UNIVERSITI PUTRA MALAYSIA

RADIATION AND TEMPERATURE EFFECTS ON OPTICAL AND ELECTRICAL PROPERTIES OF DYED POLY (VINYL ALCOHOL) ORGANIC COMPOSITES CONTAINING CHLORINE

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By

SUSILAWATI

Thesis Submitted to the School of Graduate Studies,
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for the Degree of Doctor of Philosophy

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DEDICATION

I dedicate this thesis special for my father Hj. Hambali, S.G B.A, my mother Hjh. Ahilmi, my husband Aris Doyan, PhD and my sons Muhammad Ikhsan, Ikhlasul Amal, and my late daughter Kurnia Ramadhani. I also dedicate this thesis to all my family.

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirement for the degree of Doctor of Philosophy

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Chairman: **Associate Professor Elias Saion, PhD**

Faculty: **Science**

The effects of radiation on dyed PVA-based organic blends containing chlorine have been studied for their potential applications in radiation dosimetry as well as in optical and electrochemical devices. The PVA-CH, PVA-TCA and PVA-TCE blends were doped with cresol red and blended separately with 23, 34, 45 and 57% CH and 20, 25, 30 and 35% TCA and TCE. The composite films were prepared by solvent-casting method and each film has been irradiated with γ-rays at different doses up to 12 kGy. The dosimetric and optical properties have been studied using Raman spectrometer and UV-VIS spectrophotometer in the wavelength range of 200 – 800 nm. The electrical properties have been studied using LCR meter, an impedance analyzer in the frequency range from 20 Hz to 1 MHz.

The dosimetric study has shown that the absorption spectra of the irradiated PVA-CH composite films change color from yellow to red, but for the irradiated PVA-TCA and PVA-TCE blends, the films change color from purple to yellow. The change in color is because of the lowering the pH in the films caused by the presence of acid generated by γ-ray interaction with CH, TCA and TCE. The useful critical dose at changing colour increases linearly with decreasing CH, TCA and TCE compositions in the range of (5.2 - 8.9), (5.0 - 7.5) and (6.0 - 8.7) kGy for PVA-CH, PVA-TCA and PVA-TCE respectively. The indirect dose response obtained from the absorbance at the absorption peaks has resulted in the linear increase of the dose sensitivity parameter D_0 with the increase of CH, TCA and TCE compositions. This has been confirmed by the direct dose response obtained from a decrease in the intensity of C-Cl bond of CH, TCA and TCE molecules due to radiation scission using Raman spectroscopy technique, which has resulted in the increase of D_0 with increasing CH, TCA and TCE compositions.

The optical absorption study has revealed that the absorption coefficient α increases with photon energy that is higher than the absorption edges with decreasing dose in range of (4.62 - 5.08), (4.00 - 4.74) and (4.44 - 4.88) eV for PVA-CH, PVA-TCA and PVA-TCE respectively for decreasing blend composition. The exponential relationship between the absorption coefficient and photon energy revealed that decreasing of Urbach's energy or optical activation energy ΔE with the increase of dose in the range of (0.69 - 0.64),

(0.68 – 0.61) and (0.72 – 0.65) eV for PVA-CH, PVA-TCA and PVA-TCE respectively for increasing blend composition. The direct band gap energy E_g obtained decreases with the increase of dose in the range of (4.12 – 4.02), (5.04 – 4.56) and (5.07 – 4.90) eV for PVA-CH, PVA-TCA and PVA-TCE respectively for increasing blend composition. While the indirect optical band gap energy E_g decreases with increasing dose in the range of (4.05 – 3.64), (3.8 – 3.44) and (4.62 – 4.23) eV for PVA-CH, PVA-TCA and PVA-TCE respectively for increasing blend composition. These changes are attributed to the radiation effect on the optical transitions of electrons from donor atoms to acceptor atoms in the electronic structure of the composites.

The conductivity-dose relation study revealed that increase in conductivity of the irradiated PVA-CH, PVA-TCA and PVA-TCE blends with increasing dose up to 12 kGy. The increase in the conductivity with dose is attributed to the increase of ionic carriers in the composites induced by radiation scission of CH, TCA and TCE molecules and also due to hydrolysis of water. The conductivity spectra consist of frequency-independent dc component and frequency-dependent ac component. The flat response of dc conductivity has been attributed to free ions and has Arrhenius type relationship with dose that resulted in dose sensitivity D_0 increases with increasing blend composition. The power law type response of ac conductivity has been attributed to hopping of ions trapped in the localized sites of the PVA matrix and resulted in frequency exponent s decreases with increasing blend

composition. The conductivity-temperature relation study revealed that an increase conductivity of the unirradiated PVA-CH, PVA-TCA and PVA-TCE blends with increasing temperature up to 353 K. The increase of conductivity with temperature is attributed to the increase of free ion mobility due to thermal energy kT and possible more ions gained kinetic energy via the thermally activated hopping of charge carriers between trapping sites and phonon-assisted quantum tunneling through a barrier separating two equilibrium positions. The conductivity activation energy obtained decreases with the blend composition increases.

