EFFECT OF GAMMA IRRADIATION ON DIELECTRIC PERMITIVITY OF POLYMER (PVA-CH) FILM

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Abstract - *The objectives of this study are to investigate the effects of radiation on dielectric properties of PVA-CH films. Polymer (PVA-CH**)** films were irradiated with Gamma ray at 12 kGy**.** Polymer film containing PVA (poly Vinyl Alcohol) and Chloral Hydrate (CH) has been prepared by solution casting technique. The obtained polymer composite layers were irradiated with γ – rays at various doses to investigate the radiation effect on dielectric permittivity in the frequency range of 20 Hz – 1 MHz at room temperatures. The real (ε') and imaginary (ε") dielectric constant are found to increase with increase in irradiation dose.*

Keywords: *Dielectric Permitivity, Gamma Irradiation, Polymer Film*

INTRODUCTION

PVA is a polymer, which has been investigated by many researchers and is known for many applications in industrial products due to its excellent mechanical strength, bio-compatibility, electrochemical stability, high tensile strength and abrasion resistance. Pure PVA is known for its good insulating polymer property with low conductivity and low dielectric loss, therefore it is of primary importance in microelectronic industry (Shekar et al, 1999). The electrical conduction and charge-storage capacity of PVA film blended with chlorine containing organic compounds CH (Chloral Hydrate) can be markedly increased by radiation. This solid electrolyte has electrical properties quite similar with the ionic conducting polymer electrolytes, which is useful for many electrochemical devices. Investigation of electrical conduction in polymers is aimed at understanding the nature of charge transport, while investigation of dielectric loss is aimed at understanding the polarization properties of molecules of the polymer.

Every organic material such as polymers shows great dose response to ionizing radiation. Hence, interaction between polymer and ionizing radiation produces radiation effects in the form of physical and chemical changes, which are dose dependent. The irradiated polymer may be useful as solid electrolytes potentially to be used in many applications such as cellular phones, laptop computers, rechargeable batteries, fuel cells, super capacitors and gas sensors. Radiation can cause cross-linking, grafting and scission in polymer, which modify the amorphous structure leading to an increase of the ionic conductivity and a change in the electrochemical property. The irradiated polymer may be useful as solid electrolytes potentially to be used in many applications such as cellular phones, laptop computers, rechargeable batteries, fuel cells, super capacitors and gas sensors.

The dielectric properties of heterogeneous disorder systems of polymer play important role in device applications such as chemical sensors, fuel cells, solid-state batteries, etc. When an electric field is applied across polymer placed between two electrodes, the electrical response can be described by the complex permittivity consists of the real dielectric constant and the imaginary dielectric loss (Mott and Davis, 1979). The dielectric constant is a parameter that describes the material ability to store charge due to polarizations, thus can give

information on the structure-property behavior of polymer. While the dielectric loss is a parameter describing dipole relaxation and frequency independent ionic conductivity, which give information on molecular motion and dielectric relaxation behavior of polar groups as well as bulk resistance of the material. Most studies in dielectric properties are centered on the measurement as a function of temperature, which can give information on how phonon assists the polarization mechanism, dielectric relaxation and ionic conductivity in the polymer chain (Wubbenhorst & Turnhout, 2002., Bassiouni et al., 2003). In the last several years that several work on dielectric properties of irradiated polymer with ionizing radiation have been intensive (Raghu *et al*. 2016., Gouda & Elrasasi, 2015., Kilic *et al*. 2017., Prabha & Jayanna, 2015., Ahmed et al. 2017., Swu et al, 2013., Raghua, 2014). The dose-dependent dielectric parameters can give information on how radiation-induced electric dipoles, dielectric relaxation and ions are being introduced in polymer.

The dielectric permitivity analysis technique has been applied to study structural and transport properties of gamma irradiated and non-irradiated bases polymer films and the resulting the influence of radiation and temperature on dielectric properties of polymer films (Ahmed et al, 2017; Swu et al, 2013). Singh, et al. (1998) have investigated the dielectrics properties of acid-based PVA complex and reported that acid concentration as well as humidity largely affect the dielectric characteristics of the polymer films. Dielectric properties of Polyacetate polymer composite irradiated with $10 - 10^6$ Gy γ radiation have been studied in the frequency range (42 to 1000) Hz (Swu et al, 2013). The dielectric loss of the irradiated increases as the frequency increases without any relaxation processes. Dielectric properties of PVA-Polystyrene polymer blends irradiated with γ radiation have been measured as a function of temperature at ($10^2 - 10^6$) Hz (Prabha & Jayanna, 2015). They found that the dispersion peak of dielectric constant of the polymer shifts to higher temperatures after gamma irradiation due to degradation of the polymer structure. Both the dielectric constant and dielectric loss of the gelatin increase with increasing dose. Dielectric relaxations of gamma irradiated Polyethylene have been intensively investigated (Raghu *et al*. 2016., Kilic *et al.* 2017).

