Manufacture of graphene sensors for stress/force measurements in mechatronic/robotic units

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***Abstract*—The present work shows the different production techniques used to obtain graphene nanoplates with few layers, as well as the synthesis of cross-linked polysilicone, both necessary for the manufacture of the soft matrix nanocomposite sensor based on polysilicon and graphene. It was determined that with the liquid phase exfoliation technique in N-methyl-pyrrolidone we can obtain graphene with the desired characteristics since the XDR, SEM, and TEM tests indicate it; only the sonicated time should be adjusted to achieve the desired dimensions. And after that step, to manufacture the sensor.**

***Index Terms*—graphene, sensor, nanocomposite, robotic, polisilicone.**

I. Introduction

Technological development is becoming increasingly transdisciplinary. To generate new and useful results, the idea of networking is accepted in the scientific community, following the teachings of the great physicist Werner Heisenberg when he proposes that "The whole is much more than the sum of its parts" [1]. An example of this is the discipline of mechatronics and robotics, which today is revolutionizing not only production methods and also the lifestyle. New developments in mechatronics/robotics require more and better sensors, which are integrated into different components. Today the idea of autonomation JIDOKA (Automation with a human touch) [2], implies the perfection and miniaturization of the basic components, that are: the sensors, the actuators, the mechanical structures, and also the capacity of the electronic support (hardware) for the control logic (software). Integrating components such as "stress sensors" at many points of the mechanical structure and "force-contact sensors" at key locations to generate touch effects requires highly developed and sensitive sensors. Historically and until very shortly ago, in the classical idea, a mechatronic system is calculated for a specific load state (limit) and safety coefficients are applied to it that oversize the structure. Developments based on this paradigm, not only implies higher material costs, but mainly causes a problem because it implies increasing the mass of mechanical components, masses subjected to permanent accelerations and decelerations during their operation in the mechatronic assembly, and that increase the power of the actuator and then one additional energy consumption. Changing the paradigm and in that sense, dynamically control the mechatronic-system in many points, and make the parts work at a maximum tension (without over-dimensioning), controlling the actuators (motors) involved in its movement [3], is now possible if we have multiple integrated sensors with low cost [4], miniaturized and minimum mass. That is why the development of the present work focuses on solving this problem, building and applying low-cost sensors with greater sensitivity than traditional electronic ones [5] [6]. The exponential growth of these developments in the field of mechatronics also allows the generation of micro-sensor structures to capture information analogous to touch, which is another of the great contributions sought for the development of prostheses or parts for humanoids with specific functions in industry or other areas.

II. Materials and equipment

The materials and reagents used for the graphene production process were, synthetic graphite (-20 + 100 mesh, 99.9% metal basis, ALFA AESAR), absolute anhydrous alcohol 99% RA (Anedra Research G SA), SDS Sodium Dodecyl sulfate (Cytiva), N-methyl-2-pyrrolidone (CARLO ERBA). In addition, for the synthesis of the cross-linked polysilicone (PSR) samples and the nanocomposite, 350 cst silicone oil (Dow Corning), boric acid (Anedra Research G SA), anhydrous ferric chloride ($FeCl_3$),colloidal silicon dioxide (Aerosil) and chloroform pro-analysis (Cicarelli Laboratories) were needed. A low-power sonicator (ARCANO), a heated magnetic stirrer (AREC), an analytical balance (ACCULAB) and a VT3216 centrifuge (CAVOUR) were used for the preparation of

graphene, as for the PSR and the nanocomposite, plus as a planetary ball mill (PM100 RETSCH®).

III. Graphene production techniques

In this section, the graphene production techniques that we have used for our research are listed.

A. Exfoliation of graphite through a ball-milling approach

Material obtained from 99.9% purity synthetic graphite was synthesized by mechanical milling by the method of Jeon *et.al* [7]. For this, dry ice was used in a planetary ball mill with the following parameters: speed 500rpm; milling time (1, 6, and 24 hours). For all the samples, after milling, 2 washes with hydrochloric acid and distilled water were carried out, because they all showed magnetic behavior, due to the wear suffered by the metal balls inside the milling chamber. Said wear varied between 1.5% and 3% of the weight of the balls used, its percentage increasing with the milliing time.