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 dipoles in the polymer system. The increase in dielectric loss ε'' with increasing dose can be attributed to dielectric dipole relaxation and dc conductivity of free ions in the blends. The dose sensitivity D_0 obtained increases with increasing blend composition. The dielectric-temperature relation study revealed that an increase of the dielectric constant ε' with temperature can be attributed to the increase in the ability of dipoles to rotate towards the applied field as the binding forces between ions and atoms become weak with increasing temperature in the so called free volume effect. The increase in ε'' value with temperature increase can be attributed to the dc conduction process where the charge carriers gained kinetic energy via the thermal energy kT, thus increase the mobility of the

free ions and the dielectric loss value. The electric activation energy obtained decreases with the blend composition increases.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Doktor Falsafah

KESAN SINARAN DAN SUHU KE ATAS SIFAT OPTIK DAN ELEKTRIK BAGI POLY (VINYL ALKOHOL) BERPERWARNA MENGANDUNGI SEBATIAN ORGANAN BERKLORIN

Oleh

SUSILAWATI

April 2005

Pengerusi: Profesor Madya Elias Saion, PhD

Fakulti : Sains

Kesan sinaran terhadap campuran polimer berasaskan PVA berperwarna yang mengandungi sebatian organan berklorin telah diselidiki untuk menunjukkan keupayaan aplikasinya dalam dosimetri sinaran dan peranti optik dan elektrokimia. Komposit PVA-CH, PVA-TCA dan PVA-TCE telah didopkan dengan perwarna cresol merah dan dicampurkan secara berasingan dengan sebatian organan pada komposisi 23, 34, 45 and 57% CH dan 20, 25, 30 and 35% TCA dan TCE. Film komposit disediakan dengan kaedah kimia acuan pelarut dan setiap film itu telah disinarkan dengan sinar-γ pada dos yang berbeza sehingga 12 kGy. Pengkajian sifat-sifat dosimetri dan optik telah diselidiki dengan menggunakan kaedah spektroskopi Raman dan spektrofotometer UV-VIS dalam julat panjang gelombang 200 - 800 nm. Pengkajian sifat-sifat elektrik pula telah diselidik

dengan menggunakan meter LCR, melibatkan analisis impedans dalam julat frekuensi daripada 20 Hz hingga 1 MHz.

Pengkajian dosimetri menunjukkan bahawa spektra penyerapan film PVA-CH tersinar telah berubah daripada warna kuning kepada warna merah, sedangkan bagi film PVA-TCA dan PVA-TCE tersinar perubahan berlaku daripada warna ungu kepada warna kuning. Perubahan warna ini disebabkan penurunan pH dalam yang tersebut dihasilkan oleh pertambahan asid kerana tindakan sinar-γ dengan sebatian CH, TCA dan TCE. Didapati bahawa dos kritikal di mana berlaku pertukaran warna akan berkurangan secara linear dengan pertambahan komposisi CH, TCA dan TCE iaitu dalam julat (5.2 - 8.9), (7.5 - 5) dan (8.7 - 6) kGy untuk masing-masing PVA-CH, PVA-TCA dan PVA-TCE. Sambutan dos secara tak terus didapati daripada penyerapan pada puncak penyerapan dan menghasilkan parameter dos kepekaan D_0, yang bertambah secara linear dengan komposisi CH, TCA and TCE. Ini telah disahkan dengan kaedah sambutan dos secara terus yang diperolehi daripada pengurangan keamatan ikatan C-Cl bagi CH, TCA dan TCE kerana tindakan sinar-γ secara kaedah spektroskopi Raman yang juga menghasilkan parameter dos kepekaan D_0 yang bertambah dengan komposisi CH, TCA and TCE.

