J. Chil. Chem. Soc., 61, Nº 3 (2016)

STUDY OF PHYSICAL AND CHEMICAL CHARACTERIZATION OF NANOCOMPOSITE POLYSTYRENE / GRAPHENE OXIDE HIGH ACIDITY CAN BE APPLIED IN THIN FILMS

REZA JAMSHIDI RODBARI[1], RUNE WENDELBO[2], LOURDES CRISTINA LUCENA AGOSTINHO JAMSHIDI[3], EDUARDO PADRÓN HERNÁNDEZ[4], LUCIANO NASCIMENTO[5]*

[1,4]Program of Post-Graduation in Materials Sciences -PPGMS/ Center of Exact Sciences and Nature-CESN / UFPE,Recife - PE, Brazil.*
[3,5]Program of Post-Graduation in Chemical Engineering-PPGCE/ Center of Technology and Geosciences-CTG / UFPE, Recife - PE, Brazil.
[2]Oslo-Området, Norway Kjemikalier - CEO / General Manager at Abalonyx AS, Forskningsveien 1, 0373 Oslo, Norway.

ABSTRACT

This paper shows a study of Nanocomposite formed by adding reduced Graphene oxide with high acidity and polystyrene. The interest and research in the material is due to the ability of these nanoparticles significantly altering the electrical and mechanical properties of the polymer, even addition of small levels. The existence of functional groups on the graphene oxide containing abundant oxygen such as; epoxy, hydroxyl and carboxylic acid, can be well dispersed in the polymer because of its good interaction with polymer chains. In this study we used the solution by dispersing method to that made the use of solvent tetrahydrofuran (THF), for purposes of obtaining a reaction with functionalization of graphene oxide / polystyrene in time of 48 hours. The analyses of physical-chemical characterizations were made diffraction X-ray (XRD), scanning electron microscopy (SEM), Infrared Spectroscopy (IRD), Thermogravimetric Analysis (TG) and Differential calorimeter by scanning (DSC). The results obtained by XRD diffraction pattern showed a strong expansion in the peak, indicating amorphization on single sheets of graphene oxide due to distorted sp^3 sites CO. The morphology of the nanocomposite structure was with surface roughness, folds and rough predominant oxidation process of oxygenated functional groups. Their techniques showed the range of absorption, crystallinity degree and the mass loss. Finally, current and future possible applications of formed polystyrene nanocomposite/ graphene oxide show high acidity efficiency in the use of thin films.

Keywords: Nanocomposite; Dispersion; Graphene oxide; Polystyrene; Thin films.

1.INTRODUCTION

The interest and search for new materials or end products that is efficient and cost-effective production, and is suitable for technology innovation and environmentally green. Consequently, it is the intention of the researchers is thorough knowledge in this research material that can meet the need of the world market and social sustainability. Among this wide range and technological universality, has drawn attention of the scientific community graphene.

Graphene is a material that is motivating much research due to their quality of combination with other materials and highlighting the good mechanical, electronic, optical and physical and chemical properties. In view of the potential applications in the industrial field such as; sensors are nanocomposites in polymeric matrix, batteries, super capacitors, hydrogen storage and support for heterogeneous catalysts.

However, it is common knowledge; graphene is an atom-thick hexagonal flat sheet and hybridization type sp^2 carbon. Furthermore, it is a material having a single layer of carbon atoms arranged in a two-dimensional lattice structure (2D); is regarded as the basic structural element of some carbon allotropes [1]. Graphite oxide (GO) constitutes of a layered and water-soluble nanomaterial, which is obtained by extensive, chemical oxidation of graphite, each fundamental layer of GO consists of a dense two-dimensional carbonaceous skeleton containing a larger number of sp^3 hybridized carbon atoms and a smaller number of sp^2 carbons. In accordance with Meyer and collaborators on studies showed that these ripples in 3D are seen in a side scale of 10nm, it consists of a gain of elastic energy, probably due to interaction between the phonons with large wavelength stabilizing atomically thin membranes through its deformation in the third dimension [2]. But it should say another promising application is formed of graphene oxide films. In this perspective we include a transparent conductive oxide, which can have flexibility, chemical stability and viable cost.

