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Optical and Structural Properties of Prepared Polyaniline – Graphene (PANI/GN) Nanocomposite

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Abstract

Polyaniline (PANI) polymer was successfully prepared by the chemical oxidation method at 0 °C. Polyaniline-nano grapheme (GN) powder nanocomposites were prepared by the addition of GN with different weight ratios (0.1, 1, 5, and 10 g wt. %) during the polymerization of PANI. It was found that the polymerization reaction of poly-aniline was exothermic. The effect of adding nano-graphene powder during polymerization process on the time and temperature of the reaction was studied. The resulting polymer was diagnosed using several methods, including Fourier transform infrared spectroscopy (FT-IR) and UV-VIS spectrophotometry. The results of FTIR demonstrated a shift to higher wave numbers in the peaks of nanocomposites, due to PANI peaks, in addition to the matching between the groups of active sites of the polymer with its chemical composition. The results of the optical properties showed a decrease in the energy gap of the nanocomposite compared with that of the pure PANI sample. The morphology of the samples was studied using Scanning Electron Microscope (SEM). The increase in the concentration of GN led to a change in the surface morphology of the composites. The results predict that the PANI/GN nano-composites can be used in many applications, such as those of sensors.

Keywords: - Optical properties, Polyaniline (PANI), Graphene GN, In situ Polymerization.

الخواص البصرية والتركيبية لمتراكب نانوي محضر من البولي انيلين / كرافين

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الخلاصةً

تم وبنجاح تحضير البولي أنيلين مختبريا. تم تحضير البولي أنلين بطريقة الاكسدة الكيميائية عند درجة الصفر المئوي، ثم حضرت متراكبات البولي انيلين – كرافين النانوية بإضافة مادة الكرافين النانوية وبنسب وزنية مختلفة (0.1,5, 1, 10%) غرام خلال عملية البلمرة. وجد أن تفاعل البلمرة للبولي أنيلين كان باعثاً للحرارة. تمت دراسة تأثير إضافة مسحوق الكرافين النانوي أثناء عملية البلمرة للبولي أنيلين على زمن التفاعل ودرجة حرارة التفاعل.

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شخص البوليمر الناتج بعدة طرق منها طيف الأشعة تحت الحمراء FT-IR وطيف الأشعة المرئية- فوق البنفسجية UV-Vis.من التحليلات الطيفية للأشعة تحت الحمراء , وجد ان هناك انحرافا نحو الاعداد الموجية الاعلى في قمم المتراكبات النانوية نسبة الى قمم البولي أنيلين كما واظهرت النتائج تطابق مواقع المجاميع الفعالة للبوليمر مع تركيبه الكيميائي. بينت نتائج دراسة الخواص البصرية نقصان في قيم فجوة الطاقة للمتراكبات مقارنتا مع عينة البولي أنيلين. تمت دراسة مورفولوجيا السطح باستخدام المجهر الإلكتروني الماسح SEM وقد لوحظ أن زيادة تركيز مادة الكرافين تؤدي الى تغير في مورفولوجيا السطح للمتراكبات. النتائج تتنبأ بأنه يمكن استخدام متراكبات البولي أنيلين / كرافين في العديد من التطبيقات منها أجهزة الاستشعار.

Introduction

Polyaniline (PANI) is an organic material discovered in 1834 by Runge, and was known as "aniline black". Green and Woodhead, in1912, found the interesting property of PANI, which is a mixed oxidation polymer consisting of reduced benzoid and oxidized quinoid units [1, 2]. It is well known that PANI exists in three different oxidation states, which are the leucoemeraldine, emeraldine, and pernigraniline, where only polyemeraldine is electrically conductive [3,4]. The structure of PANI chain is shown in Figure-1.

