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Elastic layered rubber-graphene composite fabricated by rubbing-in technology for the multi-functional sensors

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Abstract

In this work, the elastic layered rubber-graphene composite based multi-functional sensor has been fabricated by rubbing-in technology. The effects of temperature, displacement, pressure and humidity on the impedance of the multi-functional sensor has been investigated in the frequency range of 0−200 kHz. The impedance of the samples decreased under the effect of uniaxial compressive displacement and under the effect of pressure. The temperature coefficient of the samples was found to be −0.836 and −0.862 %/°C with the increase in temperature from 29 °C to 54 °C, respectively, while the impedance of the samples decreased 1.26 ± 0.01 times with the increase in temperature from 29 °C to 54 °C while, respectively. The humidity dependent cross-sensitivity of the samples was investigated in the relative humidity range of (58−93) %RH and no effect of humidity on the performance of the sensor has been observed. The elastic layered rubber-graphene composite potentially can be used as displacement, frequency, temperature and pressure sensors.

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1. Introduction

Several studies on the elastic substrates covered by resins filled with fillers such as metal nanoparticles for the fabrications of electronic devices have been described in literature. Electric properties of these substrates depend upon on the kind of the conductive particles, concentration and type of resin. One of the applications of these elastic and flexible conductive substrates is in strain sensors which can be used in instrumentation such as load sensors, heart beat rate measurements. Sensitivity, reliability, cost and size of these devices depends on materials, technology of fabrication and sensor circuit. At same time nano-materials can improve the sensing properties of sensors [1, 2]. Highly sensitive, flexible capacitive pressure sensors with micro structured rubber dielectric layers were fabricated and investigated by Mannsfeld et al [3]. The sensor was made on the base of elastomer polydimethylsiloxane and integrated into organic field effect transistor as dielectric layer. The flexible, stretchable and wearable multifunctional sensor array as an artificial electronic skin for static and dynamic strain mapping was fabricated in ref. [4]. This sensor could detect strain, pressure and temperature. Comparison of the sensors described in the literature and offered in this work allow us to emphasize the simplicity of the fabrication of the offered by us sensors. One of the most important properties of the fabricated multifunctional sensor the stability to the effect of humidity is. Most materials which are in use in electric and electronic devices are also sensitive to the humidity [5, 6, 7].

Considering the interesting mechanical, electrical properties of graphene, it can be considered as a suitable candidate for flexible and stretchable electronics. The development of layered structure graphene paper has been reported in reference [8] and its mechanical properties and electrical conductivity have been enhanced by thermal annealing. As described in Shi et al. [9], it was developed a cost effective high-performance strain sensors and stretchable conductors based on a composite film consisting of graphene platelets and silicon rubber. It shows a linear and reproducible sensitivity to tensile strains, which is contributed by the superior piezoresistivity of graphene platelets with tunable gauge factors 27.7−164.5. As described in Wang et al. [10], the graphene woven fabrics (GWFs) were explored for highly sensitive sensing. A flexible and wearable strain sensor was assembled by adhering the GWFs on polymer and medical tape composite film. The properties of graphene and graphene related materials for the improvement of the analytical performance of sensors and biosensors have been discussed in detail by Justino et al [11]. They provided an overview of graphene-based sensors and biosensors, comparing their analytical performance for application in clinical, environmental, and food sciences research, and gave their observations on future research trends in this field. While the research and development of two-dimensional (2D) graphene have been summarized for electrochemical sensors by M.M. Rahman and A.M. Asiri [12]. They discussed the design, fabrication, functionalization and application of graphene membranes with the focus on chemical vapor deposition techniques and solution-processing assembly approaches.

