

Improving the Compatibility of Zein/Poly(vinyl alcohol) Blends by Gamma Irradiation and Graft Copolymerization of Acrylic Acid

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The effect of gamma irradiation and graft copolymerization with different ratios of acrylic acid monomer (AAc) on improving the compatibility of polymeric blends based on zein, as natural protein, and different ratios of poly(vinyl alcohol) (PVA) up to 50% were studied. The structure property of the polymeric blends was characterized by Fourier transform infrared spectroscopy (FTIR), mechanical testing, scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The FTIR analysis indicated that grafted AAc into zein/PVA matrix was stabilized by hydrogen bonding. The stress–strain curves showed that pure zein films were brittle, whereas pure PVA and zein/PVA blends films were tough materials either before or after gamma irradiation. The SEM micrographs indicated the formation of multilayers during the blending of zein and PVA, and these layers turned to dispersion in matrix after gamma irradiation and grafting with AAc, suggesting an effectiveness of gamma irradiation on improving compatibility.

KEYWORDS: Zein; poly(vinyl alcohol); polymer blends; γ radiation; graft copolymers; compatibilization; biodegradable packaging materials; FTIR; mechanical properties; SEM; XRD; DSC

INTRODUCTION

The production, properties and potential applications of edible films and/or biodegradable films have been reviewed (1, 2). Zein is a corn protein that represents about 80% of the total proteins in corn grains. The protein body of these grains consists of three structurally distinct types of zein: α -zein, γ -zein (which includes β -zein) and δ -zein. Films of zein are brittle, but plasticizers like glycerol, oleic acid, and polypropylene glycol can be used to improve their flexibility (3). Zein is also used as a potential material for the production of biodegradable plastics due to its thermoplasticity, hydrophobicity and impermeability to gases (4–6). It is considered as a byproduct from corn milling. For these reasons, zein is considered as one of the best biopolymers that can be used for the preparation of edible and biodegradable films after some modification with plasticizers (7, 8). Poly(vinyl alcohol) (PVA) is a versatile polymer with many industrial applications with a backbone composed of C–C bonds that are biodegradable (9). The excellent chemical resistance and optical and physical properties of PVA resins have led to broad industrial applications. Moreover, PVA is often modified by combination with other polymers or fillers in order to enhance its performance and barrier properties.

During recent years, the techniques of copolymerization and blending have acquired importance in improving the performance of materials, becoming an alternative way for the creation

of new polymers (10–12). Mixing two or more polymers to produce blends or alloys is a well-established strategy for achieving specific physicochemical properties, without the need of synthesizing any new functional polymer (13). The level of miscibility obtained depends on the nature of the components and the blending technique employed. Radiation technology may serve as a tool, not only for surface grafting to improve surfaces but also for reactive compatibilization (14–16). The main advantages of the application of high-energy irradiation applied to polymer blends may be summarized as follows: (i) Strong bridges between macromolecules can be formed. (ii) The compatibilization by high energy radiation of polymer blend (one cross-linkable component and the other less stable to the high energy processing) can be achieved without the addition of any ionomer. (iii) Addition of multifunction monomers and ionomers to polymer blends is effective in accelerating and increasing the cross-linking degree in irradiated polymer blends (17).

In this study, gamma irradiation and zein/PVA blending were used to improve the mechanical and thermal properties of biodegradable zein-based films. Thus, mechanical and thermal properties of polymeric blends before and after gamma irradiation were examined. The morphology and chemical changes of the polymeric blends were also studied using scanning electron microscopy (SEM) and FTIR spectroscopy, respectively.

MATERIALS AND METHODS

Materials. Zein, poly(vinyl alcohol) (PVA), 87–89% hydrolyzed, with average molecular weight of 85,000–146,000, and acrylic acid monomer

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(AAc) were provided by Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). A laboratory grade (99.5%) of glycerol was obtained from Laboratoire Mat (Beauport, QC, Canada).

Preparation of Zein/PVA Film Blends. Stock solutions containing 5% (w/w) of zein dissolved in ethanol/water mixture (80/20%) and PVA dissolved in hot water at different ratios were prepared. The solutions were continuously stirred, and the required ratio of glycerol (20% w/w), based on blend weight, was added to the solutions. The solutions were degassed under vacuum in order to remove dissolved air. Films were then prepared by solution casting (5 mL) onto polymethacrylate (Plexiglas) plates, and placed on a horizontal-leveled surface. Solutions were allowed to dry overnight in a ventilated oven at 60 ± 2 °C. Dried films were peeled from the plate surface.

