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Effects of electron beam irradiation on properties of corn starch undergone periodate oxidation mechanism blended with polyvinyl alcohol

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ABSTRACT

This work was performed to examine the properties of pristine PVOH and PVOH-starch blends under exposure of different irradiation dosages. The periodate oxidation method was used to produce dialdehyde starch. The application of low dosages of electron beam irradiation (≤10 kGy) has improved the tensile strength by forming crosslinking networks. However, the tensile strength drastically declined when radiated at 30 kGy due to the reduction of available hydroxyl groups inside polymer matrix for intermolecular interaction. Also, the incorporation of corn starch and dialdehyde starch has significantly reduced the melting temperature and enthalpy of melting of PVOH blends due to cessation of the hydrogen bonding between PVOH and starch molecules. The crystallite size for deflection planes (101), (10$\bar{1}$) and (200) for all PVOH blends was significant reduced when irradiated. The electron beam irradiation has also weakened the hydrophilic characteristic of all PVOH blends as evidenced in infrared and microscopy analysis.

1. Introduction

Nowadays, the synthetic and non-biodegradable polymer materials have been widely applied in human daily life and various applications in industry. However, the increasing of synthetic and non-degradable polymer materials usage in human daily life have caused serious environmental problem due to accumulation of non-degradable polymer solid wastes [1–3]. Hence, biodegradable polymer materials such as polyvinyl alcohol (PVOH), polylactic acid (PLA), blends of starch (polysaccharides) and biodegradable polymer etc. are considered as promising alternatives to replace the usage of non-biodegradable polymer materials [4–5]. Currently, the development of biodegradable polymer materials such as polyvinyl alcohol (PVOH), starch (polysaccharides) based materials, polylactic acid, etc. have rapidly increased due to its environmental friendly characteristic can reduce the pollution problem caused by accumulation of polymer solid waste [1,6–8]. PVOH is a one of the most commonly used synthetic biodegradable polymers in food packaging and biomedical industries. The high melting temperature of PVOH is mainly attributed to the high crystallinity of polymer matrix and also the existence of strong hydrogen bonding among hydroxyl groups (O—H) in polymer matrix PVOH [9]. PVOH has been widely used in food packaging application due to its excellent performances in mechanical, optical and physical properties [4,10–11]. However, the applications of PVOH in various industries are limited due to its expensive price [4].

On the other hand, starch is a multi-hydroxyl polymer with the presence of vast intermolecular and intramolecular hydrogen bonds in the structure of granule [12]. Starch is widely used to blend with synthetic biodegradable polymers such as PVOH, polylactic acid, chitosan [13,14] to reduce the cost of polymer blends. Various modification methods of native starch have been carried out by many researchers to improve the irregularity problem of starch particles in the polymer matrix such as PLA/starch blends and PVOH-starch blends, etc. [12,15]. Periodate oxidation method is one of the modification methods used to improve the regularity of starch particles in polymer matrix by providing the reinforcement of polymer matrix [12,16–18]. During the periodate oxidation reaction, the C-2 and C-3 bonds of the anhydroglucose rings of native starch polysaccharide would breakdown into aldehyde groups (C=O) from the hydroxyl groups (C—OH) to form dialdehyde starch (DAS) [12,18]. In decades, dialdehyde starch attracts considerable potential market as biodegradable polymer materials in the food industries for packaging purpose. Whilst, electron beam irradiation is widely applied in polymer engineering field to improve the mechanical properties of polymer blends. Numerous of researches have

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been conducted to investigate the enhancement effect of electron beam irradiation on physical–mechanical properties of polymer blends added with types of filler [19–22]. Previous research by Bee et al. [20] reported that the application of electron beam irradiation is able to gradually improve the mechanical properties of montmorillonite (MMT) added PVOH. Hence, the current work aims to investigate the effect of electron beam irradiation on physical, mechanical and thermal properties of native corn starch and dialdehyde starch (DAS) added PVOH compounds.

2. Experimental

2.1. Materials

In this study, fully hydrolyzed polyvinyl alcohol (PVOH) with grade of Denka Poval, K-17C was used as the primary polymer base. The PVOH used in this study was manufactured by Denki Kagaku Kougyo Kabushiki Kaisya (DENKI). The hydrolysis and viscosity of the Denka Poval, K-17C graded PVOH are 87–89 mol% and 45–55 mPa.s, respectively. The food grade native corn starch was used as secondary polymer base in this study. The native corn starch was supplied by Thye Huat Chan Sdn Bhd., Malaysia. Sodium periodate with Fisher Scientific brand was used to prepare the dialdehyde starch from native corn starch using periodate oxidation reaction. The Fisher Scientific brand sodium periodate with the specification of 0.2 mL N% of acidity, 0.003% of insoluble matter in water and 0.025% of loss of drying at 110 °C, Assay > 99% was supplied by Warisan Alam Enterprise Sdn. Bhd., Malaysia. Concentrated sulphuric acid with purity of 95–98% was used to control the acidity of dialdehyde starch solution during the preparation of dialdehyde starch. The concentrated sulphuric acid was purchased from Sigma-Aldrich (M) Sdn Bhd., Malaysia.

2.2. Preparation of dialdehyde starch

Sodium periodate powder was initially dissolved into distillated water to prepare the sodium periodate solution with concentration of 0.35 mol/L. On the other hand, the native starch solution was prepared by dissolving 16 g of native corn starch into 100 mL of distillated water. After that, the sodium periodate solution and native starch solution were mixed together in a beaker and stirred slowly for five hours at room temperature to enable the occurrence of periodate oxidation reaction. During the mixing process, the concentrated sulphuric acid was used to control the pH of the mixture solution in the range of 3.5–4.0 by adding into the mixture solution. After five hours of reaction, dialdehyde starch was separated from the mixture solution in slurry form using centrifuge machine. The separation process was conducted under high stirring speed of 12,000 rpm for 30 min. The separated dialdehyde starch in slurry form was washed using distillated water for several times and then dried in the oven at 55 °C for 24 h.

2.3. Sample preparation

The samples of PVOH-corn starch blends and PVOH-DAS blends were prepared via solution casting method with the PVOH: starch ratios of 80%: 20%, 60%: 40%, 40%: 60% and 20%: 80%, respectively. Initially, the PVOH resin was dissolved in distilled water using a water bath at temperature of 97 ± 2 °C for 30 min. A driven motor was used to stir the mixtures of water and PVOH resin evenly at the rotating speed of 350 rpm until all the PVOH resin fully dissolved in distilled water. After that, native corn starch or dialdehyde starch (DAS) was added into PVOH solution and then stirred again in water bath at temperature of 97 ± 2 °C for another 30 min. The mixtures solution of PVOH-corn starch or PVOH-DAS was cast onto a petri dish into sheet form with approximately 1 mm in thickness. Then, the cast samples were dried in a vacuum oven at constant temperature of 65 °C until reach a constant weight. The dried PVOH samples were kept and stored in sealed plastic bags under room temperature of 25 °C at relative humidity of 65% for conditioning purpose.

The cast samples were further electron beam irradiated to irradiation doses of 10, 20 and 30 kGy under the EPS-3000 electron beam irradiation machine with the irradiation rate of 10 kGy per pass. The irradiation voltage, current and energy of the EPS-3000 electron were set at 15 kV, 1 mA and 1 MeV, respectively.

2.4. Gel content

The gel content test was conducted to evaluate the degree of crosslinking network induced by irradiation in accordance to ASTM D2765. Firstly, the cast samples of pristine PVOH, corn starch, dialdehyde starch and all PVOH-starch blends were cut into smaller pieces using sample cutter. After that, 0.2000 g of cut samples were weighed by using an analytical balance. The weighed samples were then gravimetrically immersed and heated hot water for two hours under a constant heating temperature of 100 °C. After two hours of extraction, the extracted samples were washed using clean water for several times to remove the stain of soluble materials. The washed samples were further dried to constant weight in a vacuum oven at temperature of 40 °C for 24 h. The dried samples were accurately weighed and recorded as remaining weight (W_f) using analytical balance. The gel content percentage of all the samples was calculated according to Eq. (1). Three specimens per sample were used to calculate the average value of gel content percentage.

$$\text{Gel content}(\%) = \frac{0.2000\ \text{g} - W_f}{0.2000\ \text{g}} \times 100\% \quad (1)$$

where W_f represents the remaining weight of samples after the extraction process.

2.5. Tensile test

Tensile test was carried out by using Instron 5848 Tensile Microtester in accordance to ASTM D882. Initially, the cast and electron beam irradiated samples were cut into the standard rectangular shape according to ASTM D882. After that, the cut samples were placed in the grips of the Tensile Microtester and tested with the crosshead speed of 50 mm/min. Five specimen were tested for each formulation and the obtained results were then averaged to calculate the mean value and standard deviation.

2.6. Differential scanning calorimetry (DSC) test

Differential scanning calorimetry test was conducted using Mettler Toledo DSC823 Differential Scanning Calorimeter. The samples of PVOH-corn starch and PVOH-DAS blends with weight of 2–5 mg was measured and loaded into a crucible. The nitrogen gas was purged into the testing column with flow rate of 2 L/min before the testing to eliminate the air inside the testing column. After that, the sample in crucible was heated from room temperature to 250 °C under nitrogen atmosphere with the heating rate of 20 °C/min.

2.7. X-ray diffraction (XRD) test

The crystalline structures of PVOH-corn starch and PVOH-DAS samples was investigated using X-ray Diffraction Shimadzu XRD 6000 diffractometer with Cu-Kα radiation (λ = 1.542 Å). The samples were scanned from 2θ = 0° to 2θ = 80° at a scanning rate of 1.0°/min. The operating acceleration voltage and current of the Cu-Kα radiation generator were set to 40 kV and 30 mA, respectively. The crystallite size, L of crystallites in polymer matrix of PVOH-corn starch and PVOH-DAS blends was calculated using the Scherrer equation as shown in Eq. (2). The d-spacing, d of crystallites in PVOH-corn starch and PVOH-DAS samples was calculated using the Bragg's equation as shown in Eq. (3).

The inter-chain separation, R of crystalline was calculated using Klug and Alexander equation as shown in Eq. (4).

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{2}$$

$$d = \frac{\lambda}{2\sin\theta} \tag{3}$$

$$R = \frac{5\lambda}{8\sin\theta} \tag{4}$$

where K is Scherrer constant (usually taken as 0.9), β is the full width at half maximum (FWHM) of the deflection peak, λ is 1.542 Å and θ is the Bragg angle in radians.

2.8. Fourier Transform Infrared (FTIR) spectroscopy

Fourier Transform Infrared (FTIR) analysis was performed using a FTIR machine of ThermoScientific Nicolet iS10 with a spectrum recorded from 4000 to 400 cm^{-1}. The PVOH-corn starch and PVOH-DAS samples were cut into small pieces before the FTIR scanning. The cut samples were then placed directly onto the sample holder for scanning.

