Effect of Ni Nano particles on Thermal, Optical and Electrical Behaviour of Irradiated PVA/AAc Films

Dalia E. Hegazy, M. Eid and M. Madani
National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

Received: 25/12/2013 Accepted: 20/1/2014

ABSTRACT

Solid electrolyte polymeric materials based on poly(vinyl alcohol-co-acrylic acid) P(VA-co-AAc) containing Ni nano particles were prepared using electron beam induced crosslinking and reduction of Ni ions technique at 30 kGy. The synthesized composites were analysed by UV-visible spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The activation energy of decomposition of the electrolytes increased with increasing salt concentration. The optical band energy gap is estimated using UV–visible spectra and it decreases with increasing dopant concentration. The DSC studies indicate that the dopant changes the thermal behavior of PVA/ AAc like glass transition temperature. Dielectric behavior was studied in the frequency range of 300 Hz- 5 MHz at room temperature. The a.c. conductivity was found to increase with the increase of dopant concentration as well as frequency. This improved properties of P(PVA/AAc)-Ni nano composite suggested to be used in optoelectronic devices.

Keywords: radiation; nano composites; dielectric; thermal analysis and optical band gap.

INTRODUCTION

Polymeric materials have attracted the scientific and technological researchers, because of their wide applications. This is mainly due to the lightweight, good mechanical strength, optical properties and makes them to be multifunctional materials\(^{(1)}\). In recent years, studies of electrical and optical properties of the polymer have attracted much attention in view of their application in electronic and optical devices. Electrical properties constitute one of the most convenient and sensitive methods for studying the physical mechanisms that determine this prop- polymer structure aiming to understand the nature of the charge transport prevalent in these materials, while the optical properties are aimed at achieving better reflection, antireflection, interface and polarization properties.

The optical absorption spectra of polymers provide essential information about the band structure and the energy gap in crystalline, semi-crystalline, and non-crystalline polymers. The electrical and optical properties of polymers can be suitably modified by the addition of dopants. Moreover, these polymers are traditionally considered as an excellent host material. The field of polymer additives has attracted strong interest in today’s materials research, in view of this it is very important to note that the dopant modifies the structure of the polymer and hence its properties. Since, the change in polymer properties are mainly depends on the nature of the dopant and the way in which it interacts with the polymer, as it achieve impressive enhancements of the polymer properties as compared with the pure polymers\(^{(2, 3)}\).

The development of nano science and nano technology has allowed us to create new nano-sized materials having unique electronic and optical properties quite different from those of their bulk state\(^{(4)}\). In various electronic and optical devices the size-dependent properties of the nano materials were used\(^{(5)}\). The optical properties of a metallic nano particle depend mainly on its surface Plasmon
resonance, and it is well known that the plasmon resonant peaks and line widths are sensitive to the size and shape of the nano particles, the metallic species and the surrounding medium. The optical properties of metal nano particles embedded in a dielectric medium have also been a subject of immense interest in recent years because of their novel characteristics.

These studies shows, the changes in the properties like electrical and optical behavior, etc. of the polymer due to doping. PVA is normally a poor electric conductor; it can become conductive upon doping with some dopant. The conducting nature of doped PVA is thought to be due to the high physical interactions between polymer chains and dopant via hydrogen bonding with hydroxyl groups as well as the complex formation. The optical absorption spectroscopy (UV–visible, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) is an established tool to investigate the effect of dopant on the microstructure of the polymer, particularly on the band structure and electronic properties including the energy gap $E_g$. Additions of the dopants to a polymer modify the energy band gap $E_g$, which depends on the type and magnitude of the defect concentration caused by the dopant. Hence, these modifications give information on the optical, electronic, thermal and microstructural behavior of the polymer.

EXPERIMENTAL

1. Materials:

The chemicals used in this study were fully hydrolyzed Polyvinyl alcohol (PVA) (average $M_w$~14000 and purity 98%) and anhydrous acrylic acid (AAc) (linear formula: $\text{CH}_2=\text{CHCOOH}$, Molecular Weight: 72.06, density 1.051 g/mL at 25 °C and purity 99%) were obtained from Merck, Germany. NiSO$_4$ and isopropyl alcohol were supplied from El-Nasr Co. for Chemical Institutes, Cairo, Egypt. All chemicals were used as received.

