Synthesis and Characterization of Conducting Polyaniline Based on ANI-PVA-MgCl₂ Composites Using Gamma Radiation Technique

NAIF MOHAMMED AL-HADA[1], **ABBAS M. AL-GHAILI**[2], **HAIROLADENAN KASIM**[3], **MUNEER AZIZ SALEH**[4], **ELIAS SAION**[5], **JIAN LIU**[1], AND **WANG JIHUA**[1]

[1]Shandong Key Laboratory of Biophysics, Institute of Biophysics, Dezhou University, Dezhou 253023, China
[2]Institute of Informatics and Computing in Energy (IICE), Universiti Tenaga Nasional (UNITEN), Kajang 43000, Malaysia
[3]College of Computing & Informatics (CCI), Universiti Tenaga Nasional (UNITEN), Kajang 43000, Malaysia
[4]Nuclear Engineering Programme, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai 81310, Malaysia
[5]Department of Physics, Faculty of Science, Universiti Putra Malaysia, Serdang 43400, Malaysia

Corresponding authors: Naif Mohammed Al-Hada (naifalhada@yahoo.com), Abbas M. Al-Ghaili (abbasghaili@yahoo.com), Hairoladenan Kasim (hairol@uniten.edu.my), and Wang Jihua (jhw25336@126.com)

ABSTRACT Conducting polymer composites such as conducting polyaniline composites have numerous attractive physical properties which could be used in several vital applications. In order to give composite materials unique physical and chemical properties that can have broad application potential in various areas, it requires appropriate adding of metal chloride through conductive polymer composites. This study employs the gamma radiation technique to produce conducting polyaniline from an aqueous solution. The solution comprises four materials, including: ANI, PVA, MgCl₂ and distilled H₂O, which serve as a binder or film support, precursor, Cl ions provider, and a solvent. To attain the conducting polyaniline composite, a film of ANI-PVA-MgCl₂ was subjected to gamma radiation under ambient conditions. Conducting polyaniline composite has been formed once the colour began to change from white to green following the doses of radiation. The results have demonstrated that the level of gamma radiation increased to 40 KGy, thereby confirming that the electrical insulation ANI-PVA-MgCl₂ film was converted into an electrically conductive polyaniline composite film, this can be applicable for energy applications. The production of conducting polyaniline composite has been observed since the colour has been changed from white to green colour alongside radiation doses.

INDEX TERMS Poly (vinyl alcohol), aniline, magnesium chloride, gamma radiation technique, energy applications.

I. INTRODUCTION

Recently, there have been advances in the production of organic-inorganic materials in respect of both their chemical and physical properties _[1]–[4]. This development has rendered them more appealing to researchers in a range of disciplines [5]–[9]. One such material which is frequently utilized is conducting polymer composite [10]. It popularity is due in large measure to its amenability to modification, it low preparation costs, and its properties as metallic support for both materials and semiconductor materials [11], [12]. In addition to the materials primary role as in conducting polymers, it also has the capacity to conduct polyaniline composite [13]. In this latter capacity, its distinctive electrical and optical properties appeal to researchers who appreciate its versatility [14], [15]. Additionally, the existence of -NH-groups helps reactions through the polymer chain to enhance their features. Hence, it offers benefits for an extensive variety of applications, including sensors and solar cells [16], [17]. One of the important property of polyaniline is that the enhancement of its electrical conductivity can be simplified using incorporation inorganic materials [18]. Furthermore, the conductivity of PANI may be contingent upon dopant ions and metallic materials which are utilized to stabilize conducting PANI [19]. The optical features of the conducting polyaniline composite also could be enhanced and developed

The associate editor coordinating the review of this manuscript and approving it for publication was Navanietha Krishnaraj Rathinam.

by using metallic salts, such as nickel chloride and silver chloride, which are also employed to increase the conductivity of polyaniline [13], [20].

Recent studies have produced conducting PANI composites by employing several techniques, including sol-gel method [21], chemical methods [22], electropolymerization method [23], in-situ chemical oxidation polymerization [24], in-situ polymerization technique [25], solution casting [26], via a sonochemical method [27], and aqueous solutions [28]. The irradiation of polymers is achieved using either gamma-rays, electron beams, or ionizing radiation [29]. Through this process, the properties of polymers are significantly altered in accordance with both the radiation employed and the features of the target materials. Whilst these processes have facilitated the identification of novel PANI conducting properties; some methods have generated products which are not merely toxic, but also possibly hazardous to the environment. Moreover, no method acted to polymerize the polyaniline in precisely the same manner using aniline, MgCl₂ and polyvinyl alcohol (PVA).

In the current study, the Gamma radiation (at different radiation doses) technique was employed to prepare polyaniline using ANI, PVA, MgCl₂ and H₂O materials. The results indicate that the properties of polyaniline are enhanced by increasing the irradiation doses [30]–[33]. The distinctive character of this study is that the radiation method adopted has multiple benefits, including its exemplary reproducibility, its low costs, and it easy application. Moreover, this method can likewise augment the electrical possessions of the product in respect of requisite composite properties.

II. EXPERIMENTAL WORK
A. MATERIALS
All the materials used in this work for the preparation and characterization of conducting polyaniline are as follows:

- Poly (vinyl alcohol) (PVA) (Mw = 85000-142000 g/mol, 99 – 100% hydrolyzed) was used as a binder or a film support and was purchased from Fluka of USA.
- Aniline (ANI) is a monomer and was used as a precursor. It was purchased from the Merck-Schuchardt Company and used without further purification.
- Magnesium chloride (MgCl₂) are chemical salts and were used as Cl ions provider.
- Finally, distilled water was employed as a solvent.

B. SAMPLES PREPARATION
The PVA solution has been prepared by dissolving 20.00 g PVA powder in 500 ml distilled water. The solution has been stirred at 80 °C temperature for 3 hours and then cooled down at room temperature. After cooling to room temperature, 25 wt% aniline has been added to PVA solution and stirred to obtain a homogeneous solution, magnesium chloride with different concentrations i.e 2%, 5%, and 8% wt of MgCl₂ were added to ANI/PVA solution. The mixtures have been stirred continuously for 2 hours using a magnetic

stirrer in nitrogen atmosphere. Then, each concentration of the blend solution of ANI /PVA/MgCl₂ was divided into two glass plates casting and left to dry at ambient temperature for 6 days in order to remove water. The ANI /PVA/MgCl₂ films were obtained by removing the blend films from the glass plate and cut into several pieces. The thickness of films has been determined by a digital micrometer model Mitutoyo no: 293-521-30-Japan. The films were packed in a sealed plastic bag in order to send them for gamma-rays exposure.

C. SAMPLES IRRADIATION
The samples have been irradiated at different doses from 0 to 40 kGy in the ⁶⁰Co γ-rays irradiation chamber (Gammacell Excel model). The ⁶⁰Co produces two main γ-rays of 1.17 and 1.33 MeV, which gives the average energy of 1.25 MeV. The dose rate was calculated based on the half-life, $T_{1/2}$, of the source, i.e. (for every 10 KGy it needs 5 mins based on the experiments and devices conditions and time) the elapsed time in which the activity of the source reduced by half, is equal to 5.27 years by the equation (1)

$$\dot{D} = \dot{D}_0 \exp(-\ln 2 \; t/T_{1/2}) \qquad (1)$$

where $\dot{D}_0$ is the dose rate at time $t = 0$. The samples were exposed to gamma radiation at room temperature to release Cl ions from the manganese salts.