However, the cohesion of the material and the influence that may occur between one interface and another material; when we treat and relate the material under study or analysis type material / product is being prepared; that is, there are conditions to specify the product that we have. When, we had referred a semiconductor or material with similar behavior.

In this case, it gives emphasis to the graphene and its electrical properties resulting from the fact that it is an electrical conductor without bandgap "zero band-gap conductors", with two linear bands that are at the extremes of the first Brillouin zone. However, graphene is a zero band semiconductor with extremely high carrier mobility that absorbs only 2.3% of visible light [3].

Polymeric nanocomposites has aroused the investigation of researchers also some technological sectors, mainly with use of graphene oxide nanoparticles. The good properties having a nanocomposite is connected adequate dispersion of the particles forming the dispersed phase.

With a view to the functionalization of graphene oxide polymer, derived primarily covalent and non-covalent binding, and numerous reactive groups of graphene oxide. However, when it is desired to obtain a nanocomposite with a combination of polymer / graphene oxide should have a good homogeneous dispersion of the materials. However, this integration is due graphene oxide group containing abundant oxygen, such as; epoxy, hydroxyl and carboxyl, can be well dispersed in a polymer matrix, due to its good interaction with polymer chains. However, in terms of functionality of the graphene oxide at the junction of a polymer, must obtain dispersions with good stability in nanoplatelets to this, it is necessary hydrophobic solvents which have activities to control the microstructure of nanocomposites.

Therefore, adsorption of the polymer is on the surface of the graphene oxide nanoplatelets via electrostatic interaction and Van der Waals force, when considering the functionality of noncovalent [4].

Whereas, some factors should be influence directly the various final properties of the nanocomposite and quality of graphene interface with the polymer matrix. Furthermore, the functionality achieved by covalent means of covalent bonding and hydrogen bonding benefits the surface of the graphene oxide sheets and also increase the degree of polymer dispersion. This work has the purpose of showing a concept for a nanocomposite with two types of materials, graphene oxide / polystyrene obtained in a dispersed form and the use of solvent tetrahydrofuran (THF), providing a significant improvement in mechanical properties of the material formed.

2.THEORY

2.1 STUDY OF THE ELECTRONIC STRUCTURE OF THE GRAPHENE SHEET

The exfoliated graphene sheets oxide contain groups with hydrophilic functionality will know:–OH; ─COOH; ─C─O─C─; C=O, which keep highly dispersible leaves in layers. It's providing more attractive and interesting properties in use and electronics applications, polymer composites, clean energy conversion and sensors. Particularly, the reduction of graphene Oxide sheets to the reduced graphene oxide sheets of considering a type of graphene derivative[5]. Knowledge already evidenced by scholar's graphene sheet containing a monolayer of carbon atoms form a planar hexagonal crystal lattice, forming a two-dimensional crystal[6].

However, it must be said that the model structure is the basis for other, as is the case of fullerene, being described as bending a sheet of graphene on a zero-dimensional structure similar to a soccer ball. Soon became intense theoretical

e-mail: rodbari.ufpe@gmail.com[1]

and interesting for the scientific community make the synthesis of graphene sheets through technical micromechanical cleavage, because too broad industrial use in transparent electrodes for liquid crystal display and transistors[7]. The graphene sheets are semiconductor gap null high mobility and relative ease of controlling the charge carriers even at room temperature[8]. Naturally, the occurrence of ripples in graphene sheets is from some local defects around a site on the network, chemical, electrical or structural uniqueness. In view of surface roughness of the sheet and of corrugations are at least 0.6 nm; and conformity of Figure 1 under reduced graphene oxide. However, the lengths of carbon monoxide connections (CO) do not exceed 0.3 nm by 26 oxygen atoms existing in the structure.