2. Preparation of Ni nano particles/ PVA- AA films:

PVA solution 6 wt% was prepared by dissolving PVA in 85°C double-distilled water with stirring for 2 h. Acrylic acid monomer dissolved in double-distilled water at room temperature was added to the PVA solution to form PVA/AAc, 50/50 w/w%, mixture solutions with stirring till homogeneous mixing at 85 °C. Different contents of NiSO$_4$.5H$_2$O (10, 20, 50, 100, 150 and 250 m mol) were added followed by adding 0.3 mL of isopropyl alcohol as scavenger of hydroxyl radical. The mixture solutions were poured into glass dishes and then irradiated using 1.5 MeV electron beam accelerator (Model ICT) at NCRRT, Cairo, Egypt, at a dose of 30 kGy. The experimental details, sample preparation procedures and samples characterization have been described in a previous work.

UV–vis absorption and transmittance spectra of the prepared samples were recorded using a double-beam spectrophotometer (JASCO model V-550, Japan). Thermogravimetric analysis (TGA) were performed using Shimadzu–50 instrument (Japan) at heating rate of 10°C / min under flowing nitrogen (20 ml/min) from ambient temperature to 500°C. The glass transition temperature of the samples was investigated by using a Perkin-Elmer DSC7 differential scanning calorimeter. The experiments were carried out in nitrogen atmosphere using about 7 mg sample sealed in aluminium pans. The samples were heated from room temperature to 135°C. The heating rate was 10°C/min in all cases.

Dielectric measurements were performed by impedance spectroscopy using a Hioki LCR meter, 3531 Z Hi-Tester, Japan, operating at a frequency range (42 Hz–5 MHz), with impedance accuracy ranges from 0.15% up to 4%. The bridge connected via a standard interface (RS-232C interface, Hioki, Japan) to a Pentium personal computer for instrument control and data processing. Silver
electrode 10 mm in diameter were used on both side of the samples. The capacitance ($C$) and the loss tangent ($\tan \delta$) were obtained directly from the bridge from which $\varepsilon'$, $\varepsilon''$ and $\sigma_{ac}$ were calculated. The permittivity ($\varepsilon'$), dielectric loss ($\varepsilon''$) and ac conductivity ($\sigma_{ac}$) for the denoted samples were conducted over a frequency range from 100 Hz to 5 MHz at room temperature.

RESULTS AND DISCUSSION

1. Preparation of P(PVA/AAc) Ni nanoparticles:

   Equal volumes of (6 wt%) PVA and (50 wt%) AAc were prepared by dissolving in double-distilled water at 85°C and room temperature respectively. The two solutions were mixed then different contents of NiSO$_4$.5H$_2$O of (10, 20, 50, 100, 150 and 250 m mol) were added followed by adding 0.3 ml of isopropyl alcohol as scavenger of hydroxyl radical. The mixtures were poured into glass dishes then irradiated by electron beam irradiation at 30 kGy. The prepared copolymers were characterized using different techniques; optical properties, thermal degradation, thermal parameters and dielectric analysis.

2. Optical characterization:

   Study of the optical absorption edge in the UV-region has proved to be a very useful method for elucidation of optical transitions and electronic band structure of the materials[14]. The law of absorption of light $I=I_0 \exp (-\alpha d)$ was used to calculate the absorption coefficient according to the Davis and Mott[15] model where $\alpha(\lambda)$ is the absorption coefficient which can be calculated from the optical absorption spectrum using the relation:

   $$\alpha(\lambda) = 2.303 A d^{-1}$$

   where $d$ is the sample thickness, $\lambda$ is the wavelength of the incident photons and $A$ is defined by $A=\log (I_0/I)$ where $I_0$ and $I$ are the intensities of the incident and transmitted beams, respectively.

   The UV/VIS Spectrophotometric scans were measured in the wavelength range 200–900 nm for all samples. Figure 1 (a, b) shows the variation of absorption coefficient and optical transmittance with wavelength for different films, respectively. Figure 1 (a) shows the optical transmittance for the doped and un-doped (PVA/AAc) nano composite. It can be seen that the transmittance percent increase with wavelength. The transmittance percent affect on the concentration of Ni salt in where the transmittance gradually with increasing salt content. It is usually presumed that the transmittance of the films decreases with grain size in the visible region of spectrum due to light scattering on their rough surfaces[16]. The un-loaded (PVA/AAc) shows high transmittance percent, it reaches 42% at 700nm.

