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Influence of Gamma Irradiation on The Electrical Conductivity and Dielectric Properties of Polypyrrole Conducting Polymer Composite Films

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ABSTRACT

Electrical conductivity and dielectric properties of polypyrrole conducting polymer composite films were investigated using gamma irradiation from 0 kGy up to 25 kGy. The AC conductivity is directly proportional to the frequency. The DC conductivity increased with the irradiation dose. In dielectric studies, relative permittivity and loss factor increased with gamma dose whereas the relaxation times decreased with irradiation dose. The study showed that gamma irradiation is capable to polymerize and induce the electrical conductivity and dielectric properties of the polypyrrole composite polymers.

1. INTRODUCTION

Since the discovery led by polymer scientists; H. Shirakawa, A.G. MacDiarmid and A.J. Heeger in 1979 [1], the 4th generation of polymer namely conjugated conducting polymer becomes a focused field in materials research [2-4]. Polypyrrole, PPy is known as one of the interesting conjugated conducting polymers because of good processability, relatively high electrical conductivity, inexpensive and good stability in environment [5]. The potential application of PPy includes batteries, capacitors, shielding and absorbing materials and corrosion protection [6]. Apart from these outstanding properties, this material still encounters difficulties for commercialization as it is not biodegradable, water insoluble and poor mechanical strength. Therefore, scientists have started to prepare composites containing conjugated conducting polymers and polymer matrixes with the purpose to improve the properties i.e. mechanical strength, better polarity and biodegradable. The newly prepared composites have a potential for commercialization due to resistance towards chemical, thermal and stress.

There are several techniques to prepare composite polymer. One of them is chemical technique, which is easy, cheap and has good optical properties. However, average conductivity was obtained and excessive amount of chemicals used thereby may affect the purity of sample [7]. Another technique by electrochemical polymerization, high conductivity can be obtained but this method is quite complicated and costly [5]. These two methods seem ineligible for mass production. Alternative technique that can be used to synthesize composite polymer is by irradiation technique. Irradiation technique has advantages of cleanliness of the process, high

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purity of composites prepared and cost-friendly for bulk scale [8-11]. Various radiation source can be used; UV, electron beam and gamma ray. Although the process which utilized UV and electron beam is much faster, it is less penetrative and could give less conductivity. Thus, gamma ray is found as a better radiation source because it is very penetrative thereby improves the polymerization process and hence contributes to the better conductivity of composites polymer [8, 9].

This paper reported the electrical and dielectric study of polypyrrole composite films prepared by gamma irradiation technique. From previous studies, the research on conductivity and dielectric studies by using radiation technique is limited [8,9,11]. This study discusses extensively and emphasizes on radiation induced conductivity and dielectric properties. This includes the process which influenced the electrical properties.

