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ABSTRACT

In this study, the optical and electrical influences of 2D graphene flakes in electrospun polycaprolactone (PCL) fibers were observed. Graphene nanoplatelets were added in different concentrations into the PCL solution, and then, using the electrospinning technique, fibers were built from that solution. Three samples were prepared with different graphene concentrations of 0% w/w, 0.5% w/w, and 2.0% w/w. From all three samples, fibers were prepared and tests were conducted for the identification of the properties of fibers. An optical spectroscopy test was performed to identify the optical behavior of the fibers. Scanning electron microscopy tests were conducted for the morphological characterization of the fibers. For the comparison of the electrical conductivity of the three samples, electrical tests were also conducted. In addition, Raman spectroscopy was conducted to characterize the graphene and PCL. This study shows that using graphene can change the properties of fibers, for example, as the graphene content increases, the fiber diameter also increases. Also, by varying the 2D graphene concentration, both electrical and optical properties can be tuned; this can be utilized in the synthesis of nanosensing surfaces and structures.

I. INTRODUCTION

Synthesis of a new generation of nanosensing surfaces has attracted a lot of attention these days as nanostructured surfaces have a larger surface area and a higher interaction with the environment, which is a key factor in sensor fabrication. Various methods have been proposed by researchers for the fabrication of sensing nanostructures induced by physical and chemical vapor deposition (PVD and CVD), atomic layer deposition (ALD), advanced lithography, advanced chemical etching, and electrospinning. Between all these methods, electrospinning is widely used for the fabrication of various porous sensing structures having enhanced properties and different fiber morphologies; however, the process is limited to organic and polymeric materials with proper electrical conductivity.

Electrospinning of composite (organic/organic and organic/inorganic) solutions enhances the resulting fiber properties as this opens up the chance for the integration of polymers to produce functional fibers with a wide range of properties. Electrospinning of nanofibers in the presence of carbon nanoparticles provides some advantages over structural properties and interconnected porosity: these hybrid electrospun fibers can be used for a wide range of applications in biomaterials, gas and chemical sensor fabrication, energy and batteries, and air and water filtration; among nanomaterials which can be added to the electrospinning process, graphene attracts extensive attention as a new emerging nanomaterial with some unique properties including superb thermal and electrical conductivity, strong mechanical property, and extremely high surface area. Graphene has extremely high charge mobility (>200 000 cm² V⁻¹ S⁻¹ for suspended graphene), zero effective mass, and ballistic transport even at room temperature; thus, it is an ideal material to enhance fiber’s electrical conductivity. In addition, graphene has broad absorption spectra, narrow emission spectra, size-dependent tunable photoluminescence, and excellent stability which make it an ideal additive to the electrospun nanofibers for biosensing and bioimaging applications.
The aim was to study the different properties of nanofibers in detail by varying the percentages of graphene nanoplatelets. Electrospun nanofibers having 2D graphene nanoplatelet concentrations of 0% w/w, 0.5% w/w, and 2% w/w were fabricated with PCL. Various characterization tests were carried out for identifying the customizing of physical properties like topology and fiber diameters of the electrospun nanofibers as well as their optical and electrical properties, which are key parameters in optical sensor fabrication. This research can open new doors for the synthesis of better nanosensing structures based on the electrospinning of hybrid materials with controlled optical and electrical properties.

II. EXPERIMENTAL METHODS

A. Material and sample preparation

The methodological approach starts with the selection and preparation of the solution. Graphene nanoplatelets were selected to mix with PCL in three different concentrations to analyze their property. Three solutions were prepared in order to carry out further experiments. One solution was prepared by adding only 15% w/w PCL with acetone to make a 50 g solution, and the other two solutions had 0.5% w/w and 2% w/w concentrations with 15% w/w PCL. All solutions were prepared by first mixing all the ingredients and then sonicating them for 2 h, followed by further stirring. Previous studies show electrospun nanofibers with a concentration lower than 2% w/w have a more uniform distribution of graphene nanoplatelets. This can be due to the fact that a higher concentration of graphene results in a possible saturation of the solution and less dispersion of the graphene nanoplatelets. Thus, the electrospun nanofibers with higher than 2 wt.% of graphene show a presence of graphene clusters.

The experiment was performed with the freshly prepared solutions using the electrospinning technique to analyze the interaction between PCL and graphene. Before starting the experiment, all pipes, needles, and syringes were washed using acetone to remove any type of clogging. Plastic syringes were filled with the solutions and placed in the machine by setting a syringe diameter of 14.3 mm. The experiment was carried out by setting the pump flow rate at 0.5 ml/h and applying a 20 kV voltage supply to the needle. Fibers from all the solutions were collected on an aluminum plate, and this collector was placed at a gap of 120 mm from the needle tip. The electrospinning test was carried out for 5 min for all three solutions so that sufficient uniform fibers could be collected.