Graft Copolymerization of AAc onto Zein/PVA Blends. Solutions containing different ratios of zein and PVA and the required amount (2, 5, 10% w/w) of AAc were stirred continuously and poured in quick-fit bottles (100 mL). The contents of bottles were degassed under flow of nitrogen atmosphere prior to irradiation. The direct method of grafting was used, in which the substrate and monomer were simultaneously exposed to gamma irradiation. The bottles were exposed to gamma-irradiation in a ^{60}Co source (Underwater Calibrator-15A Research Irradiator; MDS Nordion inc., Kanata, ON, Canada) at a mean dose rate of 20 kGy/h. Films were then cast as described above.

FTIR Spectroscopy. FTIR spectra were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high linearity lithium tantalate (HLLT) detector. Spectra were analyzed using the spectrum software (version 3.02.01). The films were previously dried in an oven at 50 °C for 24 h in order to minimize water absorbance during measurements. The films were then placed onto a zinc selenide crystal, and the analyses were performed within the spectral region of $650\text{--}4000\text{ cm}^{-1}$ with 64 scans recorded at a 4 cm^{-1} resolution. Measurements were done on three films of each formulation, and the average spectrum was then calculated and analyzed. After attenuation of total reflectance and correction of the baseline, spectra were normalized with a limit ordinate of 1.5 absorbance units.

Mechanical Testing. Films (4 cm diameter) were equilibrated in a sodium bromide saturated solution in a desiccator, to ensure 59% RH at 20 °C. Film thickness was measured using a Mitutoyo Digimatic Indicator (Mitutoyo MFG, Tokyo, Japan) at five random positions along the films.

Puncture strength (PS) and puncture deformation (PD) were carried out using a Stevens-LFRA texture analyzer (model TA-1000; Texture Technologies Corp., Scarsdale, NY). In these measurements, a cylindrical probe (0.2 cm diameter) was allowed to move perpendicularly to the film surface at a constant speed (1 mm/s) until it passed through the film. Strength and deformation values were determined at the puncture point from the recorded force–deformation curves. The PS and PD values were calculated according to the following equations:

$$\text{PS (N/mm)} = (9.81F)/x$$

$$\text{PD (mm)} = d/K$$

where F is the recorded force value (g), x is the film thickness (μm), 9.81 m/s^2 is the gravitational acceleration, d is the distance (mm) recorded between the time of first contact probe/film and the time of puncture point and K is a corrective factor related to the fixed parameters of the texture analyzer.

The stress–strain properties were determined according to an ASTM D-638 method using the Minimat Material Tester (Rheometric Scientific, England). For all mechanical measurements, the recorded data is the average of four measurements for each sample.

SEM Analysis. The structure morphology of the fracture surfaces of zein/PVA polymeric blends was examined by scanning electron microscopy (SEM). The SEM micrographs were taken with a Hitachi S-3000N electron microscope with variable pressure (Hitachi High-Technologies Canada inc., Rexdale, ON, Canada), at a magnification of $1000\times$, at room temperature. The acceleration voltage used was 15 kV. Prior to SEM examination, samples were first cooled in liquid nitrogen and subsequently fractured for observation of cross-section.

DSC Measurements. DSC measurements were performed using a Shimadzu (Japan) DSC calorimeter equipped with data station. The films