D. IMPEDANCE ANALYZER AND CONDUCTIVITY MEASUREMENT
The conductivity of the samples has been measured by using LCR- meter model HP 4284A, It operates in the frequency range from 20 Hz to 1 MHz. The system was equipped with an in-house Lab VIEW software program that controls all the measurement process and collects the data as capacitance (C), conductance (G) versus frequency. The raw data for the sample conductivity was measured by sandwiching the sample between two metal electrodes made of brass plates with the surface area of $4.87 \times 10m^2$, which are connected to LCR-meter system at room temperature. Then by applying the equation (2) the conductivity can be deduced versus frequency.

$$\sigma(\omega) = G(\omega)\frac{d}{a} \qquad (2)$$

where,

$G(\omega)$ is the conductance at a given frequency f or $\omega = 2\pi f$,
d is a thickness of the sample, and
a is the surface area of the electrode sample.

Data of samples for calculating conductivity were measured at room temperature. Values of capcitance(Cp) and conductance (G) were measured to calculate the real and imaginary parts of the complex impedance.

The Cole-Cole plots of the complex impedances has been used to determine the dc conductivity using the subsequent

equation (3):

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

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary of the complex impedance, respectively according to equations (4) and (5) for different frequencies;

The Cole-Cole plot concept is useful to deduce the impedance of the dielectric at zero frequency, which can be graphed from Z' (really impedance) versus Z'' (imaginary impedance), these parameters are given by the following equations (4) and (5):

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

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

where:

$Cp(\omega)$ is the capacitance of the dielectric,
$\omega = 2\pi f$ is the angular frequency, and
f is the frequency.

III. RESULTS AND DISCUSSION

A. POLYANILINE FORMATION INDUCED USING GAMMA RADIATION

In order to change and modify the physical and chemical features of polymers and polymer blends, it is necessary not only to adopt constant processes akin to radiation-induced oxidation but also to employ as reduction.

Generating Hydrated electrons, e_{eq}^-, radicals of hydrogen H*, radicals of hydroxyl OH*, hydrogen ions H⁺, and hydroxyl ions OH⁻ by bond scission requires the combination of γ-rays in water. C-C, C-H and C-OH covalent bonds. These are chemical bonds which will be involved in the chemical formation of poly (vinyl alcohol) (PVA) C-H and C-OH but both C-H and C-OH are weak compared to C-C. The effects of γ irradiation PVA generate the attachment scissions from C-H (binding energy 4.37 eV), in addition to several C-OH surface processions [34]–[36]. The dechlorination process from MgCl₂ formed hydrogen chloride, HCl whilst the γ-rays made contact through ANI-PVA-MgCl₂ film. In this study, Cl⁻ ions serve as an oxidant to N⁺ sides and polymerized imines collection was oxidized in conjugated units from the conducting polyaniline. The possible reaction mechanism for the production of conducting polyaniline-PVA arising thru aniline monomer and Cl⁻ induced using γ-radiation is shown in Figure 1.
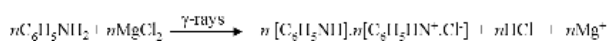
$$nC_6H_5NH_2 + nMgCl_2 \xrightarrow{\gamma\text{-rays}} n[C_6H_5NH].n[C_6H_5HN^+.Cl^-] + n]Cl + nMg^+$$

FIGURE 1. Polyemeraldin structure.

Producing metals such as $n\mathrm{Mg}^0$ and converting them into a group from atoms requires the interaction between free electrons. This was attempted using γ-rays and ions from $n\mathrm{Mg}^+$ as shown in Figure 1.

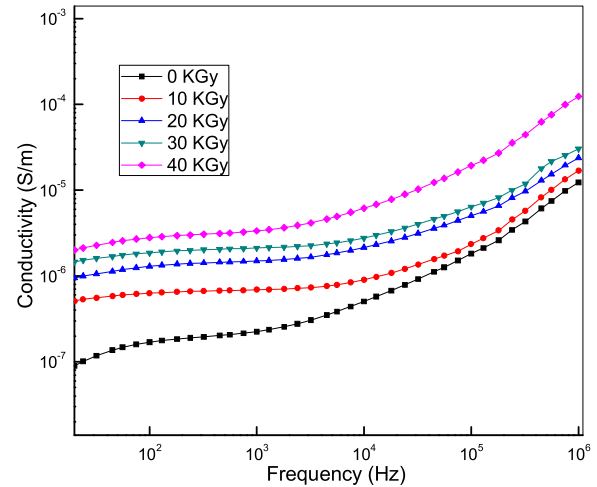**FIGURE 2.** Ac conductivity of PVA at different radiation doses of 10, 20, 30 and, 40 kGy.

When γ-rays interact with ANI/PVA/MgCl₂ films, the MgCl₂ rapidly degrades. This principally results in a loss of Cl⁻ through the dechlorination procedure. Radiation-induced Cl⁻ acts as an oxidizing agent or oxidant, which can dope the imines group of aniline and 'in-situ' polymerization of imines to form conducting polyaniline (PANI) in the form of polyemeraldine structure. The conducting PANI is formed by protonation at imines (–N=) sites. In this work, Cl⁻ ions act as an oxidant to N⁺ sides and polymerized imines group which oxidized into conjugated units of conducting PANI.

B. THE CONDUCTIVITY OF PURE PVA

Figure 2 displays the conductivity versus frequency of pure PVA films before and after irradiating with gamma-rays. In the current study, the ac conductivity has been measured in frequency variety of 20 Hz – 1MHz. The conductivity can be expressed according to Jonsher *et al.* (1976) by the relation

$$\sigma(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega) \quad (6)$$

where $\sigma_{dc}(0)$ and $\sigma_{ac}(\omega)$ are the zero frequency and ac conductivity values respectively. The conductivity of pure PVA increases with increasing dose as shown in Figure 2. The ac conductivity increment subsequent the dose is related to H⁺ and OH⁻ ions persuaded using γ radiation, trapped thru PVA host leading to the disorder of structure to amorphous, that enhances the carriage of charge carriers of one site to another in the PVA using ionic hopping mechanism [37] or even by phonon-assisted tunnelling process [38] influenced by the room temperature. The ac conductivity increases at higher frequencies as more trapped ions are released and move between the electrodes. These outcomes are in similar to the earlier findings [39] that is the conductivity of pure PVA increases as dose increases.

C. THE DC CONDUCTIVITY OF PURE PVA

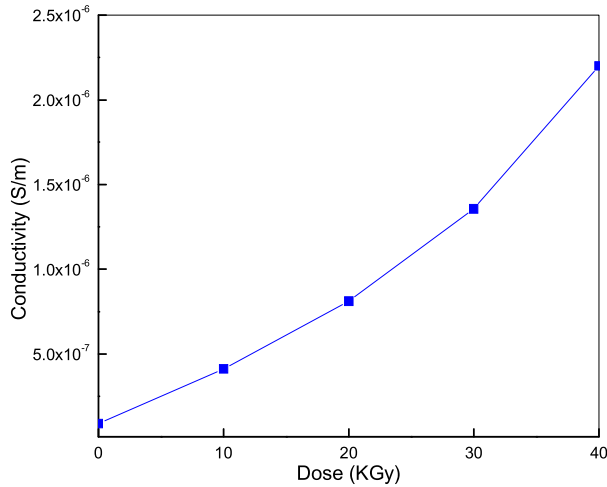The frequency-independent dc conductivity was deduced from the extrapolation of the complex impedance plots.

FIGURE 3. The extrapolation of the dc conductivity component for pure PVA at different radiation doses of 10, 20, 30, and 40 kGy.

Figure 3 displays the dc conductivity versus radiation dose of the pure PVA films by extrapolating the dc component towards the y-axis. The conductivity rises exponentially from 8.88×10^{-8} at radiation dose of 0 kGy to 2.20×10^{-6} (S/m) at radiation dose of 40 kGy. This dc conductivity appears throughout the frequency range although it cannot be seen in Figure 2 due to the increase of ac conductivity at higher frequencies. The dc conductivity increases with increasing dose due to free charge carriers H^+ and OH^- ions induced thru radiation. The data were obtained at room temperature, and we anticipated that their mobility at this temperature also increases the dc conductivity. Thus, the dc conductivity is contributed by both the charged carriers and their mobilities'.