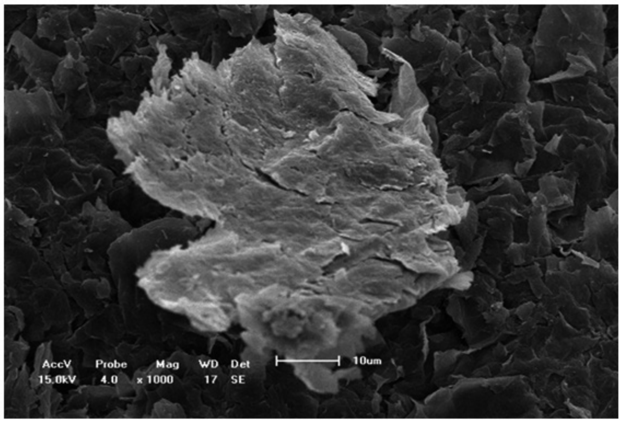

Figure 1. Representation distortions and ripples in graphene sheets.

The bonds formed in the crystalline hexagonal lattice of graphene are strong due to the sp^2 hybridization that allows three sigma bonds. The active dispersion forces is to London and induced dipole-induced dipole), which provides a space between layers of occupation of available binding agents[9].

The adsorption on the surface of the graphene sheets is by Van der Waals forces, which are weak bonds which favor the sliding of a flat on one another by applying an external force. In the vectors describing have the two triangular Bravais lattice for a graphene sheet, as can be had in equation 1 below. It can be had in equation 1 below. So we have the basis vectors: $\vec{c}_1$ e $\vec{c}_2$ with the subnet the vector is generated.

$$\vec{r}_i = n_i\vec{c}_1 + m_i\vec{c}_2 \tag{1}$$

Consequently, the subnet B is also generated by the vector.

$$\vec{r}_i = n_i\vec{c}_1 + m_i\vec{c}_2 + \vec{d} \tag{2}$$

Wherever n_i, $m_i \in \mathcal{Z}$, The origin of the unit cell system .Where each site of a network interacts with other neighboring sites of the three other sublattice via the vectors of the first neighbors 10. The excitations of quasiparticles (which appear to be fermionic) above the Fermi surface of the graphene, for propagation of the electromagnetic field in the presence of a graphene layer is then adjusted p her effective action where fermionic excitations are integrated outside, where the linear law dispersion, $\omega=v_F k$, (v_F is the Fermi velocity is the speed of light in vacuum),this law is valid for energies up to about 1eV.

2.2 FORMATION OF NANOCOMPOSITES (POLYSTYRENE / GRAPHENE OXIDE)

Industrial needs and technological advancement drives the demand for lighter materials, resistant and is durable, has flexibility with viable cost. Thus arose polymeric composites with different types of use and application to know; aeronautics, aerospace, automobile and sporting goods. Polystyrene is a well-known polymer commercially-like other plastic, and also one of the most consumed worldwide. Therefore, it is one of low cost thermoplastic in its production, possessed good electrical properties and transparency. But it is a hard material, limiting its application when required good impact resistance.

The formation of a material called polymer nanocomposites, is necessary particles with at least one of their dimensions in the nanometric scale, they are dispersed in a thermoset polymeric matrix, or thermoplastic elastomer[11]. However, the interaction between the polymer chains and nanoparticles gives nanocomposites properties superior to those presented by conventional polymers.

Scientific investigations show that the interface between the polymer and the form of nanoparticles, such as a maximum of three layers; the first layer is between essentially contact between the polymer and nanoparticles (Graphene Oxide). The second and third layer may or may not exist, and depend on the interaction between the phases of the nanocomposite [12].

Factors that influence the interface with the polymer matrix phase is dispersed, the chemical nature of the constituent materials, the shape presented by the nanoparticles, the size, concentration, orientation, and degree of dispersion occurred throughout the polymer. The structure of the films from the polymeric matrix over graphene oxide, notes a barrier in forming the layers. This existing barrier in film may have occurred in the permeation rate of the molecules of water and oxygen.

Causing defects or cracks in the layer that is produced during the process of preparing the composite preventing industrial. Many research with technological applicability, already conducted by scientists have revealed the thermal stability of nanocomposites formed in the composition of graphene oxide / polymer; Thin films exhibited a semi-conductive nature and to AM bipolar field effect[13].