Recently, our group investigated the properties of graphene/carbon nanotubes composite [13]. In another study, we described the semitransparent thermo-electric cells based on the bismuth telluride and graphene composite. Pressure sensitive sensors based on carbon nanotubes, graphene, and its composites were investigated in [14]. Flexible impedance and capacitive tensile load sensor based on CNT composite was investigated in [15] and flexible resistive tensile load cells based on MWCNT/rubber composites was investigated in [16]. In continuation of our efforts to study of the graphene containing materials and devices, in this work, we present the investigations of the effect of the displacement, pressure, humidity and temperature to the resistance and impedance of the elastic layered rubber-graphene composite fabricated by rubbing in technology. The rubbing-in technology is very simple and can be processed at normal conditions. The new point of the work is the fabrication of the flexible conductive thin films by rubbing in technology that allow to use it in elastic multifunction sensors. The elastic nature of the samples allows to place the contact points of the samples in one line or in one plane or in different planes which make these samples useful for different applications. Materials that are used for the fabrication of these samples are very low-priced and are available in the commercial market.

2. Experimental

For fabrication of the samples commercially available dense rubber and graphene were used. The polished metallic load was used for rubbing in the graphene into the substrate. Special mechanism moved the load in a horizontal plane at a frequency of (1−10) Hz into two perpendicular directions as shown in Fig. 1. Rubbing in procedure takes (1−3) min. The pressure on the surface of the sample were in the range of (5−10) g/cm^2. On rubber film the graphene powder was spread. The load moves in the horizontal plane in two perpendicular directions and in the process rubbing-in of the graphene on the flexible rubber film takes place. As the flexible rubber film is in strained condition the sizes of porous in rubber increased and rubbing in the process realized easily. After of completion of the rubbing in process the substrate released from the round plane metallic substrate and be in normal condition without of strain. In the result the pore sizes come to initial condition and the graphene particles are squeezed in the rubber substrate. Therefore, the rubber substrate shows electrically conductive and stable properties. Thickness of the graphene-rubber composite layers were in the range of 10−20 μm. The dimensions (length, width and

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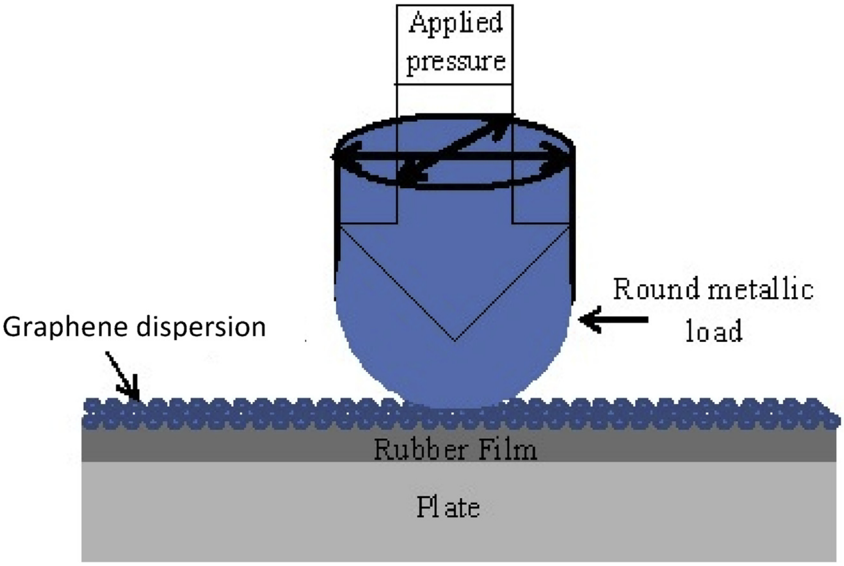

Fig. 1. Schematic of the fabrication process of the rubber-graphene composite samples by rubbing-in technology.

thickness) of the samples were equal to 16 mm × 7 mm × 7 mm, respectively. The thickness of the graphene-rubber composite layers on the surface of the substrate was in the range of (10–20) μm. The composition of the graphene & rubber in the composite layers was 74 wt.% and 26 wt.%, respectively.

