Characterization of Minerals, Metals, and Materials 2016
Edited by: Shadia Jamil Ikhmayies, Bowen Li, John S. Carpenter, Jiann-Yang Hwang, Sergio Neves Monteiro, Jian Li, Donato Firrao, Mingming Zhang, Zhiwei Peng, Juan P. Escobedo-Diaz, and Chenguang Bai
TMS (The Minerals, Metals & Materials Society), 2016

EFFECTS OF GRAPHENE OXIDE ADDITION ON MECHANICAL AND THERMAL PROPERTIES OF EVOH FILMS

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Keywords: Composites, ethylene vinyl alcohol, graphene oxide, flexible films, mechanical properties, thermal properties

Abstract

Currently, ethylene vinyl alcohol (EVOH) is one of the oxygen barrier materials most used for food packaging. The addition of graphene oxide nanosheets to the EVOH matrix is employed to improve their mechanical and barrier properties. In this work, films of EVOH-based composites reinforced with graphene oxide were prepared by melt extrusion, using a twin screw extruder machine and blown extrusion process. The graphene oxide was prepared via chemical oxidation of natural graphite and then was exfoliated into nanosheets using the sonochemical method. The composite films samples were characterized using FTIR and DSC analysis. In addition, their mechanical properties were also determined.

Introduction

In recent years there has been increased interest in improving food packaging. For this have been used new polymeric materials and polymer matrix composites, because they can increase its shelf life. Among the polymers used for this purpose is the Ethylene-Vinyl-Alcohol (thermoplastic polymer) [1-3]. Ethylene vinyl alcohol (EVOH) are copolymers of ethylene and vinyl alcohol that are widely used in the food packaging industry due to their high transparency, excellent chemical resistance, as well as very good gas barrier properties to oxygen, organic solvents, and food aromas [2].

Currently, the graphene-based nanocomposites are under intense research because they allow significantly improvement of the properties of the composites [1, 2]. The polymer composites with graphene or graphene oxide (GO) as filler, have shown improvements in properties such as elasticity modulus, tensile strength, electric conductivity, and thermal stability [1, 3-6]. Moreover,

these improvements are often observed using low filler contents, behavior related to the surface area of these materials [4, 7]. For example, it is reported that with a 0.7 wt. % graphene oxide loading on a PVA nanocomposite, were observed a 76% increase in tensile strength and 62% increase in Young's modulus [8]. Furthermore, nanocomposites of graphene oxide (0.9 wt. %) in a PS matrix showed significant improvements in the mechanical properties (57% increase in elastic modulus and 70% in strength) [9]. Also, recent work has shown that the use of nanocomposites of graphene or graphene oxide with EVOH polymeric matrix can improve the mechanical properties and oxygen permeability of EVOH films [6, 10-12]. However, to achieve significant improvements in the properties of nanocomposites, the graphene oxide should be exfoliated and well dispersed in the polymer matrix [13].

Chemical oxidation of graphite is the most used method for the preparation of graphene [14]. The graphene oxide (GO) is obtained employing concentrated acids (sulfuric acid, nitric acid, and phosphoric acid) and highly oxidizing agents (potassium permanganate or potassium perchlorate) [14, 15]. This method was developed by Hummers et al. [16] and was modified by different researchers to improve their efficiency. The GO syntheses using an improved variant of the method of Hummer was reported by Marcano et al. [17]. The advantages of this variant are the employ of a relatively simple protocol, with temperature controlled at 50 °C and no toxic gas evolution during the preparation, this make it attractive for preparing GO on a large scale. However, the method has the disadvantage that the conversion rate of graphite to GO is not 100%.

Recently, Huang et al. reported a new variant that simplify the process of synthesis of GO [14, 18]. This method has the advantages of obtaining a nearly 100% conversion of graphite to GO and further enables obtaining GO nanosheets. However, for use in composite materials, it has the disadvantage that the nanosheets have micron-scale dimensions. On the other hand, exfoliation of graphene oxide (GO) can be performed by stirring and most commonly by sonication in solvents [14, 19, 20].

In this work, GO was prepared via a simplified Hummer's method. In addition, the obtained particles were used in the manufacture of EVOH/GO composite flexible films.

Materials and methods

Materials

Graphite flakes from Quimesp Química Ltda (Sao Paulo, Brazil) were used. Sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%), potassium permanganate ($KMnO_4$, 99.9%), Hydrogen chloride (HCl, 37%) and hydrogen peroxide (H_2O_2, 30%), were purchased from Casa Americana de Artigos para Laboratórios Ltda (São Paulo, Brazil). The polymeric material used in this study was the Ethylene vinyl alcohol copolymer (EVOH) with 32% mol/ethylene (EVAL™ manufactured by Kuraray Co. Ltd.).

