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INFLUENCE OF IONIZING RADIATION TO ANILINE HYDROCHLORIDE/PVA ON CONDUCTIVITY

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ABSTRACT

Polyaniline (PANI) has been considered as one of the potential conducting polymers for various electrochemical and electronic applications. To facilitate the formation of PANI, 0.2 g of Aniline hydrochloride were dissolved in distilled water together with polyvinyl alcohol (PVA), for casting into composite film. The electrical conductivity increases from 10^{-7} S/cm – 10^{-6} S/cm when they were exposed to ^{60}Co gamma rays at dose range 0 Gy to 6 kGy. Measurements of electrical conductivity were carried out using Hewlett-Packard 4284A impedance analyzer in the frequency range of 20 Hz to 1 MHz. The dc conductivity was extracted from the Cole-Cole plots of the complex impedance Z" vs. Z'

INTRODUCTION

Conducting polymers, also known as "synthetic metals", have been the subject of widespread investigation over the past decade due to their very promising characteristics. Among conducting polymer, polyaniline stands out due to its outstanding properties. It is one of the so-called doped polymer, in which conductivity can be achieved from a process of partial oxidation and reduction. It was published earlier that the electrical conductivity of polyaniline (PANI) base polymer composites increase to a significant extent when irradiated to gamma radiation.(Sevil et al., 2003)

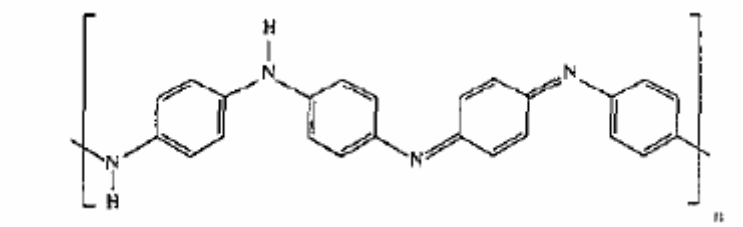

Figure 1: The repeat unit for the emeraldine base

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The discovery of electrically conductive polymer composites base on polyaniline provides conductive materials, which are soluble in selected organic solvents. These materials, which are melt processable exhibit good stability characteristics. The aniline hydrochloride undergo a high degree of side chain degradation resulting mainly loss of HCl when expose to ionizing radiation. This radiolytic products can be captured by the neighboring PANI molecules thus enhancing the electrical conductivity of the composite (Mahmad. 2004).

$$C_6H_7N.HCl + h\nu \longrightarrow H^+ + Cl^- + C_6H_7N^{\cdot}$$

MATERIALS AND METHOD

The amount of 17.5g PVA Polyvinyl alcohol (mw: 70 000, product of Aldrich) have been dissolved in 350ml distilled water in a beaker under heating condition at 80^{o}C. Aniline hydrochloride powder with different concentrations was added into PVA solution while being stirred for 2 hours, to ensure a homogeneous composition of the solution. The solution was transferred to the horizontal glass plate and dry at room temperature for one week. After drying, the films were stripped from the glass plate.

The film irradiations were carried out with 9.39 kGy/h γ-rays beam in the ^{60}Co chamber at the Malaysian Institute for Nuclear Technology research (MINT) at Bangi. The film samples of each dose were placed inside the polystyrene block for radiation equilibrium.

The ac conductivity of the polymeric film was measured by complex impedance spectroscopy using HP4284A precision LCR meter operating with the 20 Hz to 1 MHz frequency range, by using the Cp-D method. The conductivity of the film was measured at different dose. The dc conductivity was extracted from the Cole-Cole plots of the complex impedance Z" vs. Z'

RESULTS AND DISCUSSION

Changes in the conductivity under radiation, generally termed as radiation-induced conductivity, comprise three processes: generation of ionic and charge carriers by ionization; the motion of these carriers under the influence of density gradients (diffusion) and any existing electric fields (drift); and finally the immobilization of the carriers by trapping or other recombination mechanisms (Javaid at el., 1990). The PVA/AH film will change to PVA/PANI after being irradiated with gamma rays.

