SYNTHESIS, ELECTRICAL AND STRUCTURAL CHARACTERIZATION OF A COMPOSITE MATERIAL BASED ON POWDERED MAGNETITE AND HIGH DENSITY POLYETHYLENE.

SÍNTESIS Y CARACTERIZACIÓN ELÉCTRICA Y ESTRUCTURAL DE UN MATERIAL COMPUESTO A BASE DE POLIETILENO DE ALTA DENSIDAD Y MAGNETITA PULVERIZADA

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ABSTRACT

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This work describes the synthesis and characterization of a composite material based on magnetite filled HDPE, which is commonly known for its magnetic properties. Composites of this kind are used in different applications such as magnetic and microwave absorption, transducers manufacturing, and biomedical applications like targeted drug delivery, organs tagging, etc. The samples were produced according to different volume ratios of magnetite and HDPE. The samples structure was analyzed through X-ray diffraction tests and the crystallinity degree was calculated. Then, the samples were electrically characterized through volume resistivity measurements. The results showed that for ratios less than the 20% of magnetite there is not a substantial reduction in the resistivity of the composite compared to the unfilled HDPE. For magnetite ratios above the 30% the composite shows a substantial reduction of six orders of magnitude in its electrical resistivity.

Keywords: Magnetite, volumetric resistivity, High density Polyethylene.

RESUMEN

En este trabajo se describe la síntesis y caracterización de un material compuesto a base de polietileno de alta densidad (HDPE) y magnetita pulverizada, comúnmente conocido por sus propiedades magnéticas. Los compuestos de este tipo se utilizan en diferentes aplicaciones tales como la absorción magnética y de microondas, la elaboración de transductores y en aplicaciones biomédicas como la producción de capsulas para la entrega

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focalizada de medicamentos, marcación de órganos, etc. Las muestras del material compuesto fueron producidas con diferentes proporciones en volumen de magnetita y HDPE. La estructura de las muestras se analizó a través de pruebas de difracción de rayos X y se calculó el grado de cristalinidad. Posteriormente las muestras se caracterizaron eléctricamente a través de mediciones de resistividad volumétrica. Los resultados mostraron que para proporciones menores al 20% de volumen de magnetita no hay una reducción sustancial en la resistividad del material compuesto, en comparación con el polietileno de alta densidad puro. Para proporciones de magnetita por encima del 30% el compuesto muestra una reducción sustancial de seis órdenes de magnitud en su resistividad eléctrica.

Palabras Clave: Magnetita, resistividad volumetrica, polietileno de alta densidad.

1. Introduction

This paper aims to produce a composite material based on high density polyethylene (HDPE) with different proportions of powdered magnetite (Fe_3O_4). The HDPE is one of the most used polymers in the world due to its low cost, ease of processing and good performance in addition to being known as a reusable thermoplastic.

During the last decade, many studies have tried to improve the performance of this material for specific applications, adding to the polymeric matrix different kinds of reinforcements like fibers and particulate materials such as the silicates or other ferrimagnetic minerals. For instance, in Colombia the magnetite is an abundant material, economical and easy to achieve due to the good amount of mines found throughout the country, mainly those that are located in Huila and Cundinamarca.

By the addition of silicates such as montmorillonite some researchers have successfully enhanced the mechanical properties of different polymeric matrices; these composites can be used as building block for constructions. In other works the addition of some minerals, like the graphite or magnetite in different proportions into the polymeric matrix, have allowed to study the percolative properties of the composite material, these kinds of studies are useful for the design of technological gadgets such as heat sinks or packages for electronic devices with electromagnetic shielding e (**Panwar et al.**, 2007; **Weidenfeller** et al, 2002). Although the use of magnetite in thermoplastic and thermoset matrices is relatively new, these composites has been implemented in the automotive industry and in some biomedical uses, like the design of stents that can be able to change their shape in the presence of magnetic fields (**Razzaq et al.**, 2007). Some polymers filled with magnetite can also use in pharmaceutical applications including targeted drug delivery, tissue reconstruction and tumor treatments (**Zhang et al.**, 2008), primarily because of the low cytotoxicity of the magnetite [**Miles et al.**, 2010; **Wentao et al.**, 1996].

In this work the samples were synthesized using an extruder plastic machine and its resistivity and crystallinity degree for different concentrations of HDPE and magnetite were studied. Is expected to be achieved a composite with the mechanical properties and excellent machinability of the polymers, along with the conductive and ferromagnetic properties of the magnetite. This composite can be used for the development of technology or biomedical products, using economic and reusable precursors.