The Cole-Cole plots of the complex impedances have been used to determine the dc conductivity using the subsequent equations (3), (4) and (5). The cole-cole plots of the complex impedances have used based on the circuit of resistor and capacitor that are in parallel placed.

The complex impedances plots $Z''(\omega)$ vs. $Z'(\omega)$ produced almost a semicircle at different doses. Figure 4 shows the semicircles radius of pure PVA that declines with the rise of dose. The dc conductivity was determined from the resistance, Z_0, by extrapolating or extending the semicircle curve to zero frequency on the real impedance axis Z'. The dc conductivity was calculated from the relation given by Jonsher (1976) in the form:

$$\sigma_{dc} = \frac{d}{aZ_0} \qquad (7)$$

where d is the thickness of sample and a is the electrode area. The dc conductivity results are shown in Figure 5. The conductivity increases exponentially from 8.53×10^{-8} at radiation dose of 0 kGy to 2.11×10^{-6} (S/m) at radiation dose of 40 kGy. Comparing to the dc conductivity values obtained from Figure 3, the differences are not significant. Perhaps, the extrapolation method in both procedures contributed to their differences.
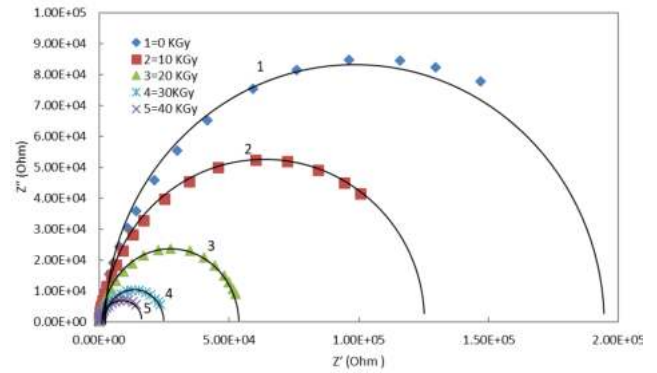

FIGURE 4. Cole-Cole plot of pure PVA at different radiation doses of 10, 20, 30, and 40 kGy.
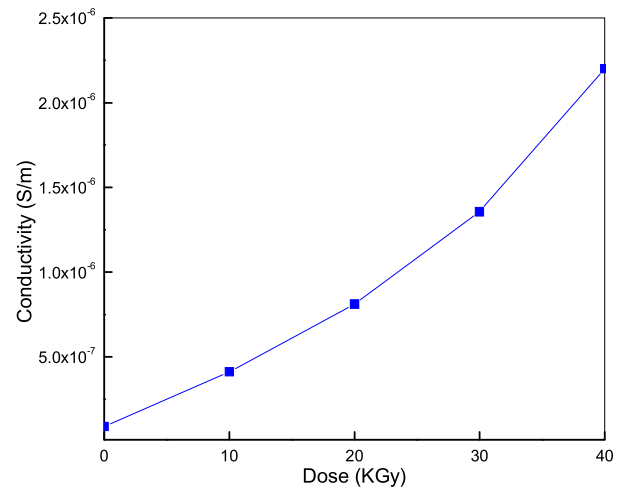

FIGURE 5. Using the Cole-Cole plot to determine the dc conductivity of pure PVA at different doses.

D. THE AC CONDUCTIVITY OF PURE PVA

The ac conductivity $\sigma_{ac}(\omega)$ of pure PVA films in Figure 6 follows (Jonsher, 1976), which is appropriate towards identical extensive materials regardless of their physical structures and the charge carriers type (Duta, 2001). The ac component may be written in the form:

$$\sigma_{ac}(\omega) = A\omega^s \qquad (8)$$

where A is a constant dependent on the dose and elemental composition, $\omega = 2\pi f$ is the angular frequency and s ($0 < s < 1$) is the frequency exponent, in need of on dose of radiation as $s(D)$. It can be evaluated the s value from the linear slope gradient of $log\sigma_{ac}(\omega)$ vs. $log\omega$ at higher frequencies as shown in Figure 6. The s value declines with the rise of radiation dose as revealed in Figure 7. These outcomes approve the domination of ac conductivity by ionic hopping when $s < 1$. The ionic carriers involved are H^+ and OH^- ions induced by radiation from radiation scission of C-H and C-OH groups and trapped in PVA. Ion hopping between the localized sites and as the radiation dose rises the dependence of conductivity on frequency decreases thus reduces the frequency exponent s with radiation dose rises.
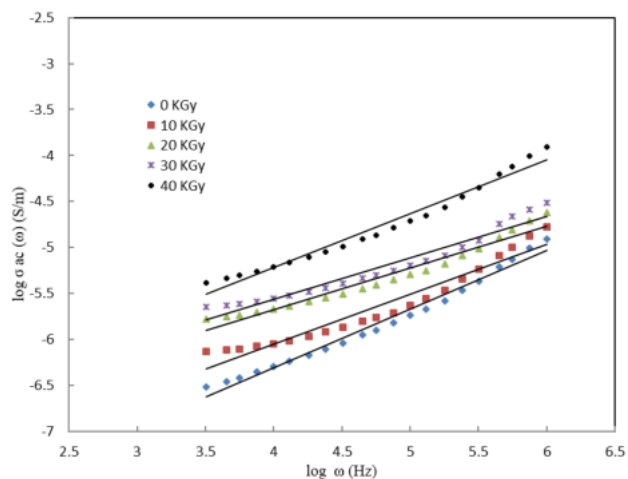
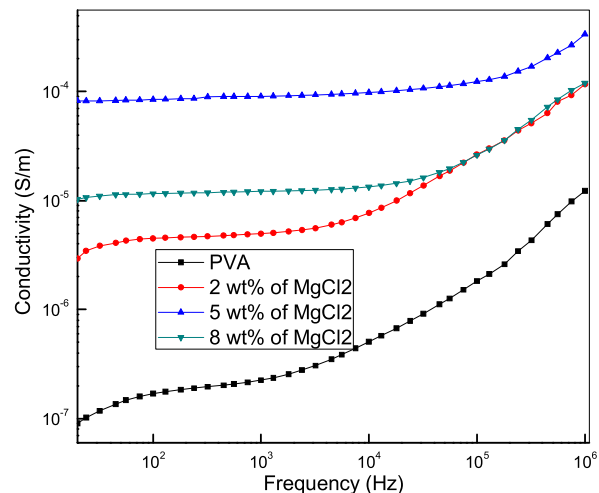**FIGURE 6.** Log $\sigma(\omega)$ of PVA at different radiation doses.