The present study attempts to investigate the effect of radiation on PVA-CH for their potential applications in electrochemical devices. Investigations of the effects of radiation dose on dielectric properties of the PVA-CH films at room temperature by using impedance analyzer. The present study is aiming to study the effect of gamma irradiation on the dielectric properties of PVA (Polyvinyl Alcohol) – CH (Chloral Hydrate) polymer film.

RESEARCH METHOD

The method of making samples in this article is the same as the method of making samples in our previously published article (Susilawati & Doyan, 2009, Susilawati & Doyan, 2015, Susilawati, 2018).

Gamma Irradiation

Dyed PVA composite films were irradiated with 1.25 MeV γ-rays from a J.L Sherperd type γ-ray Co^{60} source at a mean dose rate of 163.75 Gy min^{-1}. The new dose rate was calculated based on the half-life of the source, which is 5.27 years by using equation below:

$$\dot{D}_{\text{New}} = \dot{D}_0 \rightleftarrows e^{-ln\,2t/T_{1/2}}$$

Where $\dot{D}_0$ the initial dose rate, t is is the time leaps; $T_{1/2}$ is the half-life of the source, which is 5.272 years. The deviation of the current value to standard value is of main interest for chamber stability and are maintained to within ± 1%. The deviation was calculated using equation

$$\text{Deviation} = \frac{2.75\times10^2\times\Delta A}{1+0.007(T-25\ ^oC)} \quad (1)$$

Where ΔA is the changing absorbance, T is the temperature in Celsius. Response of Fricke dosimeter was compared to the secondary standard chamber and the consistencies of by these methods were maintained to be less than ± 3%. The solution was then sent for standardization using gamma chamber and also for calibration of routine dosimeter. The routine check source measurements were performed every three months in order to assess the long term stability of the reference standard chamber. The International Atomic Energy Agency (IAEA) has established an international network of Secondary Standard Dosimetry Labaratories (SSDL's) to provide dosimeter calibration facilities for those who are engaged in the application of ionizing radiations in areas such as radiation therapy and food preservation (McLaughlin, 1988). The IAEA's Dosimetry Laboratory is the central laboratory of the IAEA/WHO network of SSDLs, and has an established link to the international measurement system. For this study the relative combined standard uncertainty in the measured dose value was ± 1 % as obtained from a inter-comparison between Secondary Standard Dosimetry Laboratories (SSDL), and International Dose Assurance Service Radiation Processing Dosimetry (IAEA-Vienna, Austria). The agreement within ± 3 % of the measured dose between the radiation user and the IAEA is considered to be satisfactory. The samples of the composite films for each radiation dose were placed at the centre of the irradiation chamber of the facility that was surrounded by the polystyrene block of cylindrical shaped for secondary charge particle equilibrium. The composite films were irradiated with absorbed doses that ranged from 0 to 12 kGy at 1 kGy step for each composition of CH. At least three samples were represented for each radiation dose, but no significant differences in their characteristics were found during measurements.

RESULTS AND DISCUSSION

Most polymers have insulating properties. An insulator is a dielectric material, which is electrically non-conducting and exhibits or may be made to exhibit an electric dipole structure (Gaffar, 2001). Polymers having the dipole moment aligned parallel to the chain contour exhibit a dielectric relaxation due the fluctuation of the end-to-end vector of the chains. Parameter relating to the electrical insulating property is the dielectric permittivity, which may reveal the presence of dipoles in the bulk materials. This parameter is useful in dielectric study to understand the structure-property behaviour of composite polymers (Ramesh et al, 2002).

