



UNIVERSITI PUTRA MALAYSIA

**EFFECT OF RADIATION ON DOSIMETRIC AND OPTICAL
PROPERTIES OF DYED PVA/CH AND DYED PVB/CH BLENDS**

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By

AZLINA BINTI BAHA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirements for the Degree of Master of Science**

July 2005



DEDICATIONS

*To my lovely husband, Abd. Aziz Sadri,
my father, Baha Yeop and my mother, Sitah Alang Aziz, and family
for their love, support and concern....*



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Master of Science

EFFECTS OF RADIATION ON DOSIMETRIC AND OPTICAL PROPERTIES OF DYED PVA/CH AND DYED PVB/CH BLENDS

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July 2005

Chairman : Assc. Prof. Dr. Zainal Abidin Talib

Faculty : Faculty of Science

Crystal violet doped polyvinyl alcohol blended with chloral hydrate (CV doped PVA/CH) and methyl green doped polyvinyl butyral blended with chloral hydrate (MeG doped PVB/CH) films were prepared by solvent casting method. The blends were irradiated with γ radiation at doses of up to 110 kGy. The dosimetric and optical characteristics of the irradiated and unirradiated polymer blends were studied using UV-Vis-NIR and Raman Spectrometer.

The CV doped PVA/CH blends change colour from violet to blue at high dose (40 to 60 kGy) before bleaching at higher doses due to the formation of acid by radiation induced dechlorination of CH. The absorption spectra was measured and analysis spectrometrically. The absorbance at the absorption band at 590 nm, the characteristic of



violet colour, decreases with increasing dose. The dose sensitivity D_0 increases where the values were 54.6, 81.9, 84.0 and 117.6 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively. On the other hand, the absorbance at the absorption band at 620 nm, the characteristic of blue colour, also decreases with increasing dose. The dose sensitivity D_0 increases where the values were 81.9, 94.3, 100.0 and 109.1 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively. The consumption of CH has been studied using Raman spectroscopy by observing the reduction of C-Cl bond peak intensity at 780 cm^{-1} . The Raman intensity decreases with increasing absorbed dose, which produces the dose sensitivity D_0 where the values were 35.3, 52.6, 98.0 and 114.9 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively.

The influence of γ rays on CV doped PVA/CH and MeG doped PVB/CH blend films leads to bond scission and structural order/disorder changes, which reflected in the electronic transitions in the film and can be described by the empirical Urbach rule. The absorption edge, E_{opt} for CV doped PVA/CH decreases strongly with the increase of absorbed dose. However, it decreases slightly with the increase of CH concentration. The overall values decrease from 3.74 eV to 3.22 eV for doses up to 110 kGy and CH concentration from 2 g to 5 g. The optical activation energy, ΔE increases from 0.282 to 0.524 eV with the increase of CH concentration from 2 g to 5 g CH respectively at zero dose. The value does not change significantly with the change of dose from 20 kGy to 80 kGy and CH concentration from 2 g to 5 g CH. The values obtained are from 0.62 to 0.71 eV. At dose 100 kGy, ΔE is higher from 0.834 eV to 0.908 eV for CH concentration at 2 g to 5 g CH, except at 3 g the value was found to be 1.025 eV. The



optical energy band gap, E_g value for CV doped PVA/CH blend films decreases with increasing dose and CH concentration for direct and indirect allowed transitions. The values of the direct optical energy band gap, E_g are from 3.64 eV to 4.00 eV, while for indirect optical band gap are from 2.84 eV to 3.60 eV.

The MeG doped PVB/CH blends show no colour change but starts to bleach at lower γ -ray doses of 25 kGy. The absorbance at the absorption band at 425 nm, the characteristic of yellow colour, decreases with increasing dose. The dose sensitivity D_0 increases where the values were 13.5, 16.7, 18.7 and 23.0 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively. On the other hand, the absorbance at the absorption band at 650 nm, the characteristic of green colour, also decreases with increasing dose. The dose sensitivity D_0 increases where the values were 14.5, 16.4, 19.5 and 20.9 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively. Analysis from Raman spectra show that the intensity of C-Cl bond at 780 cm^{-1} decreases with increasing absorbed dose. The dose sensitivity D_0 increases where the values were 8.2, 9.5, 15.5 and 20.5 kGy for CH concentration at 2.0, 3.0, 4.0 and 5.0 g CH respectively.

