ABSTRACT: In this paper the process of manufacturing and performance analysis of piezoresistive graphite sensors on paper substrate and encapsulated with Bisphenol A epoxy resin is discussed. Piezoresistive semiconductor sensor elements used in mechanical stress sensors, pressure sensors, chemical sensors, accelerometers, and other electronic devices involve complex manufacturing systems. Graphite-based piezoresistive sensor elements have promising advantages compared to traditional materials because they have excellent mechanical, electrical and thermal properties. The processing of graphite sensing elements using mechanical exfoliation on paper, GoP method, does not generate considerable environmental impacts, does not demand complex processes and equipment that generate high costs and have controllable functionalities.

KEYWORDS - Epoxy Resin, Graphite on Paper, Mathematical Modeling, Sensors Elements, Packaging

I. INTRODUCTION

Graphite sensor elements feature high sensitivity, controlled resistivity and operate at different temperatures. The sensor elements can be integrated into microelectromechanical systems for a wide range of applications, such as automation and control systems, biomedical engineering, robotics, agricultural and industrial equipment [1,2]. A graphite film deposited on paper polymer substrate is mechanically flexible and allows measurements of deformations for different degrees of applied mechanical stresses [3,4].

Currently, the development of sensors with different materials is based on the piezoresistive effect. Its use for accuracy of measurements is excellent, which comes guaranteeing quality in batch productions. Thus, piezoresistive sensors are much needed by industries and their improvement has been a constant evolution.

Otherwise, a sensor device to function properly needs to be encapsulated which represents something around 70% of the total cost of the device. Therefore, in this work the graphite sensor element encapsulated with epoxy resin bisphenol A is characterized as an alternative to develop low-cost sensor elements.

II. ELECTRICAL CONDUCTION MECHANISMS AND GRAPHITE PROPERTIES

In graphite each carbon atom is attached to another three in a plane composed of hexagonal cells as illustrated in Fig. 1 (a). In this state, three electrons meet in sp² plane hybrid orbitals and the fourth in a p orbital plane.

The set of these orbitals forms plate known as graphene, as shown in Fig. 1 (b). These overlapping plates are joined together by covalent bonds, Van der Waals bonds, forming an infinite mesh of hexagonal type.
The structural arrangements of the graphite atoms contribute by making it a good conductor of electrical current. Its hexagonal rings are shaped by double conjugated bonds, which allow the migration of electrons. Its overlapping rings in different planes and united by weak connections allow the movement of electrons between the planes, thus occurring transfer of electricity [5].

The delocalized electrons move easily from one side of the flat layer to the other. This gives it electrical resistivity of $5 \times 10^3 \Omega \cdot m$ in the direction perpendicular to the graphene planes, characterizing it as semimetal. While in the parallel direction to the plane it has electrical resistivity of $5 \times 10^{-6} \Omega \cdot m$, characterizing it as a good electric conductor [5,6].

When a material is a good conductor, its thermal properties are dependent on its electrical properties. When the material is a semimetal, in the case of graphite, its thermal properties are influenced by the vibrations of the crystalline network [7]. This indicates that temperature changes can influence the physical properties of graphite.

The increase in the number of free electrons causes the resistivity to decrease with increasing temperature, as there is an increase in the charge carriers in the conduction band. Otherwise, the density of the graphite is very similar to that of the silicon of the order of $2.26 \text{g/cm}^3$ [7].

III. PIEZORESISTIVE SENSORS

Sensors are devices that allow to obtain information of the medium in which they are inserted and in the form of actuators are able to interact with the same [5]. Sensors are mechanisms capable of perceiving external actions or stimuli, interacting, through information of different natures. In this work the effect of piezoresistivity is explored to implement the graphite sensing elements.

