Effect of gamma irradiation and ZnO nano particles on the A.C electrical conductivity of polyaniline

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Abstract

Conducting polyaniline / ZnO nano composites are synthesized using a simplified cheap method with one step in –situ chemical polymerization, and AC conductivity (σ_{ac}) of the prepared samples is studied in the range of frequency from 50 Hz to 15MHz.). The presence of polarons in the conjugated polymer chain are responsible for the ac conductivity is reliance on the frequency in these composites. The effect of increasing the ZnO nano particle concentration irradiation and gamma radiation on the electric conductivity was analyzed. The result showed that the nanocomposite prepared has the highest conductivity, from pure polyaniline and the exponential factor S was found increasing with ZnO content it was 0.739 for PANI pure and for 0.02 ZnO it was 1.415.

Key words

Conductive polymers, ZnO nano particle, gamma radiation, A.C conductivity.

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تأثير التشعيع بأشعة كاما وجسيمات اوكسيد الزنك النانوية على التوصلية الكهربائية المتناوبة لبولي انلين

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الخلاصة

تم تحضير المتراكب النانوي اوكسيد الزنك / بوليمر موصل باستخدام طريقة بسيطة وغير مكلفة وبخطوة واحدة بالبلمرة الكيميائية للنظام، تم دراسة التوصلية المتناوبة σ_{ac} للمتراكبات ضمن مدى الترددات (50 Hz-15MHz.). ان وجود البولارون في سلسلة البوليمر المترافق هو المسؤول لاعتماد التوصلية المتناوبة على التردد. تم تحليل نتائج زيادة تركيز جسيمات اوكسيد الزنك النانوية والتشعيع كاما على التوصلية الكهربائية المتناوبة. أظهرت النتائج إن المتراكب النانوي المحضر يمتلك توصلية أعلى من البولي انلين النقي، والعامل الآسي s يزداد بزيادة محتوى، اوكسيد الزنك فقد كانت قيمته 0.739 للبولي انلين النقي والمتراكب ذو نسبة 0.02 اوكسيد الزنك أصبحت 1.415.

Introduction

In general, traditional polymers are known to be flexible, sensitive to heat, electrically insulating. The addition of inorganic compounds such as Cu, Mg, Ni, or metal oxide like ZnO, MgO can be enhance the electrical properties of these polymers [1]. The conjugated polymer are classes of molecules that containing conjugated backbone, i.e alternating double and single bounds. The attention in conjugated polymers have increased because theses polymers combine some properties of both metals and polymers [2]. Using nanoscale particles as a reinforce are affective to grant a large surface area because of their intriguing properties[3]. Also the using of nanoscale reinforcement materials may improve the electrical and optical properties of the steward polymers [4].

One of the most popular and oldest known conductive polymers is polyaniline (PANI) which is a phenylene - based polymer that has chemically flexible –NH group surrounded on either side by pheneylene ring [5]. Protonation and deprotonation and various other physic-chemical properties of polyaniline can be related to the presence of the –NH-group [6]. The polyaniline is the most interesting electro conductive polymer this is result important properties like, existence in different oxidation state, electrical and optical properties, low cost, environmental stability and ease synthesis by chemical or electrochemical [7, 8]. Because of these properties polyaniline was interested in many application such as, energy storage, electronic devices, sensors, and corrosion protection of metals [9-10]. The aim of the research is preparing nanocomposite with high conductivity. And this composite has many applications like toxic gases examination. The influence of irradiation was only to improve electric properties because when the dose increases, this would lead to sample destruction.

Experimental part

Raw materials

The following chemicals have used for synthesis of PANI and PANI -ZnO nanocomposites, which their purpose for using and the supplier companies, Aniline hydrochloric (C6H5 NH2.HCl) as a monomer 99.99% supplied by Hopkin and William-Germany, Ammonium persulphate $(NH_4)_2S_2O_8$ as initiator (oxidant agent) 99.95% supplied by Himedia Laboratories-India, Acetone (C_3H_6) purification 99.5% supplied by MEDEX-Switzerland, ZnO nano particles additive 99.99% supplied by MTI-USA, (30nm diameter).

