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Development and Characterization of a Piezoresistive Polyurethane/GNP Coating for Strain Sensing Applications

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Abstract— **In this work a simple cost-effective process is described to obtain a highly piezoresistive coating, consisting of sprayable water-based polyurethane (PU) paint filled with graphene nanoplatelets (GNPs). We investigated the morphology of the produced nanomaterials (i.e. cross-section and top surface) using a Field Emission Scanning Electron Microscope (FE-SEM). The rheological features of the polymeric blend loaded with 3.5 wt% of GNPs were analyzed at different concentrations of water (up to 20 wt%) in order to achieve a viscosity suitable for air-spraying. Moreover, the effect of humidity on the electrical resistance variation of the cured nanocomposite films was investigated and limited through the use of a covering agent. The stability of the PU/GNP based sensors protected with the covering agent was assessed repeating the same humidity test after four months. The sensor's piezoresistive response was obtained through three-point flexural tests and dc volt-amperometric measurements. The results of the electromechanical tests showed an increasing sensitivity of the sensor with the applied deformation and a maximum gauge factor of ~17 at 1% of strain, thus demonstrating the feasibility of the paint for strain sensing in structural health monitoring applications.**

I. Introduction

In recent years, there has been an increasing attention towards the development of innovative sensors for structural health monitoring (SHM). SHM represents the diagnostic process that provides in-situ real-time information to improve safety and reduce inspection costs of civil structures, industrial components and materials [1]. SHM can be implemented using a variety of sensors relying on different properties such as optical characteristics change [2]–[5], piezoelectric response [6]–[9] and piezoresistive effect [10]–[15].

Among them, piezoresistive strain sensors based on polymer matrix filled with carbon nanostructures (i.e., carbon nanotubes (CNT), reduced graphene oxide (rGO), graphene nanoplatelets (GNPs)) have gained considerable attention due to their high sensitivity, mechanical compatibility with the host structures, isotropic response and size scalability. In particular, the sensing mechanism is generally based on the formation of a percolating nanofiller network whose electrical resistance is dependent on the geometry of particles, on their mutual distances and intrinsic piezoresistivity [16].

The development of a piezoresistive paint, highly sensible to strain, with controlled thickness and multifunctional properties, easy-to-apply for different substrates and for surface areas from a few μm^2 to several m^2, is particularly intriguing for many SHM applications.

Within this context, we developed a novel water-based polyurethane (PU) paint properly filled with GNPs in order to obtain sensors which are characterized by a high piezoresistive response and that can be deposited over the surface of different materials through a simple spray coating technique. The electrical properties of the final coating can be also tuned spraying multiple layers or varying the filler concentration. In the next section the fabrication process is described; in addition, the results of morphological investigations, rheological measurements, humidity tests, and electromechanical characterizations are presented and discussed.

II. Experimental

A. Fabrication of PU/GNP strain sensor

The piezoresistive paint was produced by adding GNPs to a commercial water-based PU paint as briefly described below.

In particular, GNPs were produced from expanded graphite by liquid phase exfoliation in solvent. Successively, the GNPs-based suspension was placed in oven to obtain the complete evaporation of the solvent [1]. The PU paint, after the addition of same amount of deionized (DI) water to control the viscosity, was filled with 3.5 wt% of dried GNPs.

The mixture was then homogenized by following these steps: mechanical blending, high shear mixing and ultra-sonication, in order to promote a good dispersion of GNPs and to avoid their agglomeration.

After the addition and mixing of the curing agent, the PU/GNP paint was sprayed over the substrate and finally cured in oven at 100 °C for 20 min. Figure 1 shows a sketch of the described process (a) and an image of the produced sensor deposited on a small rectangular polycarbonate beam (b).

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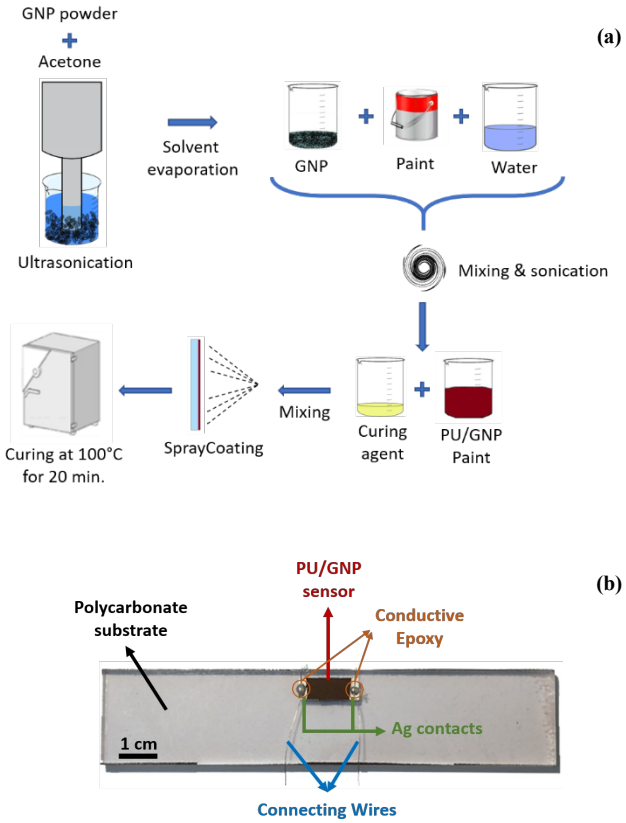