The permeate flow in the material investigated dependent on the concentration gradient of diffusion of the molecules. The concentration gradient is determined by the solubility of the diffusion inside the polymer molecules and the lateral dimension of film barrier[14].It should be noted, the presence of Graphene Oxide will evidence the nucleation sites, altering the polymer morphology crystallization. The formation of smaller crystallites tends to increase the modulus of elasticity, but the impact creep resistance characteristics of the material are also altered stems and affects the morphology of the nanocomposite.

3. MATERIALS AND METHODS

The training and preparation of nanocomposite (polystyrene / graphene oxide), consisted of polystyrene polymer provided by the laboratory LMPC-DEQ- UFPE, and graphene oxide purchased by the company Abalonyx AS-Norway- OSLO, is a graphene oxide which is below 0.02%. The solvent used was a tetrahydrofuran (THF), so there is good dispersion between the Graphene Oxide and polystyrene. The materials were weighed on a scale with precession of three digits to form proportional. The production of polystyrene film comprised of a mass 5g in 100 ml of tetrahydrofuran (THF), at room temperature; then made using magnetic stirring with a time of 3 hours to facilitate dissolution of the polymer. Polymeric film left in a desiccator for 2 days before there junction of two materials. There were dissolution of Nanoparticle with the same solvent tetrahydrofuran (THF), and then made joining the polystyrene Graphene Oxide with a stir 15 minutes. The solution containing the two substances together stood in a greenhouse at a temperature of 70°C for 48 hours; thus ends up the Nanocomposite.

The physical-chemical characterization for samples obtained from the Nanocomposite, were held in two different locations namely; the CETENE (Strategic Technologies Center Northeast) in the state of Pernambuco, did the analysis X-ray diffraction (XRD), for track formed phases of the Nanocomposite. She used using an X-ray Diffractometer model Shimadzu XRD - 6000, with Cu radiation – K_α (λ = 1, 54056 Å), with a 40kV voltage Assays were carried out at a temperature of 298K and 30 mA current were acquired at angular intervals $0^o \leq 2\theta \leq 120^o$, compass $\Delta(2\theta) = 0{,}02°\Delta t/$ and step $(2\theta) = 4s$ representing a total acquisition time of 14 h 34 min.17s. To analyze the morphology of the composite have been using a Scanning Electron Microscope (MeV) - FEI QUANTA 200 / EDAX, this appliance is located at the Chemistry Department fundamentally DQF / CCEN / UFPE. The samples were previously coated with a gold film, following traditional methods in the art, through a sputtering process (sputtering) with sputter mark CARON MODEL 2050-4, with a thin gold layer of 20 nm and a current of 5 to 6 amps for a time of 2 minutes to improve the electrical conductivity on the surface, a good homogeneity of the ions in the target material may cause collisions between the material atoms with the electron beam, leading to a good view on observed sample in SEM. Then the samples were added in small metal containers and taken to the product and then be analyzed in (SEM).The thermogravimetric analyzes (TGA) were performed on a Perkin Elmer TGA TESTA 6000 machine. Samples of the nanocomposites were properly weighed and subjected to heating from ambient temperature (approximately 27-750°C at a heating rate of 10 ° C/min under an inert atmosphere with nitrogen flow of 50 mL/min). Therefore, for the analysis of Infrared Spectroscopy Fourier transform (FTIR), nanocomposites in their proper proportions were also analyzed by a spectrophotometer Perkin Elmer Spectrum 400 IFR. Scans were achieved in the spectral range 4000-400 cm^{-1}, using a resolution of 4 cm^{-1}. The realization of these characterizations occurred at the Department of Fundamental Chemistry (DFC/CCEN/UFPE).

4. RESULTS AND DISCUSSION

4.1 X-RAY DIFFRACTION

The evaluation for the purpose of identifying peaks and crystallization of the Nanocomposite held ray diffraction analysis (XRD). Figure 2 shows the XRD pattern obtained by the method of the dispersed polymer matrix (polystyrene with graphene oxide). The peak with the greatest intensity is related to the reduced graphene oxide.