B. Liquid-phase exfoliation of graphite

Since 2008 the researchers began to study the possibility to exfoliate thin platelets of graphene directly of graphite, by sonication in different organic solvents kinds [8] [9].In this work those that gave us results are reported.

1) Surfactant assisted aqueous-phase graphite exfoliation: This technique consists in performing a surfactant-assisted graphite exfoliation in aqueous phase [10] (water + 15% Wt ethanol + 2.6 Mm SDS) by low-power sonication for 6 hr, the solution obtained must be poured into a test tube, trying only to pass the suspended particles and it is centrifuged at 1500 rpm for 30 min, to verify the effectiveness of the method to obtain supernatant after centrifugation.

2) Exfoliation of graphite in solvent N-methyl-pyrrolidone: Following the methodology reported by O'Driscoll *et al.* [11] for the preparation of graphene by liquid exfoliation, a concentration of 100 mg/ml of graphite in NMP (n-methyl - 2 - pyrrolidone) is used to prepare 5 g of graphite and sonicates at low power for 6 h, changing bathwater every 1.5 h to lower the temperature. Subsequently, the supernatant content (approx 90%) of the solution obtained is extracted and centrifuged at 1500 rpm for 90 min to remove the heaviest particles. The suspended particles after centrifugation are vacuum filtered with a 0.45 µm pore diameter nylon filter membrane, obtaining thin graphene films, changing them if necessary. As a next step, the membranes with graphene are split to be poured into chloroform and proceed by means of sonication to extract the graphene from the filters. In this case, they were sonicated for 13.5 h at low power. A second sonication was carried out on the remaining graphite, trying the same concentration as the first one to try to obtain a higher concentration of graphene with the same sonication time [12].

IV. Synthesis of cross-linked polysilicone (PSR)

Different methodologies were used to manufacture the PSR, obtaining different syntheses, most of which underwent crystallization over time and others presented characteristics different from those expected, such as high adherence and fluidity. Two of the samples conserved characteristics similar to Silly Putty®, at least at a qualitative level.

Both samples were synthesized using percentage values by weight to silicone oil (Table I); for sample 1, the mean value of Aerosil, 50% by weight of $FeCl_3$, and the mean value of percentage by volume of ethanol was used as a reference. The silicone oil and boric acid were mixed, constantly stirring until the sample homogenized, the $FeCl_3$ and ethanol were added, mixing for 5 min, finally, the Aerosil was added to the mixture and stirred constantly for 5 minutes Furthermore, the resulting solution is placed in a silicone oil bath 350 to 200 ° C for 45 min, performing permanent stirring with a magnetic stirrer. Sample 2 was prepared with the percentage weight of Aerosil and $FeCl_3$ corresponding to the maximum value of the range shown in table ref table1 and the maximum percentage value in the volume of ethanol; In this case, the silicone oil and boric acid are mixed until homogenizing, separately, the Aerosil, $FeCl_3$, and ethanol were mixed, with permanent stirring to later join the two mixtures until they are homogeneous, the resulting solution is placed in a silicone oil bath 350 to 200 ° C for 35 minutes, making permanent stirring with a magnetic stirrer.

TABLE I
Composition Of Cross-Linked Polysicone

Component	Quantity
Silicone oil 350	100 g
Boric acid	40 g
Colloidal silicon dioxide	5 - 10 g
Ferric chloride III	0.1 - 0.5 g
Ethanol	5 - 7 ml

V. Results and discussion

The unwashed and washed samples of the graphene synthesized via mechanical milling were studied using an X-ray diffractometer. The results obtained in the unwashed samples (Fig. 1-a) determine characteristic crystalline peaks of Fe product of the chamber and the beads ($2\theta \simeq 45$), in addition to the characteristic peaks of graphite. These last peaks widen showing their amorphous structure and move to the left, after the washes are carried out on all the samples (Fig. 1-b), the iron peaks disappearing.

