Optical and Electrical Characterization of Conducting Polythiophene Composite Synthesized by Gamma-Ray Irradiation Method

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Abstract: Electrical conducting Polythiophene (Pth) was prepared by the gamma radiation method from 28.6 wt.% 2-thiopheneacetyl chloride blended in Polyvinyl Alcohol (PVA) films. The film samples were irradiated at different doses of 0, 10, 20, 30, 40 and 50 kGy at ambient condition. This method was used without adding any type of chemical oxidizing agents. Upon gamma irradiation, the 2-thiopheneacetyl chloride monomer polymerized into conducting PTh by losing H^+ ions and formed conducting species of polarons. The SEM morphology of PTh/PVA composites showed that the particles have a spherical structure of about 0.7 μm in diameter and spread uniformly in the PVA matrix. The UV-visible spectrophotometry and impedance analyzer were used to characterize the optical and electrical properties of PTh particles, respectively. The absorption peak was established at 400 nm. The optical band gap energy (E_g) decreases with the increase of the absorbed dose from 2.35 eV before starting the irradiation process to 2.15 eV at 30 kGy. The dc electrical conductivity through the PTh/PVA composites increases with the increasing of absorbed dose from 2.8×10^{-4} S m^{-1} at 0 kGy to 9.8×10^{-4} S m^{-1} at 30 kGy.

Key words: Conducting polymer, polythiophene, polyvinyl alcohol, γ-ray, spectrophotometry

INTRODUCTION

The end of 1970s was the beginning of the new age of conducting polymers when the poly (Acetylene) (PAc) was synthesized to make highly conducting doped films (Shirakawa *et al.*, 1977). Alan MacDiarmid, Alan Heeger and Hideki Shirakawa won the 2000 Nobel Prize in Chemistry for their primary work with conducting polymers. They have established that polymers can conduct electricity if their carbon atoms are linked by alternating single and double bonds and electrons are either introduced by reduction or removed by oxidation. Generally, the electrons stay localized in bonds and cannot transfer an electric current but when the research team doped the polymer with iodine which is one of the strongest electron acceptors, the polymer started to conduct almost as good as a metal with a conductivity around 10^{11} times higher than the pure Polyacetylene (PAc) (Shirakawa *et al.*, 1977; Chiang *et al.*, 1977).

New types of conducting polymers include Polyaniline (PANI), Polythiophene (PTh), Polypyrrole (PPy), Polyfuran (PFu), Poly (P-Phenylene) (PPP), Polyfluorene (PFO), Poly (P-phenylene Vinylene) (PPV) and Polycarbazole (PCz). Even though none of these polymers have showed higher conductivity than Polyaniline (PANI), these polymers have been helpful in designing new structures that are stable and soluble. Electron-rich heterocycles based polymers like Polythiophene (PTh) and Polypyrrole (PPy) are stable in p-doped form for this reason these two polymers are the most studied conducting polymers among the others. Their stability is attributable to their lower polymer oxidation potential which follow the arrangement of PAc>PTh>PPy. Also, these structures are more modified than the Polyacetylene (PAc) which allowed for more varieties of structures.

Conducting polymers show very good electrical, optical and electrochemical properties thus they have a lot of applications such as rechargeable batteries, solar cells, fuel cells, super-capacitors, photoelectrochromics, electromagnetic interference shielding, corrosion protections and biosensors (Malinauskas *et al.*, 2005).

Therefore, attempts were made in the present study to form the conducting polymer PTh dispersed in PVA matrix and investigations were made for its structure, electrical conductivity and optical properties. In addition, the polymerization of PTh was fully obtained by ionizing radiation without using any kinds of chemical oxidizing agents unlike the other methods. The method under research is used for the first time to prepare PTh.