By rubbing-in technology, the graphene can also be placed on the opposite side of the same rubber film, which could decrease the electrical resistance of the sample and increases the current (sensitivity) of the proposed sensors. As graphene is built into the porous rubber, the structure of the samples can be considered as the elastic layered rubber-graphene composite. The surface morphology of the samples was investigated by optical microscope and atomic force microscope (AFM). Optical microscope images were taken by an Olympus metallurgical microscope with built-in digital camera.

Fig. 2 shows the optical and AFM images of the samples. It is seen that average roughness of the rubber surface and graphene layer was equal to ~2.7 μm and ~0.5 μm, respectively. During the impedance measurements two electrodes were fixed on the samples and the samples were placed in a controlled environment chamber. Humidity and temperature were measured by TECPEL 322 humidity and temperature meter. Resistance, impedance and capacitance in the frequency range of 100 Hz–200 kHz were measured by LCR meter MT 4090. The uniaxial compressive displacement was created and measured by a micrometer screw gauge. The pressure was measured by a laboratory made arrangement. Reusability and durability performances were tested five times on 12 samples during a week, it was found that the changes in the parameters of the sensors were within of (~3–5)%.

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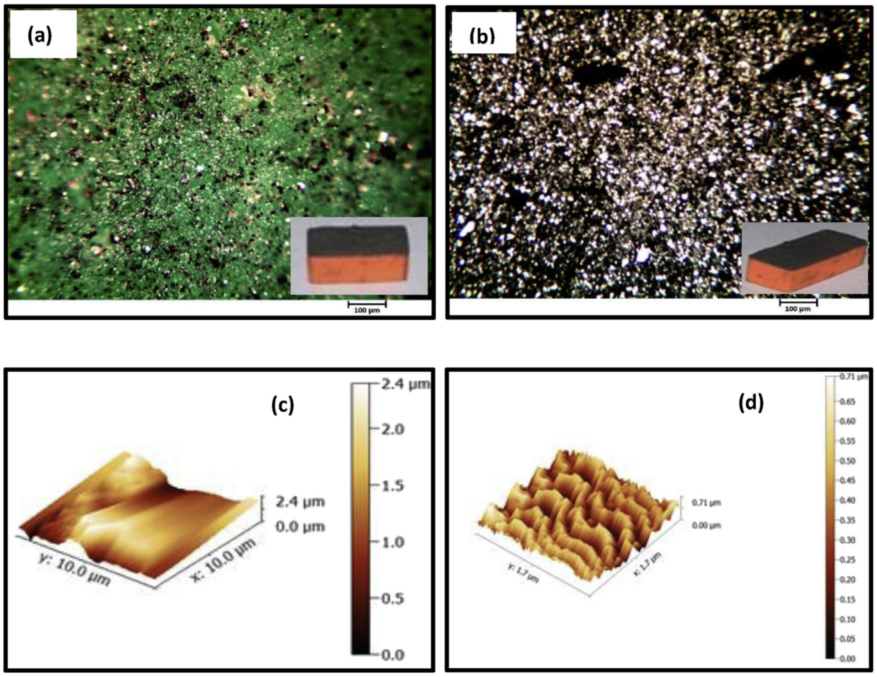

Fig. 2. (a) Optical microscope image of the rubber substrate surface. (b) The optical microscope image of the graphene film fabricated by rubbing-in technology on the surface of rubber substrate. Insets show the photo of the samples. (c) Atomic force microscope images of the rubber substrate and (d) graphene layer show the surface roughness of the samples.