Preparation of GO particles

GO was obtained from purified conventional flake graphite employing the method used by Huang et al. (simplified Hummer's method) [14]. 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. All reagents were added slowly and then stirred for 3 days to allow the oxidation of graphite. 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). The graphite oxide obtained was washed with a 1 M HCl aqueous solution and repeatedly with deionized water until a pH of 4–5 was achieved. The decantation of supernatant was realized via a centrifugation technique at 3900 rpm for 5 – 10 min. Then the GO (in water solution) was strongly sonicated at room temperature for 10 minutes (using a power of 450 W) and centrifuged at 3900 rpm for 5 minutes. The GO gel was dried at 90 ºC for 24 h in air atmosphere. Finally, the product was grind and sieved using a sieve with a 90 μm mesh size.

Preparation of EVOH/GO composite films

The EVOH/GO composites were prepared by melting extrusion process, using a twin-screw extruder Haake Rheomex P332 operating in the L/D 3:1.33 rate. The extrudates coming out of the extruder were cooled down for a better dimensional stability, pelletized by a pelletizer, dried again and fed into blow extrusion to obtain the film samples. The temperature profile used in the blow extrusion process of the EVOH films was 190/ 195/ 197/197/ 205/ 205 ºC and the screw speed was 30 rpm. The manufacture of EVOH/GO films (0.1% wt. of GO) was done using in the blow extrusion process a temperature profile of 182/ 192/ 197/197/ 205/ 205 ºC and a screw speed of 30 rpm; while, was used in the blow extrusion of EVOH/GO films (0.5% wt. of GO) a temperature profile of 177/ 179/ 184/184/ 187/ 187 ºC and a screw speed of 40 rpm.

Characterization methods

Fourier Transform Infrared Spectroscopy (FTIR): The functional groups were characterized for the as prepared GO powders and EVOH/GO films by a FTIR spectrometer, IR Prestige-21 (Shimadzu corporation, Japan).

Differential Scanning Calorimetry (DSC): Thermal characteristics such as the Tg and Tc of the composites were determined using differential scanning calorimetry (DSC). Analyses were carried out using a DSC 822e (Mettler Toledo Inc.) from 25 to 250°C at a heating rate of 10 °C/min under nitrogen atmosphere (50 ml/min).

Mechanical Tests: Tensile tests were performed using an INSTRON Testing Machine, model 5564 (Norwood, MA) according to ASTM D 882-91), in order to evaluate the mechanical behavior of the materials studied. Each value obtained represented the average of eight samples.

Results and Discussion

Functional groups

The spectral analyses (FTIR) were performed to identify the functional groups on the surface of the graphite, GO and in the EVOH/GO composite films. In the Figure 1A are shown the characteristic bands of the graphite. The spectra of GO (Figure 1B), show a broad peak between 2500–3600 cm^{-1} and two sharp peaks at 1726 and 1052 cm^{-1} , indicating the presence of hydroxyl (–OH), carboxyl (–COOH), and epoxy groups (–O–), respectively [6]. Also, the spectra of the GO

(Figure 1B) show new bands (at 529, 622, 999 cm^{-1}), demonstrating the modification of graphite to GO. Additionally, the greatest relative intensity is observed in the band corresponding to 999 cm^{-1}, which also confirms the formation of graphene oxide.