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MATERIALS AND METHODS

The PVA stock was supplied by SIGMA (Mw = 31,000-50,000 g mol^{-1}, 98-99% hydrolyzed) and 2-thiopheneacetyl chloride (98%) was supplied by ALDRICH. The PVA solutions were prepared by dissolving 5.00 g of PVA powder in 100 mL of distilled water at fixed temperature of 90°C in the water bath and stirred continuously for 3 h. Then, the solution was left to cool down at room temperature. The 2.0 g of 2-thiopheneacetyl chloride was added into 100 mL of PVA solution which gave the 2-thiopheneacetyl chloride concentration of 28.6 wt.% in comparison to the PVA weight in the solution. Magnetic stirrer was used to stir the mixture incessantly for 10 h in nitrogen atmosphere. After that the PVA/2-thiopheneacetyl chloride blended solution was divided into two 50 mL and spread into petri-dishes, 13 cm in diameter. Then, it left to dry in dark place and room temperature for 1 week to ensure that all the water has evaporated. The film was peeled off and cut into small circles of 3.2 cm in diameter and 0.195 mm in thickness. Then, each circle was put into a sealed and labeled plastic bag.

All samples were irradiated by using Co-60 γ-ray irradiation facility (Gammacell Excel Model) with different doses up to 50 kGy, i.e., 0, 10, 20, 30, 40 and 50 kGy. The structural morphology of Pth particles was studied by a Scanning Electron Microscope (SEM) Model (LEO 1455VP). The electrical and optical properties of PTh/PVA film composites were investigated at different doses to determine the amount of conducting PTh formed in films.

The optical properties were studied by an UV-vis spectrophotometer model UV-1650PC (SHIMADZU) in the wavelength range of 370-900 nm. The electrical properties were determined from the conductivity measurement by using an impedance analyzer model (HP 4284A) in the frequency range of 20 Hz to 1 MHz. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Since, there are no publications or references that describe the interaction of γ-rays with PVA/2-thiopheneacetyl chloride, the present study will try to give a logical explanation of that interaction. There are many ways for γ-rays to interact with matter. Compton scattering and photoelectric effect are the most common ones both of these interactions, interact with monomer by ejecting an electron and followed by the formation of H$^+$
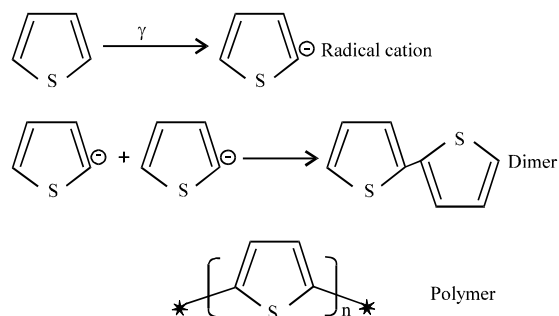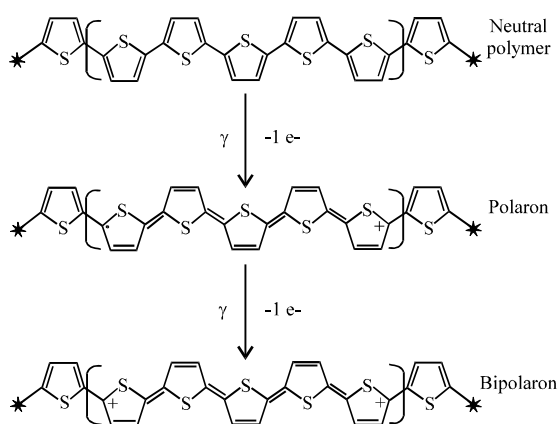

Fig. 1: Polymerization of PTh

Fig. 2: Chemical structures of polarons and bipolarons formed upon doping of PTh with γ-rays

ions and radical cation which then coupled with a second radical cation to form a dimer. This process continues to form neutral polymer as shown in Fig. 1.

After neutral polymer was formed, γ-rays start to oxidize it by removing an electron (p-doping) to form a polaron. Upon further irradiation, another electron can be released either from the polaron to form a bipolaron or from somewhere else on the polymer chain to form a second polaron as shown in Fig. 2.

Polaron can be defined as a radical cation which links with lattice distortion (Javier, 2010). Bipolarons can be formed by a high formation of polarons and they can be defined as de-ions which associate with a strong local lattice distortion (Malhotra, 1998). Figure 3 shows a polymer in neutral, polaron and bipolaron states and illustrates the significant differences between their energy levels inside the band gap.