2. Experimental

2.1 Samples Preparation

Based on the calculation of the HDPE and magnetite (Fe_3O_4) real densities, samples of filled HDPE with magnetite were obtained with different volume ratios: 90%-10%, 80%-20%, 70%-30%, 65%-35% and 60%-40%. For each volume ratio were prepared two samples.

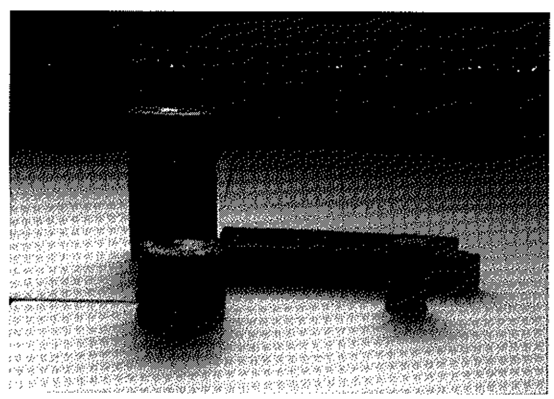

Fig. 1. Samples poured in different shapes.

The samples were made using an extruder plastic machine with three heating zones. After the extrusion process, the composite is poured into various molds with different shapes in order to facilitate the machinability of the samples, as is shown in figure 1.

For the X-ray diffraction tests and for the electrical resistivity measurements, small cylinders of approximately 1.2 mm diameter and 1mm height were cut and polished.

2.2 Resistivity Measurements

It is well known that the electrical resistivity of insulating polymers like de HDPE could decrease by dispersing a conductive filler, for instance, carbon black (CB) throughout the polymer matrix (**Wentao & Xinfang**, 1997; **Tang et al.**, 1994; **Beaucage et al.**, 1999); likewise, the magnetite as filler of polypropylene and polyamides matrices has been shown similar behaviors (**Weidenfeller** et al, 2002).

To assess the effect of the different magnetite ratios into the HDPE matrices, at room temperature, measures of volumetric resistivity were taken. The volumetric resistivity is the resistance to leakage current through the body of an insulating material, is commonly expressed in ohm-centimeters (**ASTM international**, 2007). The resistivity of the samples was measured the 6517A Keithley Electrometer and its 8009 resistivity test chamber.

2.3 X-ray diffraction Tests

The qualitative composition or phase identification of each sample is determined by the X-ray diffraction tests. The degree of crystallinity is estimated by the areas under the diffraction curves. The X'Pert PRO MPD panalytical X-ray diffractometer was used. This equipment uses a copper anode of 1.540998 Å. As analysis software the HighScore plus of panalytical was used.

3. Results and discussion

Fig. 2 shows the volume resistivity of HDPE samples filled with different volume proportions of magnetite, for each volume ratio two samples were measured. As is shown in Fig. 2 the significant drop (six orders of magnitude 10^{14} to 10^{6}) in the resistivity of magnetite filled HDPE can be observed between a filler loading of 30 vol% to 40 vol% as was predicted in previous works (**Weidenfeller et al.**, 2002; **Boettcher**, 1954; **Bruggeman**, 1937) . In contrast to this, the Fig.2 shows a high volume resistivity between the pure HDPE samples and the HDPE filled samples with 20 vol% of magnetite, that's an indicative of the predominant insulating polymeric phase.

The samples resistivity can be affected by some factors like the magnetite particles distribution and its interconnectivity into the HDPE matrix. This is why the samples with a low volume fraction of magnetite (0 vol% - 20 vol%) have a high volume resistivity, with a low magnetite particles dispersion, the resistivity is expected to be high and no conductive paths are available between the magnetite particles.

This behavior, the decrease of the resistivity between filler loadings of 30% to 40% of magnetite, and the increase of it between the pure HDPE to 20% of filler loading was also confirmed by electromagnetic polarization measures.

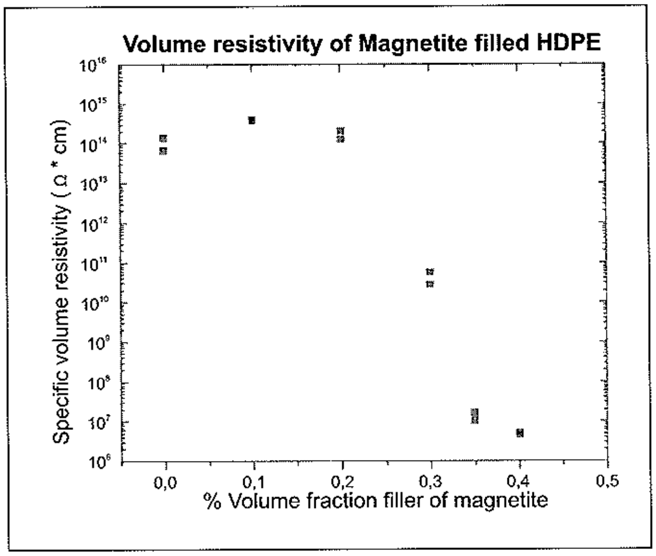

Fig.2. Specific volume resistivity of extruded and molded magnetite filled HDPE as a function of the percent of volume fraction filler of magnetite. For each volume ratio were prepared and measured two samples.