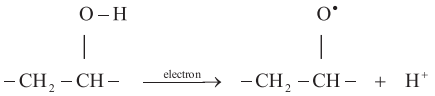
2.9. Scanning electron microscopy (SEM) analysis

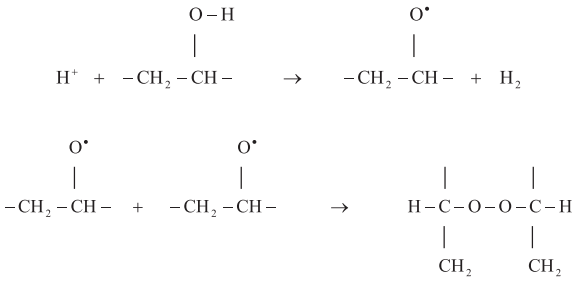
The morphologies of fractured surface for all PVOH-corn starch blends and PVOH-DAS blends were observed by conducting the scanning electron microscopy (SEM) analysis using Hitachi S-3400N Scanning Electronic Microscope (SEM). The fractured surfaces of the samples were cut into small portions and then mounted onto the copper stub with the fractured surface is facing upwards. Then, the cut samples were coated with a thin layer of palladium and gold using EMITECH SC7620 Sputter Coater. The coated samples were then scanned under the magnification of 3000 times at an electron beam voltage of 15 kV.

3. Results and discussion

3.1. Gel content

By referring to Fig. 1(a), the increasing of electron beam irradiation dosage up to 20 kGy has gradually increased the gel content of pristine PVOH. This is due to the accelerated electrons released by electron beam accelerator tend to attack the reactive O—H bonds of PVOH macromolecules by extracting the hydrogen atoms from the PVOH macromolecules to form reactive polymeric free radicals as shown in reaction Eq. (5) [23]. The released free hydrogen ions have further extracted the hydrogen atoms of other PVOH macromolecule to form hydrogen gas subsequently form polymeric free radicals as shown in reaction Eq. (6). The released polymeric free radicals would react together to form a three dimensional networks (also known as crosslinking networks) inside polymer matrix of pristine PVOH as shown in reaction Eq. (7) [19–20,24]. However, the gel content of pristine PVOH was found to marginally decrease when further electron beam irradiated from 20 kGy to 30 kGy as shown in Fig. 1(a). At higher irradiation dosage (> 20 kGy), the excessive electrons released by the electron beam accelerator would attack the backbone chains of PVOH macromolecules due to limited availability of O—H groups to release the polymeric free radicals. The breakdown of PVOH chains have further reduced the molecular size of PVOH chains and thus promote the solubility of crosslinked PVOH chains in hot water.





On the other hand, the gel contents of corn starch, dialdehyde starch and all PVOH-starch blends were also significantly increased when irradiated up to 20 kGy as shown in Fig. 1(b). The electron beam irradiation could release the polymeric free radicals by attacking the O—H groups in PVOH, corn starch and DAS chains. The polymeric free radicals would react together to from three dimensional networks in polymer matrix of PVOH-corn starch blends and PVOH-DAS blends [25]. The presence of crosslinked networks in polymer matrix could significantly resist the water penetration and thus weaken the solubility of PVOH-starch blends elevated temperature. However, further increment in irradiation dosages from 20 kGy to 30 kGy has gradually reduced the gel content of all PVOH-corn starch blends and PVOH-DAS blends as illustrated in Fig. 1(b). The reduction of hydroxyl groups (O—H) amounts in polymer matrix of PVOH-starch blends at higher irradiation dosage has significantly caused the excess electrons breaking the polymer chains of PVOH, corn starch and dialdehyde starch into shorter structure to generate polymer free radicals. The shorter chains of PVOH, corn starch and dialdehyde starch in polymer matrix promote the solubility of PVOH-starch in water and thus reduced the gel content values [16].

3.2. Tensile properties

3.2.1. Tensile strength

Fig. 2(a) illustrates the effect of electron beam irradiation on the tensile strength of pristine PVOH, PVOH-corn-starch blends and PVOH-DAS blends. By referring to Fig. 2(a), the application of electron beam irradiation dosage up to 10 kGy has significantly increased the tensile strength of pristine PVOH. As discussed earlier, the application of electron beam irradiation could induce the formation of crosslinked structures in PVOH matrix by breaking the O—H bonds of PVOH macromolecules to form reactive polymeric free radicals [25]. The formation of three dimensional networks in pristine PVOH matrix could strengthen the polymer matrix by effectively transferring the applied straining stress throughout the whole pristine PVOH matrix [20]. Thus, the application of electron beam irradiation up to 10 kGy has significantly increased the tensile strength of pristine PVOH. However, the tensile strength of pristine PVOH was observed to gradually decrease with further increment in irradiation dosages up to 30 kGy as shown in Fig. 2(a). The application of higher irradiation dosages (> 10 kGy) could induce the degree of crosslinking formed in PVOH matrix by breaking more O—H bonds inside PVOH matrix to form polymeric free radicals [23]. However, the breakdown of O—H bonds of PVOH chains inside pristine PVOH matrix (by the released electron) has significantly reduced the amount of O—H bonds in PVOH matrix. The reduction of O—H bonds (or hydroxyl groups) in pristine PVOH matrix has weakened the hydrogen bonding inside PVOH matrix [15]. Thus, the weakening effect of hydrogen bonding inside PVOH matrix has further reduced the resistance effect towards the applied straining stress and reduced the tensile strength.

By referring to Fig. 2(a), the addition of corn starch and DAS into PVOH matrix has rapidly reduced the tensile strength of un-irradiated and all irradiated PVOH blends. This is attributed to the replacement of PVOH content in polymer matrix with starch content would

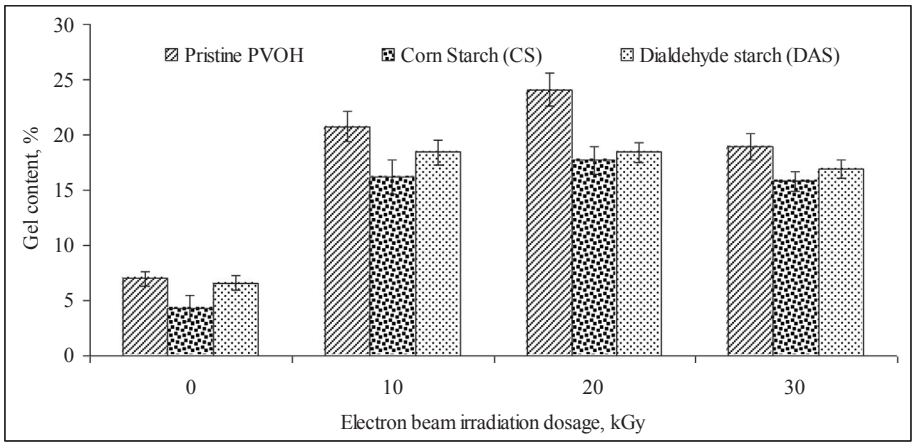


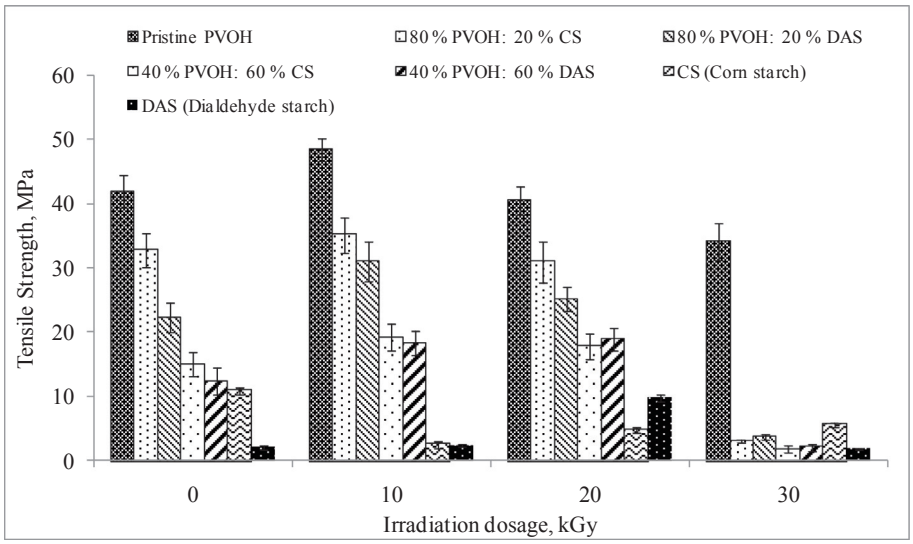
Fig. 1. Gel content of (a) pristine PVOH, corn starch (CS), dialdehyde starch (DAS) and (b) all PVOH-corn starch blends and PVOH-dialdehyde starch blends when subjected to electron beam irradiation dosages.

significantly weaken the hydrogen bonds in the polymer matrix of PVOH-starch blends. Subsequently, the increasing of starch content has significantly decreased the tensile strength of PVOH blends. On the other hand, the tensile strength of all un-irradiated PVOH-corn starch blends was observed to be higher than the tensile strength of all un-irradiated PVOH-DAS blends. This might be due to the periodate oxidation process to produce DAS could break the C-2 and C-3 bonds of the anhydroglucose units of native corn starch to form aldehyde groups by taking place the hydroxyl groups at C-2 and C-3 [12,18]. The transferring of hydroxyl groups (O—H) with stronger hydrophilic nature into aldehyde groups (C═O) has significantly reduced the hydrophilic behaviour of DAS phase and further weakened the interfacial adhesion effect with PVOH phase inside PVOH-DAS blends [5,12]. Subsequently, the poor interfacial adhesion effect between the PVOH phase and DAS phase inside PVOH-DAS blends could cause the appearance of cavities at the interfaces between PVOH phase and DAS phase [25]. The appearance of cavities at the interfaces of PVOH and DAS phases could cause the stress unable to be effectively transferred from PVOH phase to DAS phase. Thus, the tensile strength of all PVOH-DAS blends is found to be significantly lower than PVOH-corn starch blends.

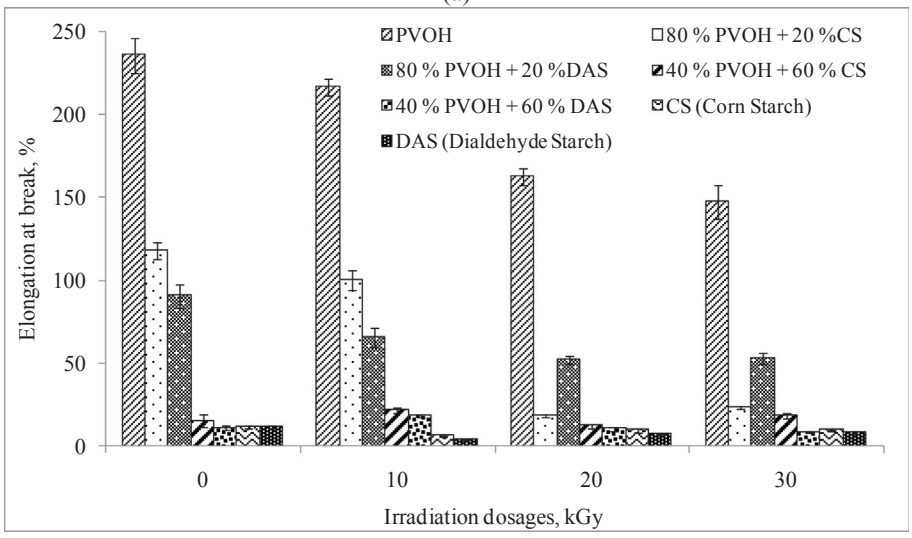
By observing the Fig. 2(a), the tensile strength of both low starch content (20%) added PVOH-corn starch blends and PVOH-DAS blends were observed to significantly increase when irradiated to irradiation dosage of 10 kGy. As discussed in earlier, the electron beam irradiation could release the polymeric free radicals by attacking the O—H groups in PVOH, corn starch and DAS chains. Then, the polymeric free radicals would react together to from three dimensional networks in polymer matrix of PVOH-corn starch blends and PVOH-DAS blends [25]. The occurrence of three dimensional networks in polymer matrix could effectively transfer the applied straining stress throughout the whole polymer matrix and thus increase the tensile strength. However, further increment in irradiation dosages up to 30 kGy has gradually reduced the tensile strength of all PVOH-corn starch blends and PVOH-DAS blends. This could be attributed to the reduction of hydroxyl groups (O—H) in polymer matrix due to irradiation process has significantly weakened the hydrogen bonds in polymer matrix of all PVOH-corn starch blends and PVOH-DAS blends [16]. On the other hand, the reduction in tensile strength of all PVOH-corn starch blends and PVOH-DAS blends also might be due to the rupture of PVOH, corn starch and DAS chains in polymer matrix as attacked by the excessive polymeric free radicals generated when subjected to higher irradiation dosages. This could further weaken the intermolecular forces between the polymer chains by reducing the molecular size of PVOH, corn starch and DAS chains inside polymer matrix [26]. Besides, the hydrogen gas released during the irradiation process would be trapped inside the polymer matrix and form bubble voids. The occurrence of bubble voids inside polymer matrix could cause an inferior effect in transferring the applied straining stress throughout the whole polymer matrix and subsequently weaken the tensile strength of all PVOH-corn starch blends and PVOH-DAS blends [17,25].