3. Results & discussion

Fig. 3(a) shows the dependence of resistance and impedance on the compressive displacement of the rubber-graphene layered composite. It is seen that resistance and impedance of the samples decreased under the effect of the uniaxial compressive displacement. It was found that, in the frequency range of up to 200 kHz, the resistance and impedance of the samples decreased to 1.08 times under the effect of the

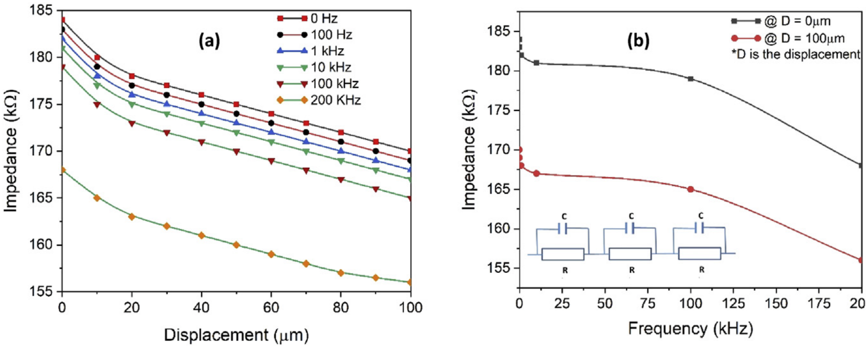

Fig. 3. (a) Dependences of resistance and impedance on the displacement for rubber-graphene layered composite. (b) The frequency vs impedance at different displacements, inset shows the simplified equivalent circuit of the elastic layered rubber-graphene composite samples.

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uniaxial compressive displacement of 100 μm. Under uniaxial compressive displacement the distances between graphene particles decreased (contact areas of the neighboring particles are increased), henceforth, the impedance decreases due to decrease of the inter-particle resistance. Moreover, the intrinsic resistance of the particles could decrease, in principle, because of the compressive displacement to the energy band structure of the graphene. The decrease of the resistance probably due to increase of the mobility of the charges under the effect of the compressive displacement other than the concentration of the graphene particles, however, further researches are required to confirm this statement. Fig. 3(b) shows the impedance-frequency relationships at different displacements. It is seen that as the frequency increases the impedance decreases. Inset in Fig. 3(b) shows the simplified equivalent circuit of the elastic layered rubber-graphene composite samples. The equivalent circuit explains the impedance-frequency relationship. The impedance dependence of the frequency can be used for demodulation of the frequency modulated signal, especially, in the frequency range of (100−200) kHz because the characteristics are quasi linear in this range. In the first approximation, the dependence of the impedance on the frequency can be represented by the use of the simplified equivalent circuit shown in Fig. 3(b). The impedance (Z) of the one (R-C) unit of the circuit can be represented in: $Z = R/(1 + \omega RC)$, where ω, C and R are the angular frequency, capacitance and resistance, respectively. The impedance - frequency relationship shown in Fig. 3(b) can be explained by the above equation.

Fig. 4 shows that the impedance and resistance of the samples decreased 1.26−1.27 times against the increase in temperature from 29 °C to 54 °C. Temperature coefficients of resistance at the specified temperatures were found to be (−0.836) and (−0.862) %/°C, respectively. The results obtained by us are related to pure graphene.

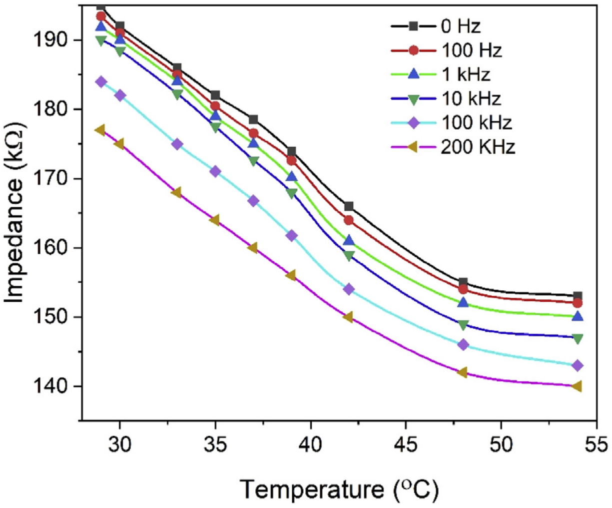

Fig. 4. Resistance and impedance dependences on temperature for rubber-graphene layered composite under different applied frequencies.