Figure 1. Sketch of the production process (a); image of the produced sensor sprayed over a polycarbonate rectangular beam (b).

B. Morphological Characterization

The morphological analysis of the produced PU/GNP paint was carried out through a Field Emission Scanning Electron Microscope (FE-SEM). The samples for SEM imaging were properly sputter coated with a homogenous Cr layer of 10 nm thickness.

Figures 2(a), (b) and 2(c), (d) show, respectively the cross-section and the top surface images of produced samples. The coating exhibits an average thickness of 40-50 µm. It is also shown that GNPs, having a lateral dimension of a few micrometers, are perfectly integrated into the polymeric matrix and homogenously dispersed into the paint.

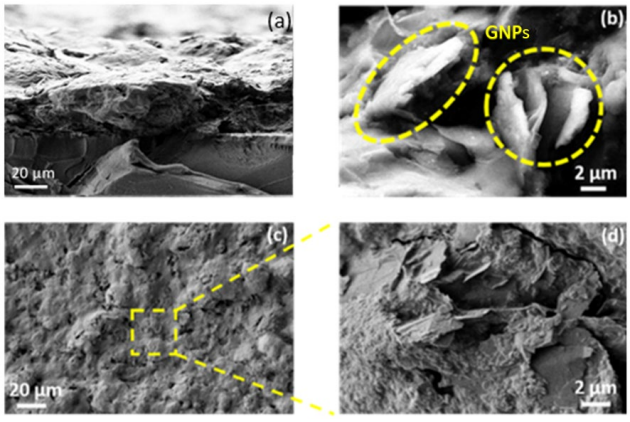

Figure 2. FE-SEM images of the cross section (a), (b) and the top surface (c), (d) of the produced sensor.

C. Rheological Characterization

Viscosity measurements were performed using a rotational rheometer (Anton Paar - MCR 302). The tests were performed at room temperature using a system of parallel plates put at a distance of 1 mm. Initially, the viscosity was investigated as a function of the weight percentage of DI water added to the neat paint up to a maximum of 20 wt%. Subsequently, the viscosity of the mixture filled with GNPs was analysed. The results of the rheological tests are reported in Figure 3. It is clearly shown that, as the water concentration increases, the viscosity of the neat paint decreases; on the other hand, the addition of the nanofillers leads to a higher value of viscosity. Therefore, to obtain a reasonable workability of the PU/GNP paint, it was necessary to use at least 20 wt% of DI water. In particular, in this condition the viscosity at high shear rates (greater than 50 s^{-1}) of the PU/GNP suspension is close to the one of the neat paint with 5 wt% of DI water.

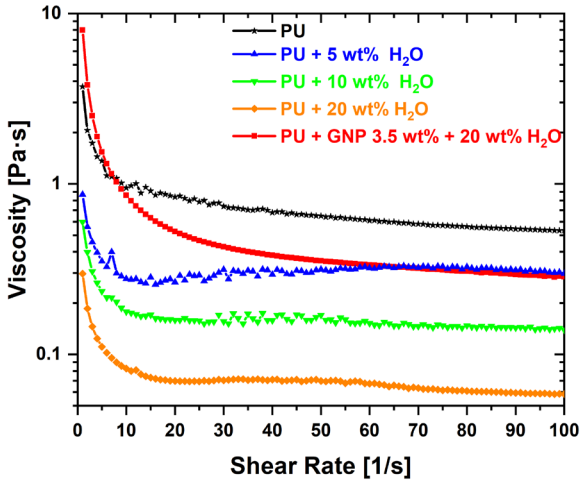

Figure 3. Viscosity curves of PU paint, with different concentrations of water, and of the PU/GNP paint with 3.5 wt% of GNPs.