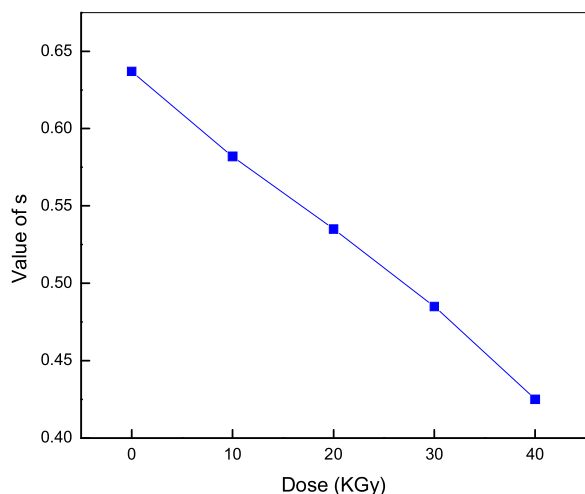**FIGURE 8.** Conductivity of the ANI/PVA film at various of MgCl$_2$.

ions obtained from MgCl$_2$ salt. The conductivity of the conducting PANI due to polarons is attributed from the motion of C = N bonds with attached free Cl$^-$ ions under an electrical field impact.
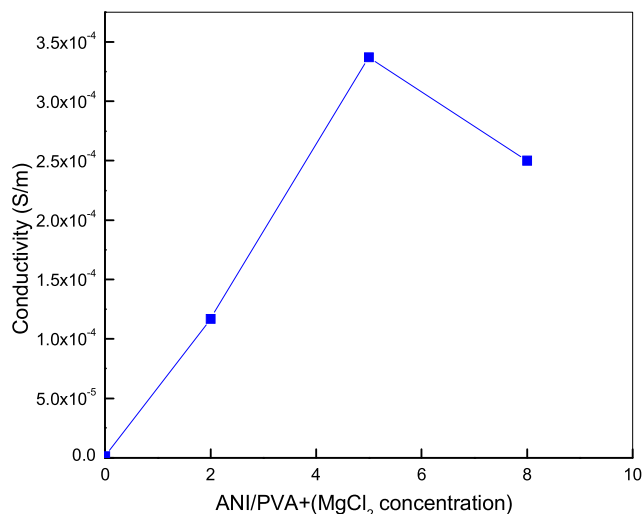

FIGURE 7. Frequency exponent s for pure PVA at different radiation doses of 10, 20, 30, and 40 kGy.

FIGURE 9. The dc conductivity of PANI-PVA composite films at MgCl$_2$ concentration wt%.

E. CONDUCTIVITY OF PANI/PVA AT VARIOUS MgCl$_2$ CONCENTRATIONS

Figure 8 revealed the ac conductivity of polyaniline composite films at various MgCl$_2$ salt in the range of frequencies from 20 Hz to 1 MHz. At low salt concentrations, the dc conductivity is frequency-independent by weakly bound electrons, H$^+$ and OH$^-$ by water residues and polarons in PANI induced by oxidation on ANI by Cl$^-$ ions obtained from MgCl$_2$ salt diluted in the residual water and also from those of phonon assisted tunnelling procedure that advantage charge mobility at room temperature. The ac conductivity at high frequencies is related to H$^+$ and OH$^-$ ions that might be trapped in sites of the samples that obligatory irregular electric field at certain higher frequencies to release these ions and donates to the conductivity by hopping between the localized sites. The conductivity rises alongside the salt concentration until 5 wt% MgCl$_2$ before the conductivity drops to the lower values at higher concentrations of 8wt% MgCl$_2$. At higher concentrations the dc conductivity is contributed mostly from polarons in PANI that induced by oxidation of PANI by Cl$^-$

The dc conductivity components at various MgCl$_2$ salt concentrations are shown in Figure 9. The conductivity rises from 1.00×10^{-7} S/m at salt concentration of 0 wt% to 3.37×10^{-4} S/m at salt concentration of 5 wt%. The dropped in the conductivity at 8wt% salt is related to the rise of crystallinity in the polymer as added crystalline chlorine are existing in the composite films. Furthermore, it may be due to high viscosity that caused resistance or impedance to oppose ion mobility [40]–[43].

F. THE CONDUCTIVITY OF POLYANILINE FILMS AT NUMEROUS RADIATION DOSES

declines. Figure 10 displays the conductivity of polyaniline polymerized with 5 wt% MgCl$_2$ salt and different radiation doses up to 30 kGy. The outcomes demonstration that the
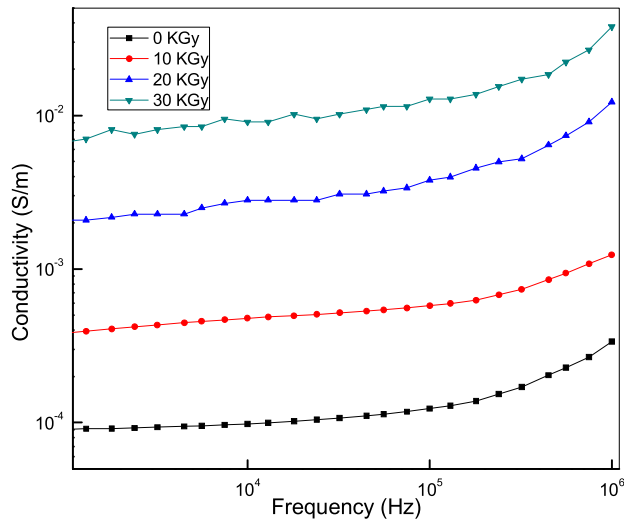
FIGURE 10. AC conductivity of PANI/PVA for 5 wt% MgCl₂ at different radiation doses of 0, 10, 20, and 30 kGy.

conductivity rises with the rise of radiation dose. This means that dose increased more polarons and lead to rise in the conductivity of conducting PANI. The polymerization of PANI by oxidation from MgCl₂ salt has been described in formation section, which attributed to the formation of $C = N$ bonds with attached free Cl^- ions from the salt in the PANI. To discuss the formation of PANI by gamma-irradiation in the presence of MgCl₂ salt it has to know the fundamentals of radiation interaction. The interaction of gamma-rays with matter releases inner electrons and outer electrons due to photoelectric effect and Compton scattering respectively. Also, the radiation chemical effect of can produce hydrated electrons, e_{eq}^- from the present of residual water in the films, with free radicals of H^* and OH^* together. These physically and chemically produced electrons can reduce Mg^+ ions in the films to produce Mg^0 atoms, which then aggregated to produce Mg. By the production of more Mg, and more free Cl^- ions originally from MgCl₂ salt can interact with $C = N$ bonds of aniline to produce PANI by attaching the $C = N$ bonds with Cl^- ions in the formation of polarons, the charged carriers of PANI. At zero doses, the conductivity of polyaniline composite films in the presence of 5 wt% MgCl₂ salt is because of the formation of polarons in PANI as discussed in the previous section and the conductivity in the measured frequency range is the dc conductivity. The ac conductivity only appears at higher frequencies above about 10^5 Hz. As the dose increases the dc and ac conductivity increase as more polarons are produced and some polarons may be trapped in the polymer. The conductivity at higher radiation doses tracks the universal power law of the form $\sigma_{ac}(\omega) = A\omega^s$ (Jonsher, 1976).

G. USING THE COLE-COLE TO DETERMINE THE DC CONDUCTIVITY OF POLYANILINE

The The dc conductivity $\sigma_{dc}(0)$ was determined using the value of resistance, Z_0, by extrapolating or extending


(a)

(b)
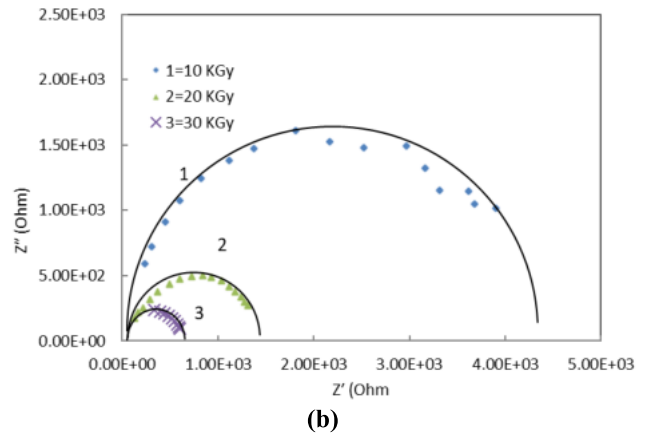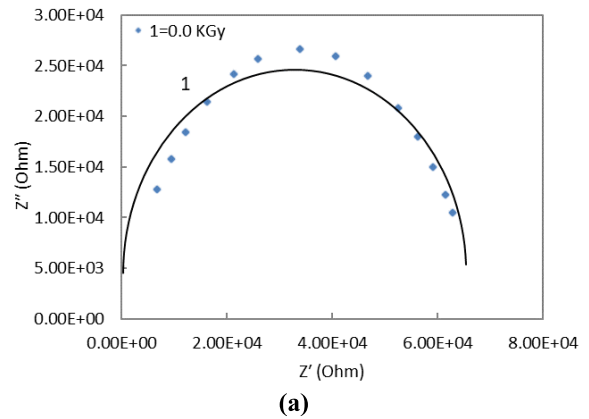
FIGURE 11. Cole-Cole plots versus frequency of PANI/PVA of 5 wt% MgCl₂ composites irradiated of (a) 0.00 KGy and (b) 10, 20, 30 KGy.