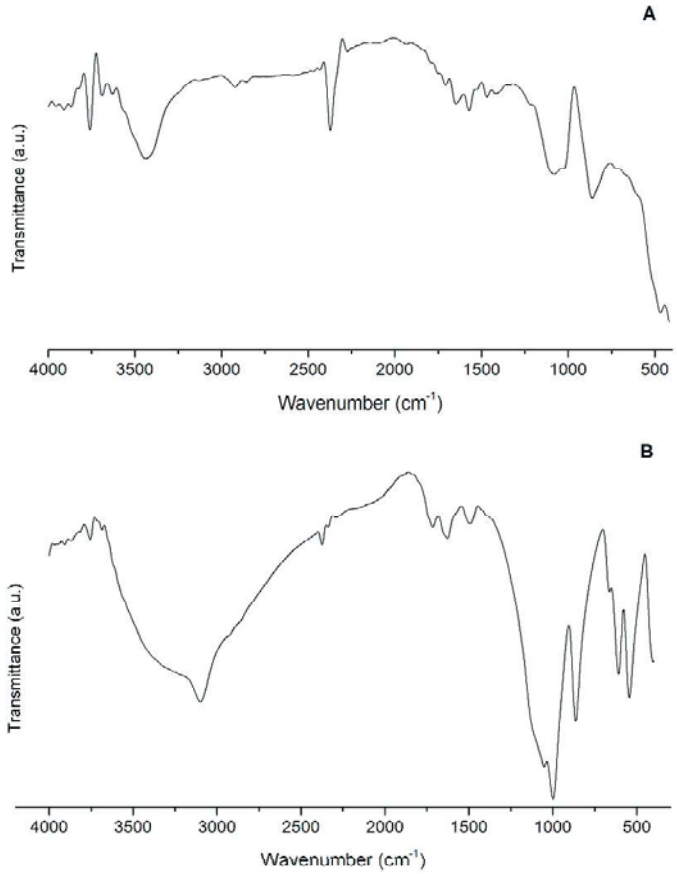

Figure 1. FTIR spectra of (A) graphite and (B) GO.

In the FTIR spectra of EVOH/GO composite films were not observed variations in comparison with spectra of EVOH films. These results are similar to the reported by Kim et al. in EVOH/EFG nanocomposite films [2]. On the other hand, this behavior can be related to the GO low content in the studied composites.

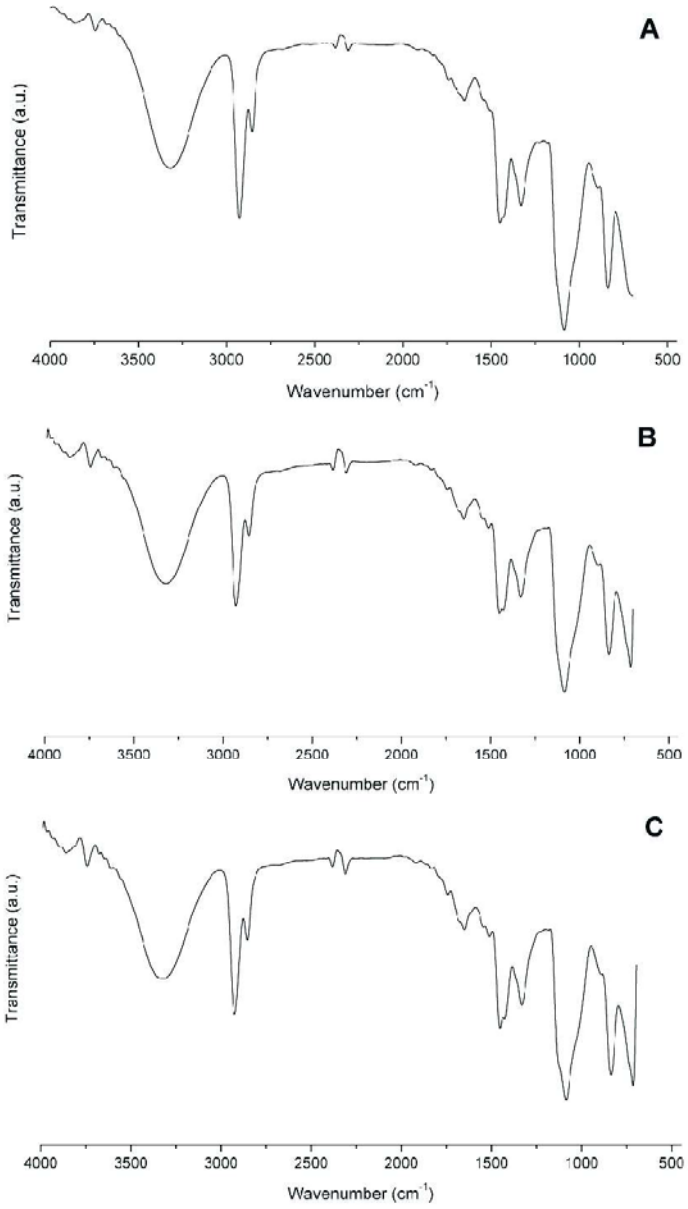

Figure 2. FTIR spectra of EVOH/GO composite films. A- EVOH film, B – EVOH/GO film (0.1 wt. % GO), C - EVOH/GO film (0.5 wt. % GO).