D. Humidity Test

Before performing the electromechanical tests, the reproducibility of the resistance in rest condition (R_0) was assessed in a climatic chamber at constant room temperature (T~21°C) and at a relative humidity which was varied intentionally from a minimum value of 10 %RH to 90 %RH. The graphs in Figures 4(a) and (b) show the relative humidity and the resistance variation of the coating as function of time. As observed in Figure 4(b) (red line) the resistance increases of about 20 % when the relative humidity increases from 10 %RH to 90 %RH.

In order to mitigate the variation of the resistance with the relative humidity, a covering agent (NG 150, HBM) was applied over the sensor. As can be noted in Figure 4(b) (green line) the covering agent makes the sensor less sensitive to relative humidity, limiting the resistance variation to 7 % of its initial value.

Moreover, the same humidity test was repeated after four months in order to verify the response stability of the sample overtime.

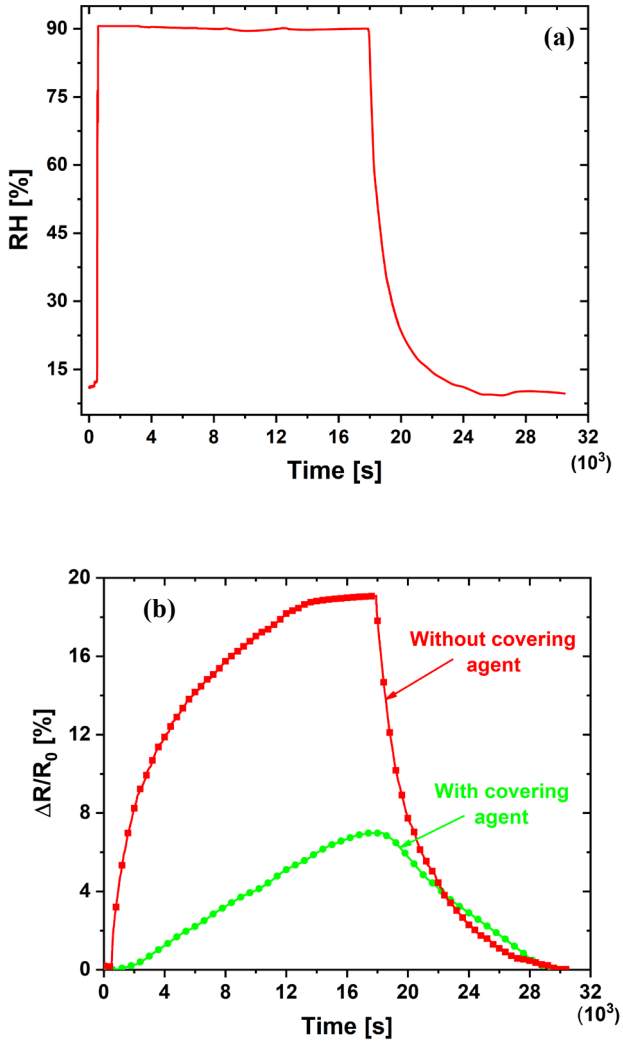

Figure 4. Variation of the relative humidity (RH) (a) and of the resistance (b) as a function of time.

The bar chart reported in Figure 5 shows the values of the resistances measured at 10 %RH and 90 %RH before and after four months.

The results demonstrate that the resistance is quite stable and that the covering agent continues to make the sensor almost insensitive to relative humidity (the variation of the resistance is lower than 4 %).

E. Electromechanical Characterization

The piezoresistive response was evaluated through a three-point bending test, using a universal testing machine (Instron 3366) with a 500 N load cell.

The sensor deposited over a polycarbonate beam was tested applying a deflection with a crosshead speed of 10 mm/min up to a maximum strain of 1 %. The flexural deformation of the beam was measured with a commercial extensometer whereas the electrical resistance was measured using a two-wire dc volt-amperometric technique. The electromechanical test setup is showed in Figure 6.

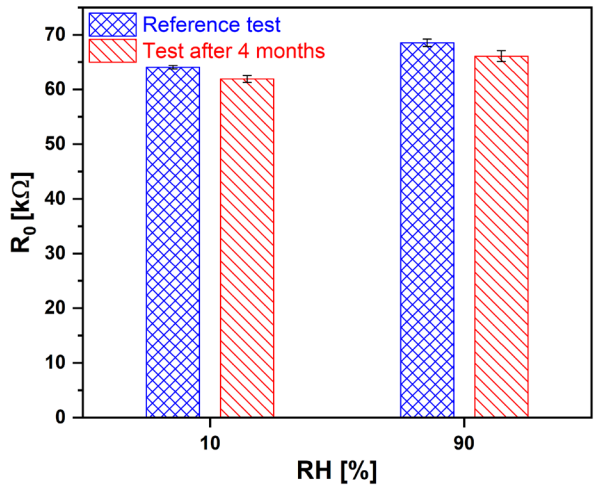

Figure 5. Stability of the resistance, at rest condition, as a function of the relative humidity (RH).