The morphology and particle size of the conducting PTh were studied by the Scanning Electron Microscope (SEM). Figure 4a-c show the SEM micrograph of PTh polymerized *in situ* by radiation doping with 28.6 wt.% of 2-thiopheneacetyl chloride and various doses of

20, 30 and 40 kGy, respectively. The micrograph was taken at the operating voltage of 10 kV and 5000 times of magnification. Figure 4a with a dose level of 20 kGy shows the PTh particles as large cubes piled over each other. On the other hand, Fig. 2c with a dose level of 40 kGy illustrates the PTh particles scattered over the surface and also not well polymerized. While Fig. 4b with a dose level of 30 kGy reveals that the formation distribution was almost uniform and it appeared like cauliflower which

Fig. 3: Schematic energy levels of polymer at neutral, polaron and bipolaron states

means it has the best polymerization among the other level of doses. The average diameter of spherical PTh particles was estimated to be 0.7 μm. This result agrees with some previous studies conducted on PTh composites (Yang *et al.*, 2007; Karim *et al.*, 2007).

The optical absorption spectra of PTh dispersed in PVA matrix films with 28.6 wt.% of 2-thiopheneacetyl chloride were measured by using UV-visible double beam spectrophotometer with air as a reference. The absorption peak is associated with electronic transitions from a Highly Occupied Molecular Orbital (HOMO) to a Lowly Unoccupied Molecular Orbital (LUMO) of electronic states (Arshak and Korostynska, 2002). Figure 5 illustrates the UV-visible absorption spectra of PTh at different doses of 0, 10, 20, 30, 40 and 50 kGy and for 28.6 wt.% of the monomer.

The UV-visible absorption spectra show one absorption peak around 390 nm (±10 nm) due to π-π* transition. The peak moved or slightly red-shifted by increasing of γ-ray dose to reach 400 nm at a dose of 30 kGy which was the maximum absorption wavelength
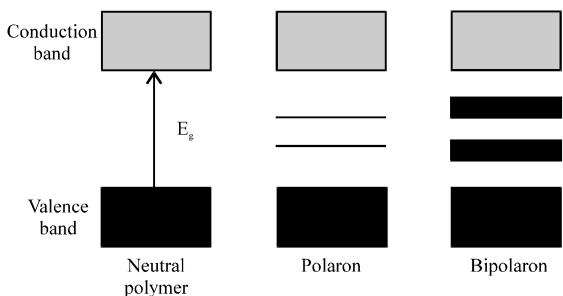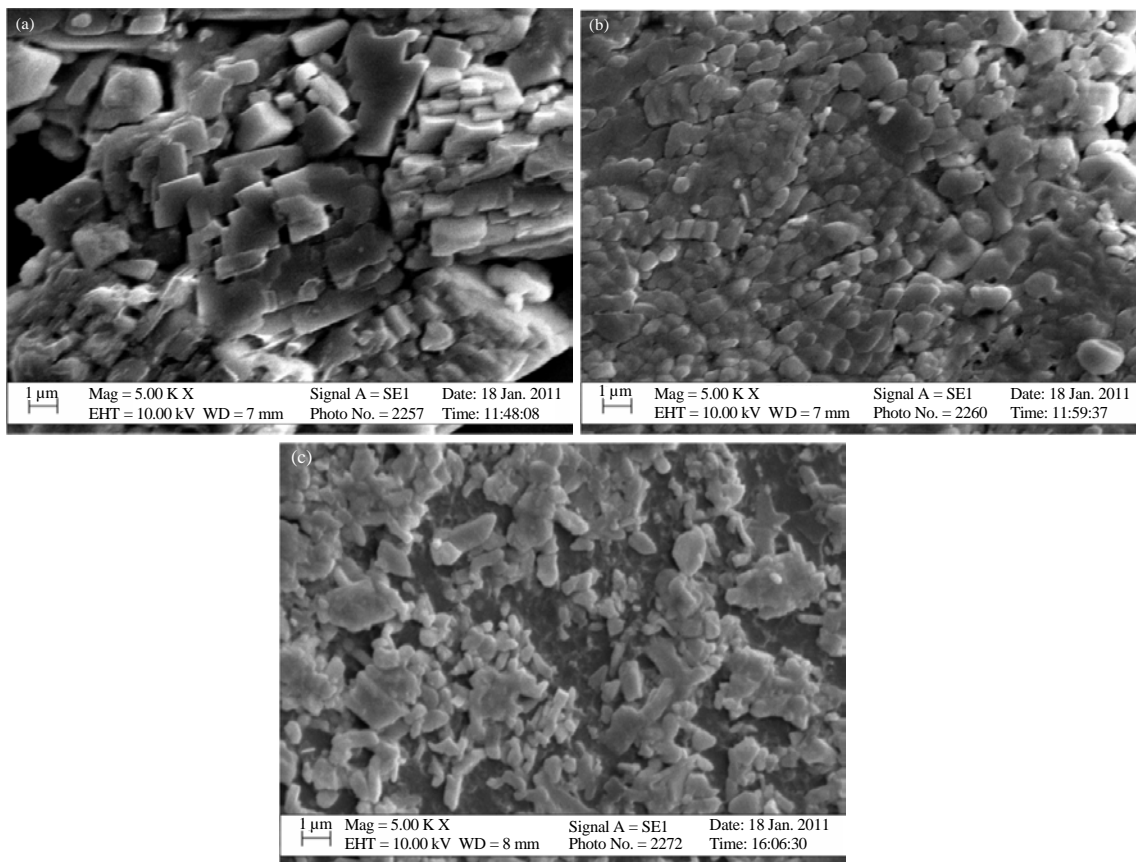