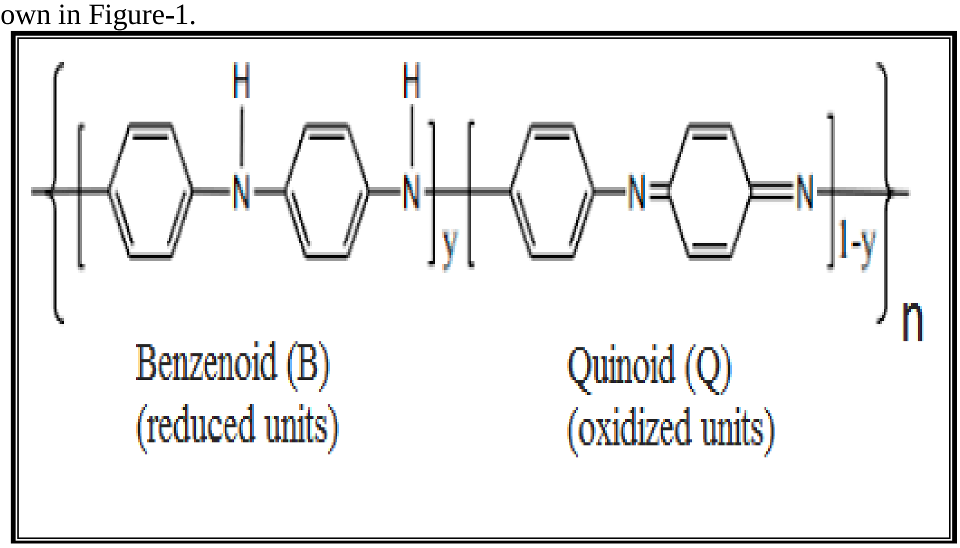


Figure 1-Structure of the polyaniline chain [5].

PANI is among the most appealing conductive polymers due to the existence of the –NH– flocks in its chain, which gives singular physical and chemical properties such as good electrical conductivity and high environmental stability. In addition, PANI is relatively inexpensive, very light, easily synthesized, and has the potential of both chemical and electrochemical synthesis. Hence, PANI is utilized in a wide spectrum of implementations, including the production of batteries, sensors, electronic devices, and supercapacitors [6, 7].

Graphene is a flat monolayer of carbon atoms that is tightly packed into a two-dimensional (2D) honeycomb lattice, with a completely conjugated sp^2 hybridized planar structure, and is a basic building block for graphitic materials of all other dimensionalities. Graphene has high thermal properties and high specific surface area [8, 9].

There are various reports on the usage of grapheme-based polymer composites where improved optical, electrical, and mechanical properties of the composites were described. Xu and his group reported the preparation of poly (vinyl alcohol) / graphene oxide composites, which could be used as high strength, flaw tolerance structural materials. Wang *et al*. prepared GO-based PANI composite with improved electrochemical performance as a supercapacitor electrode by means of *in situ* polymerization [10]. Shen and his group reported the preparation of a good thermoelectric material using polyaniline / graphene nanosheetes [11].

The aim of this work is the preparation of nanocomposites from PANI and GN by *in situ* polymerization and studying the effects of various GN concentrations on the FTIR and the optical properties of the prepared nanocomposites. Then, we aim at investigating the morphology of the surface of these nanocomposites using SEM. The main purpose of our study, in the end, is to select the best nanocomposites to be used as biosensors.

Experimental part

Aniline hydrochloride ($C_6H_5NH.HCl$) was purchased from Hopkins and William Ltd. Company (England) while acetone (C_3H_6O) was purchased from Chemistry-Lab NV (Belgium). Ammonium persulphate (APS; $(NH_4)_2S_2O_8$) and dimethyl sulphoxide (DMSO; CH_3SOCH_3) were obtained from Central Drug House (P) Ltd. (India). Graphene nano powder (6-8 nm) was purchased from Sky-spring Nanomaterial Inc. (USA).

Preparation of polyaniline

Pure PANI salt was prepared in a low temperature (0 ºC) using an ice medium during the polymerization process. PANI preparation is based on the oxidation of 0.2 M aniline hydrochloride with 0.25M ammonium persulphate in aqueous medium. Aniline hydrochloride was dissolved in distilled water in a volumetric flask to 50 ml of solution. Ammonium persulphate was dissolved in water, also to 50 ml of solution. Both solutions were kept for 2 hours at 0 ^oC, then mixed in a three-necked round bottom flask, briefly stirred, and left to polymerize. The temperature, as a function of time for this reaction, was recorded throughout the polymerization process. It turned out that the reaction of polymerization of PANI was exothermic. After 24 hours, PANI sediment was collected on a filter paper, washed with 300 ml of 0.2 M HCl and 50 ml acetone. After that, PANI powder was dried in air then in a vacuum oven at 80 ^oC for 6 hours.