3.2.2. Elongation at break

By referring to Fig. 2(b), the elongation at break of pristine PVOH, PVOH-corn starch blends and PVOH-DAS blends was gradually



(a)



(b)

Fig. 2. Effect of electron beam irradiation dosages on (a) Tensile strength and (b) Elongation at break of pristine PVOH, corn starch (CS), dialdehyde starch, all PVOH-corn starch blends and PVOH-dialdehyde starch blends.

decreased as the electron beam irradiation dosage increased from 0 kGy to 30 kGy. This might be attributable to the formation of three dimensional networks (crosslinking) by electron beam irradiation could restrict the mobility of polymer chains from slippage on each other when subjected to straining. The restriction effect of the polymer chains mobility could further significantly reduce the elongation at break of pristine PVOH, PVOH-corn starch blends and PVOH-DAS blends [6]. From Fig. 1(b), the elongation at break of pristine PVOH was observed to be significantly higher than the elongation at break of PVOH-corn starch blends and PVOH-DAS blends. This is due to the addition of corn starch and DAS with brittle behaviour and low flexibility could significantly reduce the elongation ability of polymer matrix of PVOH-corn starch blends and PVOD-DAS blends [16,27]. Besides, the addition of corn starch and DAS into PVOH matrix also could weaken the hydrogen bonds and thus further reduce the extendability of PVOH-corn starch blends and PVOH-DAS blends. According to Fig. 1(a), the elongation at break for all un-irradiated PVOH-corn starch blends was observed to be significantly higher than the elongation at break of un-irradiated PVOH-DAS blends. This is due to the interfacial compatibility of PVOH and corn starch was significantly better than the interfacial compatibility of PVOH and DAS due to stronger hydrophilic behaviour of corn starch in compared to DAS [5]. As resulted from the stronger hydrophilic of corn starch, the hydrogen bonds in polymer matrix of PVOH-corn starch were stronger than PVOH-DAS blends. Another reason was that occurrence of higher amounts of hydrophilic hydroxyl groups (O—H) inside corn starch phase could slightly absorb moisture from environment during compounding process. The absorbed moisture in polymer matrix would act as plasticizer and slightly promote the slippage effect of polymer chains inside polymer matrix of PVOH-corn starch blends [5]. However, the application of higher irradiation dosages ($\geq$20 kGy) could severely reduce the elongation at break of PVOH-corn starch blends. This might be due to the electron beam irradiation process would attack the hydroxyl groups (O—H) in corn starch chains and weaken the hydrophilic behaviour of corn starch phase. This have further weakened the interaction effect between PVOH phase and corn starch phase and subsequently reduced the elongation ability of PVOH-corn blends under high electron beam irradiation dosages.

3.3. DSC analysis

The differential scanning calorimetry (DSC) thermograms of un-irradiated and irradiated pristine PVOH, PVOH-corn starch blends and PVOH-DAS blends are shown in Fig. 3. The effect of electron beam irradiation on the melting temperature, enthalpy of melting (ΔH_m) of pristine PVOH, PVOH-corn starch blends and PVOH-DAS blends are

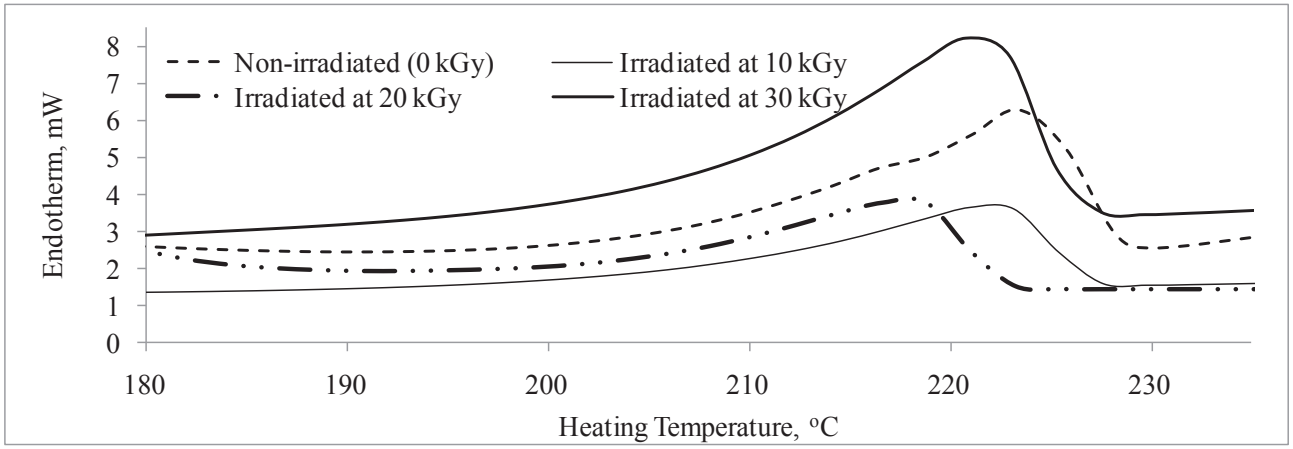
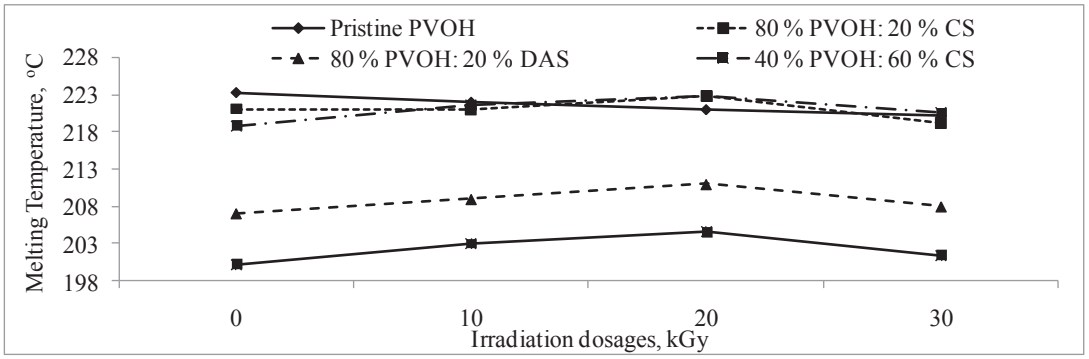
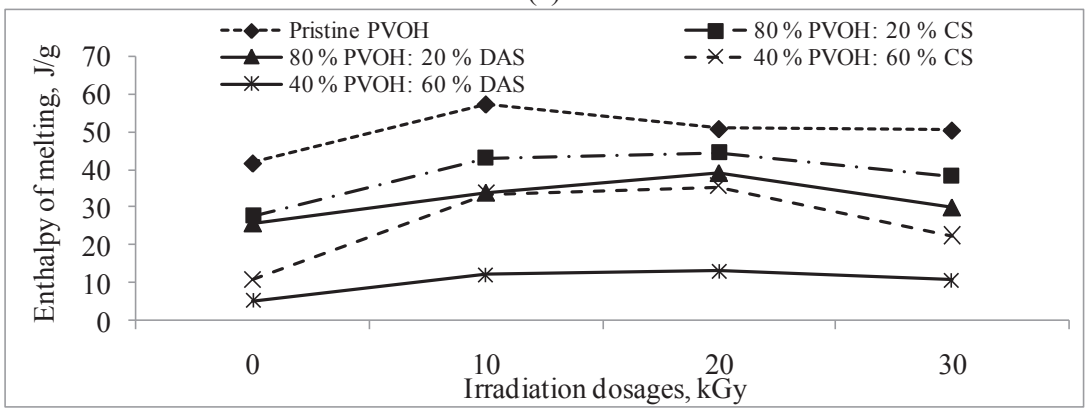


Fig. 3. DSC thermograms of (a) pristine PVOH under various irradiation dosages, (b) 40% PVOH + 60% corn starch blends and 40% PVOH + 60% DAS blends, and (c) 80% PVOH + 20% corn starch blends and 80% PVOH + 20% DAS blends under various irradiation dosages.

shown in Fig. 4(a) and (b). By referring to Fig. 3, the application of electron beam irradiation process on the polymer matrix of pristine PVOH, PVOH-corn starch blends and dialdehyde starch (DAS) blends has caused significant effects on the thermal behaviour of PVOH. By referring to Fig. 3(a), the melting peak of thermogram of pristine PVOH was observed gradually shift to lower heating temperature when



(a)



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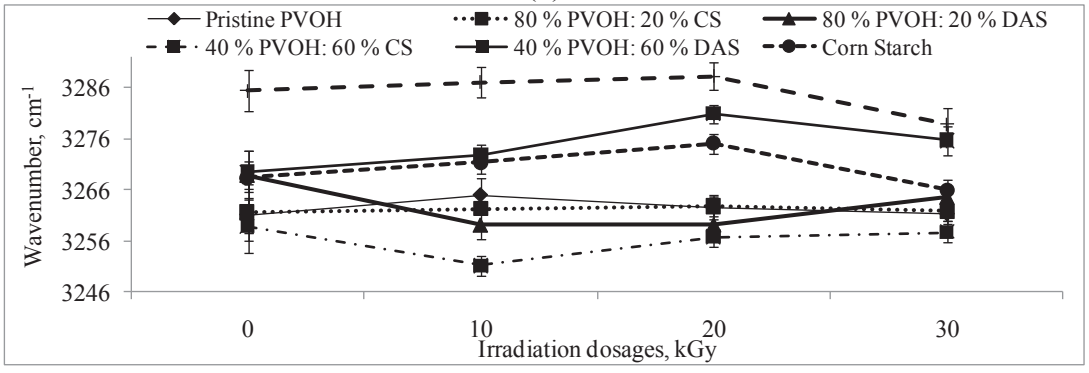
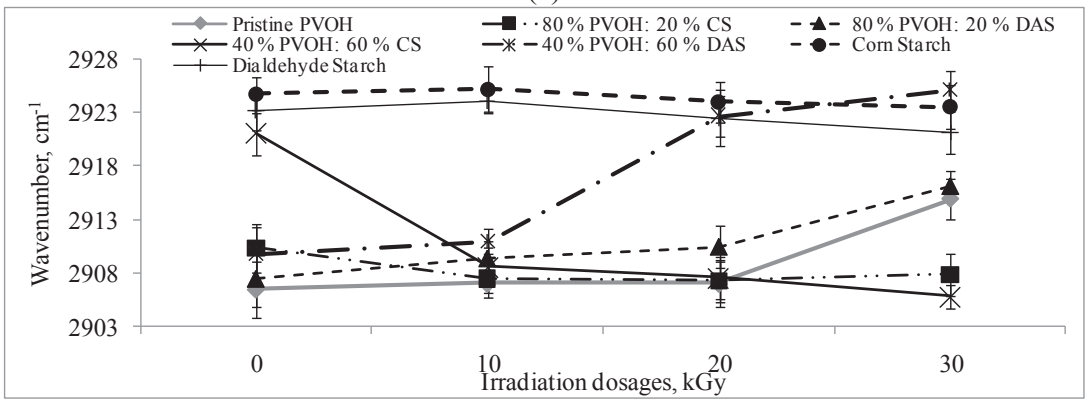