2. MATERIALS AND METHOD

Pyrrole monomer, Py with the chemical formula C_4H_4NH, was purchased from Fluka and was distilled prior to use. Polyvinyl alcohol, C_2H_4O, PVA (Molecular weight: 205,000, hydrolization degree 98%) that was purchased from Fluka was used. Organic acid reagent trichloroacetic acid, CCl_3COOH, (TCA) (Merck) was used as received. The entire experiment was conducted at room temperature (27 °C). 3 g of PVA was dissolved completely in 100 ml distilled water under permanent stirring for 1 hour while the solution was boiled up till 95 °C. Then, the solution was let to cool to room temperature while the stirring of the solution was carried out to confirm a homogenous composition. After cooling, 30 ml of PVA solution (3 part per hundred, pph PVA) was taken and was mixed with 1 g of Py monomer in 15 ml of distilled water. The solution was continuously stirred for another 5 minutes at room temperature to ensure its homogeneity. Finally, 1.5 g TCA was mixed in the solution and continuously stirred for another 10 minutes. The homogenous solution was then casted onto glass plate (dimension of 14 cm x 14 cm). The solution was left to dry at room temperature for around 120 hours. At the end of the process, the composite polymer films were peeled of from the plate and cut into 4 cm x 4 cm pieces for the gamma irradiation process. The plate was kept in desiccator to avoid from moisture. The PVA/PPy/TCA composite films were irradiated at room temperature with ^{60}Co source. The dose rate of the ^{60}Co source was 9.34 kGy/hour (as calibrated by Unit of Sinagama, Malaysian Nuclear Agency). The electrical conductivity and dielectric properties of the samples were measured by using HP Precision LCR Meter 4284A at a frequency range (20 Hz - 1 MHz) at room temperature. The proposed reaction mechanism taken place for polypyrrole composite films in PVA matrix, which are exposed to gamma irradiation, as shown in Scheme 1 [7]. The reaction does not involve PVA because PVA does not undergo scissioning process for the set irradiation dose (0 – 25 kGy) [7]:
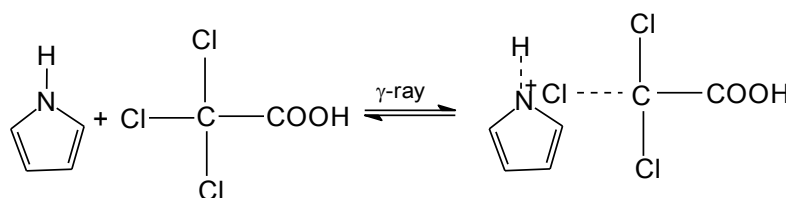
Scheme 1. The chemical reaction involved for polypyrrole conducting polymer composite films upon gamma irradiation.

3. RESULTS AND DISCUSSION

3.1 Electrical Conductivity

The measured conductance, $G(\omega)$ for the frequency varying from 20 Hz up to 1 MHz was used to measure AC electrical conductivity, $\sigma(\omega)$ using the following Equation 1 [7]:

$$\sigma(\omega) = G(\omega)\frac{d}{A} \tag{1}$$

where, d is the thickness of the composite film sample and A is the cross-sectional area. The irradiation dose range was chosen based on a previous study. If the samples are irradiated at a greater dose, the resultant films could suffer backbone scissioning thereby the sample loose its strength and mechanical properties. In addition, irradiation dose at 25 kGy is acceptable and being practiced in the industry [7].
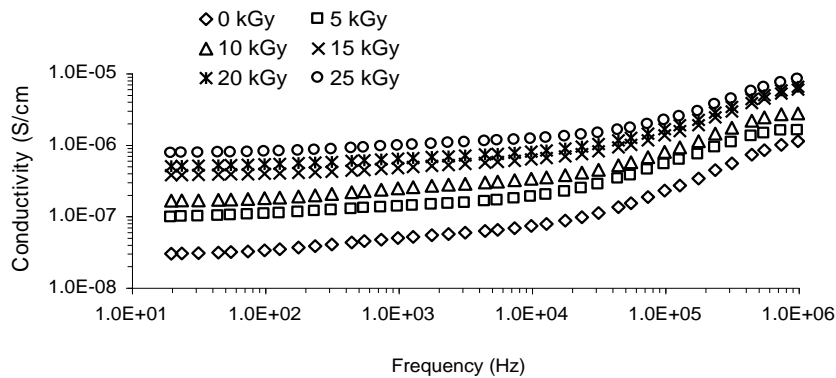
Figure 1. AC electrical conductivity of polypyrrole composite films at different doses.

The AC conductivity of the PPy composite films at different absorbed doses is shown in Figure 1. The total conductivity, $\sigma(\omega)$ of the composite films sample is determined by the relation [12]:

$$\sigma_T(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega) = \sigma_{dc}(0) + A\omega^s \tag{2}$$

where,

$$\sigma_{ac}(\omega) = A\omega^s \tag{3}$$

A is a constant depending on the dose and the frequency exponent s ($s \leq 1$) is given by [13]:

$$s = \frac{d\,\ln\sigma}{d\,\ln\omega} \tag{4}$$

The plot of conductivity versus frequency (Figure 1) shows two step variation; for the first step, the curve is horizontal and started from 20 Hz – 1 kHz. This portion of curve represents DC (0) conductivity which is the result of mobility of loosely polarons and bound ions. In the second step from 1 kHz – 1 MHz, the curves are rising which represent frequency dependent conductivity produced by the bound ions. The reaction of bound ions is mostly contributed by

PVA binder that vibrate with the increasing of frequency. Result in this study is in the agreement with the literature [12-13,15-16].