Preparation of PANI-GN Nanocomposites

The GN nano powder (6-8 nm in diameter) was measured using atomic force microscope (AFM), with various weight ratios (0.1, 1, 5 and 10 g wt.%) which were weighed in Glove Box filled with nitrogen gas. Different mixing ratios were made from GN (0.1, 1, 5 and 10 g wt.%) and the monomer and dissolved in distilled water in a volumetric flask. Ammonium persulphate was dissolved in water to 50 ml of solution. Both solutions were kept for 2 hour at 0 ^oC , then mixed in a round bottom flask and left to polymerize. The solution was left to settle to the next day. The precipitated PANI was collected in filter papers and washed with 300 ml of 0.2M HCl and 50 ml of acetone. After that, PANI powder was dried in air and then in a vacuum oven at 80 ^oC for 6 hours to avoid any effect of moisture absorption. The nanocomposites of 0.5 g were weighed using a sensitive scale. They were pressed into pellets of 1.5 – 2 mm thickness and 1 cm diameter under a pressure of 200 bar using a piston. Figures-2 and 3 show the polyaniline powder and the samples of PANI and PANI-GN nanocomposites, respectively.

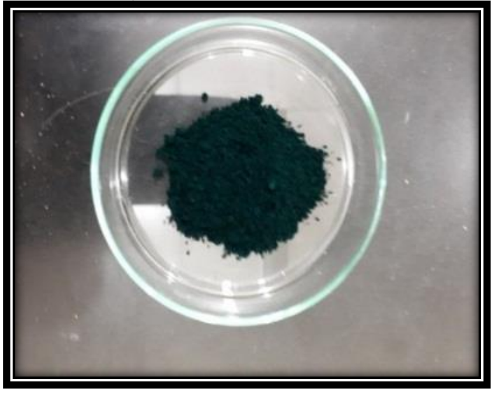


Figure 2-Polyaniline powder.

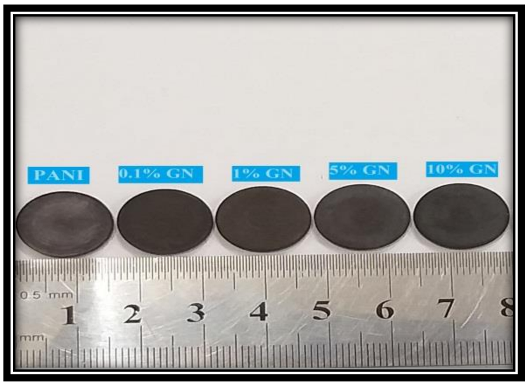


Figure 3-PANI and PANI/GN nanocomposites.

Sample Preparation for UV-VIS Measurement

PANI/ GN nanocomposites of 0.01 g weight were dissolved in 10 ml DMSO and the solution was stirred using magnetic stirrer to make the content homogeneous. Because of the partial dissolving of PANI, the solution was filtered.

Results and Discussion

Reaction temperature and polymerization time

The reaction of polymerization of PANI was exothermic. The temperature as a function of time for this reaction was recorded throughout the polymerization process. Figure-4 demonstrates the reaction temperature with the polymerization time for PANI samples prepared at 0 ºC. From this shape, three distinctive steps were observed; in the initial step of the induction period, the temperature was changed slightly and the blend reaction became blue. The second step was faster than the first one. When the polymerization started and the temperature increased, the color of the mixture turned into dark green. The post polymerization step (third step) was the oxidation-reduction, in which the temperature decreased and the reaction reached saturation stage. From Figure-4, it was found that the reaction time was decreased with increasing the concentration of GN, while the reaction maximum temperature was increased with increasing the content of GN. This indicates that an increase in the formation of free radicals leads to an increase in the reaction speed, which is reflected on the reaction temperature.