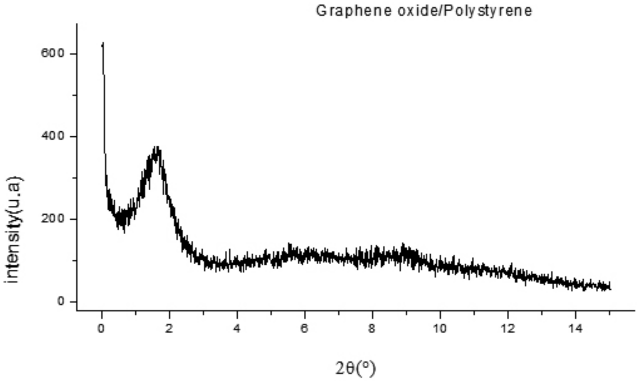

Figure 2. Characterization by X-ray diffraction *(*XRD*)* of nanocomposite of the sample after 48 hours.

The results from XRD analysis of the sample film formed has a bandwidth on the lower diffraction angle the results from XRD analysis of the sample film formed has a bandwidth on the lower diffraction angle (2θ=1,97°) corresponding to the existence of oxygen-rich groups on both sides of the leaves and the water molecule inserted between the sheets. It is existing peaks in the diffractogram similar suggests that the polymer chains are interspersed between the graphene nanoblades, maintaining the arrangement of the graphene sheets. Observed that after the functionalization of graphene oxide in the polymer, this low dislocation can be explained in the occurrence of flare spacing d is attributed to polystyrene chain between the interconnection with the Graphene sheets. In fact, the polystyrene is covalently bonded on the surface of Graphene Oxide; however, for film sample which had formed within 48 hours can be attributed to the diffraction band orientation of graphene sheets crosslink's to form a lattice.

4.2 SCANNING ELECTRON MICROSCOPY

Aiming to analyze the morphology of the nanocomposite fracture surface investigated (polystyrene/reduced graphene oxide), Figures 3 and 4 shows respectively show the results obtained in scanning electron microscopy, after mixing two materials for dispensation.

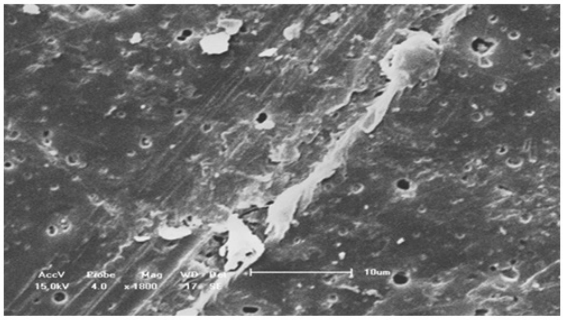

Figure 3. Morphology is showing the film surface fracture of Graphene oxide/polystyrene.

In this image the SEM of Figure 3 have a display surface in some areas of irregular morphology of fibers and various forms of holes evenly along the fiber, are structures are similar to the rod. But, there are 2 wt. % graphene oxide inclusions longer the polymer, the fibers presented in the fracture morphology is connected; indicating a high physical interaction existing between the fibers and the polystyrene nanocomposite. Overall, graphene has carboxylic acid functional group provides an intermolecular force calling itself bridge effect. Providing a cohesive bond on the system provides a more efficient load transfer to the polymer matrix. After the occurrence of functionalization will be observed that morphological change, crystallization distinguishing polystyrene and the reduced graphene oxide, this being attributed good combination of the Nanocomposite components[15].

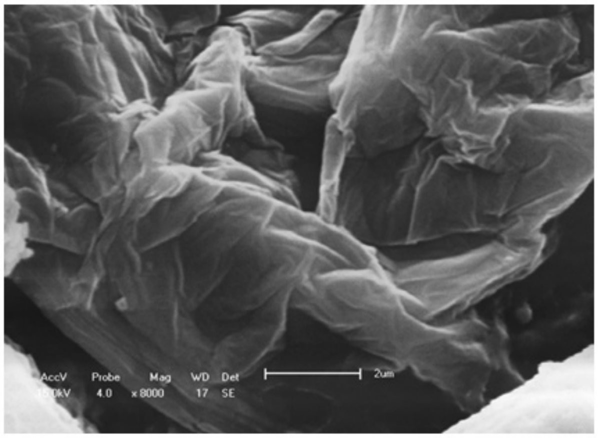

Figure 4. Morphology of SEM surface is a nanocomposite film showing the roughness and folds.