The absorption edge, E_{opt} for MeG doped PVB/CH decreases strongly with the increase of absorbed dose. Nevertheless, it decreases slightly with the increase of CH concentration. The overall values decrease from 3.68 eV to 3.25 eV for doses up to 25 kGy and CH concentration from 2 g to 5 g CH. The optical activation energy, ΔE increases with increasing of doses and CH concentration. The value does not change significantly at zero dose where the value obtained from 0.1010 to 0.1404 eV for 2 g to 5

g CH respectively. The overall values increase from 0.1010 eV to 0.7355 eV for doses up to 25 kGy and CH concentration from 2 g to 5 g CH. The optical energy band gap, E_g value for MeG doped PVB/CH blend films decreases with increasing dose and CH concentration for direct and indirect allowed transitions. The values of the direct optical energy band gap, E_g are from 3.79 eV to 3.57 eV, while for indirect optical band gap are from 3.62 eV to 2.90 eV.

In conclusion, was shown radiation effects by γ -rays on CV doped PVA/CH and MeG doped PVB/CH blend films, which affected the dosimetric and optical properties, could be evaluated with suitable reproducibility by measuring the optically stimulated.



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**KESAN RADIASI TERHADAP CIRI-CIRI PENGUKUR DOS DAN OPTIK
BAGI FILEM CAMPURAN PVA/CH DAN PVB/CH YANG BERWARNA**

Oleh

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July 2005

Pengerusi : Prof. Madya Dr. Zainal Abidin Talib

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Cristal ungu yang didopkan bersama campuran polivinil alcohol dengan kloral hidrat (CV dop PVA/CH) dan metil hijau yang didopkan bersama campuran polivinil butiral dengan kloral hidrat (MeG dop PVB/CH) disediakan dengan menggunakan teknik acuan. Filem tersebut diradiasikan dengan sinar γ sehingga 110 kGy. Ciri-ciri pengukur dos dan optik bagi campuran CV dop PVA/CH and MeG dop PVB/CH dianalisis menggunakan alat UV-Vis-NIR dan Raman Spektrometer.

Campuran CV dop PVA/CH bertukar warna dari warna ungu ke warna biru pada purata dose dari 40 hingga 60 kGy sebelum meluntur warna pada dos yang lebih tinggi hasil dari pembentukan asid kesan dari radiasi yang menyebabkan pengklorinasi CH. Spektrum serapan telah diukur dan dianalisis. Penyerapan pada puncak 590 nm,



mencirikan warna ungu menurun dengan peningkatan dos. Sensitiviti dos, D_0 meningkat di mana nilainya adalah 54.6, 81.9, 84.0 and 117.6 kGy bagi kandungan CH 2.0, 3.0, 4.0 dan 5.0 g masing-masing. Selain itu, penyerapan pada puncak 620 nm yang mencirikan warna biru juga menurun dengan peningkatan dos. Sensitivity dos, D_0 menurun di mana nilainya adalah 81.9, 94.3, 100.0 and 109.1 kGy bagi kandungan CH pada 2.0, 3.0, 4.0 dan 5.0 g masing-masing. Kepenggunaan CH telah dikaji menggunakan Raman spectrometer dengan memerhati penurunan keamatan ikatan C-Cl pada 780 cm^{-1} . Keamatan ikatan C-Cl menurun dengan peningkatan dos, di mana sensitiviti dos, D_0 adalah 35.3, 52.6, 98.0 and 114.9 kGy bagi kandungan CH masing-masing pada 2.0, 3.0, 4.0 dan 5.0 g.