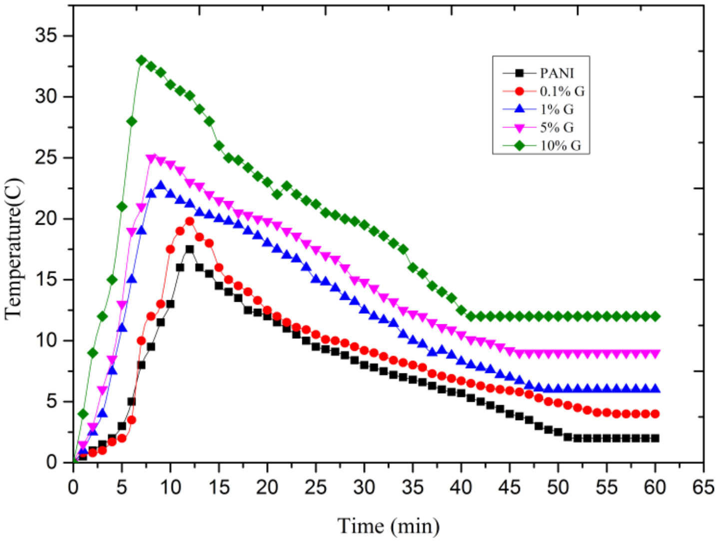
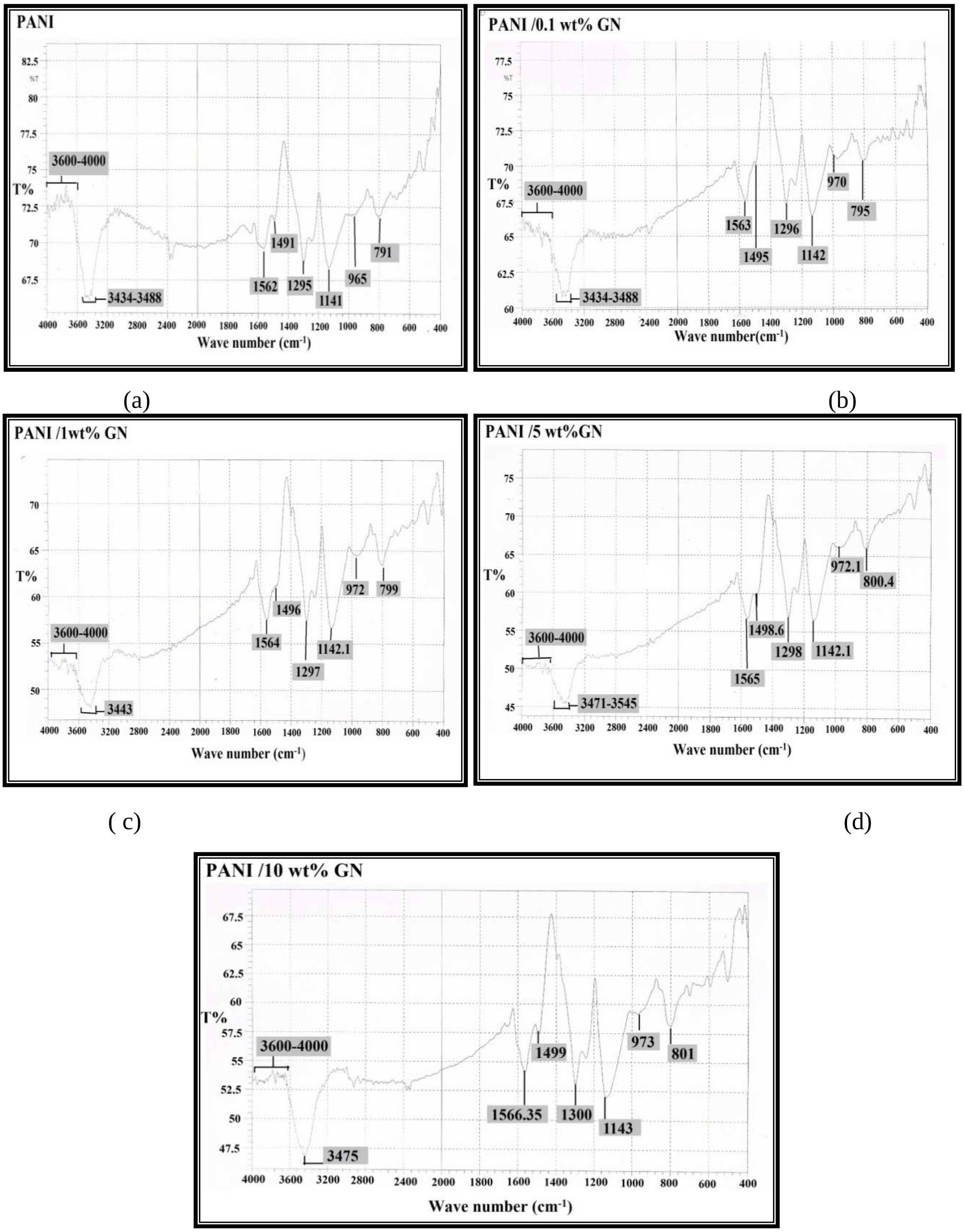


Figure 4-The polymerization time with temperature of reaction for PANI and its nanocomposites prepared at 0 °C.