(c)



(d)

Fig. 4. Effect of electron beam irradiation on the (a) melting temperature, (b) enthalpy of melting, (c) wavenumber of the hydroxyl group (O—H) on FTIR spectrum and (d) wavenumber of the C—H bonds on FTIR spectrum peak of all PVOH-starch samples.

subjected to increasing irradiation dosages from 0 kGy to 30 kGy. This indicates that the application of electron beam irradiation has significantly reduced the melting temperature of pristine PVOH as shown in Fig. 4(a). The application of electron beam irradiation has significantly reduced the required temperature of pristine PVOH to induce internal molecular kinetic energy transform the rigid solid state into molten state [14,16]. The decrement in melting temperature is mainly attributed to the weakening of hydrogen bonding between PVOH chains inside PVOH matrix [28]. The application of electron beam irradiation could introduce the formation of crosslinking networks inside PVOH matrix by attacking the hydroxyl groups inside pristine PVOH matrix. This have significantly reduced the effective amounts of hydroxyl groups inside PVOH matrix and thus further weakened the occurrence of hydrogen bonds inside PVOH matrix. By referring to Fig. 3(a), the thermogram peak of pristine PVOH was also observed to be gradually broadened when subjected to increasing irradiation dosage from 0 kGy to 30 kGy. The broadening of thermogram peak exhibits the presence range of molecular interaction within the polymer matrix of irradiated pristine PVOH. This indicates that the formation of crosslinking networks by electron beam irradiation has reduced the occurrence of physical interaction due to hydrogen bonding by introducing a variety of interaction inside PVOH matrix [16–17]. On the other hand, the incorporation of corn starch and dialdehyde starch into PVOH matrix has significantly reduced the melting temperature as shown in Fig. 4(a). The irregularity molecules of corn starch and dialdehyde has disturbed the polymer chains arrangement in polymer matrix of PVOH-corn starch and PVOH-DAS blends and weakened the interaction of PVOH-corn starch and PVOH-DAS blends [16].

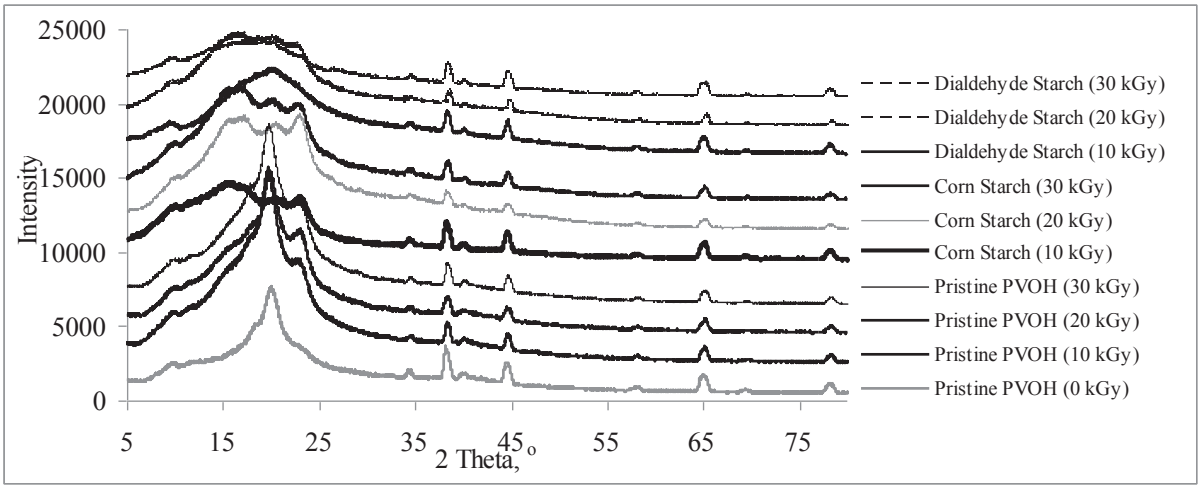
By referring to Fig. 3(b) and (c), the thermogram peaks of all the PVOH-DAS blends were found to pose lower melting temperature than all the PVOH-corn starch blends. In addition, the melting temperature of all un-irradiated PVOH-corn starch blends also found to be significantly lower than the melting temperature of all un-irradiated PVOH-DAS blends as shown in Fig. 4(a). This is due to the preparation of dialdehyde starch (DAS) from native corn starch by periodate oxidation process could break the C-2 and C-3 bond of the anhydroglucose units and convert the hydroxyl groups (C-O—H) at C-2 and C-3 into aldehyde groups (C═O) [12]. The occurrence of hydroxyl groups by aldehyde groups in DAS matrix have significantly weakened the physical bonding (hydrogen bonding) between PVOH phase and DAS phase inside polymer matrix [12]. Thus, a lower temperature is needed by PVOH-DAS blends to elevate the internal molecular kinetic energy to transform the rigid solid state into molten state. By referring to Fig. 4(a), the low DAS content added PVOH-DAS blends has higher melting temperature than high DAS content added PVOH-DAS blends. This is attributed to the occurrence of higher amounts of hydroxyl groups inside polymer matrix of low DAS content added PVOH-DAS blends which could provide higher hydrogen bonding inside polymer matrix. According to Fig. 3(b) and (c), the increasing of electron beam irradiation dosages from 0 kGy to 20 kGy have slightly shifted the thermogram peaks of all PVOH-corn starch blends and PVOH-DAS blends to higher temperature. This also indicates the application of electron beam irradiation has significantly increased the melting temperature of all PVOH-corn starch blends and PVOH-DAS blends as shown in Fig. 4(a). This is attributable to the formation of crosslinking networks has increased the molecular size of PVOH and starch chains and thus also induced the intermolecular bonding in polymer matrix [23]. This causes the PVOH-starch blends required a higher temperature to increase the internal molecular kinetic energy to overcome the strong intermolecular interaction between the molecules in order to reach the melting state from rigid solid state [14,16].

However, further increment in irradiation dosages from 20 kGy to 30 kGy has significantly shifted the thermogram peaks of PVOH-corn starch blends and PVOH-DAS blends to lower melting temperature as shown in Figs. 3(b), (c) and 4(a). This is due to higher electron beam irradiation dosages has significantly reduced the available hydroxyl groups of polymer chains in PVOH-starch matrix by breaking O—H bonds to release polymeric free radicals. The reduction of available hydroxyl groups in polymer matrix of PVOH-corn starch and PVOH-DAS blends has reduced the hydrogen bonding among the polymer chains inside polymer matrix [12,28]. Besides, the availability of hydroxyl groups to generate polymeric free radicals by electron beam irradiation was also significantly reduced at higher irradiation dosages ($>$ 20 kGy). This causes the electron released by electron beam accelerator tended to attack the main chains of polymer matrix to generate polymeric free radicals. Thus, the molecular size of polymer chains inside polymer matrix of PVOH-starch blends have been significantly reduced at higher irradiation dosages and this has further led to weaken the intermolecular bonding inside polymer matrix. The weakening effect on the occurrence of physical interaction such as hydrogen bonding and intermolecular bonding among the polymer chains inside polymer matrix of PVOH-corn starch and PVOH-DAS blends has significantly reduced the required temperature to transform the rigid solid state into molten condition.

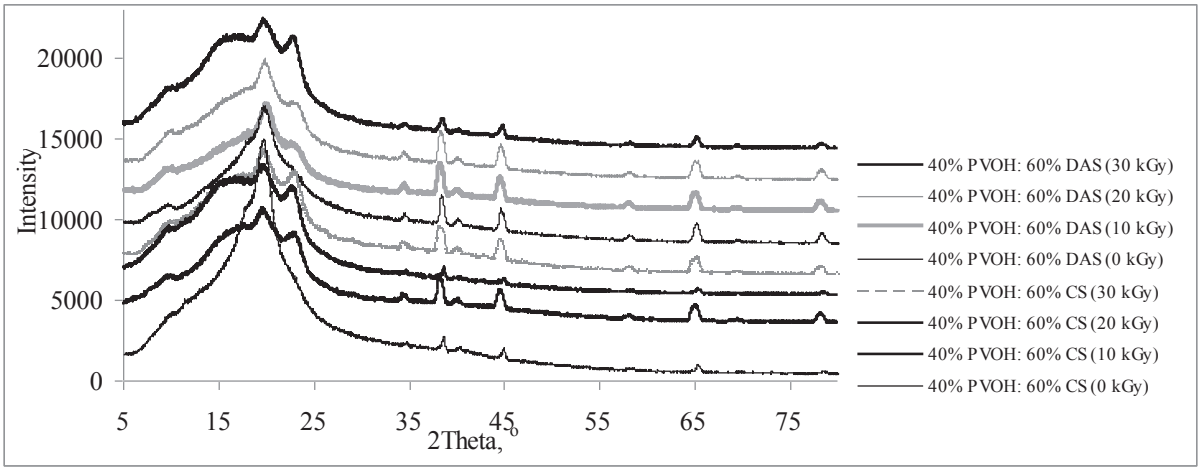
The enthalpy of melting (ΔH_m) of all PVOH-corn starch and PVOH-DAS blends is summarized in Fig. 4(b). It can be observed that the addition of native corn starch and dialdehyde starch has significantly reduced the enthalpy of melting for PVOH blends. The reduction in enthalpy of melting indicates that the incorporation of corn starch and dialdehyde starch with wide variety of irregular molecules could reduce the crystallinity of PVOH blends [16]. The large irregularity molecules of corn starch and DAS has affected the ordered chain arrangement inside PVOH blending system and thus reduced the crystallinity [16]. Moreover, the addition of DAS cause more prominent reduction in enthalpy of melting of PVOH blends in comparing to native corn starch. This is due to the periodate oxidation process could destruct the crystalline lamella structure of native corn starch granules by attacking the C2-C3 bond of anhydroglucose units of polysaccharide chains in starch [12,18]. Furthermore, the DAS with less hydrophilic behaviour unable to form strong and stable hydrogen bonding with PVOH, thus the enthalpy of melting have been significantly reduced [12]. On the other hand, the enthalpy of melting of all samples was gradually increased when irradiated to 20 kGy as shown in Fig. 4(b). This indicates that the application of low irradiation dosages ($\leq$ 20 kGy) has significantly induced the crystallinity and the physical bonding of all PVOH blends. This is due to the formation of crosslinking networks by low irradiation dosages could cause extra physical bonding between PVOH and starch. In addition, the low irradiation dosages could also slightly induce the formation of crystalline structure in polymer matrix. However, further increment in irradiation dosage up to 30 kGy has marginally reduced the enthalpy of melting of all PVOH blend. The higher electron beam irradiation dosages have highly reduced the occurrence of hydroxyl groups inside polymer matrix by attacking the O—H bonds to form polymeric free radicals. The decrement in hydroxyl group amounts has further weakened the hydrogen bonds inside polymer matrix of PVOH blends and thus reduced the enthalpy of melting. Besides, the decrement in hydroxyl group amounts also caused the electron released by the electron beam irradiation accelerator tended to attack the main chains of PVOH and starch molecules by breaking the long polymeric chains into shorter chains [20]. The breakdown of long polymeric chains into shorter chains could destroy the crystal structure in polymer matrix of PVOH blends to form amorphous regions and thus reduce the enthalpy of melting and crystallinity of PVOH blends [12].

