

FACILE EXPANSION AND FUNCTIONALIZATION OF GRAPHITE WITH NITROXIDE GROUPS

Yazmín Avila¹ and Jose Bonilla^{1*}

1 Centro de Investigación en Materiales Avanzados (CIMAV), Unidad Monterrey, Av. Alianza Norte 202, Autopista Monterrey-Aeropuerto Km 10, Apodaca, Nuevo León-México, C.P. 66600. E-mail: jose.bonilla@cimav.edu.mx

Abstract

Functionalization of carbon nanotubes (CN) with polymers have been widely studied however, CN functionalized with polymers are not available yet at industrial scale and are very expensive. On the other hand, Graphite Oxide (GO) under high both temperature and pressure leads to obtain Expanded Graphite (EG). GO is cheaper, available at large scale, and their expansion and functionalization, arises as a alternative to the CN.

In this work, a novel route to obtain EG and functionalized at the same time, using nitroxide groups is presented. Commercial natural graphite NG was expanded in the presence of solvent, nitroxides or initiator using one synthetic pathway. It is proposed that the defects in the surface of the platelets (double bonds) allow the abstraction of hydrogen atoms forming a radical centered in carbon which is trapped by the nitroxide, carrying out the functionalization of NG. EG and NG were characterized in detail by XRD and SEM. The results suggest that the NG was expanded around 20% by the covalent bonding of nitroxide groups to the platelets, which helps to the separation of graphite layers. The work proposed here has several advantages over the previous methods, including a high efficiency of expansion process, the use of a non-toxic intercalant, and the capability for mass production of expanded graphite for industrial applications.

Introduction

Currently, the use of graphite nanoplatelets (GNPs) has been of considerable attention as an alternative to metal and its low cost as conventional electrically conductive reinforcement, the composites with polymeric matrices GNPs are able to dissipate the load. [1] Some studies suggest that the composite undergoes a transition from insulator to conductor by gradually increasing the content of the conductive charging, and presents a typical behavior of percolation, which is attributed to the formation of several continuous paths for the electron or a transmission system in polymer composites with filler content above the percolation threshold. The problem of percolation of reinforced polymer nanocomposites GNPs is smaller than conventional loads, such as carbon fibers and carbon black, due to its extremely large surface area and their high aspect ratio of the GNPs. [1]

A number of works about growth and expansion of graphite have been reported. Among them, micromechanical cleavage is currently the most effective and reliable method to produce high-quality sheets of expanded graphite. However, the low productivity of this method makes it unsuitable for large-scale applications. [2]

In this first study, we speculate that using nitroxides, could be a advantage because these stable radicals can be react with the defects (double bonds) present in the graphite; these allows to find modest levels of expansion between the layers of the GN. This method involves only one chemical step under mild conditions, in which, surface is functionalized with organic groups (nitroxides). We speculated that the nitroxides can be of help to increase the degree of expansion, and the

surfacial area due to the organic groups attached to each stack of graphite. This expansion, is necessary for increase the dispersion and compatibility of expanded graphite with the polymer matrix.

Experimental

Expansion using TEMPO and initiator: The basic strategy involved in the expansion of natural graphite (GN) is carried out through the reaction with initiator and TEMPO to produce expanded graphite nanoplatelets (GNPs). The fabrication process is outlined in Figure 1. There are three main steps:

- (1) Natural Graphite was dispersed in a suitable solvent.
- (2) Graphite dispersion, TEMPO and initiator were stirred and heated in a small beaker.
- (3) On completion of the reaction, the mixture was filtered under vacuum, washed and finally dried under a vacuum.