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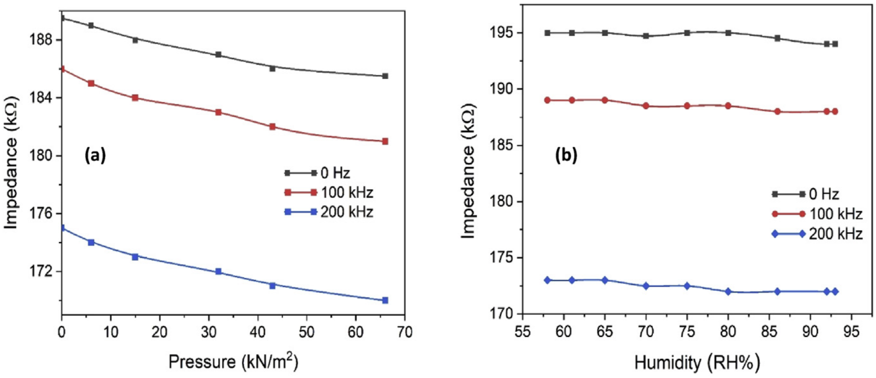

Fig. 5. (a) Dependences of resistance and impedance on the applied pressure for rubber-graphene layered composite at different frequencies. (b) Humidity dependence of the impedance of the samples.

At a high-temperature (300−500 K) electrical resistance of the single, and layer graphene drops down by 30% and 70%, respectively. It was explained by the thermal generation of the electron-hole pairs and carrier scattering by acoustic phonons.

Fig. 5(a) shows the dependence of the resistance and impedance of the samples on the uniaxial pressure. It was found that under the effect of pressure, resistance and impedance of the samples decreased by (1.02−1.03) times. A flexible pressure sensor based on the piezo-resistive effect of multilayer graphene films on polyester textile was investigated [17]. Comparison of the samples investigated by us and the sensors presented in [17] shows that the devices differ from substrates and technology of fabrication. In particular, the rubbing-in technology, which was used by us is simple and graphene powder matched well to the substrate surface, like to "ball-well" unit. Concerning the effect of humidity to the electrical parameters of the composite, it was found that the change of the relative humidity from 58% to 93% practically didn't bring any change to the resistance and impedance (at 100 kHz and 200 kHz) of the samples (Fig. 5(b)). It can be due to high conductance of the graphene with respect to the effect to its conductance of the water molecules or even oxygen and hydrogen ions.

4. Conclusion

In the paper, we described the fabrication of the elastic layered rubber-graphene composite fabricated by rubbing-in technology. The effect of displacement, pressure, humidity and temperature to the resistance and impedance of the composite is investigated. It has been found that the rubber-graphene elastic composite can be potentially used in displacement, frequency, temperature and pressure sensors. Considering the obtained results and their comparison with well-known data published in international journals, we hope that the paper would be useful for researchers, industrialists, especially, for readers who are at the initial stage of fabrication and investigation of the multifunctional sensors on the base of affordable materials by simple technology. From our point of view, the future work may be concentrated into effect of vibration to the properties of the flexible multifunctional sensors in the wider frequency range that will allow to get practically important results about the use of the sensors and optimize the condition where the sensors will show reliable performance.

Declarations

Author contribution statement

Kh. S. Karimov: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Zubair Ahmad: Analyzed and interpreted the data; Wrote the paper.

M. I. Khan: Conceived and designed the experiments; Performed the experiments.

Khalid J. Siddiqui: Conceived and designed the experiments; Performed the experiments.

T. A. Qasuria: Analyzed and interpreted the data.

S. Z. Abbas: Analyzed and interpreted the data.

M. Usman: Analyzed and interpreted the data.

Aziz-Ur Rehman: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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