The effects of radiation below 20 kGy on PVA based composites result in the formation of more ionic carriers by radiation scission of organic plasticizers, which may be immobilized by trapping at localized sites in the binder matrix and can be made in motion under the influence of density gradients (diffusion) and any existing electric fields. The electrical conduction of these materials is via ionic hopping with the hopping frequency increasing with the increase of the absorbed dose. An increase in conductivity leads to a drop in the dipole relaxation time of most segmental species of composite polymers, resulting in increase in the degree of dipole orientation and consequently enhances the dielectric permittivity. Therefore, dose sensitivity is an

important parameter in quantifying the effect of ionizing radiation on the dielectric permittivity.

This paper deals with the effects of radiation on dielectric permittivity of SCPs under investigation, PVA-CH composites. The results and the discussion will be focused on the dependence upon dose of the dielectric constant, dielectric loss, electrical modulus and dielectric relaxation time.

Dose-Dependent of Dielectric Permittivity

The dielectric response of PVA-CH composites in an electric field is described by the complex capacitance, $C^*(\omega)$ using the Debye equation (Mott and Davis, 1979)

$$C^*(\omega) = C'(\omega) - iC''(\omega) = \varepsilon_0 \frac{A}{d}\left(\varepsilon'(\omega) - i\left[\varepsilon''(\omega) + \frac{\sigma}{\varepsilon_0 \omega}\right]\right) \quad (2)$$

where $\varepsilon'(\omega)$, is the real part or dielectric constant that associates with the energy storage and $\varepsilon''(\omega)$, is the imaginary part or dielectric loss that associates with the energy loss. Dielectric loss factor mainly consists of two parts that are contributed from dipole relaxation process ε''_{dipole} and from ionic conductivity $\varepsilon''_{ion} = \frac{\sigma}{\omega\varepsilon_0}$, where σ is the ionic conductivity and $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}, is the dielectric constant of vacuum (free space). If ε''_{dipole} is small then the total dielectric loss is dominated by the ionic conductivity σ. The dielectric constant ε' and dielectric loss ε'' were determined by measuring the capacitance (C_p) and the dissipation factor (D) ($tan\,\delta$) using the following equations:

$$\varepsilon' = \frac{C_P(\omega)d}{\varepsilon_0 A} \quad (3)$$

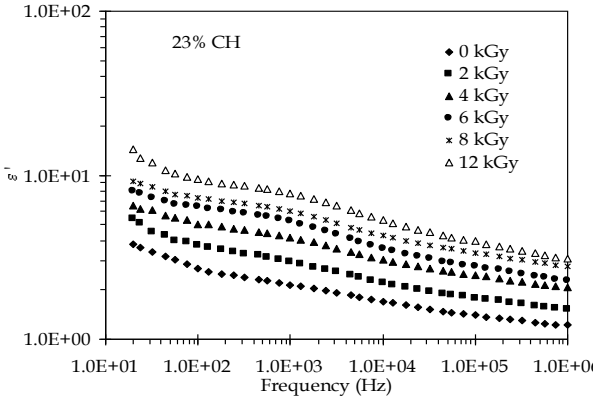
$$\varepsilon'' = \varepsilon' D$$

where A is the electrode surface area, d is the thickness of the sample and $C_P(\omega)$ is the parallel capacitance at a given frequency, $f = \omega/2\pi$, as measured by the impedance analyser.

The dielectric constant and the dielectric loss as a function of frequency (20 Hz – 1 MHz) at various doses up to 12 kGy are shown in Figure 1 and Figure 2 respectively for different CH compositions. They represent typical permittivity behavior for polar materials. $\varepsilon'(\omega)$ decreases rather slowly with increasing frequency. $\varepsilon''(\omega)$ is initially high at low frequencies, decreases rapidly with increasing frequency and attain almost a constant value at higher frequencies. Generally, $\varepsilon'(\omega)$ at low frequencies depends on dipolar orientation and space-charge polarization. The behavior of $\varepsilon''(\omega)$ can be attributed to dipole orientation relaxation process and conductivity of the weakly bounded charges in the composites. A rapid decrease in ε' value over the range frequency 20 Hz – 10 kHz indicates the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field. In the high frequency range the dipoles are hardly able to orient themselves and hence $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ will attain a constant value (Singh, 1998). Charge accumulation at the interface within the bulk of the sample is causing interface effects and the interface between the electrolyte (sample) and the electrodes is causing space charge polarization. The later may be present due to unknown impurities and other imperfections. The electronic and ionic polarizations can only occur at very high frequencies and in this region they are not present. Thus, in this composite system the dielectric constant is due to dipolar orientation and space-charge polarizations.