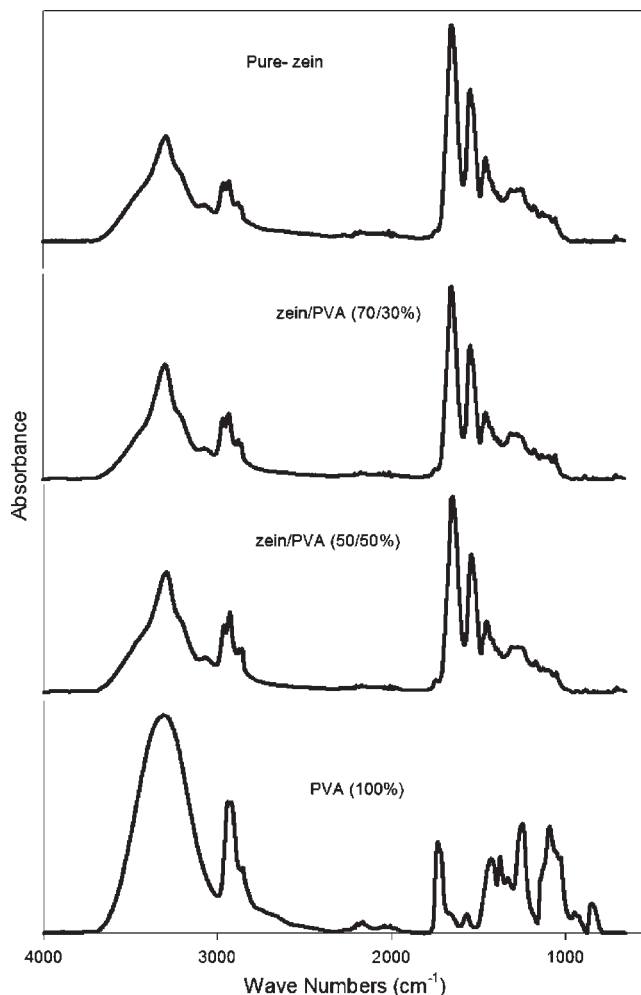


Figure 1. FTIR spectra of unirradiated zein, PVA polymers and their blends at different ratios.

were dried in an oven at 50 °C for 24 h before analysis. A heating rate of 10 °C/min was utilized, and the scans were carried out under a flowing nitrogen gas at a rate of 20 mL/min. It should be noted that glass transition temperature (T_g) was measured as the temperature of the first endothermic peak, which is the enthalpy relaxation of the amorphous part, while crystalline melting temperature (T_m) was determined as the second endothermic peak, which is due to the melting point of the crystalline part of the blend. ΔH is the melting enthalpy for the polymer, calculated from the area under the peak of the DSC heating curve. T_g , T_m and ΔH were calculated by the data software.

XRD Analysis. The films were dried in an oven at 50 °C for 24 h before analysis. X-ray diffraction (XRD) experiment of the samples was performed at room temperature by a Philips PW 1390 diffractometer (30 kV, 10 mA) with Cu/K α target irradiation at a scanning rate of 8°/min in a 2θ range of 4–90°. The typical diffraction spectrum consists of a plot of reflected intensities versus the detector angle (2θ).

RESULTS AND DISCUSSION

FTIR Analysis. FTIR spectroscopy was used to describe the chemical and physical changes that may occur in polymeric materials upon gamma irradiation and graft copolymerization of the zein/PVA blends.

Effect of Blend Composition. The FTIR spectra of unirradiated films of pure zein and PVA polymers and their blends at different ratios are shown in **Figure 1**. Absorption bands can be observed at $3200\text{--}3570$, $2850\text{--}3000$, $1725\text{--}1740$, 1430 , 1375 , 1260 , and 1100 cm^{-1} for pure PVA and at $3200\text{--}3570$, $2850\text{--}3000$, 1640 , and 1550 cm^{-1} for pure zein. The assignments of these

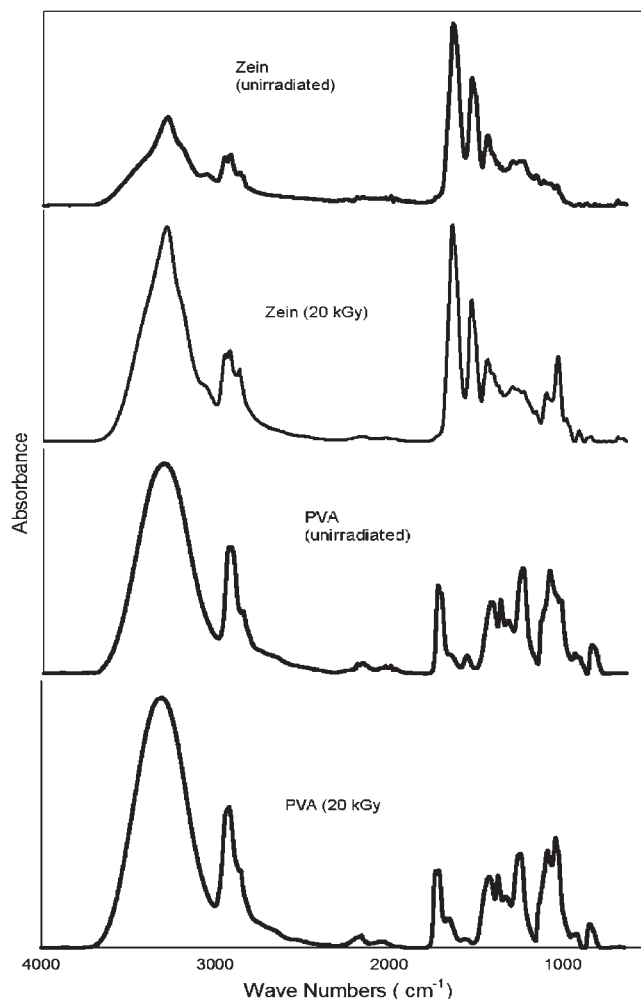
Table 1. Assignments of Some FTIR Absorption Bands for Zein, PVA and PAAc Polymers