3.4. X-ray diffraction analysis

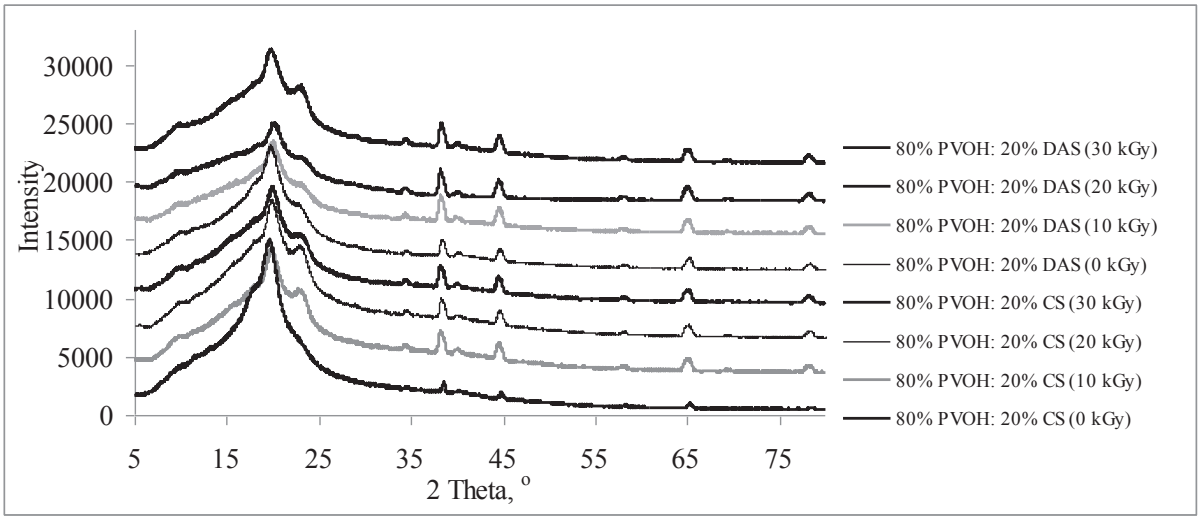
The X-ray diffraction pattern curves of pristine PVOH, all PVOH-corn starch blends and PVOH-DAS blends were illustrated in Fig. 5. A strong and significant deflection peak A can be observed to occur at 2θ = 19.5–20.1° on the XRD curves of pristine PVOH, all PVOH-corn starch and PVOH-DAS blends. The appearance of deflection peak A is due to the mixtures of deflection planes (1 0 1), (1 0 $\bar{1}$) and (2 0 0) as



(a)



(b)



(c)

Fig. 5. XRD pattern curves of (a) Pristine PVOH, corn starch (CS) and dialdehyde starch (DAS), (b) polymer blends of 40% PVOH + 60% Corn starch and (c) polymer blends of 80% PVOH + 20% DAS when subjected to electron beam irradiation dosages.

Table 1
The 2 theta, crystallite size, d-spacing and interchains separation of deflection peak A for pristine PVOH, all PVOH-corn starch blends and all PVOH-DAS blends under various irradiation dosages.

Samples	Irradiation dosages, kGy	2 Theta (2θ), °	Crystallite size (*L*), Å	d-Spacing (*d*), Å	Interchains separation (*R*), Å
Deflection peak A					
Pristine PVOH	0	20.014	48.28	4.431	5.539
	10	19.598	34.59	4.524	5.655
	20	19.797	32.00	4.479	5.599
	30	19.549	32.11	4.536	5.670
80% PVOH: 20% Corn Starch blends	0	19.503	40.17	4.431	5.539
	10	19.697	29.07	4.502	5.627
	20	19.860	33.13	4.465	5.581
	30	19.970	34.57	4.447	5.559
80% PVOH: 20% DAS blends	0	19.705	40.50	4.500	5.625
	10	19.700	31.52	4.501	5.626
	20	19.820	34.39	4.474	5.593
	30	19.760	29.10	4.488	5.609
40% PVOH: 60% Corn Starch blends	0	20.095	46.45	4.413	5.517
	10	19.834	32.32	4.471	5.589
	20	20.160	36.87	4.399	5.499
	30	19.754	28.76	4.489	5.611
40% PVOH: 60% DAS blends	0	19.680	39.16	4.506	5.632
	10	19.783	28.87	4.482	5.603
	20	19.800	29.91	4.479	5.598
	30	19.820	30.51	4.474	5.593

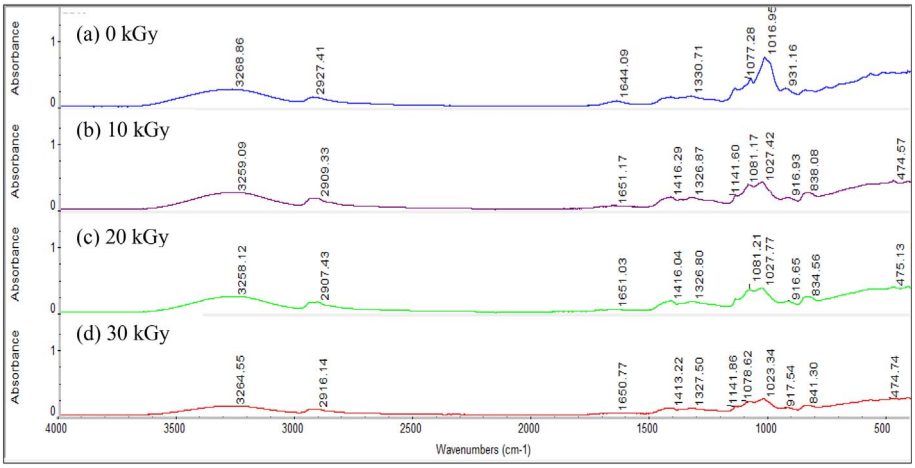
shown in Fig. 5. By referring to Fig. 5(a), the deflection peak A of pristine PVOH was observed to be significant, strong and high intensity which indicates the large crystalline size of deflection peak A for pristine PVOH. On the other hand, the deflection peak A was observed to be absent from the XRD curves of native corn starch and dialdehyde starch as shown in Fig. 5(a). The increasing of electron beam irradiation dosages up to 30 kGy has significantly broadened the deflection peak A of pristine PVOH. The broadening of deflection peak A represents the gradual collapse of the crystalline structure in crystal of deflection peak A when subjected to increasing electron beam irradiation dosages. This also indicates that the electron beam irradiation could rupture the ordered chains arrangement structure in crystallite peak A into less ordered chains arrangement [20,29]. The effect of electron beam irradiation on crystallite size of deflection peak A for all PVOH-starch blends is summarized in Table 1. The crystallite size of crystallite peak A was observed to gradually decrease with increasing of irradiation dosages from 0 kGy to 30 kGy. This also indicates that the formation of crosslinking networks in pristine PVOH (induced by electron beam irradiation) could decrease the crystallite size of crystal for deflection peak A by rupturing the crystalline structure [29]. This might be due to the decreased inter and intra molecular hydrogen bonding among the PVOH chains could disturb the highly ordered chains arrangement of crystal for deflection peak A into less ordered arrangement [1,29]. Besides, the released of polymeric free radicals is mainly due to the interaction of high energy beam and PVOH chains inside polymer matrix. At higher electron beam irradiation, the chain scissioning process tended to be predominant compared to crosslinking process due to the limited available hydroxyl groups inside pristine PVOH matrix to generate polymeric free radicals [23]. The breakdown of long PVOH chains into shorter chains has ruptured the highly ordered arrangement of PVOH chains inside crystallite peak A into random chain arrangement and thus reduced the crystallite size of crystal peak A.

The deflection peak A of un-irradiated 40% PVOH + 60% corn starch blends was found to be more significant and sharper with higher intensity than deflection peak A of un-irradiated 40% PVOH + 60% DAS blends as shown in Fig. 5(b). However, no significant change can be observed on the peak width of deflection peak A for 80% PVOH + 20% corn starch blends and 80% PVOH + 20% DAS blends as depicted in Fig. 5(c). By referring to Table 1, the crystallite size of crystal peak A for 40% PVOH + 60% DAS blends (46.45 Å) was found to be significantly lower than 40% PVOH + 60% corn starch blends (39.16 Å). This is due to the taking over of hydroxyl groups by aldehyde groups during periodate oxidation process have highly reduced the hydroxyl groups inside dialdehyde starch and thus weakened the hydrogen bonds with PVOH. The reduction of hydroxyl group amounts have weakened the interaction effect between PVOH molecules and dialdehyde starch molecules and significantly ruptured the highly ordered arrangement structure inside crystallite of deflection peak A [1,12]. The application of electron beam irradiation up to 10 kGy on 40% PVOH + 60% corn starch blends and 40% PVOH + 60% DAS blends has highly reduced the crystallite size of crystal peak A from 46.45 Å and 39.16 Å to 32.32 Å and 28.87 Å, respectively. The increasing of irradiation dosage from 10 kGy to 30 kGy has gradually decreased the crystallite size of crystal peak A of all PVOH-corn starch and PVOH-DAS blends. As discussed in earlier, the electron released by electron beam accelerator tended to attack the O—H bonds to generate free radicals and caused the reduction of hydroxyl groups inside polymer matrix. The reduction of available hydroxyl groups in polymer matrix have weakened the hydrogen bonds inside polymer matrix of PVOH-corn starch and PVOH-DAS blends and affected the arrangement structure of deflection peak A [29]. Besides, higher irradiation dosages also could further breakdown the long PVOH chains and led to increase the less ordered short chains in polymer matrix [30]. Thus, the crystallite size of deflection peak A for all PVOH-starch blends was reduced with increasing of electron beam irradiation dosages.

