained in tests for five test specimens, crosshead speed at 500 mm/min, with standard deviations less than 10 % for all tests. From the table 1 it is possible observe gain in tensile strength at break due to GO addition. The addition of only 0.1 wt. % of Go nanosheets caused a significant and important increase in the original tensile strength at break of EVOH flexible film. In addition, the elongation was not significantly affected by GO nanosheet incorporation. The addition of 0.2 wt. % of Go nanosheets led to an increase of about 160 % in tensile strength at break of neat EVOH and ca. of 40 % in elongation at break.

Table 1 - Mechanical Test results for neat EVOH and EVOH/GO flexible films

Material	Thickness (μm)	Tensile strength at break (MPa)	Elongation at break (%)
Neat EVOH	40 ± 2	6.4 ± 0.3	117 ± 12
EVOH/GO (0.1 wt. % GO)	40 ± 1.5	16.0 ± 0.7	120 ± 13
EVOH/GO (0.2 wt. % GO)	30 ± 1.7	16.9 ± 1.5	170.8 ± 14
EVOH/GO (0.3 wt. % GO)	35 ± 1.3	14.1 ± 1.3	109.8 ± 8.1
EVOH/GO (0.4 wt. % GO)	35 ± 1.6	14.6 ± 1.1	130 ± 12
EVOH/GO (0.5 wt. % GO)	30 ± 1.8	13.8 ± 1.2	106.5 ± 14

3.2. DSC analysis results of neat EVOH and EVOH/GO flexible films

Figure 1 shows the DSC analysis results for neat EVOH and EVOH/GO flexible films. It can be seen in this Fig. that the melting temperature (T_m) of EVOH/GO flexible films shows a slight increase when compared with T_m of neat EVOH flexible films.

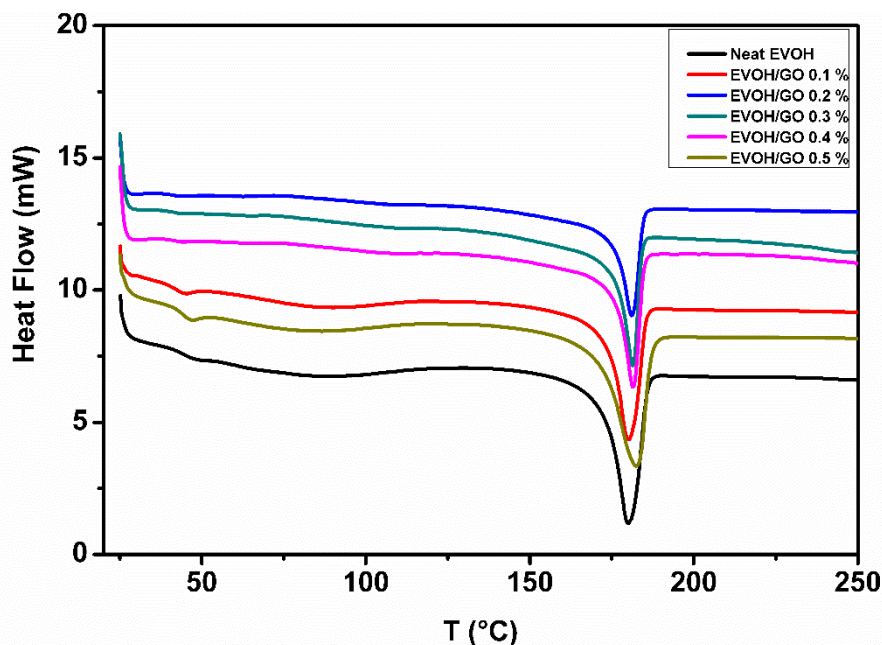


Figure 1. DSC analysis results for neat EVOH and EVOH/GO flexible films

The values of melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity percentage of neat EVOH and EVOH/GO flexible films are given in Table 2.

Table 2 - DSC analysis results for neat EVOH and EVOH/GO flexible films

Material	Melting Temperature (T_m , °C)	Melting Enthalpy (ΔH_m , Jg ⁻¹)	Crystallinity (X_c , %)
Neat EVOH	180.06	70.92	41.9
EVOH/GO (0.1 wt. % GO)	180.11	76.08	45.0
EVOH/GO (0.2 wt. % GO)	180.54	51.64	30.6
EVOH/GO (0.3 wt. % GO)	181.46	53.0	31.4
EVOH/GO (0.4 wt. % GO)	181.48	51.0	30.3
EVOH/GO (0.5 wt. % GO)	182.42	74.38	44.2

It is clear from Table 2 that there were changes in melting temperature and enthalpy of EVOH due to GO nanoosheets addition. The incorporation of 0.1 and 0.5 wt. % of GO nanoosheets increased the

melting enthalpy and consequently crystallinity % of EVOH, which means more energy needed to start the fusion process for EVOH/GO flexible films. On the other hand, the addition of 0.2 to 0.4 wt. % of GO nanosheets led to a significant reduction of melting enthalpy and crystallinity percentage of original EVOH flexible films. The reduction of melting enthalpy and consequently crystallinity percentage caused by the incorporation of GO nanosheets has also been observed and reported by various other authors [12, 17, 18]. According to Kim and Choi the reason reduction of X_c of EVOH with the incorporation of GO nanosheets is due to strong interaction between the GO and EVOH that confine the mobility of the EVOH chains close to the GO surface hindering the regular packing of the EVOH chains into crystal lattices [12]. The variation in X_c of EVOH observed in this work by GO nanosheets addition are very important for EVOH/GO packaging applications, since that in the semicrystalline polymers, like EVOH, the degree of crystallinity (X_c) and the crystalline structure induced from the crystallization process generally affect the gas barrier performance as well as their physical and mechanical properties.