polymer	wavenumbers (cm ⁻¹)	assignments
PVA	3200–3570	O–H stretching from intramolecular hydrogen bonding
	2850–3000	alkyl stretching
	1725–1740	C=O stretching from acetyl group
	1650	absorbed water
	1430	C–H bending
	1375	O–H bending
	1260	residual acetate
	1140–1100	C–O double hydrogen bonded in crystalline domain C–O deformation
916	O–H stretching from intramolecular hydrogen bonding	
zein	3200–3570	O–H stretching
	2850–3000	alkyl stretching
	1640	amide I
	1550	amide II
PAAc	3200–3570	O–H stretching from intramolecular hydrogen bonding
	2850–3000	alkyl stretching
	1725–1740	C=O stretching from acetyl group
	1447	C–H bending
	1255	OH bending
	1150	OH stretching
	1050	C–O stretching
	995	C–O deformation
	930	O–H stretching from intramolecular hydrogen bonding

bands are shown in **Table 1**. The intensity of the characteristic bands of zein/PVA blends was found to decrease with an increasing ratio of PVA in the blend. In particular, the intensity and width of the O–H stretching vibration peak was also decreased as compared to pure PVA. These lower intensities may be due to weaker polymer–water interactions when the concentration of zein increases, suggesting a relative dehydration of PVA after zein addition, as already reported by other studies (18, 19).

Effect of Gamma-Irradiation on the Structure of Pure PVA and Zein Polymers. The FTIR spectra for pure PVA and pure zein polymers before and after gamma irradiation at a dose of 20 kGy are shown in **Figure 2**. The spectrum of irradiated PVA films shows a decrease of the typical bands in the fingerprint region as compared to the unirradiated films. Moreover, although the O–H stretching band was not affected by gamma-irradiation, a shift of the C–OH stretching band from 1100 cm⁻¹ to 1000 cm⁻¹ was noticed in the PVA films. It was reported that this C–OH stretching mode (from alcohols) is influenced by hydrogen bonding, suggesting a modification in the degree of crystallinity of the PVA network (20–22). The spectrum of irradiated zein films shows a slight increase in the amide I/amide II ratio, indicating that the protein secondary structure was slightly affected by gamma irradiation and hence suggesting a decrease in the α -helical structure as a result of possible denaturation of protein conformation as described in literatures (23, 19). On the other hand, a significant increase of the bands related to O–H stretching (3200–3570 cm⁻¹) and C–H stretching (2850–3000 cm⁻¹) was observed after irradiation compared to the unirradiated films, suggesting a possible fragmentation of proteins under these conditions. As a result, this change may induce more distribution of PVA on the zein matrix and improve their compatibility.

Effect of Grafting Process on the Structure of Zein/PVA Blends. The FTIR spectra zein/PVA (50/50%) polymer blends

**Figure 2.** FTIR spectra of zein and PVA polymers before and after gamma irradiation at a dose of 20 kGy.

submitted to grafting copolymerization process in presence of 5 and 10% AAc are shown in **Figure 3**. Similarly to **Figure 2**, the effect of gamma irradiation on the zein/PVA blend (without AAc) caused changes in the typical bands related to proteins and PVA. Indeed, a slight increase in the amide I/amide II ratio suggests modifications in the secondary structure, and a strong increase of O–H stretching and C–H stretching peaks could be explained by a possible fragmentation of zein, as described above. These observations imply that the structure of zein may have been more affected than that of PVA, at a dose of 20 kGy.