the semicircle curve of Cole-Cole plots to zero frequency on the real impedance axis Z', as shown in Figure 11. At short frequency zone for a given radiation dose, the straight-line tack is related to the effect of interstitial electrodes. Mariappan *et al.* (2002) studied that the depressed semicircle at the zone of low frequency is due to parallel combination characteristics of the counterpart of capacitance and resistance for the sample phase element. Whereas Chen *et al.* (2003) described the straight line existence at zone of low frequency which related to the capacitive features of the film of sample [44]–[46].

The dc conductivity component at different doses is shown in Figure 12. At higher radiation doses the formation of polyaniline rises and thus the dc conductivity of conducting polyaniline rises.

H. THE AC CONDUCTIVITY OF POLYANILINE COMPOSITE FILM OF 5 w% MgCl₂

The ac conductivity $\sigma_{ac}(\omega) = A\omega^s$ of PANI/PVA composite film containing 5 wt% MgCl₂ salt irradiated at various doses are shown in Figure 10, which follows (Jonsher, 1976) and is applicable to conducting polymer as well. The incline of the $log\sigma(\omega)$ linear slope verse $log\omega$ is shown in Figure 13. The value of *s* declines alongside of radiation doses as Figure 14
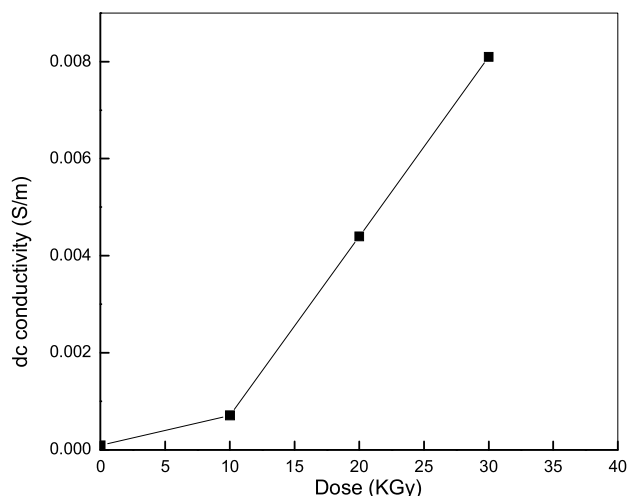
FIGURE 12. DC conductivity of PANI/PVA composite films versus dose for 5 wt% MgCl₂ concentration measured using the Cole-Cole plots.
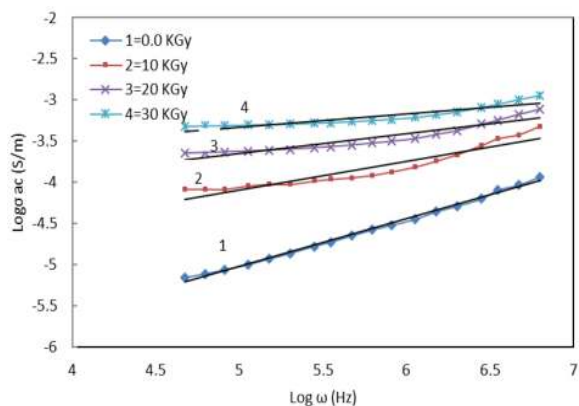
FIGURE 13. Variation of log $\sigma(\omega)$ for 5 wt% MgCl₂ at different radiation doses.

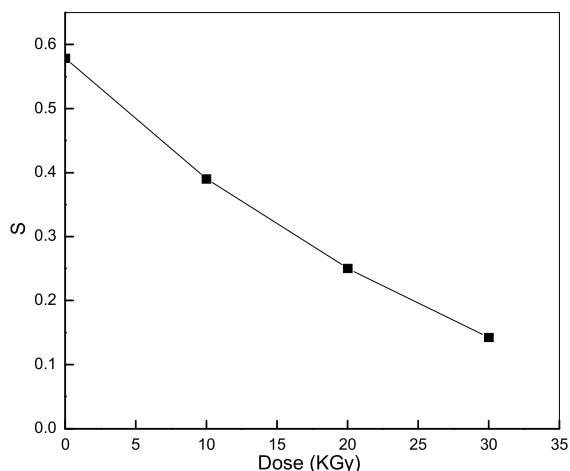**FIGURE 14.** Frequency exponent s for 5 wt% of MgCl₂ at different radiation doses.

has revealed. These outcomes approve the ac conductivity dominion using ionic hopping when $s < 1$.

I. COLOUR CHANGE OF PANI COMPOSITES

The interaction between the ANI-PVA-MgCl₂ films at different radiation doses of 10, 20, and, 30 kGy, γ-radiation and the

PVA healing electrons through the effect of photoelectric and Compton scattering is tracked with ions of H⁺ and OH⁻ thru the bond scission. These ions that association with the closing formation are not considerable. Alternatively, the interact of γ-radiations through the ANI/MgCl₂ is critical related to that the Cl is detached from H⁺ and Cl⁻ ions via emission. The protonation from the aniline through the Cl⁻ formed conducting polyaniline composite may be rendered visible through the adjusting of the colour of none irradiated ANI-PVA-MgCl₂ unify film from pale to light green at radiation of 30 kGy. This is demonstrated in the photographs in Figure 15.
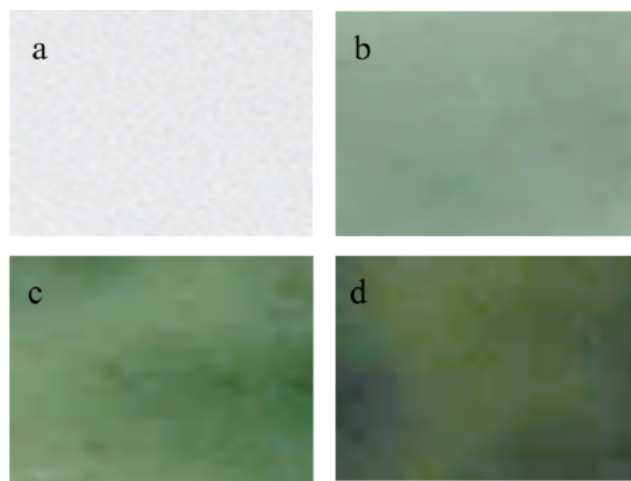
FIGURE 15. The colour of the PANI composite of 5 wt% MgCl₂ through radiation at different doses of (a) 0, (b) 10, (c) 20, and (d) 30 KGy.

Green PANI is generated by the formation of C = N double bonds of imines group. The intensity of hue is increased as the dose increases [47]. Prior to irradiation, the ANI-PVA-MgCl₂ unified films were grey when exposed to the air, thereby indicating the negative pressure in the UV-visible energy in respect of the alignment of the conducting PANI. Once irradiation has been increased to doses between 20 kGy and 30 kGy, a potent light green coloration was observed.