This Scanning Electron Microscopy (SEM) in Figure 4, we observed a morphological structure formed by several thick layers, arranged in regular patterns and characteristic stacking. Showing that the oxidation of graphene caused changes in their morphology, or it has a wrinkled appearance with multiple folds. This wrinkled aspect can be explained by the oxidation process to promote the admission of hydroxyl groups and epoxy, known as functional groups, which in turn, alter the hybridization of the carbon sp^2 (planar structure) to sp^3 (tetrahedral structure). However, the structures formed layers is due to the degree of oxidation that occurs in the material, since the greater the degree of oxidation, are more widely spaced the functionalized layers. Noting that the chemical reduction of graphene oxide causes partial removal of functional groups is still present. However, this does not completely restore the graphene structure in the material; namely, chemical reduction of the GL does not recover crystal defects caused by oxidation.

We verified this morphology the presence of well-dispersed layers, indicating that after chemical reduction the material has not organized its crystal structure. Consequently, an increase in surface area of these nanoparticles in the Nanocomposite, allowing the modification of the polymeric matrix structure, and this may result in increased elastic modulus and hardness of the sample; possibly change in the degree of crystalline because smaller nanoparticles can act as nucleation sites.

4.3 INFRARED SPECTROSCOPY FOURIER TRANSFORM SPECTROSCOPY (FTIR)

Infrared spectroscopy Fourier transform (FTIR) is shown in Figure 5. The FTIR spectra were obtained in the absorption band of 4000 to 400 cm^{-1}, but the band was found between the study between 4000 and 400 cm $^{-1}$, as is shown in figure 5 below:

The band in the range of 3445.15 cm^{-1} showed a relatively broad bandwidth that is probably related to the axial deformation of the O-H bond. The other bands in the range of 3026.35 cm^{-1} C-H show that the Nanocomposite formation process between the polymer and reduced Graphene oxide on the surface was successful. However, the characteristics and similar bands have the predominance of graphene oxide. The oxygen atoms tend to combine with carbon atoms thereby forming an array of functionality, among which can be mentioned: ketones, esters, carboxylic acids, and others.

The three faint bands were observed in the region between 1651 and 1452-1366 cm^{-1} due to bending vibrations and axial deformation of the C = C bonds is low because of graphene oxide content with respect to the polymer matrix. The two most intense peaks has its stretching vibration ascribed to C = O appeared FTIR OG/PS is in the range 1493- 1601 cm^{-1} are due to the formation of hydroxyl and carboxyl groups, resulting from the chemical reaction. The band located at 748 cm^{-1} is related to the C-axial deformation the primary alcohols and other of band and 540 cm^{-1} are due to the angular deflection of C-H with H out of plane.

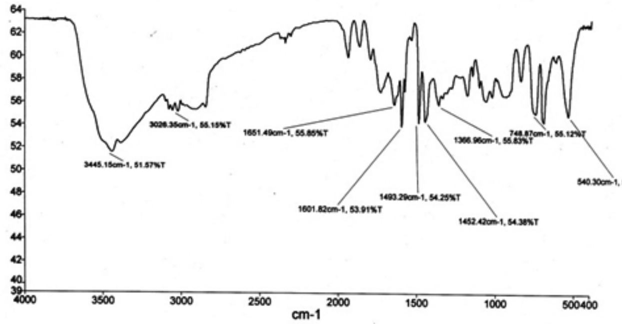

Figure 5. Spectroscopy FTIR is absorption in the region 4000-400 cm-1nanocomposite graphene oxide/polystyrene.

