

Determine the Optimum Concentration of 2-Thiopheneacetyl Chloride to Synthesize the Conducting Polythiophene by Using the Direct Irradiation Method

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Abstract: The monomer (2-thiopheneacetyl chloride) with different concentrations of 9.1, 16.7, 23.1, 28.6 and 33.3 wt.% were blended with Polyvinyl Alcohol (PVA) to synthesize conducting Polythiophene (PTh) by the gamma irradiation method. The absorbed dose of 30 kGy was applied on PTh/PVA film samples at ambient conditions. On gamma irradiation, the monomer polymerized into conducting PTh by means of losing H⁺ ions and composing polarons, the electrical conducting agent. The morphology of PTh/PVA was studied by using SEM. The SEM image indicated well distributed PTh particles spread almost uniformly in the PVA matrix which are more or less spherical and the average particle size was found to be 0.7 μm in diameter. The optical characteristics of PTh particles were measured by the UV-visible spectrometer. The absorption peak was found to be at about 400 nm with the band gap energy (E_g) which decreased from 3.19 eV at 9.1 wt.% to 2.15 eV at 28.6 wt.%. The electrical conductivity was measured by using the impedance analyzer and was found that the direct current (dc) conductivity increased from 2.6×10⁻⁵ S m⁻¹ for 9.1 wt.% to 9.8×10⁻⁴ S m⁻¹ for 28.6 wt.%.

Key words: Conducting polymer, polythiophene, polyvinyl alcohol, γ-ray irradiation method, energy

INTRODUCTION

One of the most common conducting polymers is Polythiophene (PTh) attributed to its simplicity of doping, flexibility, electrical stability and unique thermal stability. PTh is one of the most commonly used conducting polymers for the study of charge transport and a nondegenerate ground state; in addition, its structural flexibility with the very high environmental stability for undoped and doped states have led to several developments intended for applications in Organic Light-Emitting Diode (OLED), plastic photovoltaic, smart windows or electrochromic, antistatic coatings, batteries, sensors, optical devices and nanoelectronic (Jaehne *et al.*, 2001; McCullough, 1998; Roncali, 1992). PTh and its composites have succeeded in several applications like that mentioned previously and less remarkably in others. New PTh development strategies and creative designs have led to better performances in certain systems and interesting new materials. Generally, there are two major methods to prepare conducting PTh, i.e., chemical and electrochemical methods. Lately, gamma radiation has been widely used to produce new micro and nano-particles of polymeric materials accompanied with special characteristics since it can help form particles under ambient conditions. Also, it produces pure

materials since it does not need any metallic catalyst, oxidizing or reducing agent, adaptable and easy to control (Xie *et al.*, 1999; Zhang *et al.*, 2004; Seguchi *et al.*, 2002; Milojkovic *et al.*, 1997). The synthesis of PTh/PVA by the direct γ-irradiation polymerization method is presented in the present study.

MATERIALS AND METHODS

The materials used in the present study are: polyvinyl alcohol PVA (Mw = 31,000-50,000 g mol⁻¹, 98-99% hydrolyzed) (SIGMA) as a binder, 2-thiopheneacetyl chloride (98%) (ALDRICH) as a precursor, distilled water as a solvent. In addition, γ-radiation was used as an effective oxidizing agent for the polymerization process.

The PVA stock solution was prepared by dissolving 30.00 g of PVA powder in 600 mL of distilled water at 90°C in the water bath and stirred continuously for 3 h. The solution was left to cool at room temperature. Different concentration of 2-thiopheneacetyl chloride, i.e. (0.5, 1.0, 1.5, 2.0 and 2.5 g) or (9.1, 16.7, 23.1, 28.6 and 33.3 wt.%) was dissolved in 100 mL PVA solution. The mixture was thoroughly stirred for 10 h in nitrogen atmosphere; the PVA/2-thiopheneacetyl chloride blended solution was poured into petri-dishes, 13 cm in diameter.

Then, it was left to dry in dark place and room temperature for 1 week. The film was then peeled off and cut into small samples of 3.2 cm in diameter and 0.195 mm in thickness. Each sample was put into a plastic bag, sealed, labeled and exposed to γ -radiation.