Concerning the grafting process, it is interesting to note that the spectra of the grafted zein/PVA blends (with 5 and 10% AAc) display similar profiles relatively to their interactions with AAc. In particular, the presence of AAc resulted in a decrease of O–H stretching and a significant increase of the C–H stretching, that could be due to homopolymerization of AAc into poly(acrylic acid) (PAAc) after irradiation as a secondary reaction. The decrease of the O–H band, associated with a broader shape and a shift toward lower frequencies, could be due to a stronger hydrogen bonding level between the various groups formed during the grafting process. Moreover, a new band appeared at 3000–3100 cm⁻¹ and is assigned to unsaturated methylene C=C stretching from AAc in the polymer blend, as described by ref 24. Furthermore, a broad symmetric C=O stretching band also appeared clearly at ~1730 cm⁻¹, as compared to ungrafted blends, hence suggesting the presence of AAc (or PAAc) interactions within the zein/PVA blend.

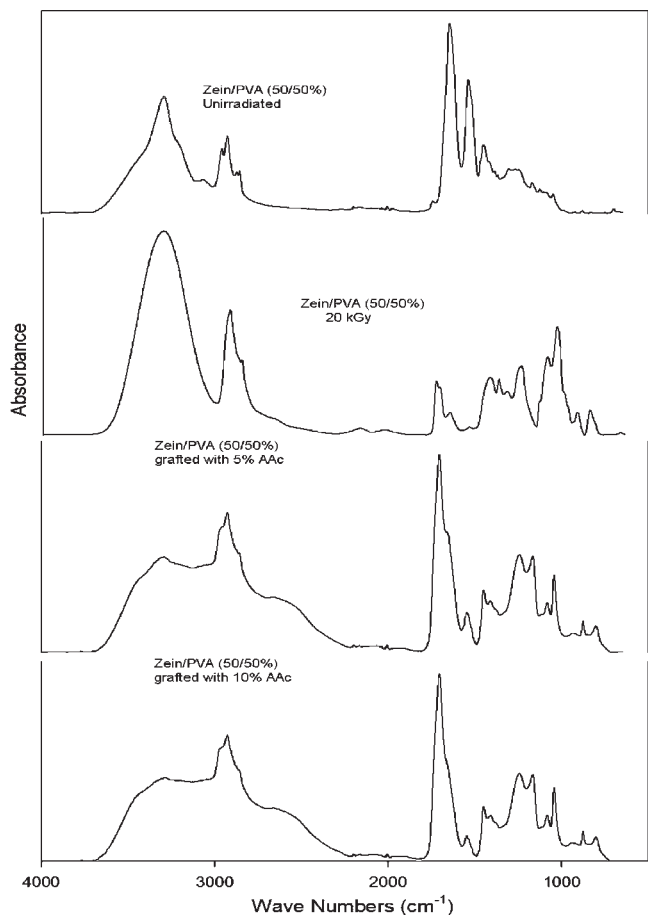


Figure 3. FTIR spectra of zein/PVA (50/50%) blend, before and after gamma irradiation at a dose of 20 kGy as well as its graft copolymers with different ratio of AAc monomer.

These characteristic peaks related to AAc interactions have already been described and are in agreement with previous studies of grafting copolymerization between starch and methacrylic acid, in which a C=O stretching band (1700 cm^{-1}) from the carbonyl groups of grafted monomer chains was observed (25–27). The compatibilizing effect of some reactive agents on polyethylene/plasticized starch blends was also supported by FTIR analysis and described by analogous observations (28). In conclusion, this FTIR analysis allowed characterizing the presence of grafted AAc in zein/PVA blend, inducing the compatibilization of the two immiscible polymers and their stabilization via hydrogen bonding.

Tensile Mechanical Properties. Mechanical properties may be considered as the most important properties of polymers for most applications. It is well-known that polymers are classified into three types according to the type of stress–strain curves (29). In brittle polymers such as polystyrene, the stress–strain curves are linear up to the fracture point. Tough polymers such as polyethylene exhibit a yield point followed by extensive elongation at almost constant stress (cold draw). The third type of stress–strain curve is exhibited by elastomers such as polyurethane, in which a nonlinear curve up to break point, and the elongation percentage may be of the order of several hundred percent.