Kesan sinar γ terhadap campuran CV dop PVA/CH dan MeG dop PVB/CH memutuskan ikatan dan berlaku perubahan struktur bahan, yang mana memberi kesan terhadap peralihan elektronik di dalam sampel seperti yang dinyatakan oleh hukum Urbach. Nilai E_{opt} bagi CV dop PVA/CH didapati jelas berkurang dengan peningkatan dos tetapi tidak jelas dipengaruhi oleh kandungan CH. Keseluruhan nilainya adalah dari 3.74 eV hingga 3.22 eV pada kandungan CH masing-masing dari 2.0 hingga 5.0 g setelah diradiasikan sehingga 100 kGy. ΔE meningkat dari 0.282 hingga 0.524 eV bagi kandungan CH dari 2.0 hingga 5.0 g pada 0 kGy. Nilai ΔE tidak jelas berubah dari dos 20 kGy hingga 80 kGy masing-masing pada 2.0 dan 5.0 g CH. Nilai yang diperolehi adalah dari 0.62 to 0.71 eV. Pada dos 100 kGy, ΔE lebih jelas meningkat dari 0.834 eV to 0.908 eV masing-masing pada kandungan 2.0 dan 5.0 g CH, kecuali pada 3.0 g CH di mana nilainya adalah 1.025 eV. Nilai E_g oleh campuran CV dop PVA/CH menurun dengan



peningkatan dos dan kandungan CH bagi $m=1/2$ dan $m=2$. Nilai E_g bagi $m=1/2$ adalah dari 3.64 eV to 4.00 eV, sementara itu bagi $m=2$ pula adalah dari 2.86 eV hingga 3.60 eV.

Bagi campuran MeG dop PVB/CH telah menunjukkan tiada berlaku perubahan warna, tetapi mula meluntur pada purata dos kurang dari 25 kGy. Penyerapan pada puncak 425 nm, mencirikan warna kuning menurun dengan peningkatan dos. Sensitiviti dos, D_0 meningkat di mana nilainya adalah 13.5, 16.7, 18.7 and 23.0 kGy bagi konsentrasi CH 2.0, 3.0, 4.0 dan 5.0 g masing-masing. Pada masa yang sama, penyerapan pada puncak 625 nm yang mencirikan warna hijau juga menurun dengan peningkatan dos. Sensitivity dos, D_0 menurun di mana nilainya adalah 14.5, 16.4, 19.5 and 20.9 kGy bagi konsentrasi CH pada 2.0, 3.0, 4.0 dan 5.0 g masing-masing. Analisis dari Raman spectrometer menunjukkan keamatan ikatan C-Cl menurun dengan peningkatan dos. Sensitiviti dos, D_0 di mana nilainya adalah 8.2, 9.5, 15.5 and 20.5 kGy bagi kandungan CH masing-masing pada 2.0, 3.0, 4.0 dan 5.0 g.

Nilai E_{opt} for campuran MeG dop PVB/CH jelas menurun dengan peningkatan dos tetapi ia tidak jelas kelihatan menurun dengan peningkatan kandungan CH. Nilai keseluruhannya menurun dari 3.68 eV hingga 3.25 eV sehingga dos 25 kGy dan pada kandungan CH dari 2.0 g hingga 5.0 g. Nilai ΔE didapati meningkat dengan pertambahan dos dan juga kandungan CH. Nilainya tidak jelas berubah pada dos 0 kGy iaitu dari 0.1010 hingga 0.1404 eV pada masing-masing 2g dan 5g. Nilai keseluruhannya meningkat dari 0.1010 eV hingga 0.7355 eV pada dos sehingga 25 kGy dan pada kandungan CH dari 2 g hingga 5 g. Nilai E_g bagi campuran MeG dop PVB/CH



menurun dengan peningkatan dos dan kandungan CH bagi $m=1/2$ dan $m=2$. nilai E_g pada $m=1/2$ adalah 3.79 eV to 3.57 eV, sementara itu nilai E_g pada $m=2$ adalah dari 3.62 eV hingga 2.90 eV.

Didapati bahawa filem blend CV dop PVA/CH dan MeG dop PVB/CH yang diradiasikan dengan sinar γ memberikan kesan terhadap ciri-ciri pengukur dos dan optik.



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