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Electrical and Dielectrical Properties of Some Novel Polyaniline Nanocomposites

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NOVEL polyaniline/silver (PANI/Ag) and polyaniline/silver/cupper (PANI/Ag/Cu) core–shell nanocomposites have been successfully prepared. The morphology and the structure of the prepared nanocomposites have been characterized and elucidated. The AC conductivity measurements in the frequency range from 1MHz to 1GHz at different temperatures for the prepared nanocomposites have been investigated. The results showed very high conductivities and dielectric constants. The ac conductivities of the prepared nanocomposites are frequency dependent and follow up hopping conduction mechanism in general. The enhanced electrical properties of the prepared nanocomposites may be attributed to the superior core shell structure and the presence of the core Ag, Ag/Co and Ag/Cu nanoparticles.

Keywords: Polyaniline nanocoposites, Core-shell nanocomposites and Ac-conductivity.

Introduction

Polymer nanocomposites (PNCs) constitute a class of hybrid materials composed of an organic material which is the polymer matrix and an inorganic material which is in general metal nanoparticles.PNCs have been incorporated in different fields such as nanoelectronics, electromagnetic and biomedical devices due to their unique properties[1-4].

Polyaniline (PANI) is one of the most widely used conductive polymers and has distinctive electrical, optical, photoelectric properties and good environmental stability [5].

Incorporation of metal or semiconductor nanoparticles [6, 7] into conducting PANI matrix is such a way to improve its electrochemical, catalytic as well as sensing properties.

Therefore intensive research work on the preparation of PNCshas been carried out in recent years[6, 8-10].

The methods of preparation of PANI are in general (chemical and/or electrochemical polymerization) using appropriate protonation media.

Electrochemical methods have been used for preparations of PNCs and offer precise control for the degree of interaction between the polymer and the metal anion[11-13].

However, the yield of material got from electrochemical methods is very little and restricted by the electrode size and the polymer/metal interface.

The insertion of nanoparticles into composite materials can enhance their chemical, thermal resistances as well as electrical conductivity. Hence an attempt has been made to enhance the ac conductivity and the dielectric properties by embedding metal nanoparticles into the core of PANI shell.

In this context, we report here the measurements of the ac conductivity as well as dielectric constant for the prepared novel core shell nanocomposites at high temperartures and different frequencies.

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Experimental

Materials

Aniline monomer (99.5%), dodecyl benzene sulfonic acid (DBSA, surfactant), silver nitrate ($AgNO_3$), Cobalt (II) Chloride ($CoCl_2$) and cupper (II) chloride ($CuCl_2$) were supplied from Sigma-Aldrich Company, USA.

Preparation of PANI/Ag nanocomposite

The polymerization reaction has been done according to the procedure of Elhalawanyetal[9] which in detail is as follows: Aniline and DBSA of ratio (1:1) have been mixed in water and isopropanol (IPA) mixture of ratio (3:1) respectively under continuous vigorous stirring using homogenizer at 10,000 rpm for 5 min to form the miniemulsion. A 20 ml of 1.5×10^{-2}M $AgNO_3$ solution has been added drop wisely to the former miniemulsion under continuous vigorous stirring at 10,000 rpm for further 10 min at room temperature. A color change from white to bluish green then to green has been observed.

At the final stage of polymerization, a stable green colloidal dispersion has been obtained. The green dispersion was further centrifuged, washed several times with water/methanol mixture of ratio (1:3), filtered and then dried and kept for further use.

Preparation of PANI/Ag/Co and PANI/Ag/Cu nanocomposites:

The same as previously mentioned except that we have used 20 ml of 1.5×10^{-2}M $CoCl_2$ and$CuCl_2$solutionsrespectively with silver nitrate solution in a separate feed. The stable dispersion was then centrifuged, washed, filtered, dried and finally kept for further use.

Characterization of the prepared composites

Fourier transform infrared (FT-IR) spectra

FT-IR analysis of the prepared composites has been carried out at Infra-Red Unit, Central Service Labs, National Research Center (NRC) using FT-IR-6100, Japan.