The normalized resistance as function of the strain is shown in Figure 7. Notice that four consecutive tests were performed to investigate the repeatability of the sensor's response. The reported results demonstrate that, after the first test, the subsequently measured curves are pretty much overlapping in the considered strain range.

In order to evaluate the performance of the produced sensors we estimated the value of the gauge factor (GF) as function of the measured strain (ε), using the following expression [17]:

$$GF = \frac{R - R_0}{R_0 \varepsilon} \quad (1)$$

where R is the resistance value as function of ε and R_0 is the resistance value in the rest condition (~21°C and ~40 %RH). Figure 8 shows the GF variation of the last test, after the electromechanical stabilization of the sensor response: the GF reaches a value of ~17 at 1 % of strain.

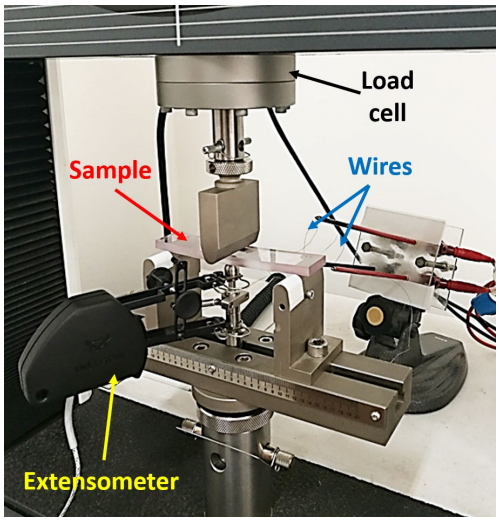

Figure 6. Electromechanical test setup.

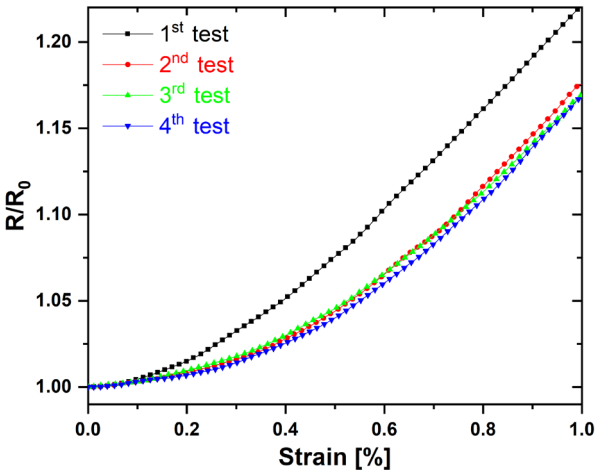

Figure 7. Piezoresistive response of the produced sensor as function of the applied deformation.

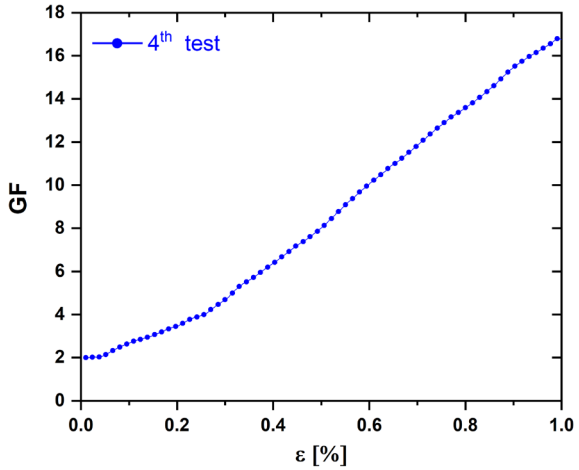

Figure 8. Gauge factor of the produced sensor as function of the applied deformation.

III. Conclusion

In this work we developed a new type of piezoresistive strain sensors with high sensitivity made with a water-based PU/GNP paint.

Morphological characterizations showed that the GNPs are well dispersed into the paint. Rheological measurements showed the necessity, with a GNP loading of 3.5 wt% to add 20 wt% of DI water in order to maintain the mixture viscosity in a range of values that enable air-spraying of the piezoresistive paint. We also observed a variation of the sensor's electrical resistance up to 20 % when the relative humidity varied from 10 %RH to 90 %RH. This variation has been reduced to 7 % by applying a protective layer. The stability of the sensors was confirmed by repeating humidity test after four months. Finally, the electromechanical tests demonstrated that a sensor made with the piezoresistive paint can follow the substrate deformation up to 1 % with a maximum GF of ~17.

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