The value of ε' and ε'' increases with dose and CH composition increase. For PVA/23% CH composite at 20 Hz, it was found that ε' increases from 2.25 before irradiation to 14.0 after irradiation at 12 kGy. When CH composition increases to 57%, ε' value increases from 6.1 at zero dose to 698 at 12 kGy. The value of ε' increase with

increasing dose indicates that the orientation polarizations of the system increase with dose. Radiation scission produces more dipoles due to the breaking up of molecules of CH and PVA, which leads to an increase of dipole orientation polarization. An increase of CH composition leads to an increase of the number of dipoles in the composites, thus increase the orientation polarization. The increase in ε' value with the irradiation dose is attributed to the formation of some defects sites in the band gaps of polymer as a result of occurrence of chain scission. Generally, these defects may indicate sign of the existence of charge carriers traps in the band gap of the polymer; it may be capturing the charge carriers. Therefore, γ-irradiation increases the ability of the polymer to store charge (Gouda & Elrasasi, 2015).



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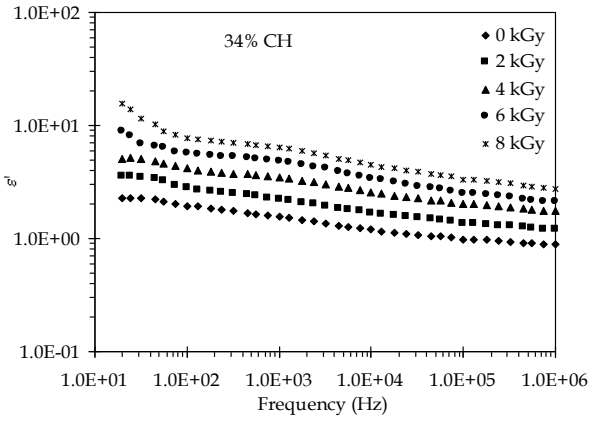

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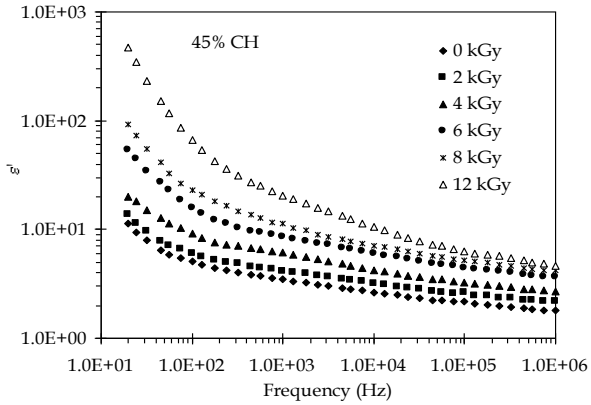

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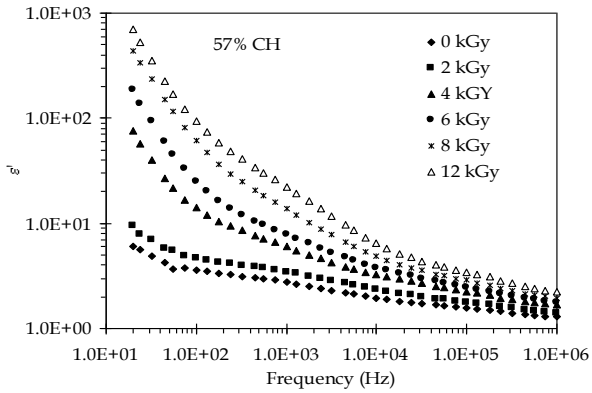
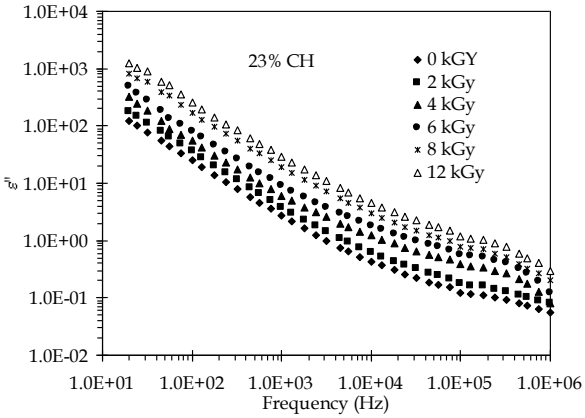