Thermal stability

In some industrial processes such as food packaging, it is required polymeric materials with thermal stability due to the heat treatments they are subjected to, such as pasteurization and sterilization [2]. In this work, the effect GO contents on the thermal stability of EVOH/GO composite films, was studied by DSC analysis. Figure 3 shows that the composite films have the same pattern that pure EVOH films; the GO addition did not change the Tg and Tm of the

composite films. Tg and Tm are strongly dependent on the polymer chains mobility and of the filler which can increase the Tg and Tm of polymeric films. However, also this behavior should be related to the low content of GO in the composite films.

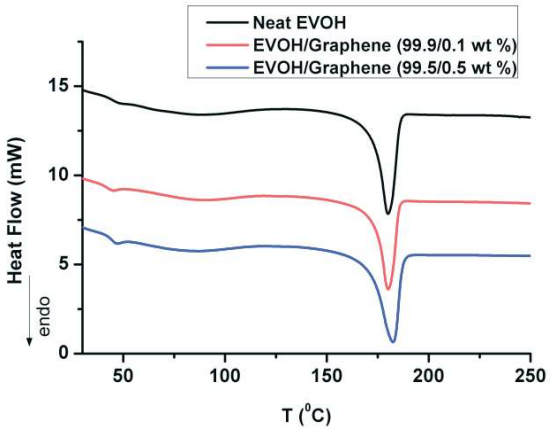

Figure 3. DSC thermograms of EVOH films and EVOH/GO composite films.

Mechanical properties

In order to evaluate the effect on the mechanical properties of the incorporation of graphene oxide particles in EVOH films, tensile tests were performed. The mechanical tests of pure EVOH and EVOH/GO composite flexible films were carried out in the longitudinal direction. Pure EVOH presented a tensile strength of 6,0 MPa. Figure 4 shows the tensile stress–strain curves of the EVOH/GO composite films, with a mean tensile strength of 36 MPa. The incorporation of only 0.1 wt. % of GO particles to the EVOH films caused a significant and important increase in the tensile strength. In addition, the elongation was not significantly affected after the GO incorporation. Such behavior may be due to the easily deformable nature of graphene oxide itself, relative to other fillers such as nanoclays.

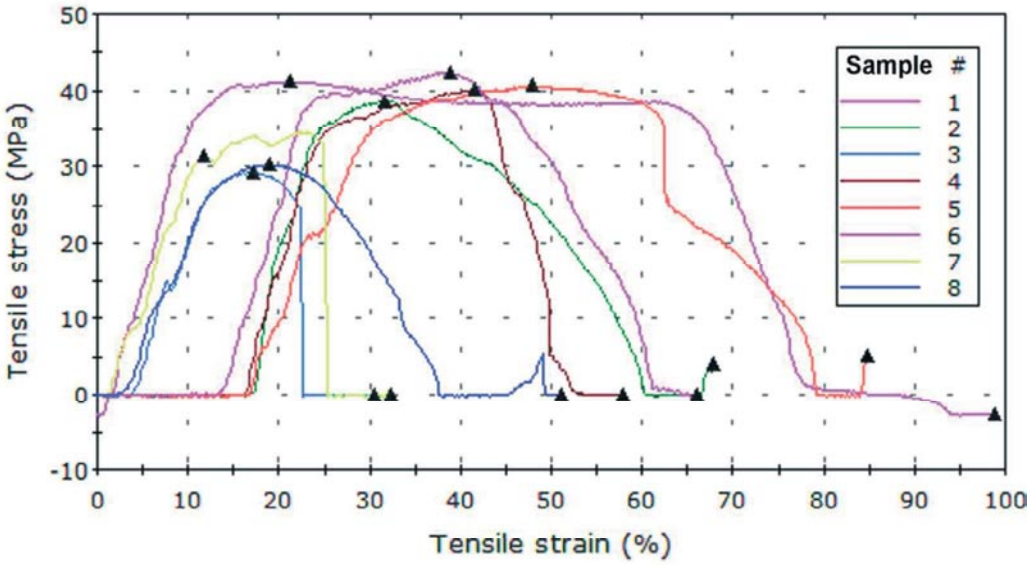

Figure 4. Tensile stress–strain curves of the EVOH/GO (0.1 wt. % GO) composite films.

Conclusions

We successfully prepared GO particles using a simplified Hummer's method. The new bands in the FTIR spectra, demonstrate the modification of graphite to GO during the chemical synthesis. In addition, we obtained EVOH/GO composite films. These films showed a significant and important improvement in their tension strength without affecting their elongation and thermal stability.

Acknowledgments

This work was supported by the project CAPES/MES Cuba № 041/2011. The authors thank the Nuclear and Energy Research Institute (Brazil) for their assistance in conducting some of the tests.

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