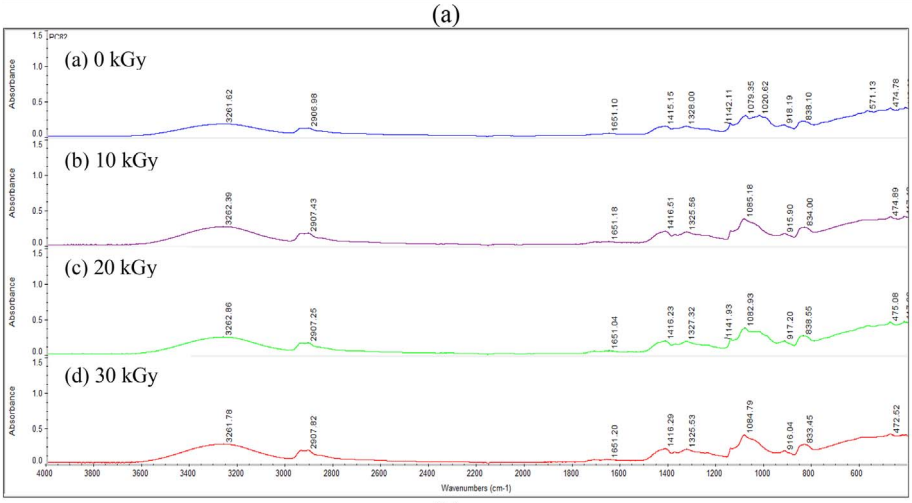
The d-spacing and interchains separation of crystallite peak A for all PVOH blends is summarized in Table 1. The addition of corn starch into PVOH matrix did not exhibit a significantly change in d-spacing and interchains separation of crystallite for deflection peak A. In other words, the occurrence of native corn starch molecules did not provide significant effect on the compactness of PVOH chains inside crystallite for peak A. For un-irradiated samples, the incorporation of dialdehyde starch into PVOH matrix has provided a very small increment in the d-spacing and interchains separation of the crystallite for peak A. This might be attributed to the dialdehyde starch with less hydrophilic behaviour cannot form strong hydrogen bonds with PVOH and slightly cause the compactness of polymer chains inside crystal peak A to be slightly reduced [12]. By referring to Table 1, the application of electron beam irradiation did not provide significant effect on the d-spacing and interchains separation of deflection peak A for pristine PVOH and all PVOH-starch blends. This also indicates that the formation of crosslinking networks by electron beam irradiation did not significantly affect the compactness of chains arrangement inside crystallite peak A. This is due to the electron released by the electron beam accelerator is more likely to attack the polymer chains in amorphous regions (outside of crystallite peak A) of polymer matrix due to un-restricted movement to form crosslinking networks [31].

3.5. FTIR analysis

Fig. 6 illustrates that the FTIR spectra of PVOH-corn starch blends and PVOH-DAS blends when subjected to increasing electron beam irradiation dosages. An obvious broad peak can be found at wavenumbers range of 3245–3305 cm^{-1} for all PVOH-corn starch blends and PVOH-DAS blends, which is attributed to the O—H stretching of hydroxyl groups (OH) [1,17]. Besides, a significant peak also observed at wavenumber range of 2903–2928 cm^{-1} for all PVOH-corn starch and PVOH-DAS blends as shown in Fig. 6, which is due to the existence of C—H stretching [1]. By referring to Fig. 4(c), it can also be noticed that the intensity of hydroxyl peaks for corn starch and dialdehyde starch (DAS) is significant higher than pristine PVOH. This is attributed to the "red shift" effect of hydrogen bonds, where the strong hydrogen bonds



(a)



(b)

Fig. 6. Infra spectrogram of (a) 80% PVOH + 20% dialdehyde starch blends and (b) of 80% PVOH + 20% native corn starch blends under various irradiation dosages.

could weaken the bonding of O—H of the hydroxyl groups and thus reduce the wavenumbers of O—H stretching [16]. This also indicates that the presence of hydrogen bonds in pristine PVOH is significantly higher than the hydrogen bonds in corn starch and dialdehyde starch (DAS). On the other hand, the O—H stretching of hydroxyl (—OH) groups of native corn starch was found to be significantly lower in wavenumbers when compared to dialdehyde starch (DAS) as shown in Fig. 4(c). The reduction of O—H stretching is mainly attributed to the presence of stronger hydrogen bonds between the hydroxyl (O—H) groups and subsequently weakened the O—H stretching of the hydroxyl groups. This is because the formation of aldehyde groups (C═O) from C—OH of the anhydroglucose ring during periodate oxidation have significantly reduced the amounts of O—H groups in DAS and thus further weakened the strength of hydrogen bonds in DAS [12]. The mechanism model of the presence of hydrogen bonding in polymer matrix of non-irradiated PVOH-corn starch blends and non-irradiated PVOH-DAS blends is illustrated in Fig. 7. The oxidation of hydroxyl group (O—H) of native starch molecules into aldehyde groups (C═O) to produce dialdehyde starch has significantly reduced the hydrogen bonding in polymer matrix of PVOH-starch blends due to the reduction amounts of hydroxyl groups in polymer matrix. The reduction of hydrogen bonds in polymer matrix of PVOH-DAS blends has further caused the O—H stretching of PVOH-DAS blends to be stronger than PVOH-corn starch blends as illustrated in Fig. 7. Besides, the increasing of native corn starch and DAS amount up to 80% has highly induced the wavenumbers of O—H of hydroxyl groups as depicted in Fig. 4(c). As discussed in earlier, the increment of wavenumbers is mainly attributed to the weakening effect of hydrogen bonding action in PVOH blending system by the addition of native corn starch or DAS where the presence of native corn starch or DAS could disrupt and weaken the hydrogen bonds in polymer matrix. As shown in Fig. 7, the presence of bulky anhydroglucose rings in molecules of native corn starch and dialdehyde starch could hinder the interaction effect between hydroxyl (O—H) groups of PVOH chains and thus weaken the hydrogen bonding in polymer matrix of PVOH-starch blends. Furthermore, the hydrogen bonding between the hydroxyl groups on the native corn starch and dialdehyde starch molecules and the hydroxyl groups of PVOH chains has also been weakened due to the presence of bulky anhydroglucose rings which induced the distance between the molecules in polymer matrix.

The effect of electron beam irradiation on the stretching of O—H bonds and C—H bonds of pristine PVOH, corn starch, DAS and all blends of PVOH-corn starch and PVOH-DAS was summarized in Fig. 4(c) and (d). By referring to Fig. 4(c), the increasing of electron beam irradiation dosages up to 20 kGy has gradually increased the wavenumber of O—H stretching of hydroxyl groups of pristine PVOH, corn starch, dialdehyde starch (DAS) and all blends of PVOH-corn starch and PVOH-DAS. This indicates that the application of electron beam irradiation at lower dosages ($\leq$20 kGy) could induced the wavenumber of O—H stretching by weakening the strength of hydrogen bonds in polymer matrix. This might be due to the released electrons from electron beam accelerator could attack the O—H groups to generate the polymeric free radicals, where the generated polymeric free radicals would react with each other to form crosslinked chains in polymer matrix as illustrated in Fig. 8 [20]. The formation of crosslinked chains in polymer matrix has significantly reduced the available

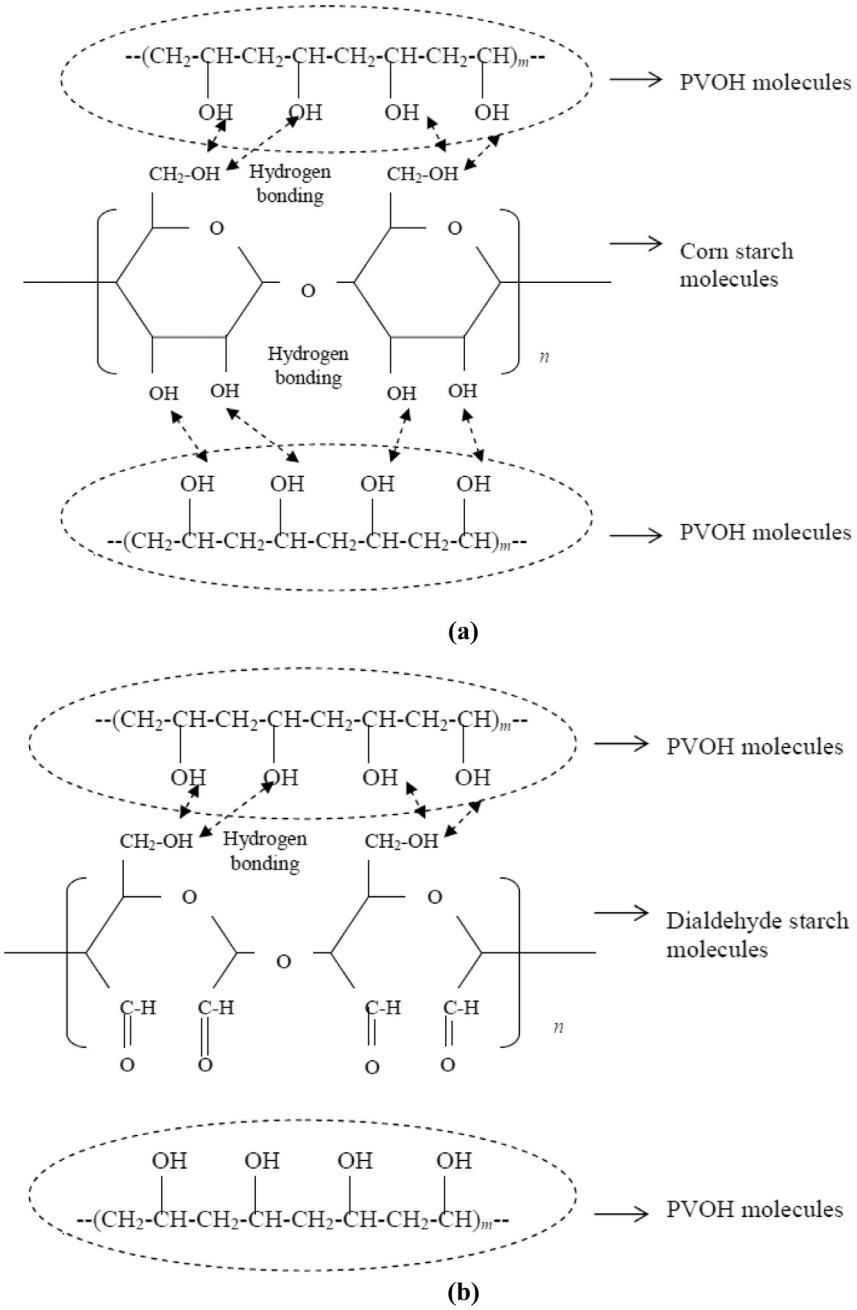


Fig. 7. Mechanism model of hydrogen bonding in polymer matrix of (a) PVOH-corn starch blends and (b) PVOH-dialdehyde starch blends before electron beam irradiation.

hydroxyl groups (O—H) in polymer matrix of PVOH-starch blends (as shown in Fig. 8) and thus weakened the hydrogen bonds in polymer matrix of all PVOH-starch blends. Subsequently, the O—H groups in polymer matrix of pristine PVOH, corn starch, dialdehyde starch (DAS) and blends of PVOH-corn starch and PVOH-DAS have been significantly reduced, thus weakened the presence of hydrogen bonds in polymer matrix as illustrated in Fig. 8. However, further increment in electron beam irradiation dosage up to 30 kGy has significantly reduced the wavenumber of O—H stretching of all samples as shown in Fig. 4(c). This also indicates the higher electron beam irradiation could weaken the O—H bonds of hydroxyl groups in polymer matrix of all samples. This might be due to the available amounts of O—H stretching in polymer matrix at higher irradiation dosage ($\geq$30 kGy) has been rapidly reduced by generating the more polymeric free radicals and thus weakened the O—H stretching in polymer matrix of all samples [20,32].