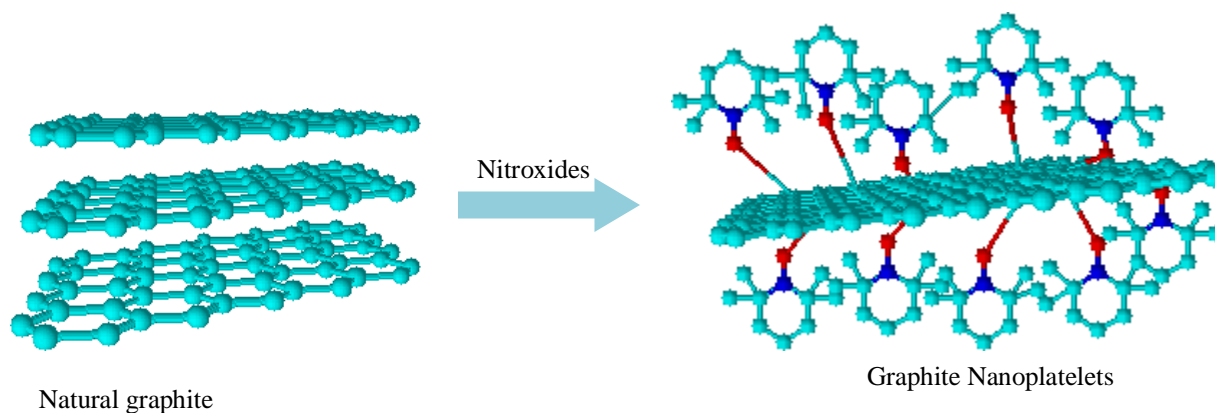


Figure 1. Process using TEMPO

X-Ray Diffraction. Analysis by X-ray diffraction was carried out on a PANalytical Empyrean, radiation CuK α 1, Cu anode, $\lambda = 1.54060$ Å, operated at 35 mA, 40 kV, with a 2θ scan of 9.9 at a 99.9 of total time in a continuous scan mode with a Bragg-Brentano geometry.

Scanning Electronic Microscopy (SEM). The surface morphology, was conducted by a 15kV HV SEM analysis in a SEM Field Emission Model FEI Nova 200 Brand NanoSEM. The sample preparation was performed using a drop of the dispersion on a sample holder for SEM. The study was performed using the secondary electron detector.