4.4 THERMAL ANALYSIS TG AND DSC

Figure 6 is showing two curves that refers TG blue, red and other DSC curve. More we have a curve representing weight loss obtained by the thermogravimetric analysis events occurring three weights at certain temperatures. For the DSC curve observed melting temperature, crystallization temperature and degree of crystallization of the obtained nanocomposite (polystyrene/ graphene oxide). The influence of the dispersion method are and the presence of the nanoparticles this property.

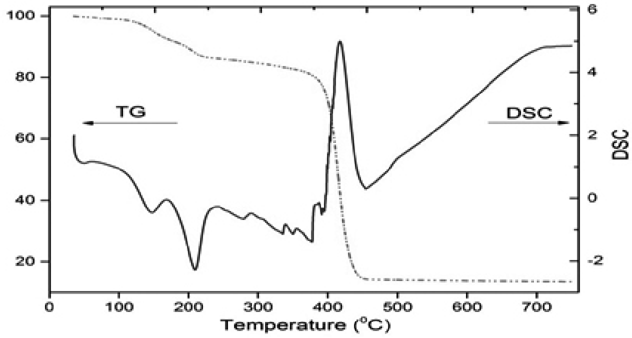

Figure 6. TG curves of during heating being studied by Differential Scanning Calorimeter (DSC).

The first mass loss observed with 3.3% percent at 100°C for the graphene oxide is lost can be attributed to physically adsorbed water removal water on the surface of the graphene oxide. The second mass loss event occurs at 200°C with 19.4% considering the thermal stability of the nanocomposite graphene/ polystyrene oxide. The homogeneity of the polymeric matrix in the dispersion is preventing the output of small gas molecules during thermal degradation. The third mass loss is about 15.4% in a 417°C temperature will ascribe removal of more stable functionality oxygen. The crystallization temperature (T_c) of the Nanocomposite with a reduced Graphene/ Polystyrene oxide; mean there was a good spread between sheets of graphene and polymer.

Indicating that they are nanoparticles tend to act as nucleating agents. Factors such as polarity of the phases and free energy interfere with the interaction between nanoparticles and polymer matrix; there is interference with the potential nucleation. In general, there is a tendency of increasing the degree of crystallinity by reducing the size of the nanoparticles thus exfoliated or dispersed states tend to have the highest crystallinity results. The melting temperature of the nanocomposite has no change compared will pure polymeric matrix, according to studies by the scientific literature.

CONCLUSIONS

In summary we can mention the following conclusions:

- Found in this study topological defects may have negative or positive inflections in the graphene sheet; it has an effect on the behavior of the electrons, since this material exhibits intrinsic undulations its structure;
- The solubility of graphene oxide in water and other solvents allows it uniformly on the deposition substrate which vary in width in the form of films or networks; making it potentially useful for electronic industries;
- The combination of the reduced graphene oxide high acidity solvent tetrahydrofuran (THF), exhibited good dispersion and a strong interfacial;
- The surface of the film structures in the nanocomposite with folds formed in layers and roughness is due to the degree of oxidation that occurs in the material, since the greater the degree of oxidation will be at spaced more functionalized layers;
- Observed by Infrared Spectroscopy Fourier Transform, the Nanocomposite formed by (reduced Graphene Oxide/polystyrene),the two most intense peaks has its stretching vibration ascribed C = O, is in the range 1601 e1493cm^{-1} are due to the formation of hydroxyl and carboxyl groups, it is the result of a chemical reaction;
- Thermogravimetric analysis enabled us to verify the homogeneity of the polymeric matrix in the dispersion, prevent the output of small gas molecules during thermal degradation;

- The state of dispersion of nanoparticles, the effectiveness of the dispersion technique and possible difficulties of interfacial adhesion is due to the difference in chemical nature of the constituent phases.

ACKNOWLEDGMENTS

The authors have thanks special to Dr. Rune Wendelbo Chief of the Company Abalonyx AS, that support and procurement of all raw materials and help to development of this research and CETENE/Strategic Technology Center of the Northeast, Department of Fundamental Chemistry-DFC/UFPE and laboratory LMPC/ DEQ/ UFPE.