Besides, another significant peak can be found at the wavenumbers of 2905–2930 cm^{-1} as shown in Fig. 6. This peak is attributed to the C—H bonds stretching of pristine PVOH, all PVOH-corn starch blends and all PVOH-DAS blends. By referring to Fig. 4(d), the wavenumbers of C—H stretching of native corn starch and all PVOH-corn starch blends are observed to be slightly higher than DAS and all the PVOH-DAS blends. This indicates that the amount of saturated C—H bonds in non-irradiated PVOH-corn starch blends is slightly higher than non-irradiate PVOH-DAS blends. This is attributed to the periodate oxidation of native corn starch could slightly break and transfer the saturated C—H bonds of the anhydroglucose rings into unsaturated O=C—H bonds. This could further slightly reduce the wavenumbers of C—H stretching to lower values [12,33–34]. The increasing of electron beam irradiation dosage up to 30 kGy has gradually reduced the wavenumber of saturated C—H stretching of all PVOH-corn starch blends to lower value as shown in Fig. 4(d). This indicates that the application of electron beam irradiation has significantly reduced the amount of saturated C—H stretching in polymer matrix of all PVOH-corn starch blends. This is because the some of electron released from electron beam accelerator

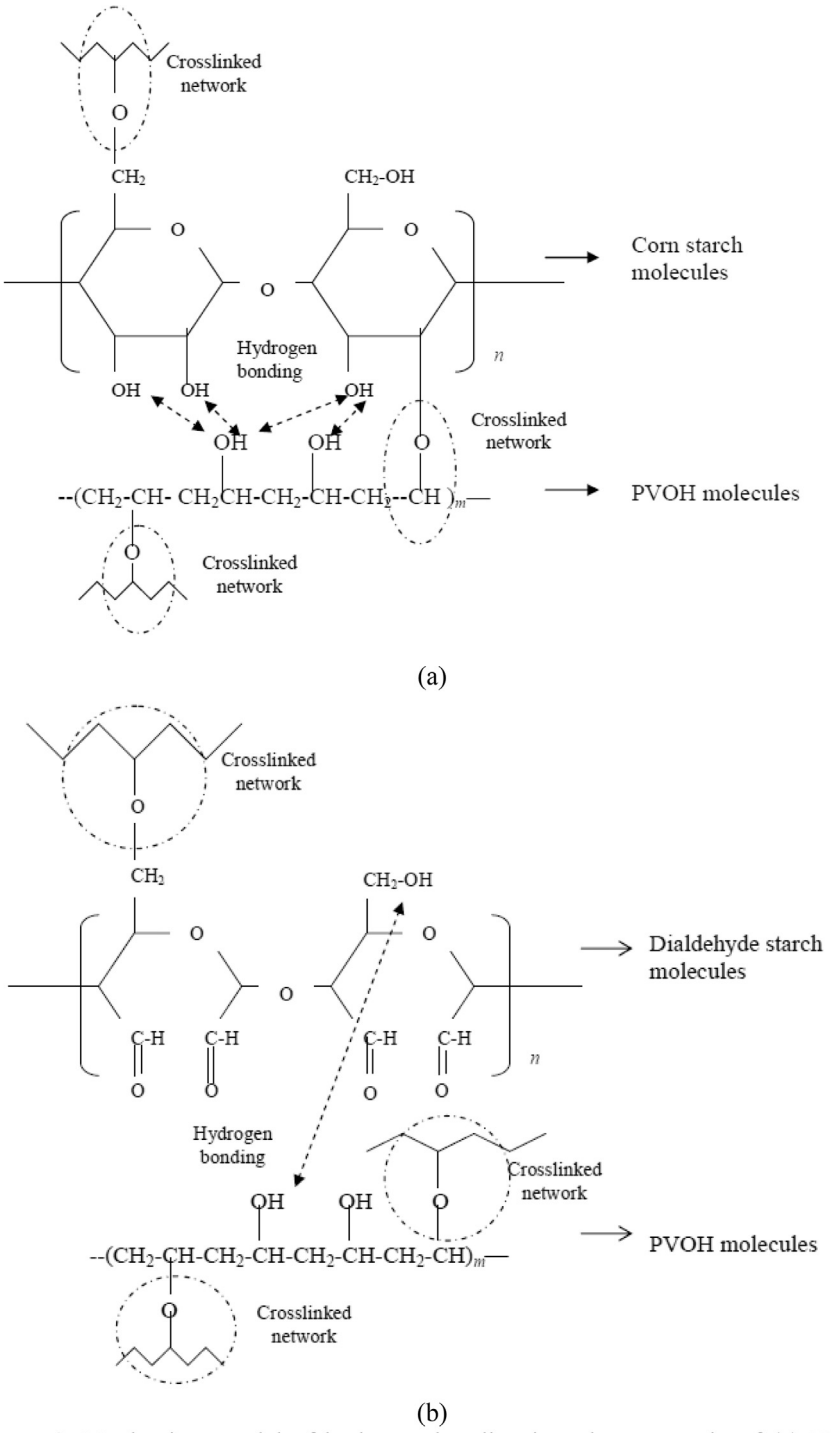
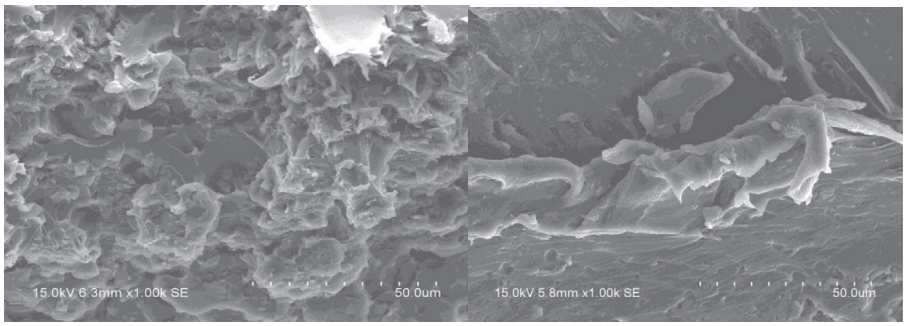


Fig. 8. Mechanism model of hydrogen bonding in polymer matrix of (a) PVOH-corn starch blends and (b) PVOH-dialdehyde starch blends when subjected to electron beam irradiation.

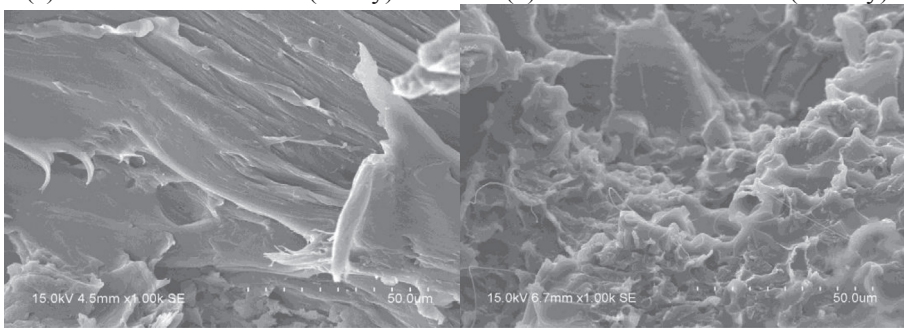
would attack the saturated C—H bonds of polymer chains to generate the polymeric free radicals by releasing the hydrogen atom due to the limited amount of hydroxyl groups in polymer matrix [20,22]. These released hydrogen atoms would react with other released hydrogen atoms or released ion $(OH)^-$ to form hydrogen gas and water vapour during irradiation [22,35]. As the results, the C—H stretching of all PVOH-corn starch blends was significantly decreased when subjected to electron beam irradiation. However, the application of electron beam irradiation up to 30 kGy has gradually increased the wavenumber of C—H stretching for all PVOH-DAS blends as shown in Fig. 4(d). This also indicates the increment in amount of saturated C—H bonds in polymer matrix of all PVOH-DAS blends by electron beam irradiation. This might be due to the released electrons from electron beam accelerator tended to attack C═O bonds of H—C═O to form polymeric free radicals and then these polymeric free radicals would react with other polymeric free radicals to form crosslinking networks. Thus, the amounts of saturated C—H stretching in polymer matrix of all PVOH-DAS blends have been significantly increased by increasing the wavenumber of saturated C—H stretching [12].

3.6. Scanning electron microscopy (SEM) analysis

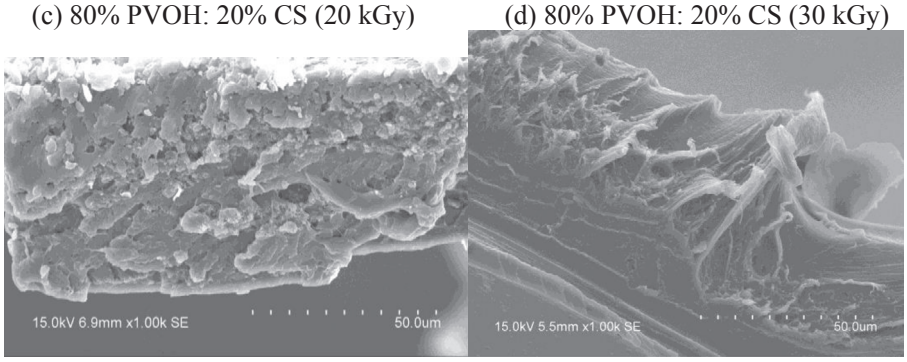
The surface morphologies of the fractured surfaces for all un-irradiated and irradiated PVOH-corn starch and PVOH-DAS blends were



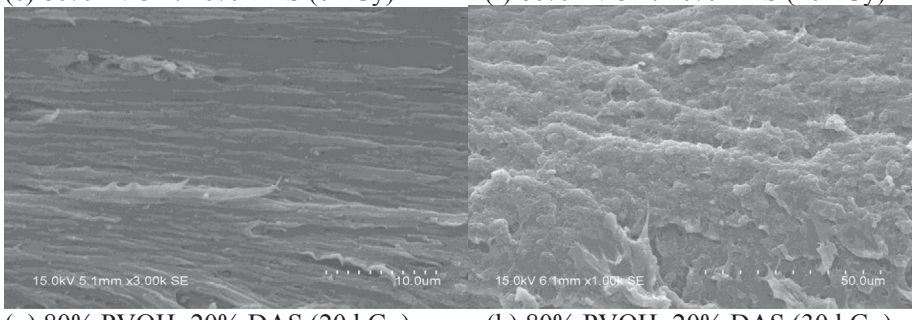
(a) 80% PVOH: 20% CS (0 kGy) (b) 80% PVOH: 20% CS (10 kGy)



(c) 80% PVOH: 20% CS (20 kGy) (d) 80% PVOH: 20% CS (30 kGy)



(e) 80% PVOH: 20% DAS (0 kGy) (f) 80% PVOH: 20% DAS (10 kGy)