The average thickness of films obtained after casting was in the range of $80\text{--}120 \pm 2\ \mu\text{m}$. Zein films exhibited brittle-type polymers behaviors with a linear relationship between stress and strain, whereas PVA and zein/PVA polymeric blends behaved like tough polymers as shown in **Figure 4**. However, the increase of PVA ratio in the blends increased the toughness of the blends.

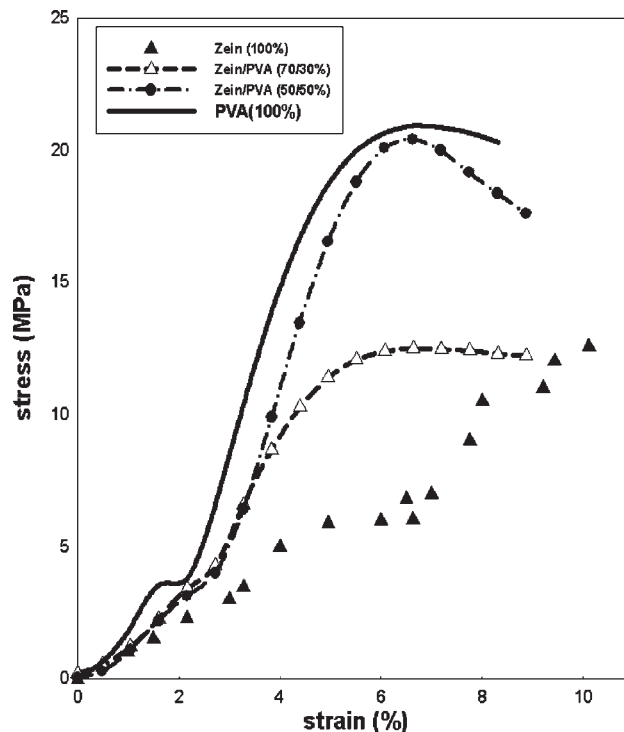


Figure 4. Stress–strain curves of unirradiated zein and PVA polymers and their blends of different ratios.

Table 2. Mechanical Properties of Zein/PVA Blends of Different Ratios before and after Gamma Irradiation to a Dose of 20 kGy and Their Graft Copolymer Blends with 5% AAc Monomer

zein/PVA ratio (%/%)	dose (kGy)	graft copolymer	PS ^a ($\text{N}\cdot\text{mm}^{-1}$)	PD ^a (mm)
100/0	0	no	$48.0 \pm 8.9\text{ bc}$	$2.16 \pm 0.28\text{ a}$
90/10	0	no	nd	nd
	20	no	nd	nd
80/20	20	yes	$55.7 \pm 2.2\text{ c}$	$3.00 \pm 0.27\text{ cd}$
	0	no	nd	nd
70/30	20	no	$54.5 \pm 5.3\text{ c}$	$4.14 \pm 0.08\text{ e}$
	0	no	$29.2 \pm 1.7\text{ a}$	$2.58 \pm 0.20\text{ ab}$
50/50	20	no	$67.5 \pm 6.0\text{ d}$	$2.72 \pm 0.21\text{ c}$
	20	yes	$40.3 \pm 4.3\text{ b}$	$6.47 \pm 0.39\text{ f}$
0/100	0	no	$69.9 \pm 6.2\text{ d}$	$3.40 \pm 0.30\text{ d}$
	20	no	$234.0 \pm 16.8\text{ e}$	$5.50 \pm 0.30\text{ f}$
	20	yes	$37.0 \pm 3.9\text{ b}$	$9.82 \pm 0.32\text{ g}$
	0	no	$201.0 \pm 11.1\text{ e}$	$5.88 \pm 0.36\text{ f}$

^a Values in the same column with different letters are significantly different ($P \leq 0.05$); nd, not detected.

Table 2 shows the mechanical properties of zein/PVA polymeric blends at different ratios before and after gamma irradiation to a dose of 20 kGy. It can be seen that, due to noncompatibility of the blends containing 90 and 80% of zein component, the mechanical properties were undetectable and broken during testing due to insolubility of PVA polymer in the zein matrix. Before gamma irradiation, a ratio of 30% PVA in the blend was the minimum ratio to obtain a compatible phase with zein. In general, the mechanical properties of unirradiated blends are higher than those of zein and lower than those of PVA. Usually, mechanical properties are controlled by three morphological factors, the number of tie molecules, lamellar thickness and molecular chain entanglement. From **Table 2**, it can be concluded that the addition of PVA would increase the entanglement and tie molecules but