The irradiation facility, model (Gamma cell) which is using ^{60}Co as γ -ray source was used to irradiate all samples with a dose of 30 kGy. The Scanning Electron Microscope (SEM) Model (LEO 1455VP) was used to study the morphology structure of PTh composite particles. UV-vis Spectrometer Model (UV-1650PC) was used to study the optical characteristics in the wavelength range of 300-900 nm. The impedance analyzer, model (HP 4284A) was used to determine the electrical characteristics by means of measuring the electrical conductivity in the frequency range of 20 Hz to 1 MHz. All the measurements were conducted at room temperature.

RESULTS AND DISCUSSION

In order to study the morphology structure of the electrically conducting PTh, SEM was used. Figure 1 shows the SEM image of the conducting PTh which polymerized by using gamma radiation with 28.6 wt.% of the monomer and a dose of 30 kGy. The image was taken at 10 kV of the operating voltage and magnification of 10,000 times. It exposes that PTh particles have uniformly distribution and assumed cauliflower-like shape. The result showed that the conducting PTh has a good polymerization. The PTh particles have spherical shapes

an average diameter of 0.7 μm . This result agrees with some previous studies conducted on PTh composites (Yang *et al.*, 2007; Karim *et al.*, 2007).

Figure 2 illustrates the absorption spectra of the conducting PTh with different monomer concentrations, i.e. (9.1, 16.7, 23.1, 28.6 and 33.3 wt.%) and at a dose of 30 kGy. The spectra revealed one absorption peak at approximately 390 nm due to π - π^* transition. The peak is a little bit red-shifted by the increased of monomer concentrations to reach 400 nm at 28.6 wt.% which was attributable to its extended conjugation (Takahashi *et al.*, 2012; Subramanyam and Blumstein, 1992). This peak corresponds with the absorption peaks of other PTh composites as evaluated by other researches (Ngamna, 2006; Karim *et al.*, 2006; Cihaner and Onal, 2005).

The band gap wavelength can be determined by using the direct extrapolation method (Cihaner and Onal, 2005; Park *et al.*, 2010; Martinez-Castanon *et al.*, 2005; Boldish and White, 1998) as shown in Fig. 2. In order to find the band gap energies E_g , Eq. 1 was used:

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

Where:

h = Planck's constant (6.626×10^{-34} Jsec)

c = The speed of light (2.998×10^8 m sec $^{-1}$)

λ = The wavelength of light

The results of the band gap energies E_g were found to be decreasing when the monomer concentration

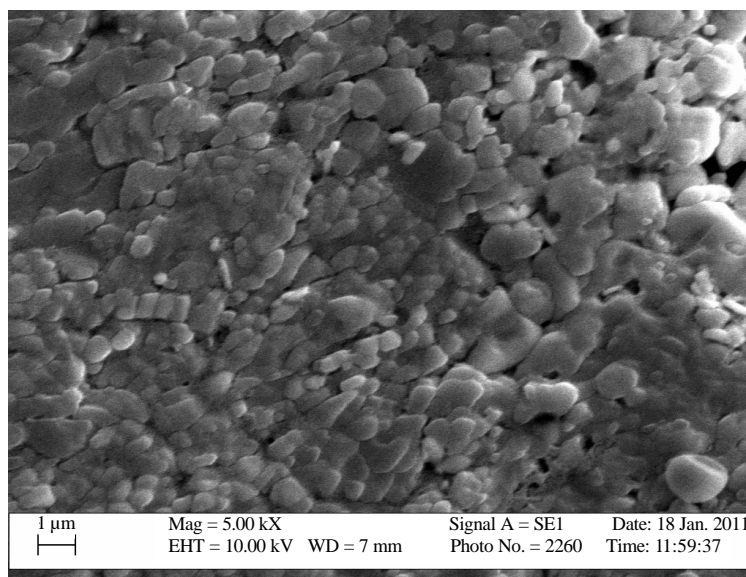


Fig. 1: SEM micrographs of PTh particles polymerized by 30 kGy for 28.6 wt.% monomer