The uniformity generated by the sharing of conducting PANI film is observed in the distribution of the green spectrum in the PVA matrix. The dominance of the energy beam ensures standardization throughout the irradiation and the ANI-PVA-MgCl₂ combination blend during the current study. In order to benefit from the ANI-PVA-MgCl₂ mixed tests and the images taken between the polyethylene layers that built up the inferior charge subdivision stability, an agreement has been constructed. Furthermore, a magnetic mixer in inert nitrogen ambience was used throughout the training to blend the PVA solution and the ANI/MgCl₂ powder constantly for 180 mins.

J. FTIR ANALYSIS

Employing the FTIR spectra, as showed in Figure 16, it has been possible to accrue additional data regarding the chemical composition of PANI/PVA. The stretching vibration of the O-H and N-H bonds of PVA and PANI [33], [48],
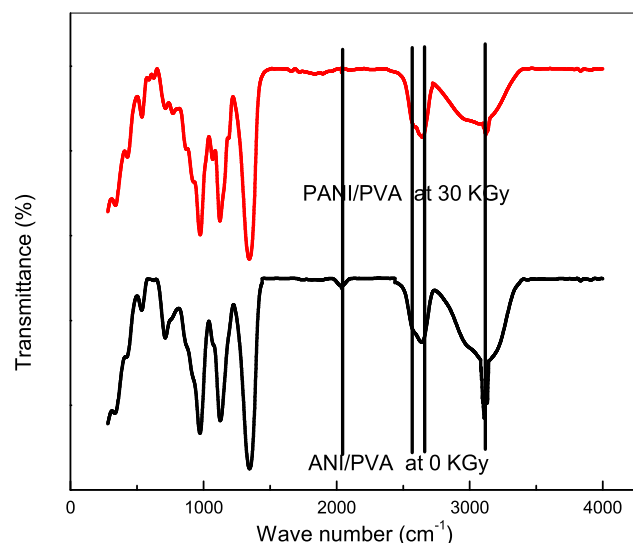
FIGURE 16. FTIR spectra of PANI/PVA composite films.

can be identified as the cause of the visible peaks in the region within ranges of 3400-2350 cm^{-1}. In Figure 16, the value 3140 cm^{-1} denotes the peak of the superposition of multiple polymeric H bonds. This peak has a relationship with both the crystalline and the amorphous stages of conventional semi-crystalline PVA and where the stretching of the O-H bond from the PVA matrix are in evidence [49]. The syndiotactic structure of samples, which matches to C-H vibration, was observed at the peak at 990 cm^{-1}. Moreoever, it is clear that the intensity was decreases after irradiation. These results suggest that hydrogen bonding is weaker due to a reduction in the number of OH groups, and a disturbance in the polymeric due to interruptions from the PANI during irradiation. The plane structure disruption is further maintained via the declining intensity after the irradiation, which approximates absorption bands of 2713, 2610, 2054, and 1307 cm^{-1}, corresponding to C-H stretching, C-H bending, C-H vibrations, and C-O stretching vibrations, respectively [49], [50].

IV. CONCLUSION

This article has discussed the successful synthesis of conducting polyaniline composite film from 10 kGy to 30 kGy doses at ambient surroundings using the gamma radiation method. At high doses, gamma irradiation ANI-MgCl$_2$ undergoes significant chain degradation due to the loss of Cl$^-$, which consequently acts as an oxidant for doping the imines group of aniline and insitu'polymerize aniline monomer into conducting polyaniline in the procedure of emeraldine salt. The dc conductivity of conducting PANI composite was exposed by conductivity measurement. Conductivity principally qualified the establishment of polarons in the PANI arrangement.

Colour change and electrical properties were a variety of ways that approved the configuration of PANI. The dc conductivity of conducting PANI composite augmented beside gamma dose was exposed by the conductivity measurement. Through three folds from 8.29×10^{-5} S/m at a radiation dose

of 10 kGy to 2.29×10^{-1} S/m at a radiation dose of 30 kGy. The conductivity is primarily qualified for the establishment of polarons in the PANI arrangement.

The most excellent electrical and optical properties were found to be surrendered to by conducting PANI prepared from 5 % MgCl$_2$.

REFERENCES

[1] Y. Shan, Z. Lyu, X. Guan, A. Younis, G. Yuan, J. Wang, S. Li, and T. Wu, "Solution-processed resistive switching memory devices based on hybrid organic–inorganic materials and composites," *Phys. Chem.*, vol. 20, no. 37, pp. 23837–23846, 2018.

[2] N. M. Al-Hada, A. M. Al-Ghaili, H. Kasim, M. A. Saleh, M. H. Flaifel, H. M. Kamari, H. Baqiah, J. Liu, and W. Jihua, "The effect of PVP concentration on particle size, morphological and optical properties of cassiterite nanoparticles," *IEEE Access*, vol. 8, pp. 93444–93454, 2020.

[3] N. M. Al-Hada, "Down-top nanofabrication of binary (CdO)$_x$ (ZnO)$_{1-x}$ nanoparticles and their antibacterial activity," *Int. J. Nanomed.*, vol. 12, pp. 8309–8323, Nov. 2017.

[4] N. M. Al-Hada, H. M. Kamari, M. A. Saleh, M. H. Flaifel, A. M. Al-Ghaili, H. Kasim, A. A. Baqer, E. Saion, and W. Jihua, "Morphological, structural and optical behaviour of PVA capped binary (NiO)$_{0.5}$ (Cr$_2$O$_3$)$_{0.5}$ nanoparticles produced via single step based thermal technique," *Results Phys.*, vol. 17, Jun. 2020, Art. no. 103059.

[5] M. L. Foresti, A. Vázquez, and B. Boury, "Applications of bacterial cellulose as precursor of carbon and composites with metal oxide, metal sulfide and metal nanoparticles: A review of recent advances," *Carbohydrate Polym.*, vol. 157, pp. 447–467, Feb. 2017.

[6] Z. Hawash, L. K. Ono, and Y. Qi, "Recent advances in Spiro–MeOTAD hole transport material and its applications in Organic–Inorganic halide perovskite solar cells," *Adv. Mater. Interface*, vol. 5, no. 1, Jan. 2018, Art. no. 1700623.

[7] N. Al-Hada, E. Saion, Z. Talib, and A. Shaari, "The impact of polyvinylpyrrolidone on properties of cadmium oxide semiconductor nanoparticles manufactured by heat treatment technique," *Polymers*, vol. 8, no. 4, p. 113, Apr. 2016.

[8] H. Kamari, N. Al-Hada, E. Saion, A. Shaari, Z. Talib, M. Flaifel, and A. Ahmed, "Calcined solution-based PVP influence on ZnO semiconductor nanoparticle properties," *Crystals*, vol. 7, no. 2, p. 2, Feb. 2017.

[9] A. A. Baqer, K. A. Matori, N. M. Al-Hada, A. H. Shaari, E. Saion, and J. L. Y. Chyi, "Effect of polyvinylpyrrolidone on cerium oxide nanoparticle characteristics prepared by a facile heat treatment technique," *Results Phys.*, vol. 7, pp. 611–619, 2017.

[10] J. G. Ibanez, M. E. Rincón, S. Gutierrez-Granados, M. Chahma, O. A. Jaramillo-Quintero, and B. A. Frontana-Uribe, "Conducting polymers in the fields of energy, environmental remediation, and Chemical–Chiral sensors," *Chem. Rev.*, vol. 118, no. 9, pp. 4731–4816, May 2018.

[11] N. Aydemir, J. Malmström, and J. Travas-Sejdic, "Conducting polymer based electrochemical biosensors," *Phys. Chem.*, vol. 18, no. 12, pp. 8264–8277, 2016.

[12] P. Sengodu, "Conducting polymers/inorganic nanohybrids for energy applications," in *Polymer-Engineered Nanostructures for Advanced Energy Applications*. Springer, 2017, pp. 365–417.