Preparation of polyaniline (PANI)

Pure and doped PANI composites were prepared at the ambient conditions and zero temperature. Three – necked round bottomed flask equipped with a thermometer was putted in ice medium (to provide the zero temperature), and electromagnetic stirrer was used to polymerize polyaniline. The preparation of PANI is achieved by the oxidation of 0.25M aniline hydrochloride with 0.3M ammonium peroxydisulphate in 2M HCl aqueous medium. The solution was leaved to settle for 24 hours. Then the PANI dark green precipitate was extract by filter paper then washed with 200ml of 0.2M HCl and 100ml of acetone. Then left the collected PANI in air for 30 minutes, after that it entered to an oven at 85°C for 4 hours to avoid the moisture absorption. Finally the dried powder was grinded by a mortar to get a fine particles as can [11].

Preparation of PANI -ZnO nanocomposites

Polyaniline –ZnO nanocomposites were prepared with different weight percentages wt.(0.1%, 0.5%, 1% and 2%) of ZnO. Nanoparticles (30nm diameter) from 0.5g of polyaniline monomer were synthesized by in-situ – oxidation polymerization method in the same way of preparation pure PANI. and then the resulting samples were compressed under pressure of 250 bar for by using hydrolic pressure device 10 minutes in the form of disk shape.

Irradiation of samples

The samples are irradiated to gamma rays, using $^{60}C_O$ gamma cell-900 of strength rate 4.5Ci.which giving photon energy (1.17 and 1.33MeV) and has the dose rate 250Gy/hr). The samples were painted with conducting paint (silver) to give a good electrical contact between the electrodes. The

dose was 10 kG for one day and 16 hours.

Measurement of electrical conductivity

Measurement of AC -electrical conductivity, σ_{ac}, at room temperature was carried out using LCR type Avcitive Awia - Agilent 4294A, of frequency range 50Hz-110MHz. The samples with thickness about 0.2cm and 1cm diameter were prepared for this study.

Results and discussion

Fig. 1 represents the results of the total conductivity for the PANI -ZnO nanocomposite. It can be expressed the conductivity using the following equation [11]: $\sigma_t(w) = \sigma_{ac}(w) + \sigma_{dc}$ where $\sigma_{ac}(w)$ represents the AC conductivity while σ_{dc} (DC conductivity), and w (frequency). The σ_{ω}, results from this figure show an increase with the angular frequency increasing. The $\sigma_{d.c}$ of the specimens is due to the presence of some free ions H^+, OH^- and Cl^- that induced by (γ) radiation which increases with the dose increasing and also due to the polarons of PANI [12]. or by doping with acidic solution protonation (adding protoins to the polymer chaine). In the common polymer, the ac conductivity is change with the frequency according to the following equation ($\sigma_{ac}(w) = \sigma_{\omega} - \sigma_{d.c} = Aw^s$ Where A represents a constant independent on temperature, $w = 2\pi F$ where w refer to frequency and s refer to exponent. Fig. 2 shows the σ_{ac} of the frequency for pure and doped polyaniline with different ZnO nano particle ratios (0.1%, 0.5%, 1%, and 2%). It was observed that, σ_{ac}, is obtained by the measured total conductivity and the dc conductivity according to above Eq. It is clear from the figure that the σ_{ac} increases with the frequency increasing. From the slope of the straight lines in Fig. 2, we can calculate the exponent s which is less than unity for pure PANI and increases with increasing concentration of ZnO as shown in Fig.3. In general the values of the exponent s appears to be consistent with a hopping process of the protons (the charge carriers) between polymer chains. The AC conductivity may be came from the ions like H^+, OH^-, and Cl^- which induced by irradiation or doping or from the trapped polarons. By the increasing of the precursor concentration and the dose, the conductivity was increased, corresponds with the polarons increasing in the polymer matrix [13, 14].

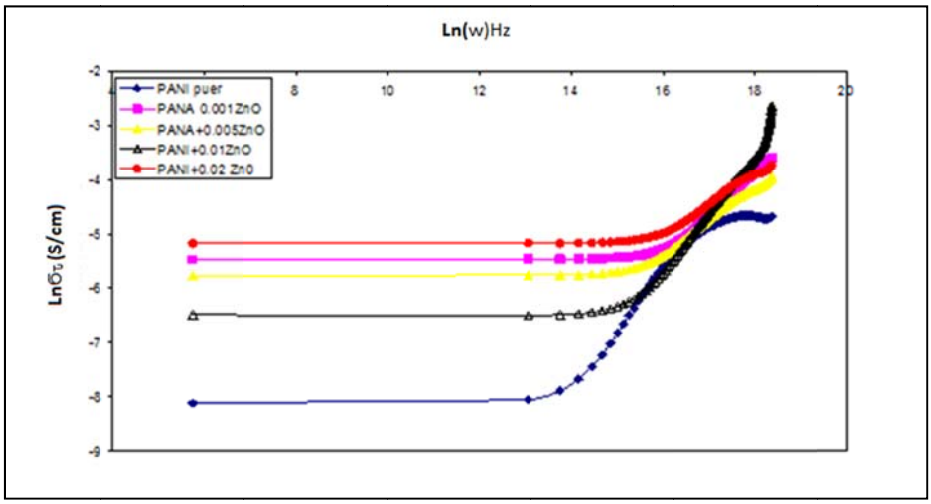

Fig .1: The σ_{ω} as a function of the frequency for pure & doped PANI nanocomposites.