   Another observation about these transmission spectra is that after adding nano-Ni in polymer matrix, an absorption peak starts emerging at 410nm with its intensity continuously increasing with increasing concentration of the dopant. The appearance of this peak in the visible region is due to the surface plasmon resonance (SPR) nature of the Ni nanoparticles embedded in a dielectric medium[17]. Figure 1(b) shows the changes in adsorption coefficient with wavelength for Ni-doped and undoped P(PVA/AAc) nano composite.

   Further, it is apparent from Fig. 1 (b) that the observed absorption edge at 307 nm, in undoped P(PVA/AAc) due to n$\rightarrow$\pi$^*$ transitions [17], shifts gradually towards the higher wavelength side with increasing concentration of Ni nanoparticles as dopant. The absorption edge shifts depend on the composition of the films, indicating a change in the optical band gap of the films. This shift in the absorption edge towards the higher wavelength side suggests a reduction in the band gap value[18].
The band gap of the films was estimated using the fundamental absorption, which corresponds to electron excitation from the valence band to conduction band\(^{(18)}\). The band gap \(E_g\) is the value of optical energy gap between the valence band and the conduction band. The band gap of the films was calculated using the following equation\(^{(14)}\):

\[
\alpha(\nu) = \alpha_0 \frac{(h \nu - E_g)^n}{h \nu}
\]

Where \(h \nu\) is the energy of incident photons, \(\alpha_0\) is a constant related to the extent of the band tailing, and \(n\) is the power, which characterizes the transition process in the K-space. Specifically, \(n\) is 1/2; 3/2; 2 and 3 for transitions direct allowed, direct forbidding, indirect allowed and indirect forbidden, respectively. \(\alpha_0\) depends on the transition probability and can be assumed to be constant within the optical frequency range. The dependence of \((\alpha h \nu)^{1/n}\) and photon energy \((h \nu)\) was plotted for the studied films using different values of \(n\), the best fit was obtained for \(n=2\). This indicates that the transition energy for electrons is indirect in K-space and interactions with lattice vibrations (phonons) take place. Figure 2 shows the plots of \((\alpha h \nu)^{1/2}\) vs. \(h \nu\) for various films. The \(E_g\) values were determined by extrapolation the linear portion of the curves until they intercept the photon energy axis. The band gap of the pure \(P(\text{PVA/ AAc})\) was calculated to be 3.4 eV and it found to be decreases by increasing Ni content in the matrix as shown in table (1). Very similar trend in optical band gap for copper nano particles doped PVA films was observed\(^{(19)}\).
Fig. (2): $(\alpha h \nu)^{1/2}$ vs. $(h \nu)$ plots of the various films.

Table (1): Analysis of the thermograms and the energy of activation ($E_a$) for the thermal decomposition of for Ni/ PVA-AAc at 30 kGy.

<table>
<thead>
<tr>
<th>NiSO_4 content (mmol)</th>
<th>$E_a$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>10</td>
<td>3.3</td>
</tr>
<tr>
<td>20</td>
<td>2.9</td>
</tr>
<tr>
<td>50</td>
<td>1.6</td>
</tr>
<tr>
<td>100</td>
<td>1.3</td>
</tr>
<tr>
<td>150</td>
<td>1.2</td>
</tr>
<tr>
<td>200</td>
<td>1.1</td>
</tr>
</tbody>
</table>

It has been well quoted in literature that PVA, more generally, exhibits the indirect band transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) band edges\(^{20, 21}\). The gradual decrease in the value of $E_a$ by increasing Ni concentration may be attributed due to the formation of chemical bonding between polymer chains and Ni nanoparticles responsible for the generation of localized states (charge transfer complexes, CTCs) between the HOMO and LUMO energy bands making the lower energy transitions feasible\(^{22}\). The reduction in energy gap value in P(PVA/AAc) after embedding Ni nanoparticles make them efficient materials for optoelectronic devices. This is because of the fact that such devices require the band gap tunability.

3. Thermal decomposition kinetics:

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer degradation. The thermal stability of the polymer composites plays a crucial role in determining the limit of their working
temperature and the environmental conditions for uses, which are related to their thermal decomposition temperature and decomposition rate. Since the thermal decomposition has a direct relationship with the stability of the compounds, TGA was used to measure the energy of activation $E_a$ of the prepared samples to determine its stability. $E_a$ for the thermal decomposition of P(PVA-AAc)-Ni nanocomposite was determined according to Horowitz and Metzger method\(^{(23)}\). In this method, a plot of $\ln(\ln((W_0- W_f)/(W_t- W_f)))$ against $\theta$ (Fig. 3) gives a straight line with a slope of $E_a \times 10^3 / RT_s^2$, in which the activation energy can be calculated from the slope. $W_0$ and $W_f$ are the initial and final weights of the samples, respectively. $W_t$ is the weight of the sample at time $t$ and