Fig. 4: SEM micrographs of PTh particles polymerized by; a) 20; b) 30 and c) 40 kGy for 28.6 wt.% monomer
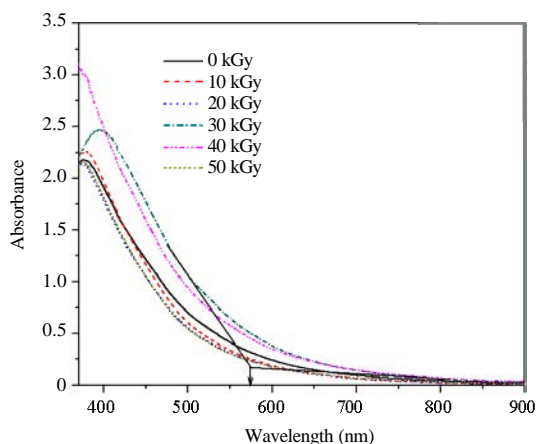
Fig. 5: The UV-visible absorption spectra of PTh dispersed in the PVA matrix for different doses and 28.6 wt.% of the monomer

due to its extended conjugation (Takahashi *et al.*, 2012). This peak corresponds with the absorption peaks of other PTh composites as evaluated by other researches (Karim *et al.*, 2006; Cihaner and Onal, 2005). The band gap E_g energies can be calculated by using the Eq. 1:

$$E_g = \frac{hc}{\lambda} \tag{1}$$

Where:
h   = Planck's constant $(6.626 \times 10^{-34}$ Jsec)
c   = The speed of light $(2.998 \times 10^8$ m sec$^{-1})$
λ = The wavelength of light (Park *et al.*, 2010)

Figure 5 shows how the band gap wavelength was determined by the extrapolation of the base line and the absorption edge; the wavelength on the opposite side crossing the two lines was taken to calculate the optical band gap (Cihaner and Onal, 2005; Park *et al.*, 2010; Martinez-Castanon *et al.*, 2005; Boldish and White, 1998). The results of the band gap were found to decrease when the radiation doses changed from 0-30 kGy as 2.35-2.15 eV.

Figure 6 shows a unique behavior of changing the band gap energies with radiation doses to describe this behavior; the graph was divided into two regions. The first region was from 0-30 kGy by increasing doses the band gap decreases which means that more of conducting PTh particles were formed. The second region was >30 kGy, the band gap energies were increased by increasing radiation doses. Although, the formation of conducting PTh particles was going on at high doses (>30 kGy), radiation degradation was more effective in making E_g to increase. The best band gap energy was
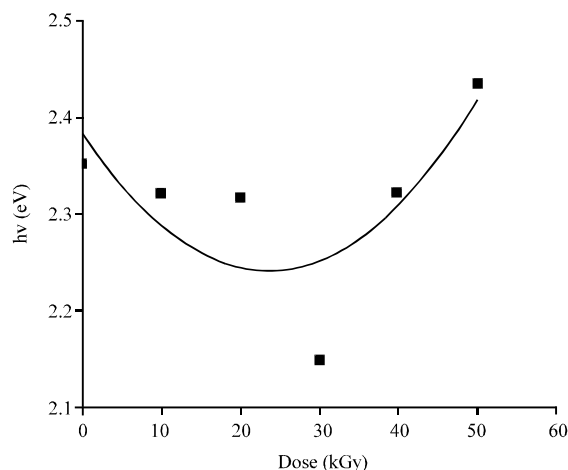