Table 1 shows the parameter of *s*, which has been calculated from the above Equation 4. It was found that value of *s* obeys the power law (0.54≤ *s* ≤ 0.71). In addition, the parameter of *s* obtained was weakly dependent to irradiation dose; in which contradict with the parameter of *s* obtained at different temperature [13, 14]. The difference is ascribed to the different mechanisms involved for gamma irradiation and temperature difference. Gamma irradiation is capable to break the bond and produce radicals. For temperature dependent, the irradiation produces heat and enhance the vibration of molecules within the samples via phonon-phonon interaction without breaking any bonds [12].

Table 1 Parameter of *s* at different doses for polypyrrole composite polymer films

| Dose (kGy)	Parameter of *s*
0	0.71
5	0.55
10	0.58
15	0.61
20	0.57
25	0.54
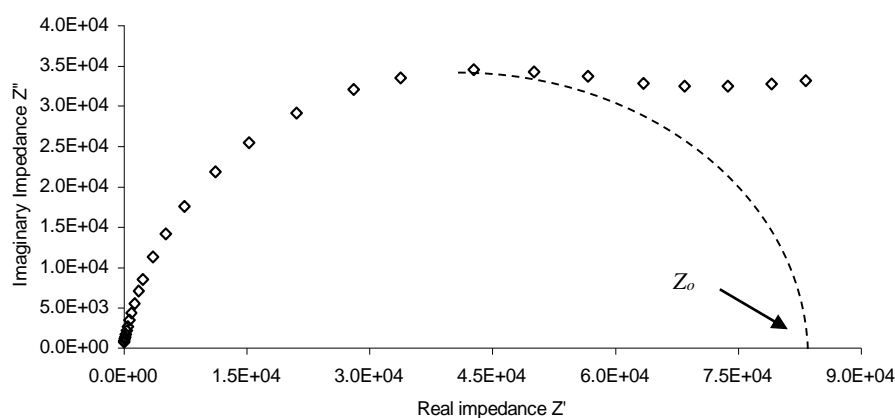
Figure 2. Complex impedance plot of PPy composite polymer to characterize Z_o.

Figure 2 shows the Cole-cole plot for impedance which is responsible to be used in determining the DC conductivity of the samples. Figure 3 shows the DC conductivity of the irradiated polypyrrole composite films. The DC electrical conductivity is calculated from the impedance obtained the extrapolation of the impedance, Z_o where $Z_o=R$ (resistance) at zero frequency for different doses as shown in Figure 2 [7]. The DC electrical conductivity is measured using Equation 5:

$$\sigma_{dc} = \frac{d}{RA} \qquad (5)$$

The DC conductivity increases from 10^{-9} S/cm to 10^{-7} S/cm with gamma dose from 0 to 25 kGy because of the formation of radical species. This is due to occurrence of dechlorination [8-10]. The radical species formation is already explained in Scheme 1. A similar observation is reported by Kim *et al.* [8] and Felix *et al.* [11].
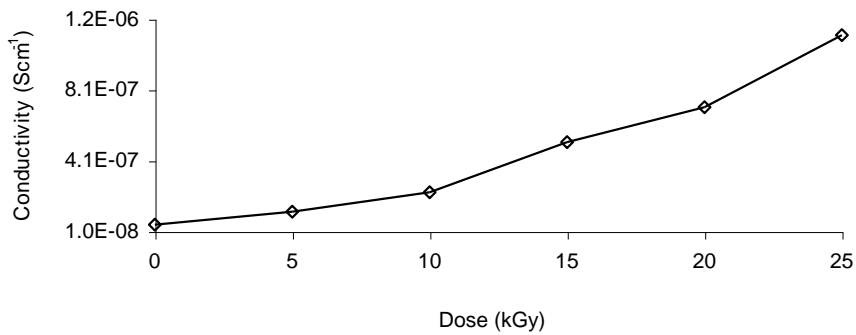
Figure 3. DC electrical conductivity of polypyrrole composite films at different doses.