[13] J. Stejskal, "Interaction of conducting polymers, polyaniline and polypyrrole, with organic dyes: Polymer morphology control, dye adsorption and photocatalytic decomposition," *Chem. Papers*, vol. 74, no. 1, pp. 1–54, Jan. 2020.

[14] X. Li, A. Rafie, Y. Y. Smolin, S. Simotwo, V. Kalra, and K. K. S. Lau, "Engineering conformal nanoporous polyaniline via oxidative chemical vapor deposition and its potential application in supercapacitors," *Chem. Eng. Sci.*, vol. 194, pp. 156–164, Feb. 2019.

[15] T. Rauhala, F. Davodi, J. Sainio, O. Sorsa, and T. Kallio, "On the stability of polyaniline/carbon nanotube composites as binder-free positive electrodes for electrochemical energy storage," *Electrochimica Acta*, vol. 336, Mar. 2020, Art. no. 135735.

[16] S. Biswas, Y.-J. You, J. W. Shim, and H. Kim, "Utilization of poly (4-styrenesulfonic acid) doped polyaniline as a hole transport layer of organic solar cell for indoor applications," *Thin Solid Films*, vol. 700, Apr. 2020, Art. no. 137921.

[17] S. Kundu, R. Majumder, R. Ghosh, M. Pradhan, S. Roy, P. Singha, D. Ghosh, A. Banerjee, D. Banerjee, and M. Pal Chowdhury, "Relative humidity sensing properties of doped polyaniline-encased multiwall carbon nanotubes: Wearable and flexible human respiration monitoring application," *J. Mater. Sci.*, vol. 55, no. 9, pp. 3884–3901, Mar. 2020.

[18] N. Zamani, A. R. Modarresi-Alam, M. Noroozifar, and M. Javanbakht, "The improved performance of lithium-ion batteries via the novel electron transport catalytic role of polyaniline (PANI) in PANI/Co$_3$O$_4$–CuO raspberry as new anode material," *J. Appl. Electrochem.*, vol. 49, no. 3, pp. 327–340, Mar. 2019.

[19] J. P. F. Santos, M. Arjmand, G. H. F. Melo, K. Chizari, R. E. S. Bretas, and U. Sundararaj, "Electrical conductivity of electrospun nanofiber mats of polyamide 6/polyaniline coated with nitrogen-doped carbon nanotubes," *Mater. Des.*, vol. 141, pp. 333–341, Mar. 2018.

[20] C. Anju and S. Palatty, "Ternary doped polyaniline-metal nanocomposite as high performance supercapacitive material," *Electrochimica Acta*, vol. 299, pp. 626–635, Mar. 2019.

[21] N. H. I. Hussain, M. K. Mustafa, and S. Asman, "Synthesis of PANI/Iron (II, III) oxide hybrid nanocomposites using sol-gel method," *J. Sci. Technol.*, vol. 10, no. 1, p. 5, 2018.

[22] B. Manjunatha, "Chemical mediated synthesis of polyaniline/tungstenoxide (PANI/WO$_3$) nanocomposites and their antibacterial activity against clinical pathogenic bacteria," *BioNanoScience*, vol. 5, pp. 1–8, Nov. 2019.

[23] Y. He, X. Wang, H. Huang, P. Zhang, B. Chen, and Z. Guo, "*in-situ* electropolymerization of porous conducting polyaniline fibrous network for solid-state supercapacitor," *Appl. Surf. Sci.*, vol. 469, pp. 446–455, Mar. 2019.

[24] S. Bai, Y. Zhao, J. Sun, Z. Tong, R. Luo, D. Li, and A. Chen, "Preparation of conducting films based on $\pm$-MoO$_3$ /PANI hybrids and their sensing properties to triethylamine at room temperature," *Sens. Actuators B, Chem.*, vol. 239, pp. 131–138, Feb. 2017.

[25] M. Revanasiddappa, D. S. Swamy, K. Vinay, Y. Ravikiran, and S. Raghavendra, "Synthesis, characterization and DC conductivity studies of conducting polyaniline/PVA/Fly ash polymer composites," *AIP Conf. Proc.*, vol. 1953, Dec. 2018, Art. no. 090070.

[26] D. Jaaoh, C. Putson, and N. Muensit, "Enhanced strain response and energy harvesting capabilities of electrostrictive polyurethane composites filled with conducting polyaniline," *Composites Sci. Technol.*, vol. 122, pp. 97–103, Jan. 2016.

[27] M. Maruthapandi, L. Eswaran, J. H. T. Luong, and A. Gedanken, "Sonochemical preparation of polyaniline TiO$_2$ and polyaniline SiO$_2$ for the removal of anionic and cationic dyes," *Ultrason. Sonochem.*, vol. 62, Apr. 2020, Art. no. 104864.

[28] S. Zaghlol, W. A. Amer, M. H. Shaaban, M. M. Ayad, P. Bober, and J. Stejskal, "Conducting macroporous polyaniline/poly(vinyl alcohol) aerogels for the removal of chromium(VI) from aqueous media," *Chem. Papers*, vol. 74, no. 9, pp. 3183–3193, Sep. 2020.

[29] A. Alyan, S. Abdel-Samad, A. Massoud, and S. A. Waly, "Characterization and thermal conductivity investigation of copper-polyaniline nano composite synthesized by gamma radiolysis method," *Heat Mass Transf.*, vol. 55, no. 9, pp. 2409–2417, Sep. 2019.

[30] A. Meftah, E. Gharibshahi, N. Soltani, W. Yunus, and E. Saion, "Structural, optical and electrical properties of PVA/PANI/Nickel nanocomposites synthesized by gamma radiolytic method," *Polymers*, vol. 6, no. 9, pp. 2435–2450, Sep. 2014.

[31] R. G. Sonkawade, V. Kumar, L. Kumarc, S. Annapoornic, S. Vaijapurkard, and A. Dhaliwal, "Effects of gamma ray and neutron radiation on Polyanilne conducting polymer," *Indian J. Pure Appl. Phys.*, vol. 48, pp. 453–456, Jul. 2010.

[32] M. Ali, "Chemical modification and control of polyaniline nanocomposites conductivity by radiation technique in PVA matrix," *J. Eng. Sci. Technol*, vol. 2, pp. 280–289, Oct. 2007.

[33] A. Bahrami, K. Behzad, N. Faraji, and A. Kharazmi, "Electrical characteristics of PVA-PANI-ZnS nanocomposite film synthesized by gamma irradiation method," *Mater. Sci.-Poland*, vol. 36, no. 1, pp. 102–106, 2018.

[34] F. A. Mir, A. Gani, and K. Asokan, "Gamma irradiation studies of composite thin films of poly vinyl alcohol and coumarin," *RSC Adv.*, vol. 6, no. 2, pp. 1554–1561, 2016.

[35] S. Sasaki, S. Omata, T. Murakami, N. Nagasawa, M. Taguchi, and A. Suzuki, "Effect of gamma ray irradiation on friction property of Poly(vinyl alcohol) cast-drying on freeze-thawed hybrid gel," *Gels*, vol. 4, no. 2, p. 30, Mar. 2018.

[36] G. Jayson, B. Parsons, and A. J. Swallow, "Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter," *J. Chem. Soc., Faraday Trans.*, vol. 69, pp. 1597–1607, 1973.

[37] N. F. Mott and E. A. Davis, *Electronic Process in Non-Crystalline Materials*, 2nd ed. Oxford, U.K.: Clarendon, 1979.