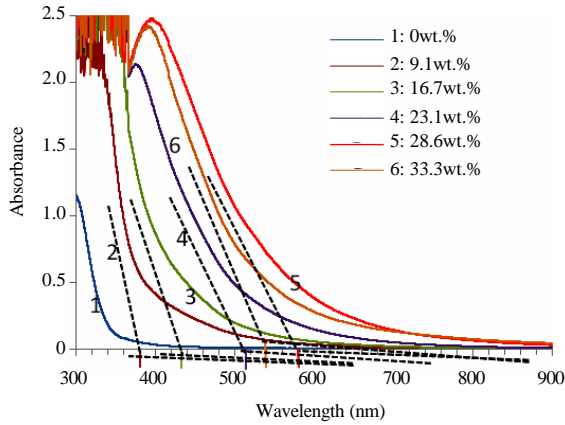


Fig. 2: The UV-visible absorption spectra of PTh dispersed in the PVA matrix for different concentration of the monomer and dose of 30 kGy

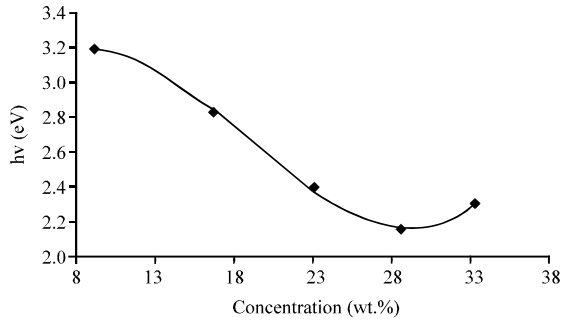


Fig. 3: The band gap energies E_g for the different concentration of the monomer at an absorbed dose of 30 kGy

increases. For instance, E_g decreased from 3.19 eV for 9.1 wt.% to 2.15 eV for 28.6 wt.% at a fixed absorption dose of 30 kGy as shown in Fig. 3.

Figure 3 exhibits the changing of E_g with monomer concentration. Firstly, an E_g decreases with the increase in monomer concentration until it reaches 2.15 eV at 28.6 wt.% which means more polarons were formed. Then, it increases when the monomer concentration is >28.6 wt.%. The reasons behind this phenomenon will be discussed later. Equation 2 can be used to calculate the conductivity (Jonscher and Frost, 1976):

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

Where:

$\sigma_{dc}(0)$ = The dc conductivity

$\sigma_{ac}(\omega)$ = The ac conductivity

Figure 4 exhibits the conductivity of pure PVA and PTh polymerized with different concentrations of

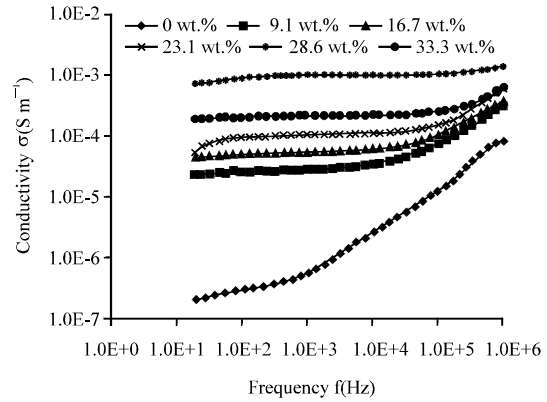


Fig. 4: Conductivity of different monomer concentration at a dose of 30 kGy

2-thiopheneacetyl chloride, i.e. (9.1, 16.7, 23.1, 28.6 and 33.3 wt.%) at a dose of 30 kGy. The conductivity initially increases with the increase of monomer concentration until it reaches 28.6 wt.%. This concentration gives the highest conductivity. Then, the conductivity decreases with the concentration of 33.3 wt.%.

This behaviour, either due to the increase of crystallinity (Omer, 2007) or high viscosity in which can cause resistance or impedance to mobility of oppose ions in the polymer composites (Guo *et al.*, 2004; Bidstrup and Simpson, 1995). This explanation can be applied for all similar behaviours.