FTIR spectroscopy

FTIR spectroscopy is a highly useful approach for studying the structure's functional groups. Figure-5-a shows the FTIR spectra of the prepared PANI specimens, where the transmittance is plotted as a function of wave number (cm^{-1}). PANI characteristic peaks are observed at 791 1/cm "N-H out of plane bending absorption ", 965 1/cm "C=C bending ", 1141 1/cm "C=N imines bending ", 1295 1/cm "C-N stretching mode for benzoid ring N=Q=N ", 1491 1/cm "C=C benzenoid ring stretching N=B=N), 1562 1/cm "C=C stretching modes for quinoid ring ", broad peak at 3434-3488 1/cm "O-H stretching, intermolecular bonding ", and small peaks from 3600 to 4000 1/cm "band of OH". Our results are consistent with those of previous reports [12, 13].

The GN nanopowder at different filling ratio (0.1, 1, 5, and 10 wt.% g) influenced the property peaks of PANI; quiniod and benzeniod peaks in Figure-5 (b-e) were shifted to higher wave numbers (red shifted).



(a) (b)

(c) (d)

(e)

Figure 5-FTIR spectra of PANI and its nanocomposites.

UV-VIS Spectrophotometry

The UV-visible absorption spectroscopy is an efficient technique to monitor the optical behavior of materials. The optical properties of matters can be described as any feature that includes the interaction of light with the matter. A UV-VIS spectrophotometry was utilized to study the transmission and absorption spectra for PANI/CN specimens at a wave length range of 200-1100 nm. The absorption was utilized to evaluate the energy gap. Figure-6 shows that the absorption of PANI has two characteristic absorption bands. The first band occurred at 336 nm, which could be attributed to the π-π^* transition of the benzenoid ring, while the second band appeared at the high wave length of 612- 630 nm, which could be attributed to quinoid excitation and π- polaron transition, respectively. These peaks are typical for doped PANI emeraldine salt. The reason for the emergence of two peaks in the UV spectrum of PANI is that it has the property of alternating double bonds in the absorption spectrum.

Figure-7 shows the UV-VIS absorption for the doped PANI material. For the 0.1 % , 1%, and 5 %, the band was shifted to a higher wavelength. When the concentration of GN was increased, as in the sample of 10%, the band was shifted to a lower wavelength.

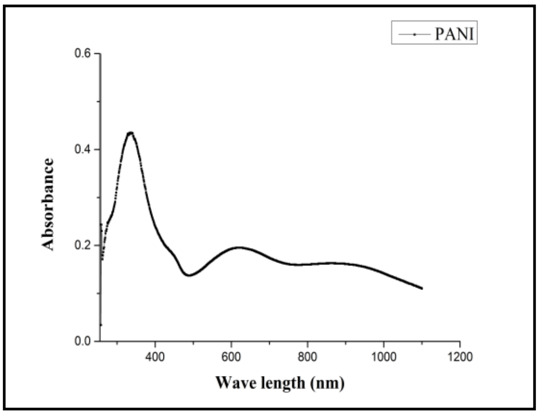


Figure 6-Absorption spectra of PANI.