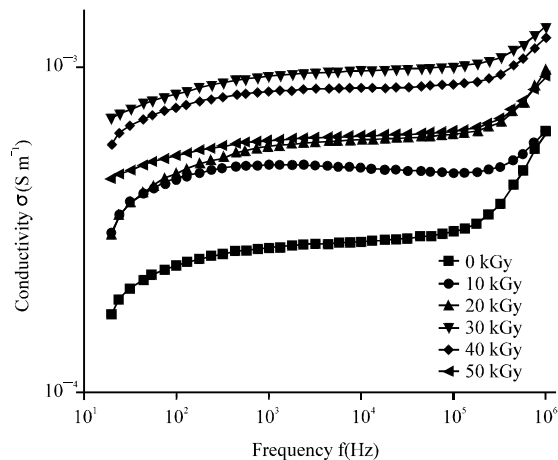Fig. 6: The band gap energies E_g at different doses

Fig. 7: Conductivity of 28.6 wt.% of monomer concentration with different doses

found to be 2.15 eV at 30 kGy. According to Jonscher and Frost (1976), the conductivity can be expressed by the Eq. 2:

$$\sigma(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega) \tag{2}$$

Where:
$\sigma_{dc}(0)$ = The dc conductivity
$\sigma_{ac}(\omega)$ = The ac conductivity

Figure 7 shows the conductivity of PTh particles dispersed in PVA matrix polymerized at doses up to 50 kGy for a 2-thiopheneacetyl chloride concentration of 28.6 wt.%. The graph shows two steps in the behavior of the conductivity. The first step, the conductivity increased with the increase of dose until it reached 30 kGy. As the dose increased to the optimum amount more polarons were formed, therefore increasing the conductivity of conducting PTh. The second step, the

conductivity decreased with the increase of dose (>30 kGy) as shown in Fig. 7. This incident returned to the effect of radiation degradation which broke the polymer chain and change the physical properties of the polymer. Hayashi *et al.* (1987) claimed that the PTh which was prepared by the electrochemical method and induced by γ-radiation under the vacuum, its conductivity decreased gradually with the increase of doses which was attributable to the radiation degradation effect (Hayashi *et al.*, 1987). The dc conductivity can be calculated by using the Cole-Cole plots of the complex electrical impedances given by the following Eq. 3:

$$Z^*(\omega) = Z'(\omega) - iZ''(\omega) \qquad (3)$$

where, $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary components of the complex electrical impedance, respectively (Dutta *et al.*, 2001) which was given according to the relation:

$$Z'(\omega) = \frac{G(\omega)}{G^2(\omega)+\omega^2 C^2(\omega)} \qquad (4)$$

$$Z''(\omega) = \frac{C_p(\omega)\omega}{G^2(\omega)+\omega^2 C^2(\omega)} \qquad (5)$$

Where:
G = The conductance
C = The capacitance of the sample

The plots of the complex electrical impedances $Z''(\omega)$ vs. $Z'(\omega)$ with varying frequencies at different doses gave semicircle curves which were typical behaviors of the Cole-Cole plot as shown in Fig. 8. The dc conductivity was deriv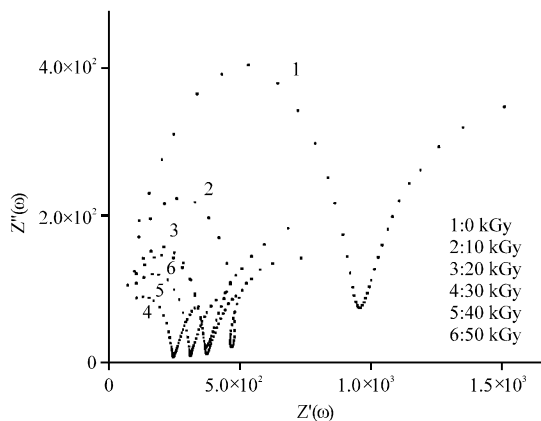ed by using the impedance Z_0 which can be obtained from the Cole-Cole plot by extrapolating the curves to zero frequency on the real component impedance (axis Z'). From the Eq. 6 which was given by Jonscher and Frost (1976), the dc conductivity was calculated:

$$\sigma_{dc} = \frac{d}{aZ_0} \qquad (6)$$

Where:
d = Thickness of the sample
a = The electrode area

At the low frequency region as shown in Fig. 8, there was a straight line spike related to the interstitial effect of the electrodes. Also, Mariappan and Govindaraj (2002) reported that a depressed semicircle at the low frequency part was due to characteristics of the parallel combination of bulk resistance and capacitance phase element of the samples (Mariappan and Govindaraj, 2002). Whereas Chen *et al.* (2003) attributed the presence of a straight line at the end of semicircles to the capacitive characteristics of conducting polymer film. While Lewandowski *et al.* (2000) attributed it to non-secured verticality of electrode spikes as well as to the capacitance interface between the dielectric and the electrode. The radius decreased with the increasing of dose until the dose level reached 30 kGy then it increased at higher doses due to the same reason that was discussed before.

The dc conductivities were found 2.8×10^{-4} S m^{-1} at 0 kGy and 9.8×10^{-4} S m^{-1} at 30 kGy which were the lowest and the highest dc conductivities, respectively as shown in Fig. 9. This conductivity agrees with the conductivity of bulk PTh powders which evaluated in previous study (Karim *et al.*, 2008).

Fig. 8: The Cole-Cole plots for PTh with 28.6 wt.% of monomer at different doses
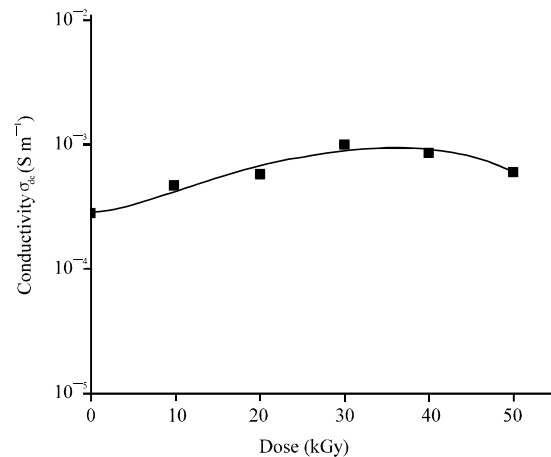

Fig. 9: The dc conductivities of PTh with 28.6 wt.% of monomer versus dose

CONCLUSION

In the present study, it was found that the gamma radiation can be used to synthesis the conducting Ploythiophene (PTh) dispersed in PVA as a binder by irradiating the solid phase of PVA/2-thiopheneacetyl chloride films at ambient conditions and without addition any kind of chemical oxidants to the samples.

On the oxidation process by gamma radiation the 2-thiopheneacetyl chloride monomer changed from isolated state to become conducting PTh by the loss of H^+ and *in situ* polymerization. The formation of PTh particles was examined by SEM morphology and found that the PTh particles assumed spherical shapes around 0.7 μm in diameter and spread uniformly in the PVA matrix. The optical properties of PTh were studied and illustrated that the absorption peak was at 400 nm attributed to π-π^* transition.

The dose of 30 kGy was found to be the optimum amount which gave the best optical property and electrical property. The band gap energy E_g changed from 2.35 eV at 0 kGy to 2.15 eV at 30 kGy; the conductivity was commonly due to the formation of polarons in the PTh structure and its analysis showed that the dc conductivity of the conducting PTh composite changed from 2.8×10^{-4} to 9.8×10^{-4} S m^{-1}.

Although, this study did not show a significant improvement in the band gap energy E_g and the dc conductivity, it leaves the door open for further investigation about the method under study.

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