[38] R. Mishra, "Optical and electrical properties of some electron and proton irradiated polymers," *Nucl. Instrum. Methods Phys. Res. Sect. B, Beam Interact. with Mater. At.*, vol. 168, no. 1, pp. 59–64, 2000. [Online]. Available: http://www.sciencedirect.com/science/article/B6TJN-402K8P8-8/2/33dfb6e34c09608d1ec1ab8cf5d29eb7

[39] D. Zainuddin, J. T. Hill, and T. T. Le, "An ESR study in gamma rdaiation poly(vinylalcohole)," *Radiat. Phys. Chem.*, vol. 62, pp. 283–291, Oct. 2001.

[40] A. F. Nogueira, C. Longo, and M.-A. De Paoli, "Polymers in dye sensitized solar cells: Overview and perspectives," *Coordination Chem. Rev.*, vol. 248, nos. 13–14, pp. 1455–1468, Jul. 2004.

[41] R. Komiya, L. Han, R. Yamanaka, A. Islam, and T. Mitate, "Highly efficient quasi-solid state dye-sensitized solar cell with ion conducting polymer electrolyte," *J. Photochem. Photobiol. A, Chem.*, vol. 164, nos. 1–3, pp. 123–127, Jun. 2004.

[42] C.-H. Tsao, H.-M. Su, H.-T. Huang, P.-L. Kuo, and H. Teng, "Immobilized cation functional gel polymer electrolytes with high lithium transference number for lithium ion batteries," *J. Membrane Sci.*, vol. 572, pp. 382–389, Feb. 2019.

[43] N. M. A. Al-Hada, "Radiation-induced Synthesis, electrical and optical characterization of conducting polyaniline of PVA/aniline/MgCl$_2$ and PVA/aniline/CaCl$_2$ composites," Universiti Putra Malaysia, Kembangan, Malaysia, Tech. Rep. FS 2011 9, 2011.

[44] C. R. Mariappan and G. Govindaraj, "AC conductivity, dielectric studies and conductivity scaling of NASICON materials," *Mater. Sci. Eng., B*, vol. 94, no. 1, pp. 82–88, Jun. 2002.

[45] E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy: Theory, Experiment, and Applications*. Hoboken, NJ, USA: Wiley, 2018.

[46] A. Michalska, and K. Maksymiuk, "Optimization of capacitance of conducting polymer solid contact in ion-selective electrodes," *Electrochimica Acta*, vol. 187, pp. 397–405, Jan. 2016.

[47] M. A. Omer, E. Saion, M. G. Elnabi, and K. M. Dahlan, "Synthesis of polyaniline HCl pallets and films nanocomposites by radiation polymerization," *Gamma Radiat.*, vol. 4, p. 115, Oct. 2012.

[48] A. Shehap, "Thermal and spectroscopic studies of polyvinyl alcohol/sodium carboxy methyl cellulose blends," *Egypt. J. Solids*, vol. 31, no. 1, pp. 75–91, 2008.

[49] O. Norfazlinayati, Z. Talib, N. Nik Salleh, A. Shaari, and H. M. Hamzah, "Synthesis and characterization of polyvinyl alcohol/polyaniline/functionalized multiwalled carbon nanotube composite by gamma radiation method," *Int. J. Nanoelectron. Mater.*, vol. 11, no. 4, pp. 435–448, 2018.

[50] R. M. Silverstein and G. C. Bassler, "Spectrometric identification of organic compounds," *J. Chem. Edu.*, vol. 39, no. 11, p. 546, Nov. 1962.

NAIF MOHAMMED AL-HADA received the B.Sc. degree in physics from Thamar University, Yemen, in 2002, and the M.Sc. degree in applied radiation physics and the Ph.D. degree in nanoscience and nanotechnology from Universiti Putra Malaysia (UPM), in 2011 and 2015, respectively. From 2015 to 2019, he was appointed as a Postdoctoral Researcher with the Department of Physics, UPM. From June 2019 to October 2019, he was a Visiting Researcher with Universiti Teknologi Malaysia (UTM), Malaysia. Since October 2019, he has been a Lecturer with the Shandong Key Laboratory of Biophysics, Dezhou University (DZU), China. His research interests include nanoparticles synthesis and applications, metallic oxides nanostructures and its antibacterial activity, binary oxide nanostructures for solar cell and sensor applications, renewable energy, polymer composites/nanocomposites, conducting polymer nanocomposites, semiconductor nanotechnology, and applied radiation.

ABBAS M. AL-GHAILI received the B.Eng. degree (Hons.) in computer engineering from the University of Science and Technology, Sana'a, Yemen, in 2005, and the M.Sc. and Ph.D. degrees in computer systems engineering from Universiti Putra Malaysia (UPM), Serdang, Malaysia, in 2009 and 2013, respectively. Since February 2018, he has been a Postdoctoral Researcher with the Institute of Informatics and Computing in Energy (IICE), Universiti Tenaga Nasional (UNITEN), Malaysia. His research interests include image processing, artificial intelligence, and energy informatics. He is a member of the International Association of Computer Science and Information Technology and the Universal Association of Computer and Electronics Engineers.

HAIROLADENAN KASIM is currently a Senior Lecturer with the College of Computing and Informatics (CCI), UNITEN, Kajang, Malaysia. His research interests include energy informatics and energy and computing.

MUNEER AZIZ SALEH received the B.Sc. degree in physics from Sana'a University, Yemen, the M.Sc. degree in applied physics from the National University of Malaysia, Malaysia, and the Ph.D. degree from University Technology Malaysia (UTM), in January 2014. He is currently a Lecturer with the Nuclear Engineering Program, Faculty of Chemical and Energy Engineering, UTM. His research interests include environmental radiology, radiation dosimetry, nuclear powerplant siting, radiation protection, and reactor physics.

ELIAS SAION received the B.Sc. degree (Hons.) from Universiti Kebangsaan Malaysia, in 1975, the M.Sc. degree from the University of Survey, in 1978, and the Ph.D. degree from the University of St Andrews, U.K., in 1989. He joined UPM, in 1976. He is currently a Professor at Universiti Putra Malaysia (UPM), where he leads the fundamental and applied researches in ionizing radiation and nanoscience at the Department of Physics. His major research areas include the radiation synthesis of conducting polymers, ionic electrolytes, metal nanoparticles, semiconductor quantum dots, nanocrystals, and the diagnostic medical physics and quantum computing of nanostructures. He is the pioneer in the radiation synthesis of conducting polymers and the quantum mechanical calculations of the optical absorption spectra of metal nanoparticles. His calculation successfully describes quantum mechanically the electronic structures of the conduction electrons of metallic nanoparticles, with otherwise were based on the classical electrodynamic description of the Mie's theory.

JIAN LIU received the B.S. degree in biotechnology from Yantai University, China, in 2003, the M.Sc. degree in genetics from Nanjing Agriculture University, China, in 2007, and the Ph.D. degree in microbial and enzymatic engineering from INSA-Toulouse, France, in 2015. From 2015 to 2017, he was appointed as a Postdoctoral Researcher at Toulouse White Biotechnology, France. Since June 2018, he has been a Lecturer with the Shandong Key Laboratory of Biophysics, Dezhou University (DZU), China. His research interests include microbiology, microbiome, plant disease, and biotechnology.

WANG JIHUA is currently the Director of the Institute of Biophysics, Dezhou University, China. He is also a Ph.D. Tutor with Shandong Normal University. He is a Council Member of the Chinese Biophysics Society. He has published more than 70 articles in well-known journals, such as *Nucleic Acids Research*, *Nature Communications*, *Biophysical Journal*, *Physics Review*, *Journal of Theoretical Biology*, and *Biophysics* journal. He holds five national patents. His research interests include long non-coding RNAs, intrinsically disordered proteins, and modern biophysical cross-discipline technologies. He received the Special Allowance of the State Council and is nominated as Scientists with Outstanding Contribution of Shandong. He has undertaken more than ten scientific research funds, including funds from the National Science Foundation of China.

• • •