In order to select the most promising composition of the film samples, six different compositions of PVA/AH film were irradiated to 6 kGy with ^{60}Co gamma rays. The conductivity of the film was then measured and compared to the non-radiated film

samples. The conductivity was calculated using the equation (1), G is the conductance, d is the thickness of the sample and A is the surface area of the electrodes.

$$\sigma = \frac{Gd}{A} \qquad (1)$$

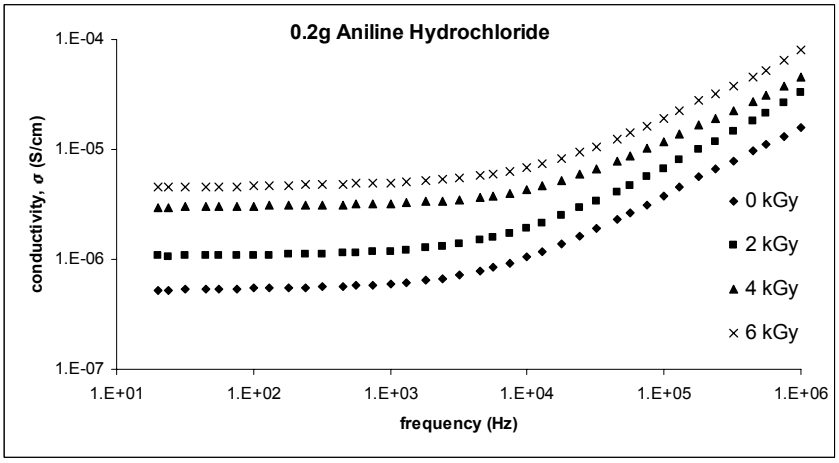

Figure 2: Variation of conductivity with frequency of PVA/PANI for 0.2 g Aniline hydrochloride

Figure 2 shows the conductivity increases with the increasing dose of gamma rays. As the dose increased, hydrolysis of moisture and scission of covalent bonds of aniline hydrochloride produces more mobile Cl, OH, and H ions that lead to increase in the conductivity of the polymer blends. At low frequency the conductivity is independent of frequency for all doses. At higher frequencies, there is a strong frequency dependence of the conductivity for all doses. This strong dispersion is due to non-homogeneities in amorphous structure of the polymer blends in which the transport of charged carriers is via a hopping mechanism (Mott et.al, 1979). Poly(vinyl alcohol) (PVA) contains carbon chain backbone with hydroxyl groups attached to methane carbons. These OH groups can be a source of hydrogen bonding hence the assistance in the formation of polymer blends (Rajendran et al., 2004).

The total frequency dependent conductivity $\sigma(\omega)$ at a given doses and frequency can be expressed as

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

where σ_{dc} is the dc electrical conductivity and $\sigma_{ac}(\omega)$ the ac conductivity. The dc and ac conductivity was calculated from the relationship

$$\sigma dc = \frac{d}{Z_0 A} \qquad (3)$$

$$\sigma ac = A\omega^s \qquad (4)$$

where A is a constant dependent on dose and the exponent $s<1$. The value of s for various doses has been determined from the linear slope of log $\sigma_{ac}(\omega)$ versus log ω as as depicted in Figure 5. The value of s increases with the decrease of doses as exhibited in Figure 6.

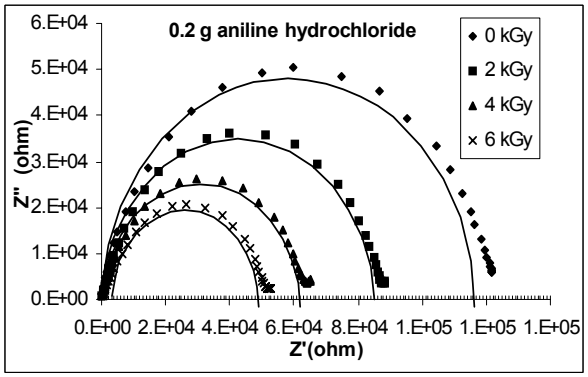

Figure 3:Complex impedance Nyquits plot at different dose for 0.2g aniline hydrochloride