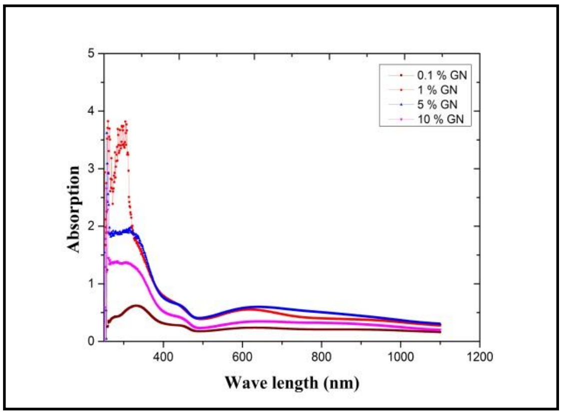
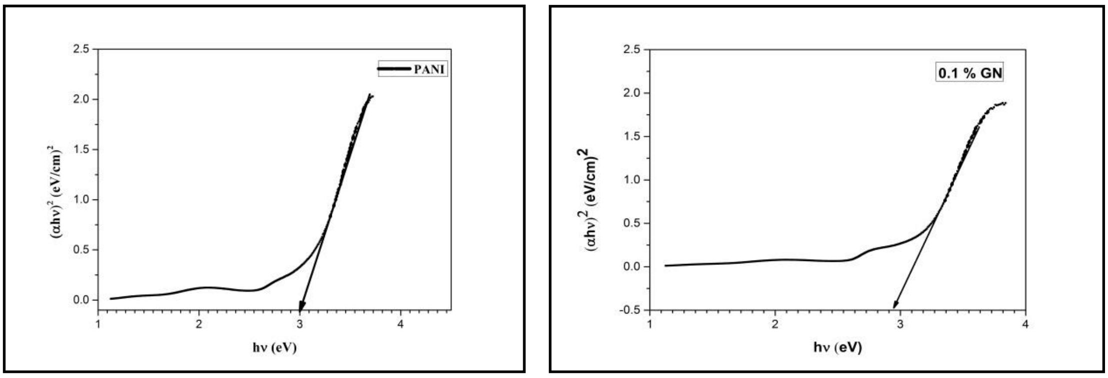
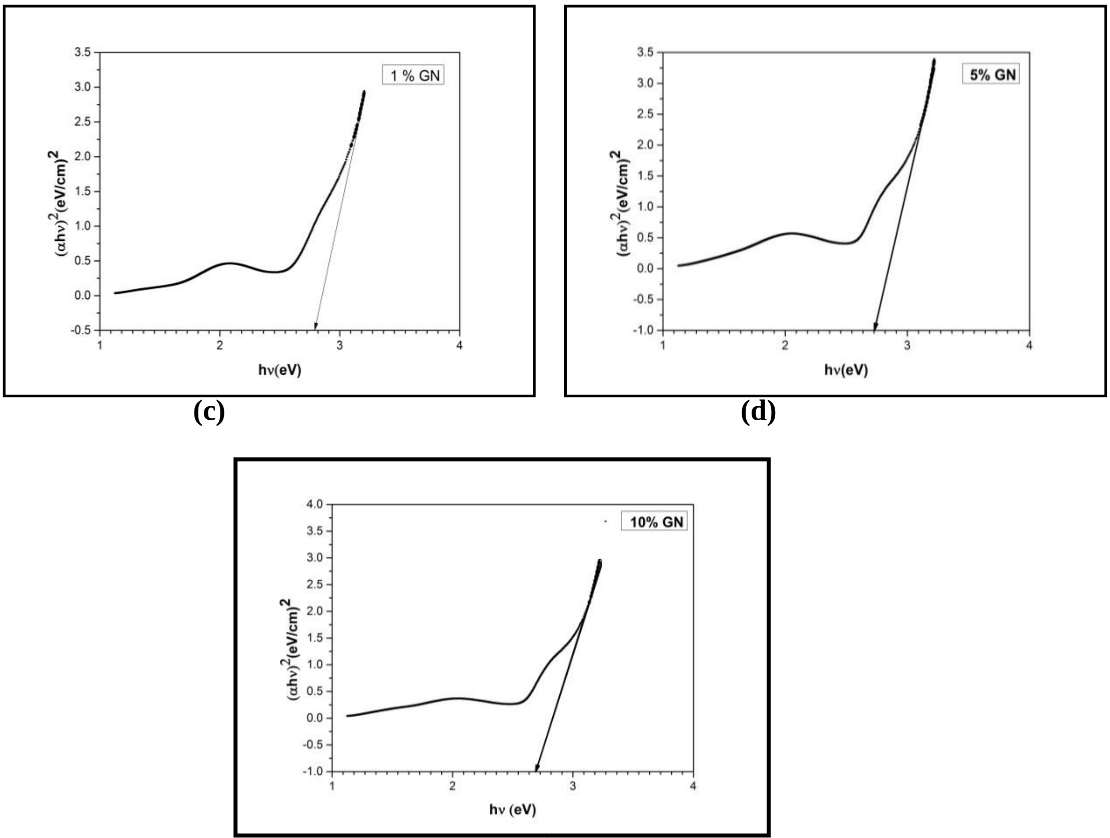