Pengkajian sifat optik menunjukkan bahawa pekali penyerapan α bertambah dengan pertambahan tenaga foton yang melebihi tenaga sisi penyerapan

dengan pengurangan nilai dos dalam julat (4.62 – 5.08), (4.00 – 4.74) dan (4.44 – 4.88) eV bagi masing-masing PVA-CH, PVA-TCA dan PVA-TCE untuk komposisi berkurang. Hubungan bereksponen antara pekali penyerapan dan tenaga foton telah menunjukkan bahawa tenaga Urbach atau tenaga pengaktifan optik berkurangan dengan pertambahan dos dalam julat (0.69 – 0.64), (0.68 – 0.61) and (0.72 – 0.65) eV bagi masing-masing PVA-CH, PVA-TCA and PVA-TCE untuk komposisi yang bertambah. Jurang tenaga terus E_g berkurangan dengan penambahan dos dalam julat (4.17 – 4.02), (5.04 – 4.56) and (5.07 – 4.90) eV bagi masing-masing komposit PVA-CH, PVA-TCA dan PVA-TCE untuk komposisi yang bertambah. Manakala jurang tenaga takterus E_g berkurangan dengan pertambahan dos dalam julat (4.05 – 3.64), (3.8 – 3.44) and (4.62 – 4.23) eV bagi masing-masing PVA-CH, PVA-TCA dan PVA-TCE untuk komposisi yang bertambah. Perubahan ini disebabkan oleh kesan sinaran terhadap peralihan optik bagi electron dari atom penderma ke atom penerima bagi struktur elektronik komposit tersebut.

Pengkajian tentang hubungan kekonduksian-dos menunjukkan bahawa penambahan kekonduksian PVA-CH, PVA-TCA dan PVA-TCE tersinar dengan penambahan dos sehingga kepada 12 kGy. Penambahan kekonduksian elektrik disebabkan oleh penambahan pembawa ion yang diinduksikan oleh pemecahan ikatan molekul sebatian CH, TCA dan TCE oleh sinaran dan juga oleh ion hasil daripada hidrolisis air. Spektra kekonduksian terdiri daripada komponen arus terus (a.t) yang tak bersandar

kepada frekuensi dan komponen arus ulangalik (a.u) yang bersandar kepada frekuensi. Sambutan kekonduksian a.t yang mendatar adalah disebabkan oleh ion-ion bebas dan mempunyai hubungan jenis Arrhenius yang menghasilkan parameter dos kepekaan D_0 bertambah dengan peningkatan komposisi campuran. Sambutan jenis hukum kuasa bagi kekonduksian a.u pula disebabkan oleh mekanisma loncatan (hopping) ion-ion antara kedudukan setempat bagi ion-ion yang terperangkap dalam polimer matrik PVA yang menghasilkan eksponen frekuensi s berkurangan dengan peningkatan komposisi. Pengkajian tentang hubungan kekonduksian-suhu menunjukkan bahawa penambahan kekonduksian komposit PVA-CH, PVA-TCA dan PVA-TCE tak tersinar kepada suhu sehingga 353 K. Penambahan kekonduksian dengan suhu disebabkan pertambahan kelincahan ion bebas setelah menerima tenaga terma kT dan kemungkinan juga oleh banyak ion menambahkan tenaga kinetik melalui mekanisma lompatan pembawa cas antara kedudukan-kedudukan terhalang dan juga oleh terowong terkuantum dengan bantuan fonon melalui satu hadangan yang memisahkan antara dua kedudukan keseimbangan. Tenaga pengaktifan kekonduksian yang dihasilkan berkurangan nilainya dengan komposisi yang bertambah.

Pengajian tentang hubungan dielektrik-dos menunjukkan bahawa penambahan pemalar dielektrik ε′ dengan peningkatan dos kerana orientasi pengutupan dalam sistem polimer. Penambahan lesapan dielektrik ε″ pula

disebabkan oleh santaian dwikutub dan kekonduksian a.t bagi ion bebas dalam komposit tersebut. Parameter dos kepekaan D_0 yang dihasilkan bertambah dengan komposisi campuran. Pengkajian tentang hubungan dielektrik-suhu menunjukkan bahawa penambahan pemalar dielektrik ε' dengan peningkatan suhu disebabkan oleh keupayaan dwikutub untuk berputar ke arah medan kerana ikatan daya antara ion-ion dan atom-atom bertambah longar kerana kesan isipadu bebas bertambah dengan suhu. Penambahan lesapan dielektrik ε'' dengan suhu pula disebabkan oleh proses kekonduksian a.t yang mana pembawa cas meningkatkan tenaga kinetik melalui tenaga terma kT dan dengan demikian menambahkan kelincahan ion bebas dan menambahkan nilai lesapan dielektrik. Tenaga pengaktifan elektrik yang dihasilkan berkurangan nilainya dengan komposisi yang bertambah.

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