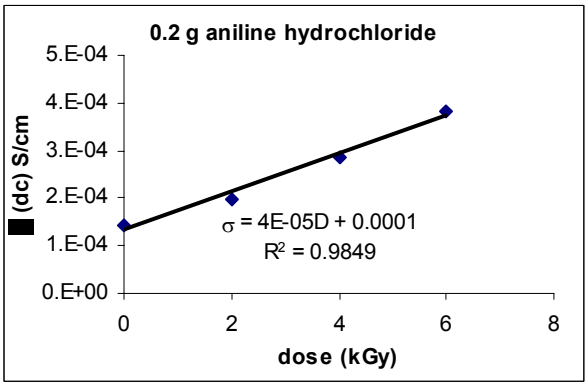

Figure 4: σ_{dc} value versus doses

Graph above (Figure 3) show the complex impedance graph, the increases of doses will decrease the resistance; this will leads to an increases of conductivity values. The measured capacitance (Cp) and conductance (G) values were used to calculate the real (Z') and imaginary (Z") parts of complex impedance, according to the formula

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

$$Z'' = \frac{C_p \omega}{G^2 + \omega^2 C_p^2}$$

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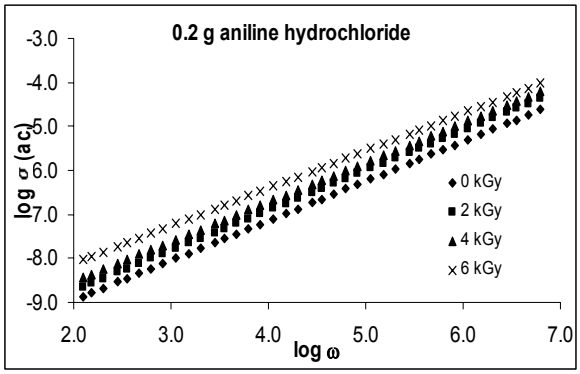

Figure 5: log-log plot of ac conductivity vs. frequency at various doses for 0.2g aniline hydrochloride

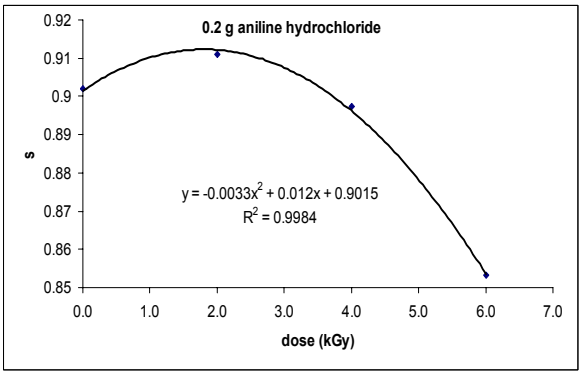

Figure 6: Variation of *s* with doses for 0.2g aniline hydrochloride

The frequency-dependent conductivity of sample is investigated. The variations of conductivity σ(ω) as a function of frequency at difference doses are show in Figure 5. The increasing of doses will increase the ac conductivity. The value of s at each dose has been calculated from the slope of figure 5. The estimated values of s are between 0.85 and 0.92 for 0.2 g PVA/AH composite as shown in figure 6. The frequency exponent, s decreases with the increase of dose.

CONCLUSION

A PVA/AH were synthesized in different concentration and irradiated to 6 kGy with ^{60}Co gamma rays. The uniform composite film containing PANI was successfully prepared in this study, which has a conductivity value of 10^{-7} S/m to 10^{-6} S/m. The value increase with the increases of doses. The increase of doses will increase the mobile ions: Cl, OH, and H that lead to increase in the conductivity of the polymer blends The almost semicircle behavior of the complex impedance Nyquits plot indicates the ionic hopping. The conductivity increases with the increase of dose. The influence of ionizing radiation on polymer film is to capture chemical bonds and create energetic free electron, ion and radicals. Therefore, the change in the mobility of these carries due to the energy absorbed in irradiation polymer film will affect the electrical conductivity, due to migration of ions or electrons or both. This suggests that the ionic conductivity increased with the presence of aniline hydrochloride. An increase of dose leads to a decrease of resistance, and an increase of conductivity.

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