3.2 Dielectric Properties

The dielectric properties of the samples were studied through complex permittivity as depicted in Equation 6:

$$\varepsilon * (\omega) = \varepsilon'(\omega) + \varepsilon''(\omega) \tag{6}$$

where $\varepsilon'(\omega)$ is real permittivity and $\varepsilon''(\omega)$ is imaginary part of permittivity representing energy storage and energy loss respectively in each cycle of electric field applied. $\varepsilon'(\omega)$ using Equation 6:

The real part $\varepsilon'(\omega)$ was found through Equation 7:

$$\varepsilon' = C(\omega)\frac{d}{A} \tag{7}$$

and imaginary part, $\varepsilon''(\omega)$ using Equation 8:

$$\varepsilon''(\omega) = \varepsilon'(\omega)\tan\delta \tag{8}$$

where d and A is the thickness and the surface area of the sample, C is capacitance and tan δ is the loss tangent.

From the plot of ε' and ε'' shown in Figure 4 (a) and (b), it is obvious that relative permittivity, ε', has two step variation. In step I, reduction in ε' for all doses is obvious in the frequency range of 20 Hz to 10 kHz. In step II, the curves are almost horizontal and smooth in the frequency ranging from 10 kHz up to 1 MHz. The initial high value of ε' (relative permittivity) in the region I is possibly due to electrode polarization [18-20] whereas in the region II, the decrease in ε'' is almost constant within the frequency range. This trend of variation may be due to the periodic reversal of electric field that is fast at high frequency because of ion diffusion may not be possible in the direction of the field [18]. The reduction of the value of permittivity, ε' is because of reduction in capacitance, C may cause dipoles to align with the field, which results into reduction in the value of relative permittivity [18,19]. In Figure 4 (b), the variation of ε'' has also shown two step variation. In step I, it is obvious that the reduction is linear within the frequency range of 20 Hz to 10 kHz. In step II, the curves for all doses are almost smooth and horizontal, showing that there is no significant loss in ε'' in the frequency range from 100 kHz to 1 MHz. The