(d)

Figure.1 $\varepsilon'(\omega)$ vs. frequency at different doses for PVA-CH composites containing (a) 23% (b) 34%, (c) 45% and (d) 57% chloral hydrate

Furthermore, it was found that for PVA/23% CH at 20 Hz, ε" increases from 79.5 before irradiation to 1,234 after irradiation at 12 kGy. In the same measurement condition for PVA/57%CH, ε" increases from 242.43 before irradiation to 24,432 after irradiation at 12 kGy. The mode of dielectric loss component $\varepsilon''(\omega)$ is dominantly contributed from ionic conduction of Debye type with single relaxation time indicated by a single semicircle of the complex impedance diagram. This can be attributed to ions that are weakly bound, trapped within microstructures and partially free to move in the polymer and composite segment of the samples (Pissis and Kyritsis et al., 1999). These effects are prominent at high doses as more charge carriers are formed and trapped in the composite molecules after undergoing

radiation scission. As the composition of CH increases, the dipole relaxation and dc conductivity of unbounded charges increase, which leads to an increase of dielectric loss factor of the composites.



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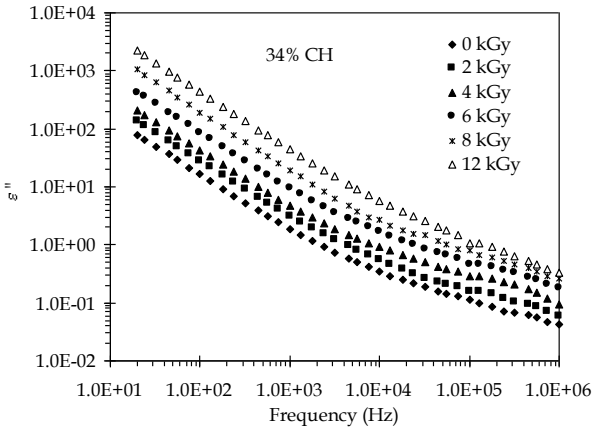

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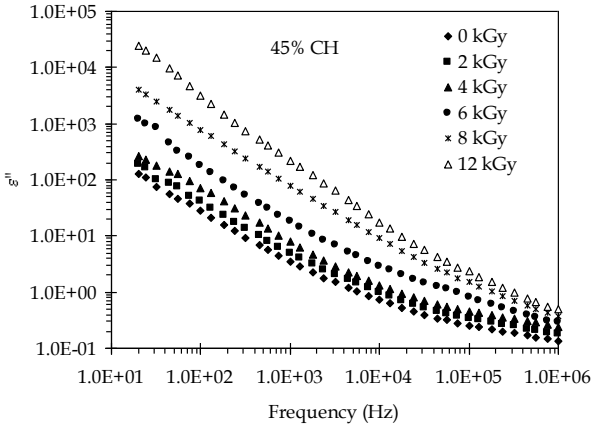

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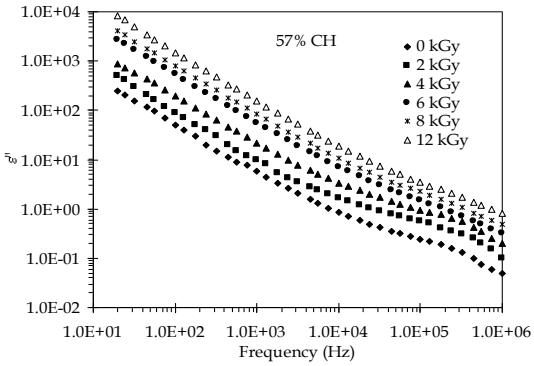

(d)

Figure. 2 $\varepsilon''(\omega)$ vs. frequency of PVA-CH composites at different doses and for CH compositions of (a) 23% (b) 34%, (c) 45% and (d) 57%

CONCLUSION

The effects of γ irradiation on dielectric properties of the composite films with different composition of CH have been investigated. The dielectric-dose relation study revealed that an increase of the dielectric constant ε' of the composites with increasing dose, which is attributed to the orientation polarizations of the dipoles in the polymer system. Increase in the dielectric loss ε" with increasing dose can be attributed to the dielectric dipole relaxation and the dc conductivity of the free ions in the blends.

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