$$\theta = T - T_s$$

where $T$ is the temperature of the sample and $T_s$ is the reference temperature defined as the temperature where

$$[(W_t - W_f)/(W_0 - W_f)] = 1/e$$

where $R$ denotes the gas constant ($R = 8.314$ JK$^{-1}$mol$^{-1}$). The activation energies calculated for all prepared films and the results are presented in Table (2). It can be seen that the activation energy for the thermal decomposition of the prepared samples increases steeply with increasing the Ni nano particle concentrations in the polymer matrix. The values of the activation energy for thermal decomposition reflected the improvement of the thermal stability of the prepared composites. The increase in thermal stability of Ni nano particles embedded P(PVA-AAc), as indicated by the results of the TGA study, can be due to two reasons. Ni nano particles have higher thermal stability as compared to the polymeric chains of the hydrogel. Hence, the presence of Ni nano particles in the system may make it thermally more stable. The other reason for this change could be the reduced mobility of the polymeric chains due to entrapment of metal salt / metal forming a complex with the hydroxyl group of the polymer chains and thus decreasing heat transfer process for decomposition of polymer composites. The char residue value found to be increased systematically with increasing Ni nano particle embedded in P(PVA/AAc) chains in Table (2).

The improvement in thermal stability may be due to restriction of polymer chain motion. In order to ascertain this possibility, the differential scanning calorimetric studies were carried out for P(PVA/AAc) and P(PVA/AAc)-Ni nano particles with various compositions to notice the possible change in the glass transition temperature ($T_g$). Figure 4 shows typical plot of the DSC curves for pure P(PVA/AAc) and P(PVA/AAc)-Ni nano particles which have been recorded on the heating run from 298K to 403 K. The glass transition of P( PVA/AAc) is found to be 345 K it is in agreement with the reported value\(^{(24)}\). The values for glass transition temperatures ($T_g$) for P(PVA/AAc) and P(PVA/AAc)-Ni nano particles with various concentrations are presented in Table 2. The transition is preferably attributed to the glass
transition \( (T_g) \) relaxational process resulting from micro-Brownian motion of the main-chain backbone. The significant shift in the glass transition temperature is noticed in case of all composites containing metal salts. When the salts are reduced to metallic form in the polymer matrix, the composites thus formed also exhibit decrease in \( T_g \). Glass transition temperature \( (T_g) \) however, depends on the nature of dopant, its capability to trap free radicals formed during the polymer degradation and found to be dependent of dopant concentration. The \( T_g \) values decreases gradually with increasing Ni content. The significant decrease in the glass transition temperature can be due to a decrease in the number of hydroxyl groups available for hydrogen bonding caused by an increase of the metallic form ions which hinders other hydrogen bonding formation from weakening of physical network and decreasing \( T_g \)\(^{(25)} \). The nanoparticles (metal salts / metal oxides / metals) when added to the polymer might have obstructed polymer chain mobility. This supports our observation that the
addition of nanofillers to a polymer increases the thermal stability\(^{(26)}\). Khanna et al. observed improved in the thermal stability of composites prepared by doping nano Ag nano particles in PVA\(^{(27)}\).

\[ \text{Temperature (K)} \]
\[320 \quad 340 \quad 360 \quad 380 \quad 400\]

\[\begin{align*}
\text{Exo} \\
(a) \\
(b) \\
(c) \\
(d)
\end{align*}\]

**Fig. 4.** DSC curves for PVA/AAc with different concentration of NiSO\(_4\):
(a) 0.00, (b) 20, (c) 100 and (d) 150 mmol.