dielectric loss in region I may be due to the motion of free charge carriers within the materials, which is associated with DC conductivity [20]. Therefore, power law dispersion is observed thus no peak is revealed in the measured frequency range. This peak is easily observed for pure dielectric materials (e.g. mica and alumina) or non-polar polymers. On the other hand, it can be observed that higher value of relative permittivity for irradiated samples is obtained and this trend continuously increases as the dose increases. The reason for this finding is due to high polarity of irradiated sample as they are exposed to gamma irradiation. Therefore, the number of dipoles is believed to be increased, thus increases the value of relative permittivity. The formation of free radical via dechlorination of trichloroacetic acid upon irradiation is believed to be the main factor for this behavior, which is discussed in the previous section.
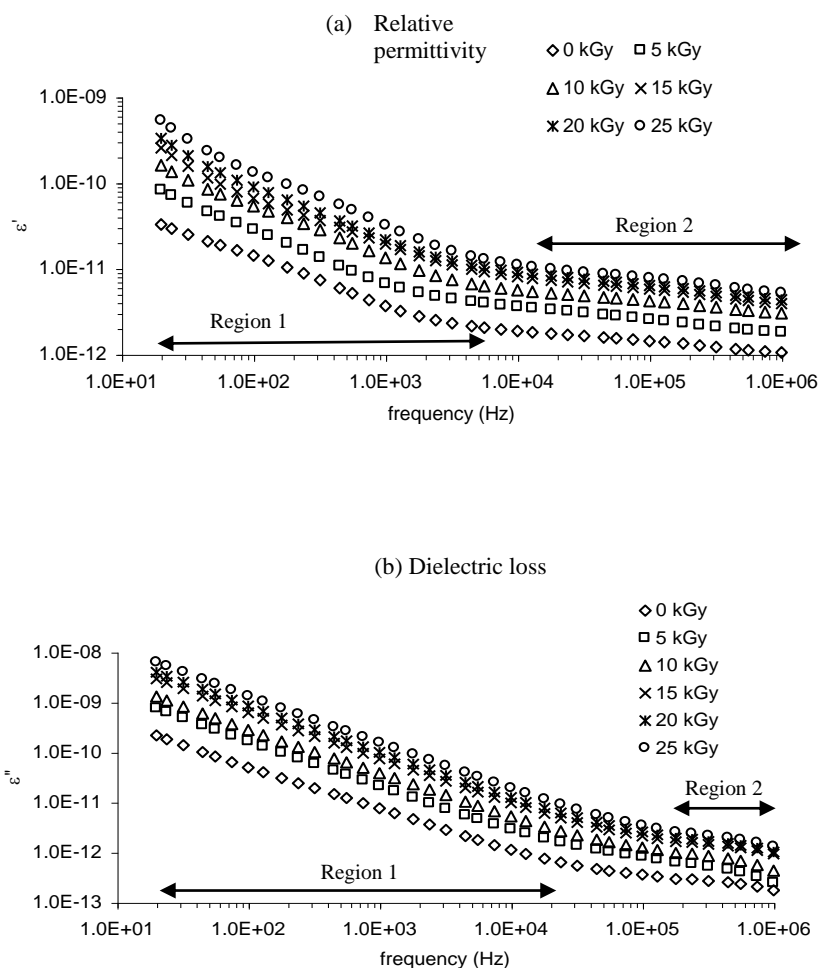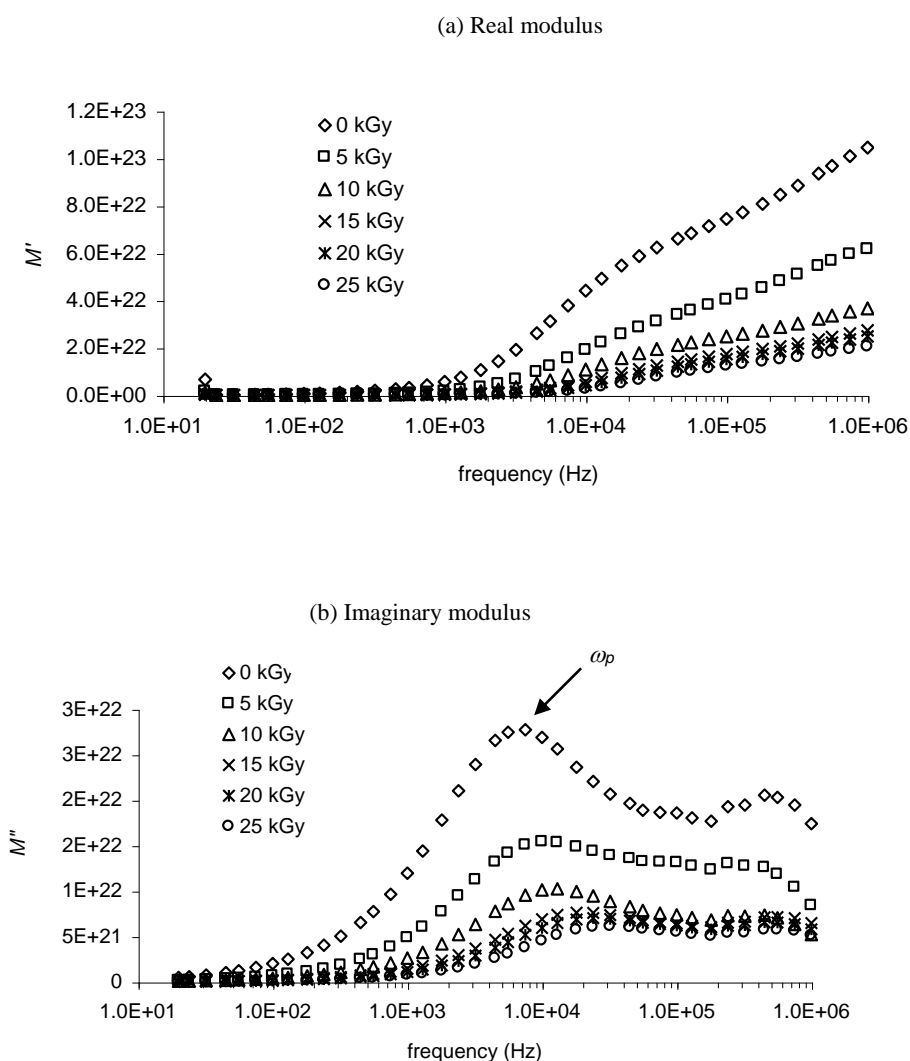