The piezoresistivity, $\frac{\Delta \rho_{ij}}{\rho}$, is the modification of the electrical resistance, $R$, of the semiconductor material when it undergoes a certain mechanical stress, $T_{xy}$, according to Equation (1),

$$\frac{\Delta \rho_{ij}}{\rho} = \pi_{ijkl} T_{kl}$$

In which, $T_{kl}$ is the mechanical stress performed on the material structure. The relationship between mechanical stress and mechanical deformation is given by the modulus of elasticity $E$, being described by Equation (2),

$$T_{kl} = E \varepsilon_{ijkl}$$

For some cases mechanical stresses, $T_{kl}$, are components along the axis of the crystal, but for others, an arbitrary oriented coordinate system is employed, so that the generalized Hooke Law must be used to determine the coefficients of elastic deformation, $S_{ijkl}$, expressed by Equation (3),

$$\varepsilon_{ijkl} = S_{ijkl} T_{ij}$$

Where $S_{ijkl}$ is a fourth-order tensor of elastic deformation constants of the material used as sensor element.

The knowledge of the constants is important for making sensors from a given material, since it is possible to determine the relationships between the mechanical stress and the mechanical deformation and, consequently, the behavior of a piezoresistor that will be manufactured on a given substrate. In the matrix form, the mechanical stress resulting from the constants can be described by Equation (4),

$$T_{ij} = C_{ijkl} \varepsilon_{ijl}$$

The piezoresistive coefficient is dependent on the crystallographic orientation and the resistivity, which in turn are intrinsic properties of the material itself to be considered or chosen as a sensor element and will be the focus of determination in this article [7].

![Graphite structure and (b) graphene plane](image)
IV. ENCAPSULATION OF SENSORS ELEMENTS

Encapsulations in addition to protecting the sensors from the action of environmental factors such as temperature, magnetic fields, atmospheric pressure, corrosion, humidity, electrical discharges also guarantee the useful life of the properties and desired parameters of the sensor.

For an encapsulation to be considered efficient, it must comply with three basic requirements, that is, to have good performance, to be reliable and to have a low cost. However, many developed encapsulations end up negatively influencing the performance of the sensors, in addition to having high costs, which makes their manufacturing and use disadvantageous.

The determination of the material used to encapsulate the piezoresistive sensor element Epoxy-Bisphenol A was based on its ability to maintain the mechanical functions of the sensor, protecting it electrically, thermally and chemically, in addition to guaranteeing the reading of the parameters of the device [8].

Epoxy resins are widely used as adhesives coatings and laminates in the chemical, electrical and mechanical industries. Generally, epoxy resins exhibit good resistance to mechanical and chemical stresses, however, their properties depend on the type or amount of hardeners used and curing conditions.

Bisphenol A, also known as BPA, is an organic chemical, as shown in Fig. 2, derived from petroleum and constitutes the basic (intermediate) unit of high performance polymers and coatings, mainly polycarbonate plastics and epoxy resins.

![Figure 2. Molecular structure of bisphenol A type epoxy resin.](image)

Applications with Bisphenol are many and varied, ranging from DVDs, computers and home appliances to glasses and construction frames and lenses, paints, coatings for food and beverage cans. Small amounts of Bisphenol A are also used as components of formulations of antioxidant additives in soft PVC, wires and cables and as a color preparer in thermal papers. In this work the epoxy resin is used to encapsulate sensor elements in paper substrate.

V. EXPERIMENTAL PROCEDURES AND STRUCTURE OF THE SENSOR ELEMENT

For the manufacture of flexible systems it is used as insulation substrate, white paper, since its fiber-based structure allows the application of forces, causing mechanical tension and changes in the sensor device. The sensor element is made of commercial hardness graphite 2B by traces of pencil directly on paper. The steps of making each sensor element and the electromechanical characterization process are shown in Fig. 3.

![Figure 3. (a) Schematic of the sensor element and (b) Real image of the sensor element.](image)
The deflection method of a crimped beam at one end illustrated in Fig. 3 is used to obtain and characterize sensor elements [6]. In the crimping beam the contact force, $F$, the mechanical stress, $T$, are related by the modulus of elasticity, $E$, and the geometry of the material (length, $l$, width, $w$, and thickness, $t$, of which it is composed). The space between the center of the sensor and the crimped end of the beam is given by the value of $d$, while the measurement from the center of the sensor to the point where the mechanical stress is applied is given by the value of $x$. The obtained equations are all linear, which guarantees a linear correspondence between the mechanical deformation, $\varepsilon_{ij}$, and the mechanical stress, $T_{kl}$.