Figure7-Absorption spectra of PANI / GN

The energy gap of the specimens was calculated using the equation "$\alpha h\upsilon = D(h\upsilon - E_g)^r$" where D is a constant, hν is the energy of incident photon (nm) that can be evaluated utilizing the equation "hυ (eV) = 1240 / λ", and r is the order of the optical transition depending on the kind of electronic transition. The transference is called direct if the ends of "V.B." and "C.B." are located at the same point in k-space, whilst it is called indirect if the transition is conceivable only with phonon assisted "$\Delta k \neq 0$". Thus the value of r may be 1/2, 2, 3/2, and 3, reflecting the allowed direct, permitted indirect, prohibited direct and prohibited indirect transition, respectively. Figure-8 shows the results of the determination of the energy gap (Eg) for the samples. The plot of $(\alpha h\upsilon)^2$ versus hυ is showing the results of pure PANI and PANI/GN nanocomposites. The linear part of the plot indicates the direct band gap nature of the polymer. Extrapolation of this line to the hν axis, which gives the value of the energy band gap, is indicating the direct band gap nature of the polymer. The optical energy gap represents the energy difference between the localized states. Therefore, increasing GN content caused an overlapping in the localized states and, consequently, the optical energy gap was decreased. Figure-9shows the variation of energy gab (E_g) with the GN% content.



(a) **(b)**



(c) **(d)**

(e)

Figure 8-Determination of the optical energy gab for PANI and its nanocomposites.

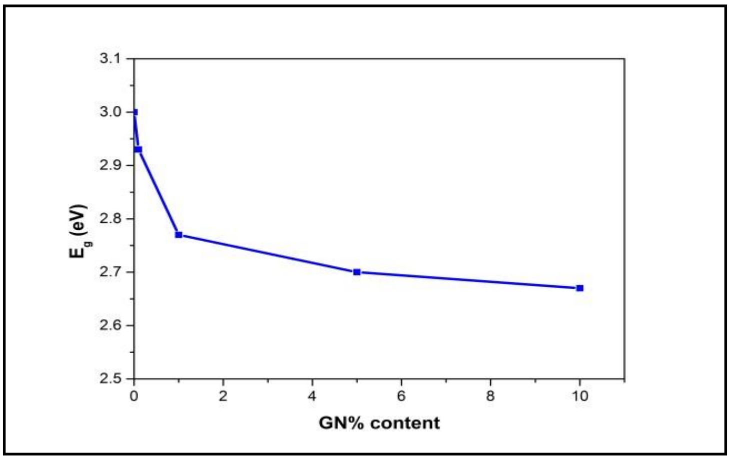


Figure 9-The variation of E_g with the GN% contents.

Results of Scanning Electron Microscopy

The morphologies of the pure PANI and PANI / GN nanocomposites were studied by SEM. Figure- 10 shows SEM images of the surface structure of GN, PANI, PANI/0.1% GN, PANI/1% GN, PANI/5% GN, and PANI/10% GN at a high magnification of the samples . SEM imaging of GN (Figure-10-a) showed a 2D nanosheet morphology. GN sheets are rippled and crumpled, with dimensions ranging from several nanometers to twenty nanometers or less. Figure-10-b shows the SEM image of PANI sample obtained by the chemical oxidation route. This image also shows the irregular particles in nano range, with size range of 30–46 nm and spherical accumulation. However, careful examination revealed that a small amount of nanofibers also appear in the product. Apparently, these nanofibers are formed without any additional structural directing factors, suggesting that the nanofibers may represent the natural morphology of polyaniline [14]. Figure-9 (c-e) shows the SEM images of PANI/GN nanocomposites at different weight ratios. This image shows that the GN was decorated on the surface of PANI. The micrograph of PANI/GN nanocomposites was incorporated into PANI matrix with average grain size less than 50 nm.