On the other hand, the degree of exfoliation of graphene obtained by way of the liquid phase in NMP, is studied by X-ray diffraction; it can be verified that the graphite presents a characteristic peak in the XRD pattern ($2\theta = 26.5$) assigned to the plane (0, 0, 2) [13]. The graphene produced shows almost the same diffraction peak of graphite ($2\theta = 26.61$) (Fig. 2) which can be interpreted as that graphene still conserves the structure of the carbon atoms. It is also observed that the peak is very intense and narrow (Fig. 2), this is due to the

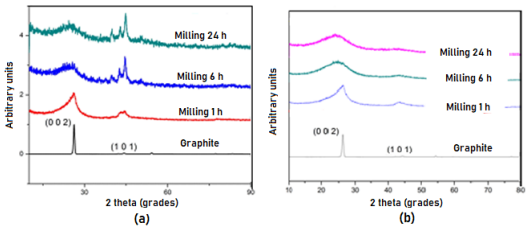

Fig. 1. Graphite diffractograms (99.9%) with different mechanical milling times: (a) unwhased, (b) whased

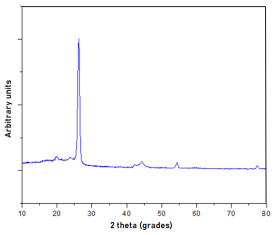

Fig. 2. Graphite diffractograms graphene diffractogram obtained by exfoliation in liquid phase in NMP and redispersed in chloroform.

appearance of exfoliated plates of less thickness when the graphite was transformed into graphene [14].

Using Bragg's law (1) we calculate the spacing between graphene sheets, from the washed samples, understanding that the amorphous peaks shown in Fig. 1-b are the product of the stacking between sheets and the samples obtained. by exfoliation in liquid phase in NMP (Fig. 2), whereby the separation between the sheets is given by:

$$D = \frac{n}{2Seno(\theta)} \tag{1}$$

Where, *D*= interlaminar distance, *n*=integer number, θ=angle of incidence.

Once the spacing between the sheets has been obtained, using Debye Scherrer (2) the size of the graphene sheet stack is calculated as:

$$d = \frac{k}{\beta Cos(\theta)}\lambda \tag{2}$$

Where, *d* = size of the crystal domain (stacking size in our case), *k*= dimension factor that depends on the shape of the particles, λ= wavelength, β= width of the peak at mid-height and θ= Bragg angle of the corresponding maximum. Finally, to obtain the number of stacked sheets *nl*, we divide the size of the stack *d (nm)* by the spacing between the sheets *D (nm)*. The values obtained are shown in Table II.

It has been shown that milling of more than 24 hours does not decrease the number of layers obtained, with this method having a limit of obtaining for commercial graphene of 6 layers by mechanical milling [15]. These arrangements are in the form of graphene nanoplates as observed in Fig. 3-A.

TABLE II
DATA OBTAINED FROM THE XRD

Material	**2θ_{max}**	**D (nm)**	**d(nm)**	**nl**
Milling 1 h	26.25	0.34	4.80	14
Milling 6 h	24.82	0.36	2.29	7
Milling 24 h	23.78	0.37	2.22	6
NMP+$CHCl_3$	26.61	0.115	0.31	3

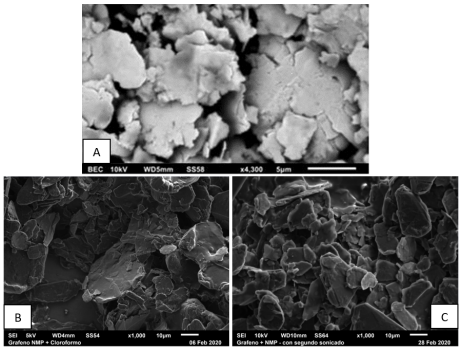

Fig. 3. SEM micrograph of graphene nanoplates obtained: A- with 24 hours of mechanical milling, and exfoliation of graphene in liquid phase in NMP, redispersed in chloroform, B- first sonication, C- second sonication.