Scanning electron microscope (SEM)

Samples have been measured using SEM JOEL 6060 LV, Japan at NRC, Central Service Labs.

Electrical conductivity measurements

The ac conductivity measurements have been carried out in the frequency range from1MHz to 1GHz at different temperatures using Agilent E4991 B 1M- 1G Impedance/Material Analyzer with Measurement range from 0.13 Ω to 20 kΩ (within 10 % accuracy), 0.8 % basic accuracy and 0 to ± 40 V, ± 50 mA DC bias (Opt. 001) from USA, at Electron Microscope Laboratory, Physics Department, National Research Center (NRC), Cairo, Egypt.

Results and Discussion

In this study a novel core shell nanocomposites have been successfully prepared [9].

The formation mechanism for the prepared core shell nanocomposites is shown in Fig. 1.

Characterization of the prepared composites

FTIR analysis

IR spectra reveal strong absorption bands at 1600 and 1490 cm^{-1} corresponding to stretching frequency C=N and C=C groups that are characteristic for N-B-N and N=Q=N formation. [14].

The bands at 1146 cm^{-1} correspond to polyaniline in the composites. In comparison with the spectrum of PANI, the intensity of peaks of PANI/Ag, and PANI/Ag/Cu were stronger and the peak of the N-H vibration at 3450 cm^{-1} has been shifted to 3445 cm^{-1} due to overlapping between the formed metallic nanoparticles and PANI. This red-shift is the consequence of the conjugated electron cloud between silver nanoparticles and PANI chains.

Scanning electron microscope (SEM)

SEM graphs and EDS analysis of the prepared core shell nanocomposites are shown in Fig. 3. It is clearly seen from the figure that Ag, Ag/Co and Ag/Cu nanoparticles are the bright spots and spherical in shape. It is also shown from the figure that the metal nanoparticles bright spots are widely separated and embedded into darker PANI matrix. Figure 3 shows also the SEM graph for the pure PANI which has the shape of stone and rod like structures. Elemental analysis by energy-dispersive spectrometry (EDS) is shown in the figure where characteristic peaks at2.9,6.9 and 7.9 eV have been arisen which confirms the presence of silver, cobalt and copper nanoparticles respectively.

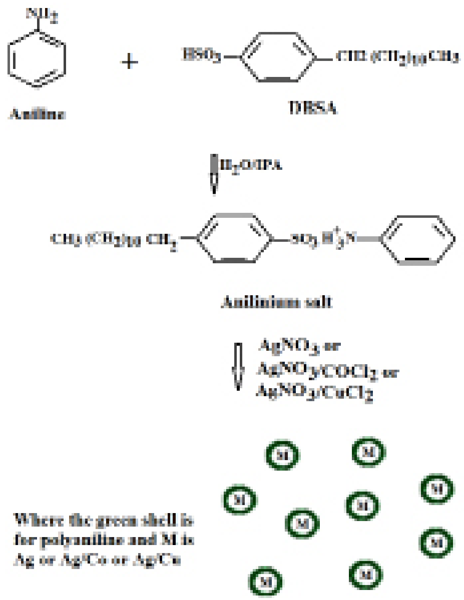

Fig. 1. Polyaniline encapsulated Ag and Ag/Cu nanoparticles.

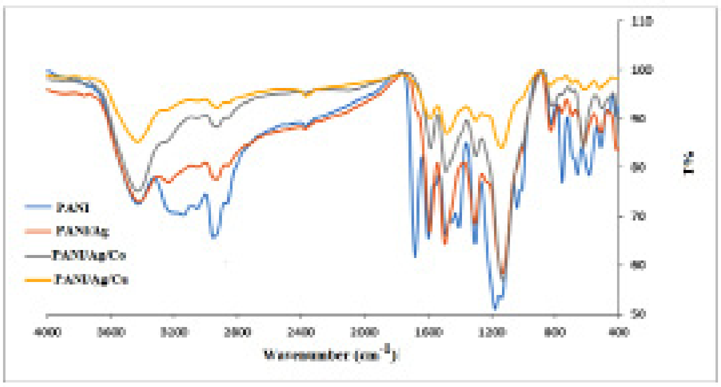

Fig. 2. FT-IR of the prepared pure PANI and PANI nanocomposites.