B. Characterization

To characterize the influence of graphene and understand the morphology of the fibers, a scanning electron microscopy (SEM) test was conducted. The fiber diameter was analyzed for all the samples to study the effect of the graphene content on it. Statistical and image analysis were performed via ImageJ and MATLAB, to ensure authenticity of the results. The 5% of error is assumed for individual fiber diameter measurement. Also, the average fiber diameter is shown with an error bar marked on the graph representing standard deviation. In addition, one way Anova with one factor was carried out to check the difference between means with 95% confidence level.

Prior to the fiber analysis, the graphene nanoplatelets were also analyzed using transmission electron microscopy (TEM). To study the graphene powder, epoxy was mixed with the powder, which was then sliced into 90 nm slices using a diamond knife. The slices were used for TEM analysis.

To study the chemical composition of all samples, a Raman spectroscopy test was conducted (the machine used was a Renishaw system 2000 imaging microscope). Testing of each sample was conducted with a 532 nm wavelength laser and at 50 mW power.

To study the optical properties of the samples, optical spectroscopy was used to collect the amount of reflected light in the visible range. These were obtained using a receiving probe connected to the Ocean Optics 2000+ spectrometer (200–800 nm); the samples were irradiated at 45°C by a light source (Ocean Optics HL-2000: 360–2500 nm). The spectroscopy probe was positioned at an angle of 45° to obtain specular reflection and then placed at 90° to obtain diffuse reflection. In all tests, the reflectance data were observed to analyze the effect of graphene over the optical properties of the nanofiber.

The electrical resistivity of the electrospun nanofiber, as well as the nonelectrospun samples of PCL + graphene, was measured. The electrical resistivity results were collected using both an impedance analyzer and 4-point probe resistivity measurement system. Certain trends were observed in resistivity with respect to the increase in graphene content in the samples. The thin-film thickness for the electrical resistivity measurement was set to 250 μm for all measurements, and the substrate thickness was 0.5 mm (the Al sheet). All measurements were collected at least four times, and error bars indicate the standard deviation.

III. RESULT AND DISCUSSION

A. TEM and Raman analysis for graphene

Graphene nanoplatelets (GNPs) were analyzed using TEM at 19,000× magnification. For the analysis of GNP s, epoxy was used to mold the powder. Nanoslices of epoxy were analyzed, and it was observed that nanoplatelets aggregated randomly, as shown in Fig. 1. It was also observed that graphene nanoplatelets have multiple layers (~10 layers), as shown in Fig. 1.

Raman spectroscopy is useful to understand the chemical composition in terms of graphitic nature, structural order, and more. In this study, a 514 nm laser was used to analyze the peaks. Different bands, such as D, G, 2D, and D + D′, were noticed from this study. Each band has its own significance: for instance, the D band signifies defects in the domain, whereas the G band signifies first-order dispersion of the E2g phonon. An increase in the intensity of the D bands results in the increase of the sp2 lattice due to oxidation, whereas with an increase in the intensity of the G band, the C−C tangential vibration and stretching increases. From this spectroscopy method, we found various main peaks at different wavelengths: ~(D band), (G band), (2D band), and (D + D’ band). Identification of the intensity ratio of the D and G bands is also crucial because it represents the lattice size. As the intensity ratio of the D/G band increases, it will decrease the lattice size, and the sp2 defect domain increases.
B. SEM analysis

The characteristics of graphene nanoplatelets were analyzed using TEM, and their multilayer behavior was discovered. The fibers were then manufactured using different concentrations of graphene and studied using SEM. Fibers of all three samples were analyzed at a common scale of 50 μm, and their diameters were studied using the open-source software ImageJ.26,27

As shown in Fig. 2, the fibers of all the samples exhibit similar surface morphology. Analysis of diameter distribution was also performed, as shown in Fig. 3. The electrospun fibers of the solution having 0% graphene by weight are the smallest of all. The reason behind this could be that increasing graphene content improved the conductivity and viscosity of the solution, which affects the electrospinning mechanism.28,29 Viscosity was considered a significant factor for fiber diameter distribution. As the graphene content increased in the solution, it was easily converted into flakes in the solution, resulting in the increment in the viscosity of the solution and leading to an increase in the diameter of electrospun fibers.28,29

C. Raman spectroscopy results

In this study, micro-Raman spectroscopy is used for the characterization of all three samples of the electrospun fibers (Fig. 4). The electrospun fibers contain two components: PCL and graphene nanoplatelets.
The micro-Raman spectra of the electrospun fibers showed corresponding peaks for both PCL and graphene nanoplatelets. Multiple peaks within this spectrum referred to the crystalline fraction of PCL in the fibers. It represents several narrow peaks for C−COO stretching and peaks for C−C skeletal stretching; other peaks represent the deformation vibration of CH₂ group twisting and bending; finally, the last peak on the right side of the graph represents the crystalline component of C=O stretching. In addition to the main peaks corresponding to PCL, there is also the presence of a hump in the range of 1550–1600 cm⁻¹, which corresponds to the presence of graphene nanoplatelets. For the electrospun fibers having 2% graphene, a band with an intense peak can be seen, whereas this band is missing in the fiber with no graphene. This is the G band, which shows the presence of graphene. As the graphene content increases from 0% to 2%, the peak of the G band became more intense.