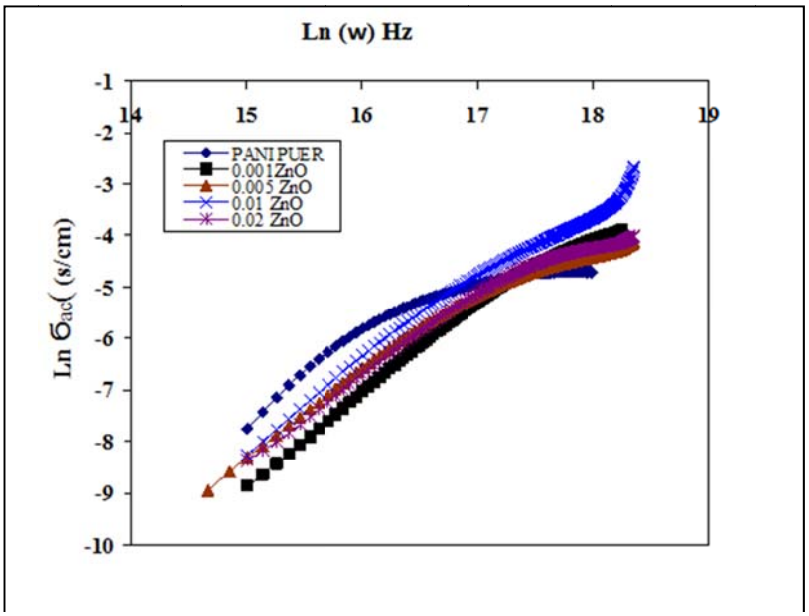

Fig. 2: The $\sigma_{a.c}$ as a function of frequency for pure PANI & PANI -ZnO nanocomposites.

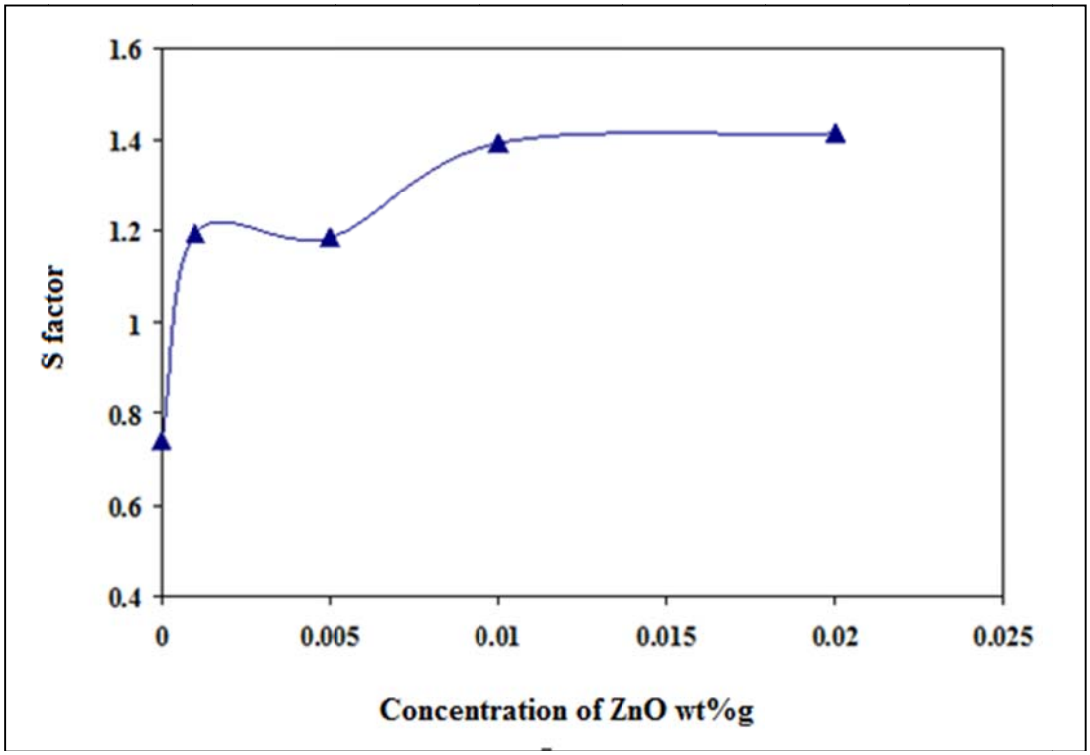

Fig.3 The value of S factor as a function of ZnO wt% concentration in PANI -ZnO nanocompsites.