Electrical conductivity measurements

Electrical properties

The A.C conductivity for the common polymer changes with the frequency according to the following formula:

$$\sigma_{ac}(\omega) = \sigma t - \sigma_{d.c} = A\omega^{s}$$

where (A) is a constant independent on temperature, ($\omega = 2*\pi*f$) and (s) is the frequency exponent.

The AC conductivity and dielectric properties of the formed nanocomposites have been studied under different temperatures and different frequencies in the range from 1MHz to 1GHz KHz. The presence of Ag, Ag/Co and Ag/Cu nanoparticles and the superior core shell structure of the nanocomposites make them having high conductivities as well as dielectric permittivities than that of pure PANI. Figures 4-6 show the variation of Ac conductivity against variation of angular frequency (ω) at different temperatures. It is shown from the figures that the ac conductivity increases with increase in temperature for every applied frequency.

It also is shown from figures that the ac conductivity increases with increase in temperature for every applied frequency. The ac conductivity increases with increasing temperature due to improvement in the mobility of charge carriers.

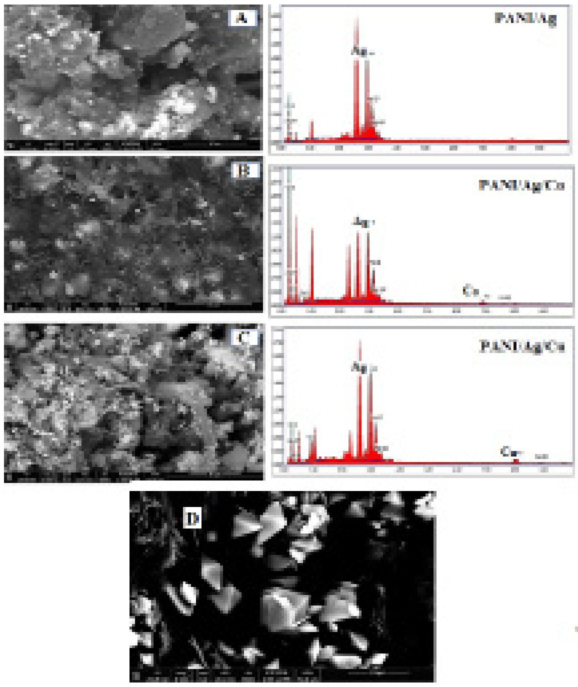

Fig. 3. EDS and SEM micrograph of (A) PANI/Ag, (b) PANI/Ag/Co, (C) PANI/Ag/Cu and (d) PANI.

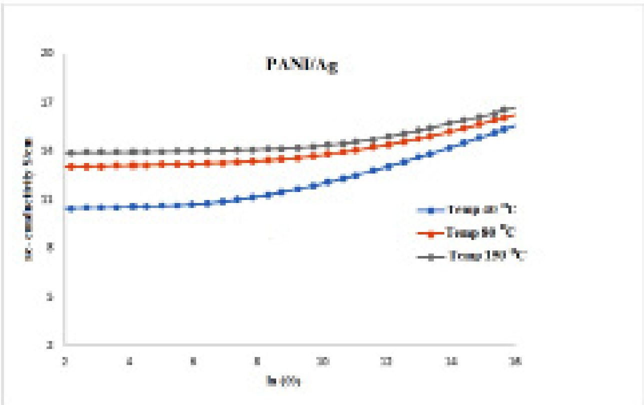

Fig. 4. The variation of ac conductivity with angular frequency at high temperatures.

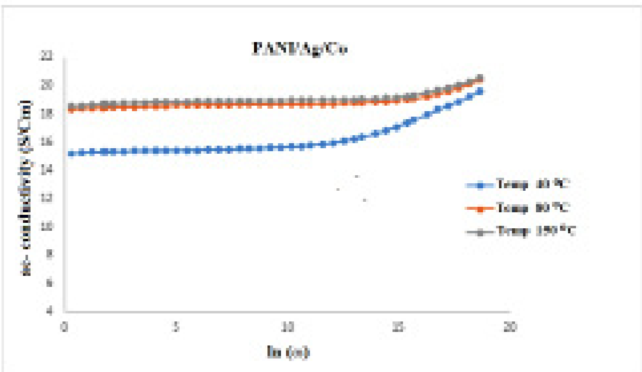

Fig. 5. The variation of ac conductivity with angular frequency at high temperatures.