REFERENCES

1.- TZALENCHUK A.; LARA-AVILA S.; KALABOUKHOV, A;. PAOLILLO, S.M.; SYVAJARVI, R.; YAKIMOVA, O.; KAZAKOVA, T.; JANSSEN, V. FALKO, E.; KUBATKIN, S. Graphene: Setting New Standards, ***Nature Nanotechnology, 5, 186-189 (2010).***

2.- J. C. MEYER, A. K. GEIM, M. I. KATSNELSON, K. S. NOVOSELOV E T.J. BOOTH, S. ROTH. The structure of suspended Graphene sheets, ***Nature, 446, 60-63 (2007).***

3.- BLAKE, P., HILL, E. W., CASTRO NETO, A. H., NOVOSELOV, K. S., JIANG, D., YANG, R., BOOTH, T. J., GEIM, A. K. (2007) Making Graphene visible. ***Applied Physics Letters. 91:1-3.***

4.- MA, P.C.; SIDDIQUI, N.; MAROM, G., KIM, J.K. Dispersion and functionalization of carbon nanotubes for polymer-based Nanocomposites: A review. Composites Part A: ***Applied Science and Manufacturing, v. 41, p. 1345-1367, 2010.***

5.- EDA, G., FANCHINI, G., & CHHOWALLA, M. (2008). Large-area ultrathin films of reduced in Graphene oxide as a transparent and flexible electronic material. ***Nat Nano, 3(5), 270-274.***

6.- LAMBIN, P.; FINK, E J .Electronic states of carbon materials. ***Encyclopedia of Condensed Matter Physics* 1**. pp.142-151,2007.

7.- BLAKE, P., BRIMICOMBE, P. D., NAIR, R. R., BOOTH, T. J., JIANG, D., SCHEDIN, F., PONOMARENKO, L. A., MOROZOV, S. V., GLEESON, H. F., HILL, E. W., GEIM, A. K., NOVOSELOV, K. S.(2008) ***Graphene-Based Liquid Crystal Device. Nano Lett. 8:1704–1708.***

8.- Y. ZHANG, Y. TAN, H. L. STORMER E P. KIM. Experimental observation of the quantum Hall effect and Berry's phase in graphene. ***Nature, 438 201-204 (2005).***

9.- PEI, Q. X.; ZHANG, Y. W.; SHENOY, V. B. A molecular dynamics study of the mechanical properties of hydrogen functionalized ***Graphene. Carbon, v. 48, n. 3, p. 898-904, 2010.***

10.- BUENO, J.M .***Propriedades Eletrônicas de Grafeno com Defeitos***. Tese (Doutorado no Departamento de Física)-João Pessoa-PB, Universidade Federal da Paraíba-UFPB,14p,2001..

11.- FISCHER, H. Polymer Nanocomposites: from fundamental research to specific applications. ***Materials Science and Engineering* 23**. pp. 763-772, 2003.

12.- TANAKA, T.; KOZAKO, M.; FUSE, N.; OHKI, Y.Proposal of a multi-core model for polymer Nanocomposite dielectrics.***Transactions on Dielectrics and Electrical Insulation*** **12**, pp. 669-681, 2005.

13.- HEO C; MOON H-G; YOON, C.S; CHANG, J-H: ABS Nanocomposite films based on functionalized-Graphene sheets. ***J App PolymSci.*****124**. pp.4663–4670,2012.

14.- WHA-YONG LEE.; SEUNG-YEOL, YANG.; JIN-NAM, JEON.; YOUNG, JAE ,CHO.; YONGWOO, KWON.; YONG-SEOG, KIM. Ultra-thin Graphene Oxide/Polymer Multi-Layer Encapsulation for Flexible OLED. Displays.***Dept. of Materials Science and Engineering,***Hongik Univ., Seoul, Korea. SID 2014 DIGESTS.

15.- F.A, HE. H-J, WU. X-.L, YANG. K-H, LAM.; L-W,H,CHAN. Novel exfoliated graphite Nanoplates/syndiotactic polystyrene composites prepared by solution-blending***, Polym. Test. 42 (2015) 45.***