From Fig. 3 the value of "S" was changed for composite samples and has value greater than unity if the value of "S" increases one, this means energy levels of materials would be very equal. And when "S" is close to two, this means "S" the distance between the levels is less than KT as the dipole would be in resonance, "S" would give a sort of conductivity mechanism hoping or tunnel which would be between polymer chains. This increasing in the values of "S" can be explained as when the photon energy of the applied field is less than the thermal energy KT, the loss due to

resonant process will vary as w^2 [13] and this dominates only high frequency, Fig. 4 shows the variation of electrical conductivity as a function of frequency with effect of gamma irradiation, from the Fig. 4. the conductivity increased because the polyaniline is a polar polymer and when radiated with gamma that's led to recognized the polymer chain, that's mean recognized configuration of polymer chain which led to increased polarons hoping between polymer chain [15, 16].

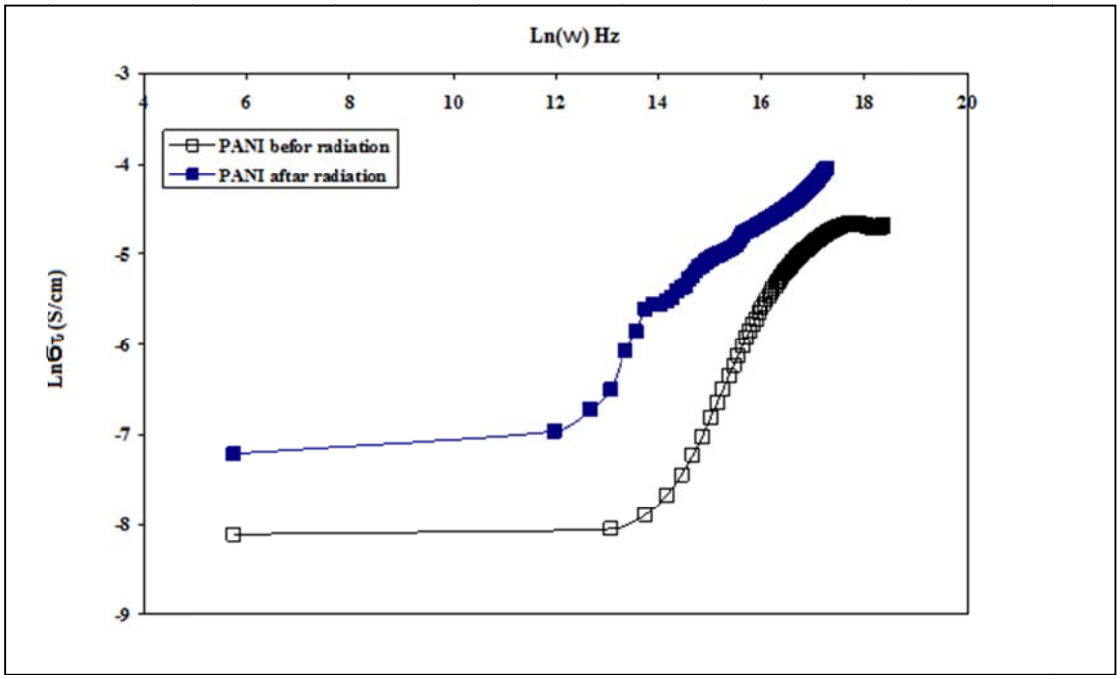

Fig.4: The effect of gamma irradiation with (10 kGy) on the total conductivity as a function of frequency for pure PANI, before & after.

Conclusions

The PANI /ZnO nanocomposites has been synthesized by the chemical oxidation polymerization at different concentration of ZnO nano particles. The ac conductivity and s factor were measured at frequency range (50Hz-15MHz) and gamma radiation. The result indicate that AC conductivity and s factor increased with the increase ZnO content and with gamma irradiation due to increase polarons hoping between polymer chain.

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