Results and discussion

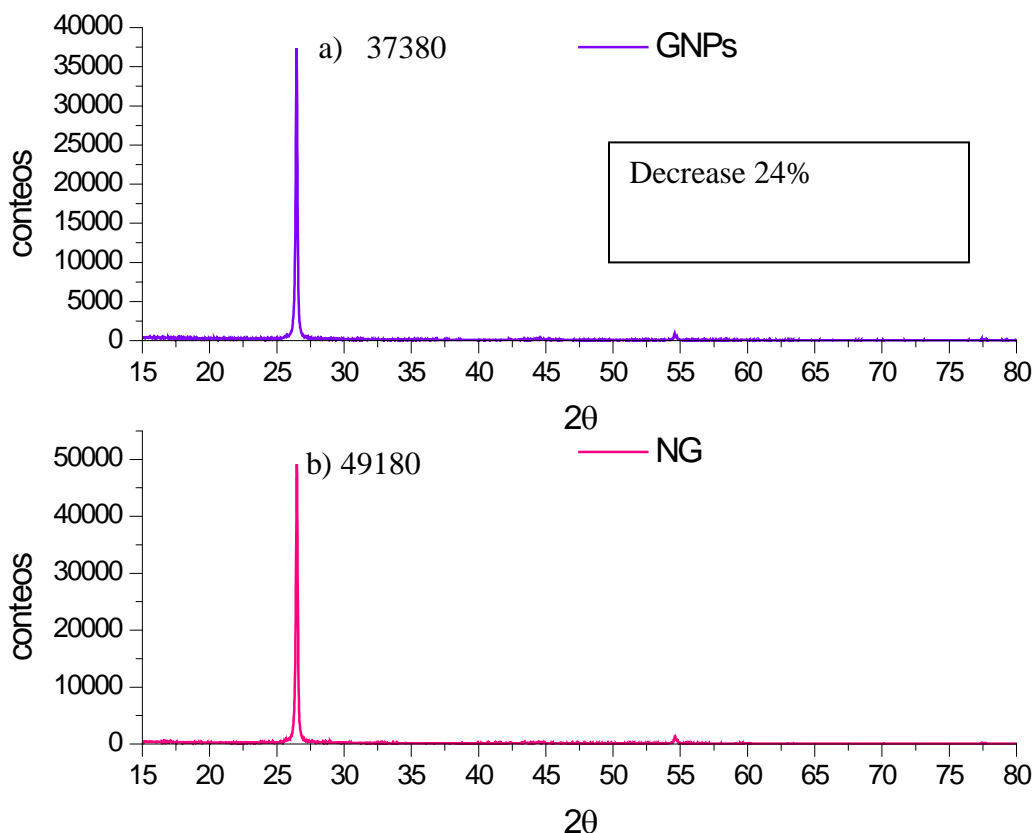


Figure 3. XRD patterns a) NG and b) GNPs

XRD patterns of samples from natural graphite and expanded graphite are showed in figure 2. In XRD pattern, the peaks coincide exactly, before and after treatment of expansion, the only difference, is the main peak intensity, which decreased from 49180 to 37380 counts. Using these values we calculate the percent of expansion, equivalent to reduction of 24%.

For NG peak intensity at $2\theta = 26^\circ$ indicates a highly organized crystalline structure. The main peak for expanded graphite decreases its intensity. This was attributed to: i) The graphite layers have been separated due to the presence of functional groups, and ii) the disordered structure of expanded graphite caused by the binding of functional groups.

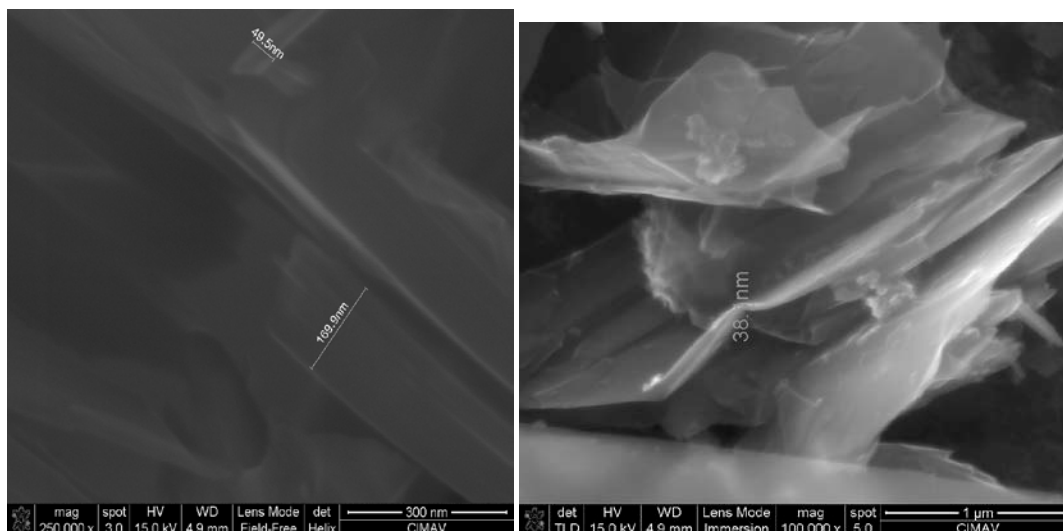


Figure 3. SEM micrographs. a) NG and b) GNPs

SEM micrographs of NG and GNPs are presented in Figure 3a and 3b respectively. For NG stacks are observed with a flat and smooth, well-defined borders with a thickness of 100 nm, with dense distribution. For there is a distribution GNPs is less dense, irregularly shaped, rough surface, rounded edges and spots on the surface, probably due to the presence of organic groups have an increased separation and there are some platelets with thickness less than 100nm.

Conclusions

This study has provided a novel method in order to expand and functionalize natural graphite to produce GNPs, which can then be dispersed in polymer matrices or non-polar solvents.

This method is relatively inexpensive and friendly, because it involves a single step

The techniques used for characterizing reveals that the natural graphite was expanded slightly, in other words, TEMPO groups were intercalated into the galleries of the natural graphite.

References

- [1] Jing Li, et al., *Composites Science and Technology*, **2007**, 67, p. 2114.
- [2] Jianfeng Shen, et. al., *Chem. Mater.*, **2009**, 15, p. 3514-3520.