D. Optical spectroscopy

The analysis was performed using the optical spectroscopy system in the visible range, and the reflectance data were collected for the electrospun nanofibers and control samples in a specular reflection at 45° (both source light and spectroscopy were installed at 45°) and diffuse reflection (the source light was radiated at 45°, and the diffused light was collected at 90°). Although the source light did not change, it was noticed that there was only one peak in the specular method and two peaks in the diffuse method.

Figures 5(a) and 5(c) show the optical spectroscopy results (specular and diffuse methods) of the electrospun nanofibers with 0.5%–2% w/w graphene. In Figs. 5(b) and 5(d), the optical spectroscopy results of the thin-film of the same materials have been presented (there was no electrospinning process; graphene was simply coated on the substrate). Generally, the light absorption for the electrospun fibers is significantly higher in the specular configuration [Fig. 5(a) vs Fig. 5(b)]. However, we did not observe significant light absorption changes in the case of diffuse reflectance spectroscopy [Fig. 5(c) vs Fig. 5(d)]. In specular data for nanofibers [Fig. 5(a)], increasing the graphene content from 0% to 0.5% resulted in a significant change in the optical behavior (absorption); however, on further increasing the graphene content, there was no...
significant change even when the graphene content was increased four times to 2%. On the other hand, for specular reflection of thin-films [Fig. 5(b)], a significant decrease in the intensity was noticed on increasing the graphene content from 0% to 2%. For reflectance by the diffusion method, the drop in reflectance with an increase in graphene nanoplatelet concentration was observed [Figs. 5(c) and 5(d)]. This shows the potential of using hybrid electrospun nanofibers embedded by graphene nanoplatelets for the fabrication of optical filters with controlled light reflection/absorption. More studies will be conducted in the future in a positive direction of this research project. From the results, it can be concluded that the light absorption by increasing the concentration of graphene increases for both specular and diffuse reflectance spectroscopy; however, for the specular configuration, it would be saturated in the 0.5% w/w of graphene.

E. Electrical resistivity

In order to use the proposed nanofibers for chemical sensor fabrication, the structure requires appropriate electrical resistivity or conductivity. In this study, electrical resistivity was evaluated by using both an impedance analyzer (LCR meter) and a four-point probe resistivity meter system (Fig. 6). From the data collected via both methods, it was noticed that the bulk electrical conductivity of the thin-film (nonelectrospun PCL-graphene thin-film) is higher than that of the electrospun nanofibers. This is due to the fact that nanofibers are more porous than the nonelectrospun thin-film samples. Although the electrospun fibers have a higher surface area, the high porosity results in an increased distance between the conductive particles of the fibers; because of this, resistivity increases in comparison with the nonelectrospun samples. On increasing the graphene content, there are also some changes in the resistivity, for example, for both the nonelectrospun samples and the electrospun nanofibers, increasing the graphene content from 0% w/w to 2% w/w causes the resistivity to decrease. This directly relates to the presence of conductive graphene nanoplatelets existing in the structure of the samples.

IV. CONCLUSIONS

This study was conducted to evaluate the change in the optical and electrical properties of fibers by the addition of graphene nanoplatelets. The SEM results show that on increasing the graphene concentration from 0% w/w to 2% w/w, the diameters of the fibers increase. The Raman spectroscopy tests identified the presence of both PCL and graphene in the fibers. However, only the G-peak was significantly observed in all three samples. The G-peak was intense in the fibers in which the graphene concentration was 2% w/w. Optical spectroscopy was also performed to identify the nature of fibers toward different wavelengths of light. From optical spectroscopy, the redshift was observed, meaning the change in the intensity was observed after ~670 nm wavelength of light. On the other hand, the change in electrical properties was also observed. Electrical tests using a 4-point probe and an LCR meter were conducted. The tests show that increasing the graphene concentration increases electrical conductivity. The results show that both optical and electrical properties of the electrospun fibers embedded by graphene can be controlled by graphene concentration for different purposes. The results of this research can lead to further opportunities for the fabrication of nanostructured materials with customized properties (optical and electrical properties). Such novel structures can be used in different types of sensors from biosensors to wireless-optical and chemical sensors.

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The authors declare that they have no competing interests.

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