In the Table II we can see that by this method it was possible to obtain microplates with a smaller number of sheets, it should be clarified that this analysis is for the graphene obtained in the second sonication of graphite in NMP (Fig.3-C). It is also highlighted that even in this instance, although the desired "nano" size was not achieved,it can be verified that it was possible to reduce the average size of the microplates that are presented with a first sonication (Fig.3-B).

As a complementary study, observations were made with a transmission electron microscope (TEM-Phillips EM 301), applied as a suspension of diluted ethanol on a Formvar/carbon 300 mesh copper grid, of the samples obtained by the different synthesis methods. ; Fig.4-a shows a micrograph of graphene obtained by mechanical grinding of 24 h, in which a deformed multiplanar arrangement of thin sheets is observed under the application of different weak forces [15] [16], so when used for the manufacture of the sensor, it presented instability, degrading the nanocomposite in a matter of hours; Fig.4-b is an image of a sample obtained through the surfactant assisted aqueous phase exfoliation method, a stable but very low concentration of graphene nanoplates with few layers (Fig.4-c) suspended and Surfactant remaining particles (SDS), which like the incompatibility of water with chloroform, represent a problem to be used in the manufacture of the nanocomposite. Fig.4-d is of a sample obtained by exfoliation of graphite in NMP, in which we can see that graphene microplates with a few sheets were obtained, with a quite acceptable concentration, which is very promising to be used in manufacturing. of the sensor, only the sonication process must be adjusted to obtain nanoplates, which is the ideal size

to synthesize the nanocomposite [5] [11].

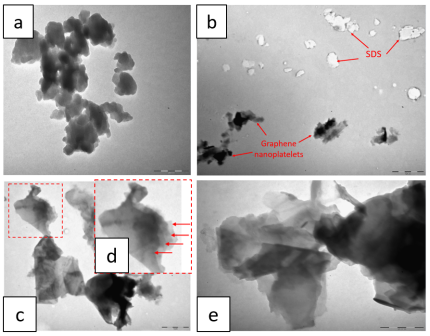

Fig. 4. TEM micrograph of graphene nanoplates obtained: a- with 24 hours of mechanical milling, b- surfactant assisted aqueous-phase graphite exfoliation, d- is a magnification of the area enclosed in dotted lines of "c", in which at least 4 edges of layers of the nanoplate can be distinguished, indicated with the arrows, e- exfoliation of graphene in liquid phase in NMP, redispersed in chloroform, second sonication.

Since Boland *et al.* [5] developed the first reported sensor for a soft matrix nanocomposite based on polysilicone and graphene and comparatively demonstrated the gauge factor (500 vs 82 [17]) far exceeded its nanocomposite predecessors, the application of these showed excellent performance in biomedical applications. Then, the manufacture of this type of sensor has presented great advances concerning its optimization in the manufacturing methodology [11]. Thus expanding its field of application in this branch. Hébert *et al.* [6] reported the use of a nano pressure sensor for soft materials, with which the conventional sensor gauges did not show good functionality. In this way, the possibility of its application in soft robotics where traditional deformation sensors have great limitations becomes more efficient. In the same sense, Peña-Consuegra *et al.* [18] are working on the fabrication, characterization, and calibration of a PSR and graphene nanocomposite sensor for applications in robotic devices and structural dynamics.

VI. Conclusion

In this work, the techniques used to obtain graphene as well as the synthesis of the PSR, both of our own manufacture, to manufacture a nanomaterial to apply it in stress/force sensing tasks were shown. From the reported development we can draw some important conclusions:

- Due to the amorphization suffered by graphene nanoplates in the mechanical grinding method, it is not possible to obtain the properties required for the nanocomposite sensor.
- The method of exfoliation of graphite in aqueous phase assisted by surfactant, gives us suspended nanoplates, stable over time, but at a very low concentration, showing inefficient the process. Furthermore, the incompatibility of water with chloroform represents a drawback for the manufacture of the nanocomposite.
- The liquid phase exfoliation method in NMP will be used to produce graphene for the sensor manufacturing, based on the evidence obtained by the XDR, SEM, and TEM tests reported, which show that modulating the sonication time they comply with the characteristics of graphene used in the manufacture of successful previous sensors, reported in our sensor cited references.

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