4. Dielectric analysis:

The permittivity (\(\varepsilon'\)), or dielectric constant, and dielectric loss factor (\(\varepsilon''\)) can be used to characterize molecular relaxations. The dielectric constant (\(\varepsilon'\)) was evaluated from the capacitance measurement using equation (5)

\[
\varepsilon' = \frac{C}{C_0} \quad \text{and} \quad C_0 = \varepsilon_0 \frac{A}{d}
\]

(5)

where \(C_0\) is the vacuum capacitance of any configuration of electrodes and \(C\) is the capacitance with an isotropic material filling the space, \(\varepsilon_0\) (=8.85\(\times\)10\(^{-12}\) F/m) is the permittivity of free space, \(A\) is the cross-sectional area of the sample and \(d\) is its thickness. While the dielectric loss (\(\varepsilon''\)) was obtained from the equation, with \(\tan \delta\) being measured

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

(6)

Figure 5 depicts the variation of real part of dielectric permittivity (\(\varepsilon'\)) with frequency for various composites. The measurements were made isothermally at room temperature (300 K) in the
frequency range from 300 Hz to 5 MHz. At low frequencies, permittivity attained higher values, in all cases, which diminished rapidly with frequency. From the plots it is clear that $\varepsilon'$ decreases monotonically with increasing frequency and attains a constant value at higher frequencies. Similar behaviour was observed in other materials\(^{(28)}\). This is because, for polar materials, the initial value of the dielectric permittivity is high, but as the frequency of the field is raised the value begins to drop which could be due to the dipoles not being able to follow the field variation at higher frequencies and also due to the polarization effects\(^{(29)}\). The low frequency dispersion region is attributed to the charge accumulation at the electrode–electrolyte interface, i.e., charge carriers being blocked at the electrodes. At higher frequencies the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Hence $\varepsilon'$ decreases with the increase of the frequency in all the samples of PVA polymer electrolytes. Also it is found that the value of $\varepsilon'$ increases gradually due to the increase of Ni nano particles in the polymer matrix. Enhanced values of ($\varepsilon'$), especially at low frequencies, can be attributed to increased conductivity, and/or interfacial polarization, and/or electrode polarization. Electrode polarization is related to the build up of space charges at the specimen-electrode interfaces and is characterized by very high values of both real and imaginary part of dielectric permittivity\(^{(30)}\). Interfacial polarization results from the accumulation of unbounded charges, at the interfaces of the constituents, where they form large dipoles.

![Dielectric Permittivity vs Frequency](image)

**Fig. (5):** The permittivity against frequency for various samples at room temperature.

Its intensity is connected to the extent of the existing interfacial area within the composite system, giving thus indirect evidence of the achieved distribution of nanoinclusions\(^{(31)}\). The imaginary part of complex permittivity $\varepsilon''$ (dielectric loss factor) vs frequency for various samples are shown in Fig. 6. It is clear that, at low frequency range, $\varepsilon''$ decreases exponentially with frequency and attains a constant value at higher frequencies. These results suggest that dc conductivity process is more significant than interfacial polarization in these materials\(^{(32)}\). The higher value of $\varepsilon''$ at low frequency range is due to the mobile charges within the polymer backbone. While the increases in $\varepsilon''$ value with dopant can be understood in terms of electrical conductivity, which is associated with the dielectric loss.
Fig. (6) : Variation of dielectric loss against frequency for various samples at room temperature.

The ac conductivity ($\sigma_{ac}$) results introduce a better understanding of the conduction process. The frequency dependence of $\sigma_{ac}$ at room temperature are plotted in Fig. 9 for various samples. The ac conductivity was determined by the relation:

$$\sigma_{ac} = \omega \varepsilon_{\infty} \varepsilon'$$  \hspace{1cm} (7)

As shown in figure 7 the Conductivity appears to be frequency dependent. In the low frequency range, conductivity tends to acquire constant values approaching its dc value, while after a critical value varies exponentially with frequency$^{[33]}$. This type of behaviour is common in disordered solids, appears to be in accordance with the so-called ‘ac universality law’, and is considered as a strong indication for charge migration via the hopping mechanism$^{[34]}$. The conductivity increases manually with increasing salt concentration. The local contact regions, between conductive particles and polymer matrix, control the overall conductance of the system.
**CONCLUSIONS**

Conductive polymer electrolytes have been prepared from Ni nano particles embedded poly(vinyl alcohol) and poly(acrylic acid) using electron beam irradiation. The characteristic properties of the prepared samples have been studied using DSC, TGA, UV-vis spectroscopy and dielectric spectroscopy. The activation energy of the thermal decomposition was calculated according to Horowitz and Metzger method. The activation energy for the thermal decomposition of the prepared samples increases steeply with increasing the Ni nano particle concentrations in the polymer matrix which reflects the improvement of the thermal stability of the prepared composites. Also the conductivity increased manually with increasing salt concentration.

The reduction in optical energy gap value in P(PVA/AAc) after embedding Ni nanoparticles make them efficient materials for optoelectronic devices. Also the conductivity increases manually with increasing salt concentration.

**REFERENCES**