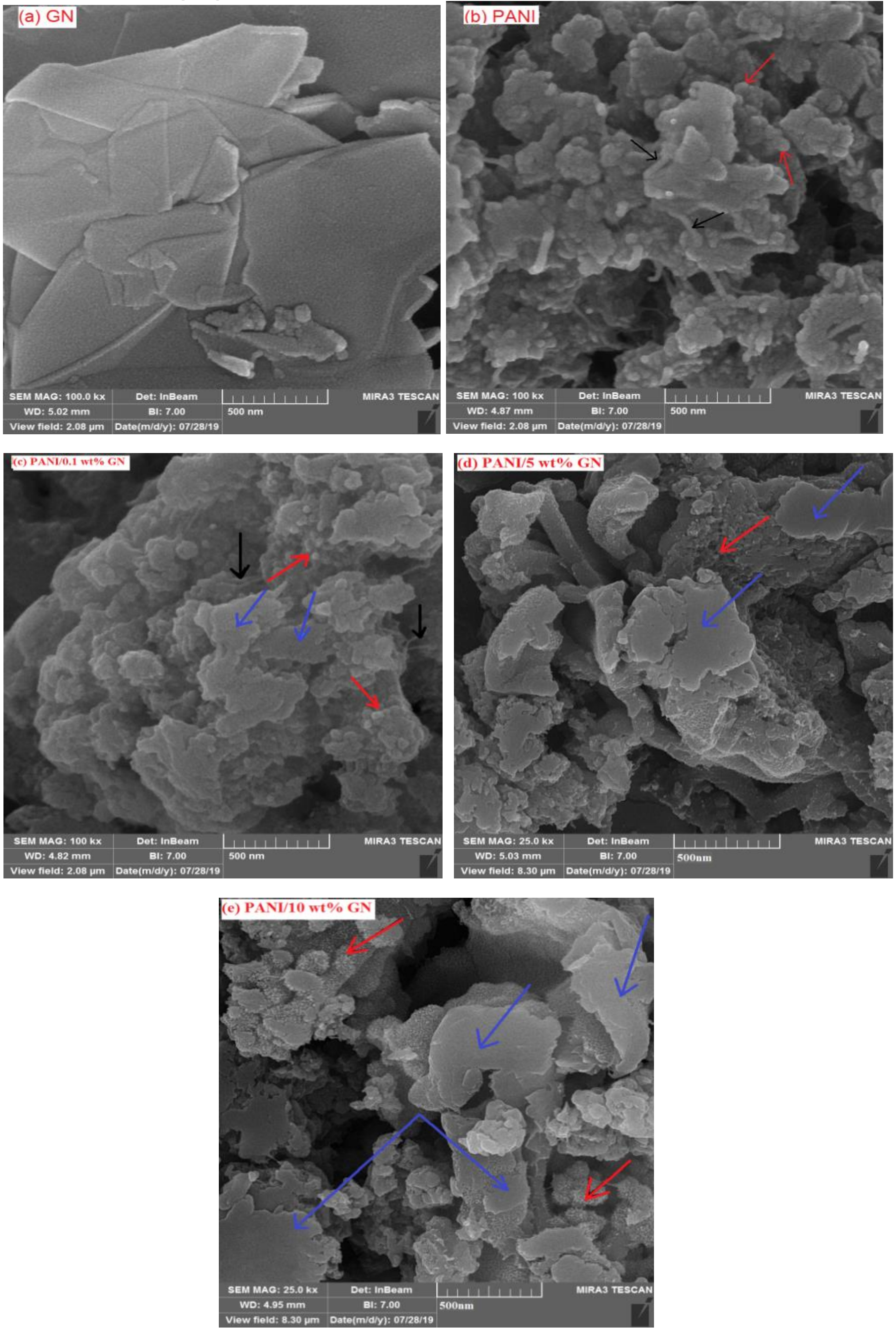


Figure 10-SEM images of PANI ,GN and PANI/GN nanocomposites.

Conclusions

This study demonstrated that the reaction of polymerization of PANI was exothermic. According to FTIR spectroscopy, GN interacted physically with PANI causing a shift in the peaks of quinoid and benzoid rings to higher wave numbers. Scanning electron microscopy showed that the increase of the concentration of GN led to a change in the surface morphology of the composites. The results of the optical properties of polyaniline and its nanocomposite solutions showed a decrease in the energy gap with the increase the concentration of GN. Overall, the results proved that, with the addition of GN to PANI , the intermolecular interaction between the two substances was improved. The results also showed that the nanocomposites have a high potential in a range of applications, including those of sensors.

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