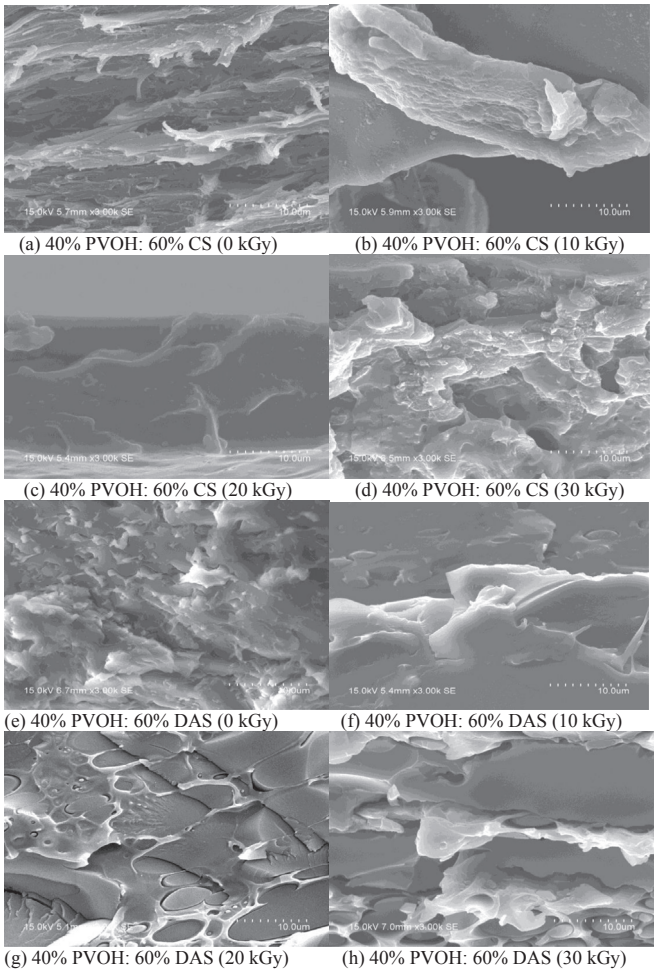


(g) 80% PVOH: 20% DAS (20 kGy) (h) 80% PVOH: 20% DAS (30 kGy)

Fig. 9. (a)–(h): Surface morphologies of fractured surfaces for all 80% PVOH + 20% corn starch blends and 80% PVOH + 20% DAS blends when subjected to various irradiation dosages.

depicted in Figs. 9 and 10. By observing the Fig. 9(a)–(c), the application of electron beam irradiation dosages of 10 kGy and 20 kGy was observed to improve the matrix continuities of 80% PVOH + 20% CS blends by reducing the occurrence of fibrils on fractured surface of polymer matrix. Furthermore, the width of fibrils formed on fractured surface of 80% PVOH + 20% CS blends also observed to be significantly larger after electron beam irradiated to 10 kGy and 20 kGy. This is due to the electron beam irradiation could induce the formation of crosslinked networks inside polymer matrix. The existence of crosslinked networks has significantly reduced the tearing effect of polymer matrix under straining and increased the width of fibrils formed by reducing in the occurrence of fibrils amounts [32]. The higher matrix continuities of polymer matrix also indicates the formation crosslinking networks has provided significant enhancement effect in tensile strength of 80% PVOH + 20% CS blends as discussed earlier in tensile strength. Besides, the occurrence of cavities in polymer matrix of 80% PVOH + 20% CS blends also observed to be highly reduced when subjected to electron beam irradiation dosages of 10 kGy and 20 kGy. However, the matrix continuities of 80% PVOH + 20% CS blends was found to be severely reduced when further irradiated to 30 kGy as depicted in Fig. 9(d). On the other hand, the occurrence of flakes-like structures also can be obviously found on the fractured surface of 30 kGy irradiated 80% PVOH + 20% CS blends. The occurrence of flakes-like structures indicates higher irradiation dosages could reduce the tensile strength and led to the brittle behaviour of polymer matrix of 80% PVOH + 20% CS blends.

For un-irradiated 80% PVOH + 20% DAS blends, the flakes like structures can be significantly found to occur on the fractured surface as



(a) 40% PVOH: 60% CS (0 kGy) (b) 40% PVOH: 60% CS (10 kGy)

(c) 40% PVOH: 60% CS (20 kGy) (d) 40% PVOH: 60% CS (30 kGy)

(e) 40% PVOH: 60% DAS (0 kGy) (f) 40% PVOH: 60% DAS (10 kGy)

(g) 40% PVOH: 60% DAS (20 kGy) (h) 40% PVOH: 60% DAS (30 kGy)

Fig. 10. (a)–(h): Surface morphologies of fractured surfaces for all 40% PVOH + 60% corn starch blends and 40% PVOH + 60% DAS blends when subjected to various irradiation dosages.

depicted in Fig. 9(e). The occurrence of flakes like structures on fractured surface indicates the brittle behaviour of polymer matrix. By referring to Fig. 9(e)–(h), the occurrence of cavities and flakes like structures were observed to be significantly reduced when irradiated to 10 kGy. This is due to the electron beam irradiation process at low dosage could induce the formation of crosslinking networks inside polymer matrix of 80% PVOH + 20% DAS blends. The formation of crosslinking networks inside polymer matrix could induce and enhance the interaction effect between the PVOH and dialdehyde starch and thus increase the tensile strength of 80% PVOH + 20% DAS blends. However, the increasing of electron beam irradiation dosages from 10 kGy to 30 kGy has gradually embrittled the polymer matrix of 80% PVOH + 20% DAS blends due to no significant elongation effect (no appearance of fibrils) on the fractured surface. In other words, the brittle polymer matrix of 30 kGy irradiated 80% PVOH + 20% DAS blends broke immediately when subjected to straining stress without any resisting ability towards the applied stress [32].

By comparing the Fig. 10(a) and (e), the polymer matrix of un-irradiated 40% PVOH + 60% corn starch blends is observed to be compatible to each other with no phase separation occurred between PVOH and corn starch. For 40% PVOH + 60% DAS blends, the PVOH and dialdehyde starch phases are found to be stay separated from each other which indicates the incompatible between these phases due to poor interaction effect between the PVOH and DAS phases. The compatibility between PVOH and corn starch phases is mainly due to the occurrence of hydroxyl groups (O—H) group with hydrophilic behaviour in PVOH and corn starch which could further induce the hydrogen bonds of PVOH and corn starch [16]. The strong hydrogen bonds of PVOH and corn starch has significantly induced the interaction between PVOH and corn starch without the occurrence of separated phases. On the other hand, the poor compatibility between PVOH and dialdehyde starch is due to the less hydrophilic behaviour of dialdehyde starch unable to form strong and stable hydrogen bonds with PVOH with strong hydrophilic nature [12]. Thus, the PVOH and dialdehyde starch regions in polymer matrix of 40% PVOH + 60% DAS blends cannot interact well with each other and stay as separated regions.

By referring to Fig. 10(a) and (b), the occurrence of thin fibrils on fractured surface of 40% PVOH + 60% CS blends was significantly reduced when irradiated at 10 kGy. The application of electron beam irradiation dosage up to 10 kGy also observed to highly increase the width of fibrils formed as depicted in Fig. 10(b). This is due to the low electron beam irradiation dosages (10 kGy) could induce the formation of crosslinking networks inside polymer matrix of 40% PVOH + 60% CS blends. The existence of crosslinking networks could further increase the matrix continuity of polymer matrix by reducing the tearing effect of polymer matrix into thin fibrils when under straining. The matrix continuity of polymer matrix for 40% PVOH + 60% DAS blends is observed to be increased when further irradiated to 20 kGy as shown in Fig. 9(c). Besides, the fibrils also observed to be disappeared from the fractured surfaces of 40% PVOH + 60% CS blends when further irradiated to 20 kGy. This indicates that higher degree of crosslinking networks has reduced the elongation ability of polymer matrix for 40% PVOH + 60% CS blends under straining. The flakes like structures and cavities can be observed to occur on the fracture surface of polymer matrix for 40% PVOH + 60% CS blends as depicted in Fig. 9(d). The occurrence of flakes like structures indicates the brittle behaviour of the polymer matrix. This is attributable to higher irradiation dosages ($\geq$30 kGy) could predominate the occurrence of chains scissioning process over the crosslinking process in the polymer matrix of 40% PVOH + 60% CS blends. The chains scissioning process could degrade the polymer matrix of 40% PVOH + 60% CS blends by breaking the long polymeric chains into shorter chains.

By referring to Fig. 10(e)–(h), the application of electron beam irradiation dosage up to 10 kGy has significantly improved the interaction effect between PVOH and dialdehyde starch inside polymer matrix of 40% PVOH + 60% DAS blends. The PVOH and dialdehyde starch phases were observed to be compatible to each other without the occurrence of separated phases. This observation also indicates that the application of low irradiation dosage ($\leq$10 kGy) could effectively improve the compatibility between PVOH and dialdehyde starch and thus further enhance the tensile strength of 40% PVOH + 60% DAS blends as discussed in earlier. However, further increment in electron beam irradiation dosages from 10 kGy to 30 kGy has severely weakened the interaction between the PVOH and dialdehyde starch phases by separating the PVOH and dialdehyde phases as observed in Fig. 10(g) and (h). This indicates that the application of higher electron beam irradiation dosages ($\geq$20 kGy) has provided a severe inferior effect on the compatibility between the PVOH and dialdehyde starch phases of 40% PVOH + 60% DAS blends. The poor interfacial adhesion effect between PVOH and dialdehyde starch phases also caused the occurrence of cavities in between the interfaces of PVOH and dialdehyde starch phases. Thus, the incompatibility effect between these phases would cause the tensile strength of polymer matrix for 40% PVOH + 60% DAS blends to be weakened.

4. Conclusions

The investigation on the effect of electron beam irradiation on thermal and mechanical-physico properties of PVOH-starch blends have been conducted. The incorporation of corn starch and dialdehyde starch has significantly decreased the mechanical properties of all PVOH blends by reducing the tensile strength and elongation at break. The

application of low electron beam irradiation dosages of 10 kGy has significantly increased the tensile strength of all samples. This is due to the electron beam irradiation could induce the formation of crosslinking networks inside polymer matrix of all PVOH-starch blends. The formation of crosslinking networks could enhance the reinforcing effect to the polymer matrix. However, the tensile strength of all samples was gradually decreased with further increasing of irradiation dosage up to 30 kGy due to significant reduction in the hydroxyl groups inside polymer matrix by electron beam irradiation. The elongation at break of all samples was gradually decreased when subjected to increasing of irradiation dosages. This is due to the formation of crosslinking networks by electron beam irradiation could restrict the mobility of polymer chains inside polymer matrix when under straining. On the other hand, the melting temperature and enthalpy of melting of PVOH-DAS blends also observed to lower than PVOH-corn starch blends. This indicates the interaction bonding effect among PVOH and dialdehyde starch molecules is significantly weaker than the interaction bonding effect among PVOH and corn starch molecules. Thus, a lower temperature is required to breakdown the internal interaction bonding effect of PVOH-starch blends. The increasing of irradiation dosages up to 20 kGy has significantly increased the melting temperature of all PVOH-corn starch blends and PVOH-DAS blends. This is attributed to the formation of crosslinking networks could increase the intra- and intermolecular bonding inside polymer matrix. Thus, the temperature required to overcome the internal interaction bonding effect also have been significantly increased. According to the XRD analysis, a significant deflection peak A is observed to occur on XRD curves of all samples and it is assigned by the mixtures of deflection planes (1 0 1), (1 0 $\bar{1}$) and (2 0 0). The increasing of electron beam irradiation dosages has significantly reduced the crystallite size of deflection peak A for all samples. This might be due to the formation of crosslinking networks would hinder and disrupt the highly ordered chains arrangement structure into less ordered chain arrangement. The application of electron beam irradiation dosages up to 20 kGy has gradually weakened the hydrogen bonds in polymer matrix of all blends of PVOH-corn starch and PVOH-DAS by attacking the O—H bonds to form crosslinking networks.

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