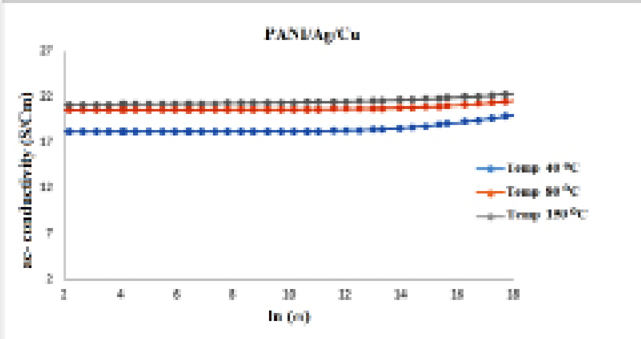

Fig. 6. The variation of ac conductivity with angular frequency at high temperatures.

The ac conductivities at high temperature at (80ºC) are 16.54, 20.54 and 22.4S/m for PANI/Ag, PANI/Ag/Co and PANI/Ag/Cu respectively. The PANI/Ag/Cu nanocomposite has the highest conductivity. It is shown also from the figures that the ac conductivities of the nanocomposites are much higher than that of pure PANI which is well known from literature in the range from 10^{-3}-10^{-4} S/cm.

The ac conductivity increases as the frequency increases in case of hopping conduction while vise versa in case of band conduction[15]. The frequency exponent (s), can be calculated from the slope of the straight lines in Fig. 4-6

Table 1 shows the variation of frequency exponent factors with frequency at 80°C. It is obvious that as the s values decrease as the conductivity increases. In general, when s values are less than unity, the conduction mechanism would be hopping conduction. According to hopping conduction mechanism, the conduction occurs via a bipolaronhopping process in which two electrons instantaneously hop or jump over the potential barrier between two charged defect states (D+ and D-) and the barrier height is associated with the intersite separation via a Coulombic interaction[15].

This matches well with our results where the lone pairs of electron of nitrogen atoms overlap with the vacant orbitals of core nanoparticles which in turn increases the polarity of the composites and hence conductivity increases.

Frequency dependence on dielectric constant
The dielectric constant, has been calculated from the measured capacitance value. The dielectric constant (ε′) was calculated from the equation:
$\varepsilon' = dC_p/A\varepsilon_o$

where C_p is the capacitance, (ε_o) is the permittivity of free space and A is the cross sectional area.

Figures 7-9 show the variation of dielectric constant (ε′) with frequency. It is obvious from figures that (ε′) decreases with increasing in frequency.

At low frequencies, the formed dipoles can certainly revolve nearby the applied electric field, so maximum polarization arises leading to high dielectric constant [16]. At high frequencies, the formed dipoles are no longer able to revolve fast and hence dielectric constant decreases.

The dielectric permittivity mainly depends on the particle size of the polymeric chains. Presence of metal nanoparticles in the core of the PANI matrix increases the net polarization and hence the dielectric constant increases. It is also shown from figures that as the temperature increases as the dielectric constant increases.

This may be attributed to increase in dipole movements towards the boundaries between the core metallic nanoparticles and the PANI shells which in turn increases the interfacial polarization and hence enhancement of the dielectric constant occurs[17].