The represented beam reacts in a manner similar to a spring, where its rigidity suffers direct dependence of the geometry and the composition of the materials used in its composition. In order for the material to not rupture, the mechanical stress limit applied to the beam should not exceed the elastic limit of the compounds used in accordance with Hooke’s Law [9].

The application of force at the free end of the beam results in a deflection perpendicular to the axis of the beam, so that the force of contact can be expressed by Equation (5),

$$ F = \frac{3EI}{L^3} y $$

Where, $I$, represents the moment of inertia and, $y$, is the deflection perpendicular to the axis of the crimped beam.

The application of force on the crimped beam causes the carbon atoms to expand significantly, inducing a change in electrical resistivity and, consequently, producing a variation of the piezoresistive coefficient of graphite [10].

VI. RESULTS AND DISCUSSIONS

To verify the piezoresistive effect in graphite sensors, the results from the model proposed by Equation (1) and experimental results are presented with fifteen samples positioned longitudinally and fifteen samples positioned transversely, as shown in Fig. 3 (a).

Figure 4 shows the behavior of the piezoresistive coefficient as a function of the mechanical deformation for piezoresistors without encapsulation and comparisons are made between the (ideal) situation and the (real) experimental situation. Ten different forces were applied in the free region of the crimped beam in order to obtain the variation of the piezoresistive coefficient at room temperature.
Figure 4: Piezoresistive coefficient variation as a function of the mechanical deformation of longitudinal (a) and transverse (b) encapsulated sensor devices.

A longitudinal average piezoresistive coefficient of the order of $5.03271 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$ was obtained in the paper substrate samples. The transversely positioned sensors had a mean piezoresistive coefficient of the order of $3.04394 \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$.

The results shown in Figure 4 that as the forces are raised, the deformation of the material increases and the piezoresistive coefficients tend to a value in the order of $10^{-10}$, indicating a stability in the accommodation of the granules in the material.

Figure 5 illustrates ten sensor elements are encapsulated with Epoxy-Bisphenol A resin and again subjected to the action of the different forces.
Figure 5. Illustrates ten sensor elements are encapsulated with Epoxy-Bisphenol A resin and again subjected to the action of the different forces.

The data obtained from the sensors encapsulated with the Epoxy-Bisphenol A resin were little dispersed from the values presented before the encapsulation, with a mean decrease of the piezoresistive coefficient around 5.75%.

Figure 6 shows the result obtained for the variation of the piezoresistive coefficient of transversely positioned piezoresistive sensor elements.

Figure 6. Variation of the piezoresistive coefficient as a function of mechanical deformation in transverse sensor devices encapsulated with Epoxy-Bisphenol A resin.
The average of the piezoresistive coefficient variation of the sensor devices encapsulated with Bisphenol A Epoxy Resin resembles the non-encapsulated ones, with a mean decrease in the piezoresistive coefficient of 4.63%.

The variation of the piezoresistance as a function of the mechanical deformation presents a polynomial behavior, where the resistance is increasing for values of the different forces, being that the results tend to a growing line, being in agreement with the behavior of the proposed model.

Although there are samples that present a greater amplitude of variation of the piezoresistive coefficient as a function of the mechanical deformation, it is possible to perceive a tendency to linearize the piezoresistive coefficient as the forces are elevated, the deformation of the material increases.

VII. CONCLUSION

The results showed that it is possible to estimate with ease and with good precision the piezoresistive behavior of a graphite sensor element since the model proposed in the literature tends to experimental data with little variation range.

The same result can be verified with encapsulation of Bisphenol A Epoxy Resin. The encapsulated sensors present relevant performance without manifesting great variations with the proposed model.

The methods used to make graphite sensor elements, besides being inexpensive and easy to process, if they show promising, do not cause any induced stress on the sensor element.

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