The Cole-Cole plots of the complex electrical impedances were used in order to calculate the dc conductivity as expressed in the following equation:

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

Where:

$Z'(\omega)$ = The real component

$Z''(\omega)$ = The imaginary component of the complex electrical impedance

These components can be given by the following relations:

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

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

Where:

G = The conductance

C = The capacitance of the sample

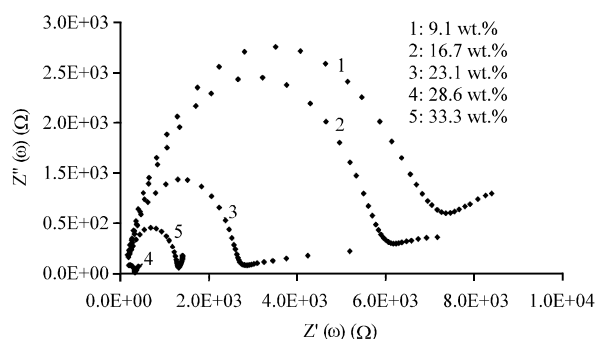


Fig. 5: Cole-Cole plots of PTh at different monomer concentrations irradiated at a dose of 30 kGy

Figure 5 shows the Cole-Cole plot of the complex electrical impedances, $Z'(\omega)$ versus $Z''(\omega)$ with different monomer concentrations and a dose of 30 kGy. The plots produced semicircle curves of standard behaviors that represent the Cole-Cole plot as shown in Fig. 5. In order to calculate the dc conductivity, Eq. 6 was used (Jonscher and Frost, 1976). To obtain the impedance Z_0 from the Cole-Cole plot, the curves were extrapolated to zero frequency on the axis Z' :

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

Where:

- d = The thickness of the sample
- a = The electrode area

Also, Fig. 5 exhibits that the radius of the semicircle curves decrease with increased monomer concentrations till the concentration reach 28.6 wt.%. Then, it increases at higher concentration, attributable to the same reasons that mentioned before. The semicircle curves have straight-line spikes as shown in Fig. 5. This phenomenon has been explained as: it is due to the interstitial effect of the electrodes (Omer, 2007).

Also, it was attributable to the characteristics of the parallel combination of bulk resistance and capacitance phase element of the samples (Mariappan and Govindaraj, 2002). In addition, it was caused by the capacitive characteristics of conducting polymer film (Chen *et al.*, 2003). Furthermore, it was due to the capacitance interface between the dielectric and the electrode as well as to the non secured verticality of electrode spikes (Lewandowski *et al.*, 2000).

The dc conductivities are $2.1 \times 10^{-7} \text{ S m}^{-1}$ with 0 wt.% and $9.8 \times 10^{-4} \text{ S m}^{-1}$ with 28.6 wt.% which are the lowest and the highest dc conductivities, respectively as shown in Fig. 6.

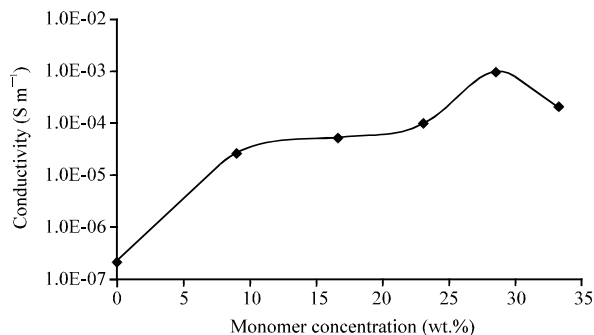


Fig. 6: The dc conductivity at different monomer concentrations at a dose of 30 kGy

CONCLUSION

This study established that the direct irradiation method can be used to form the conducting Ploythiophene (PTh) via irradiating the films of PVA/2-thiopheneacetyl chloride with γ -rays at a dose of 30 kGy under ambient conditions.

As a result of the oxidation process of gamma radiation, the monomer (2-thiopheneacetyl chloride) was polymerized into conducting PTh by losing H^+ ions and forming the polarons. The PTh particles were studied by SEM and showed that they have spherical shapes approximately of 0.7 μm in diameter. The PTh particles spread almost uniformly in the PVA matrix and exhibited an excellent environmental stability. The optical characteristics of PTh were examined and found that the absorption peak was more or less 400 nm. Also, this peak was attributed to π - π^* transition.

The monomer concentration of 28.6 wt.% was found to be the optimal value that gave the best amount of optical and electrical characteristics. The band gap energy E_g for 28.6 wt.% was 2.15 eV. The PTh conductivity is normally attributable to the formation of polarons in its structure. The dc conductivity for 28.6 wt.% was $9.8 \times 10^{-4} \text{ S m}^{-1}$. All the measurements were conducting at a dose of 30 kGy under ambient conditions.

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