3.3. TG analysis results of neat EVOH and EVOH/GO flexible films:

Figure 2 shows the TG thermograms of neat EVOH and EVOH/GO flexible films. TG of the composites showed a great difference in weight loss and in the onset degradation temperature when compared with the neat EVOH. The more important change was observed for EVOH/GO with 0.2 wt. % GO content that presented an increase of the onset degradation temperature.

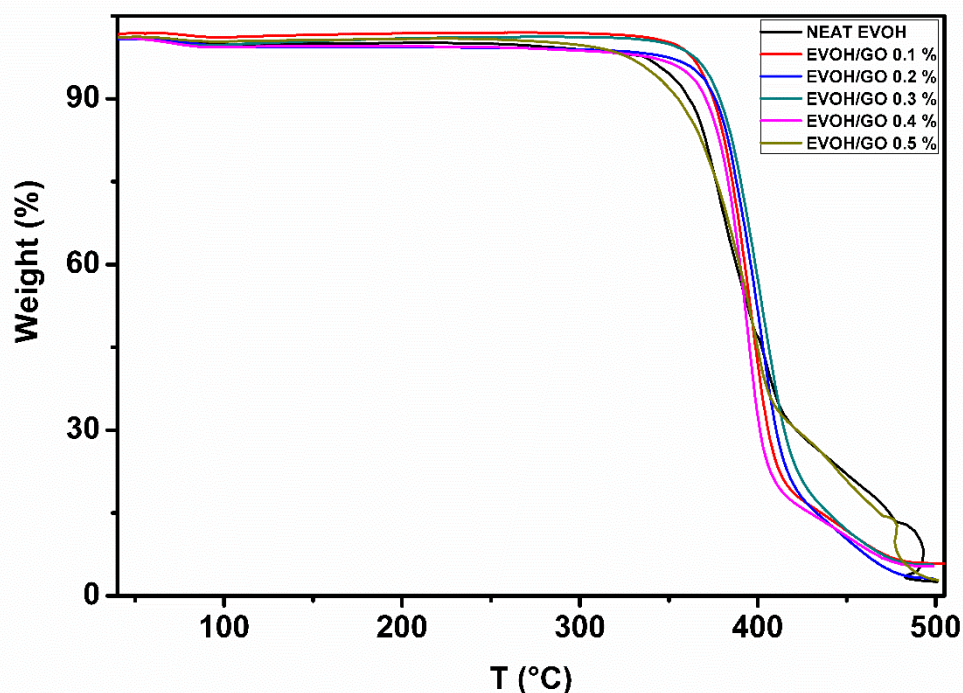


Figure 2. TG thermograms of neat EVOH and EVOH/GO flexible films

The decomposition temperature and weight loss of neat EVOH and EVOH/GO flexible films are given in Table 3. It is clear from Table 3 that the onset degradation temperatures of EVO/GO flexible films increase compared to neat EVOH with Go nanosheets addition except to 0.5 wt. % of GO addition. For all samples, the weight loss in the temperature range between 100 and 200 °C is attributed to the absorbed water and also the pyrolysis of oxygen-containing functional groups such as $-OH$ and $-COOH$. The degradation temperature for 50 % of weight loss of EVOH presented an important

increase with addition of GO, except for EVOH/GO content 0.4 wt % of GO incorporation. As can be seen in Table 3 the maximum weight loss for EVOH/GO flexible films content 0.1 - 0.4 wt % GO nanosheets takes place at 599 °C, that is, ca. 100 °C higher than neat EVOH. This results confirm that incorporation of GO in EVOH led to a significant improvement of the thermal oxidation stability of EVOH.

Table 3. Decomposition temperature, weight loss of neat EVOH and EVOH/GO flexible films

Flexible Films	T _{onset} (°C)	T _{max} (°C)	T _{WL (50 %)} ^(f) (°C)	Total Weight Loss (%)
Neat EVOH	356.5	501.1	396.5	97.4
EVOH/GO (0.1) ^(a)	363.3	599.2	397.6	94.2
EVOH/ GO (0.2) ^(b)	367.4	599	400.1	97
EVOH/ GO (0.3) ^(c)	365.9	599.4	403.8	94.8
EVOH/ GO (0.4) ^(d)	360.7	599.6	393.7	94.9
EVOH/ GO (0.5) ^(e)	355.2	501	397.4	97.1

^(a) EVOH/Graphene Oxide (99.9/0.1 wt %); ^(b) EVOH/Graphene Oxide (99.8/0.2 wt %); ^(c) EVOH/Graphene Oxide (99.7/0.3 wt %); ^(d) EVOH/Graphene Oxide (99.6/0.4 wt %); ^(e) EVOH/Graphene Oxide (99.5/0.5 wt %); ^(f) Temperature for 50 % of weight loss.

4. CONCLUSIONS

Results showed that the addition of GO nanosheets in EVOH matrix improved tensile strength at break without important effects on the elongation at break properties of EVOH/Graphene oxide flexible film. The variation in EVOH degree of crystallinity (X_c) observed in this work due to GO nanosheets addition are very important for EVOH/GO packaging applications, since that in the semicrystalline polymers, like EVOH, the X_c and the crystalline structure generally affect the gas barrier performance as well as their physical and mechanical properties. It can be concluded that the addition of GO is an effective means to improve the EVOH properties and led to the obtaining of packaging materials with superior properties suitable for several industrial applications.

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