Conclusion

Polyanilinecore–shell nanoncomposites have been successfully synthesized.FT-IR analysis showed that the NH bond shifted due presence of metal nanoparticles. The SEM showed that the metal nanoparticles are randomly embedded into PANI shell. The AC-conductivity of the prepared composites are frequency dependent and the charge transport mechanism is hopping. The enhanced electrical properties of the prepared

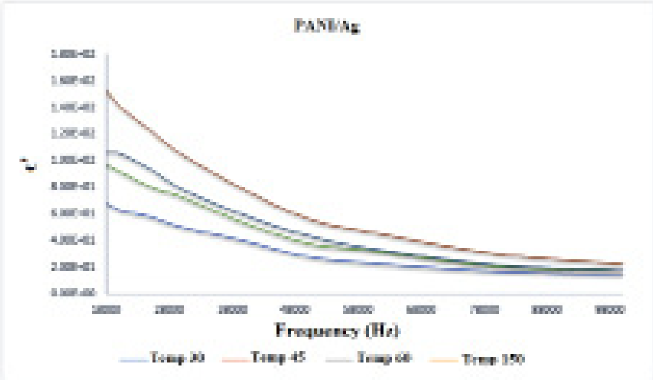

Fig. 7. The variation of dielectric constant with angular frequency.

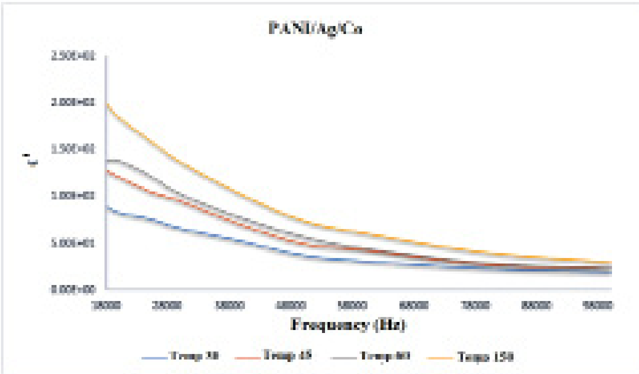

Fig. 8. The variation of dielectric constant with angular frequency.

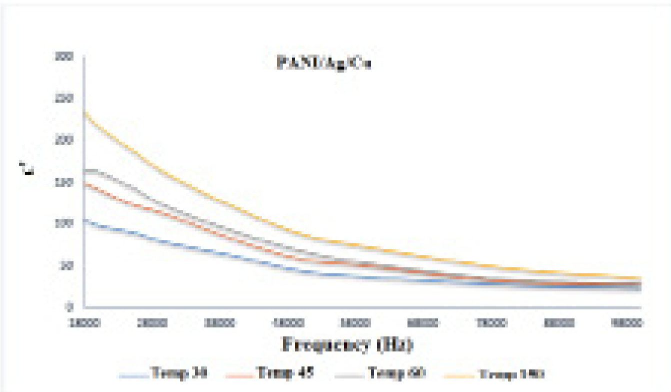

Fig. 9. The variation of dielectric constant with angular frequency.

TABLE 1. Variation of s factor for the prepared nanocomposites at 80°C

Nanocomposite	s factor
PANI/Ag	0.48
PANI/Ag/Co	0.39
PANI/Ag/Cu	0.31

composites arising from the superior core shell structure. These characteristic composites will open the gate for further use in different applications especially electronic devices.

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الخصائص الكهربية والعازلة لبعض متراكبات البولى انيلين الجديدة

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متراكبات البولى انيلين مع كلا من الفضة والفضة والكوبالت والفضة والنحاس ذات البنية الخاصه (نواة وغلاف) قد حضرت بنجاح. تم توصيف التركيب والمورفولوجيا لهذه المتراكبات بنجاح. كما تم ايضا قياس الخصائص الكهربية لهذه المتراكبات عند درجات حرارة مختلفة وترددات مختلفة تبدأ من 1MHz- 1GHz. واظهرت النتائج ان هذه المتراكبات المحضرة لها توصيلية كهربية عالية جدا وكذلك ثابت عزل كهربائى عالى. اثبتت ايضا النتائج ان التوصيلية الكهربية لهذه المتراكبات تعتمد على التردد المستخدم وكذلك تتبع ميكانيكية القفز فى التوصيل. وتعود الزيادة العالية فى التوصيلية الكهربية الى التركيب المميز ذو النواة والغلاف ووجود جزيئات النانو من كلا من الفضة والفضة والكوبالت والفضة والنحاس فى النواة.