Figure 4. (a) Relative permittivity and (b) dielectric loss of polypyrrole composite films at different doses.

Figure 5 shows the dielectric modulus for polypyrrole composite films at different doses. The purpose is to investigate dielectric spectra. The main advantage of M^* formalism is the electrode effect can be suppressed which is within the agreement of the context as found in literature [18-19]. The dielectric modulus can be determined from the relation:

$$M'(\omega) = \frac{\varepsilon\prime(\omega)}{\varepsilon\prime(\omega)^2 + \varepsilon''(\omega)^2} \tag{9}$$

and

$$M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon\prime(\omega)^2 + \varepsilon''(\omega)^2} \tag{10}$$

(a) Real modulus

(b) Imaginary modulus

Figure 5. (a) Real dielectric modulus and (b) imaginary modulus of polypyrrole composite films at different doses.

From Figure 5 (a), the asymptotic value M_∞ (i.e. high frequency limit of M' (ω)) increases with the dose. The almost zero value of real modulus indicates the removal of electrode polarization. The curve of M'' (ω) shows an asymmetric peak approximately centered at the dispersion region of peak real modulus. The peaks slightly shift to higher frequency with the increasing of the dose.

From the imaginary part of electrical modulus, M'', the relaxation time of the orientation of dipoles can be calculated by determining the peak for angular frequency, ω_p which is available from the inset of the graph M'' vs log frequency. Table 2 shows the relaxation time, τ for polypyrrole composite film at different concentration of the dopants. The relaxation times were obtained from renowned Havriliak Negami relationship [15] as written in Equation 11, where ω_p is the peak of angular frequency and τ is relaxation time.

$$\tau = \frac{1}{\omega_p} \tag{11}$$

Almost similar values of τ are obtained for the samples irradiated from 5 kGy to 20 kGy. However, significant differences of ￼￼values are calculated for unirradiated sample for the

sample irradiated with the highest dose, 25 kGy. This observation supports the explanation for dielectric constant and loss as the values increase as relaxation time decreases with the increasing of irradiation dose.

Table 2 Relaxation time, $\tau(\omega)$ for polypyrrole composite samples at different doses

Dose (kGy)	Relaxation time, $\tau(\omega)$ x10^{-5}
0	2.8
5	2.1
10	1.6
15	2.1
20	2.1
25	1.2

4. CONCLUSION

The results of this study revealed that gamma irradiation produced changes in electrical conductivity and dielectric properties of polypyrrole composite films. The value of *s* obeys the power law $s(\omega) \propto \omega^s$ as the values lie in the range of $(0.54 \leq s \leq 0.71)$. The complex modulus i.e. the real and imaginary parts are dependent to gamma irradiation dose. The same results are also observed for the relaxation time, $\tau(\omega)$ in which tends to decrease as a function of dose. From this study, it can be concluded that gamma irradiation can be used as alternative technique for polymerization of conjugated polymers as well as to enhance the electrical conductivity of their polymer composites.

ACKNOWLEDGEMENTS

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