On the other hand, in the samples with the highest filler content (30 vol% - 40 vol%) some particles seem to have contacts points among them or are separated only by very small gaps, that produces conducting paths according to the theories of **Boettcher** (1954) and **Bruggeman** (1937). This indicates an ideally and homogenous dispersion of the magnetite particles in the polymeric matrix of HDPE. Therefore charge carriers can migrate from one magnetite particle to a neighboring one by hopping or tunneling. It's also possible according to the figure 2 make an approximation of the percolation threshold for the magnetite filled HDPE samples near to the 30 vol%.

Figure 3 shows the diffraction pattern of the pure magnetite, this describes the normal crystalline behavior of the ferrites. Figure 4 shows the diffraction patterns of each sample. Excepting the unfilled HDPE and the pure Magnetite it was observed three main phases: Magnetite, Hematite and HDPE. The Hematite phase belongs to the magnetite used as precursor material for the experiments and was not previously isolated.

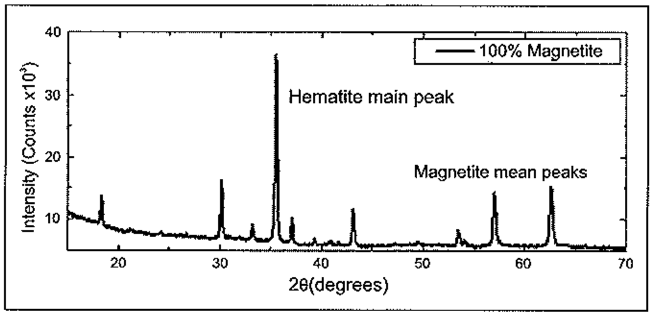

Fig. 3. Pure magnetite diffraction pattern.

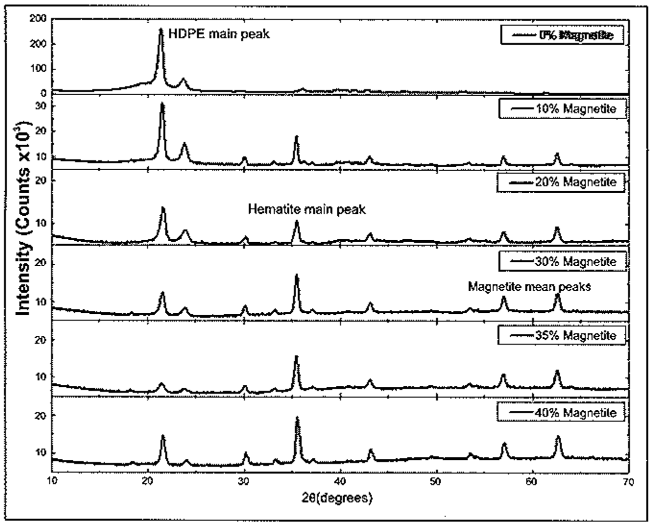

Fig. 4. Diffraction patterns of the magnetite filled HDPE samples.

As was expected, when the content of the magnetite is increased into the composite, the main peaks of the magnetite and hematite phases becomes more significant, while the main peak of the HDPE phase is gradually reduced (300.000 to 15.000 counts), in other words the degree of amorphousness decreases. The percentage of crystallinity for each diffraction pattern is measured as the ratio of the crystalline area over the total area, and the results are summarized in Table 1. Note that the percentage of crystallinity is higher as the volume of the magnetite increases.

Conclusions

Electrical and structural properties of magnetite filled HDPE samples were investigated. Samples were prepared with different volume ratios of magnetite. Electrical resistivity measurements show a rapid drop for filler loadings of the HDPE over the 30 % of volume, it is a result of point contacts between magnetite particles which are surrounded by the HDPE matrix. The increasing number of magnetite particles can be confirmed through the diffraction patterns and the cristallinity degree. The structural changes in the composite started with 20 vol% of filler. Therefore, the resistivity values of the investigated materials mainly depend on the magnetite grade.

Table 1. Magnetite filled HDPE samples degree of cristallinity.

% Vol Magnetite	% Cristallinity
0 %	16 %
10 %	24,4 %
20 %	22,4 %
30 %	24,5%
35 %	27 %
40 %	27,4 %

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