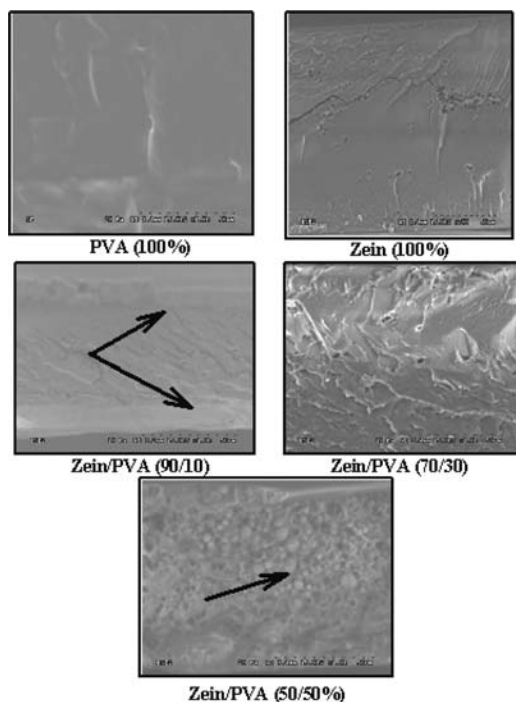


Figure 5. SEM micrographs of unirradiated zein and PVA polymers and their blends of different ratios.

would decrease the lamellar thickness and this effect decreases the brittle failure with increasing PVA ratio in the blend (28).

As shown in **Table 2**, the mechanical properties of films increased after gamma irradiation. This may be due to the occurrence of cross-linking to PVA component and oxidative degradation to zein. This state of affairs would lead to a high distribution of zein into PVA. It can also be seen that the grafting of AAc monomer onto the blends followed by gamma-irradiation had a significant effect on the mechanical properties of films ($P \leq 0.05$). In this regard, the grafted blend ratios 90/10 and 80/20, the obtained films showed the highest tensile properties. On the other hand, the tensile properties of grafted blends decreased with an increasing ratio of PVA. This may be explained based on the expectation that the grafting of AAc would prevent the cross-linking of PVA compared to the gamma-irradiated ungrafted blends. As shown in **Table 2**, the deformation properties of grafted blends are higher than those of unirradiated and irradiated ones, suggesting that the grafting process improved the compatibility of the zein/PVA network.

SEM Analysis. In immiscible blends such as zein/PVA, mechanical properties depend on the phase dispersion as well as the phase size. In most cases, the major component of the blend forms the matrix, whereas the minor component forms the dispersed phase. Therefore, in zein/PVA blend, zein is the matrix and PVA is the dispersed phase. **Figure 5** shows the SEM micrographs of the fracture surfaces of unirradiated zein and PVA as well as their polymeric blends of different ratios. It can be seen that the surface of pure polymers is smooth and uniform. However, the surface of zein showed some cracks which may be arise from casting in methanol/water mixture (30). On the other hand, the SEM micrographs of zein/PVA polymeric blends showed a multilayer view (as shown by the arrows), in which PVA formed a thin film containing zein in between. This multilayer formation is due to immiscibility of the two components and consequently involved a decrease in mechanical properties. After gamma irradiation, PVA was cross-linked and zein was degraded. As a result, SEM micrographs also showed multilayers with larger PVA layers, as illustrated in **Figure 5**. On the other hand, the SEM micrographs of the graft

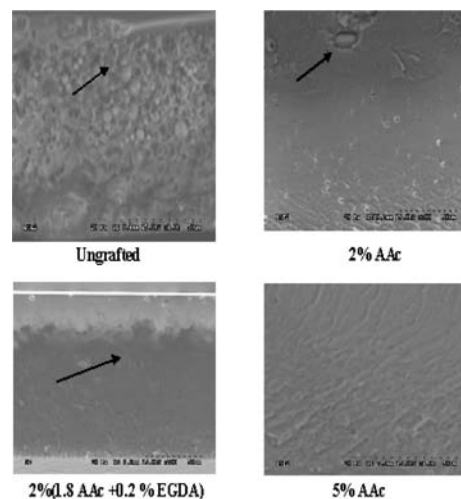


Figure 6. SEM micrographs of zein/PVA (50/50%) graft copolymerized blend with different ratio of AAc.

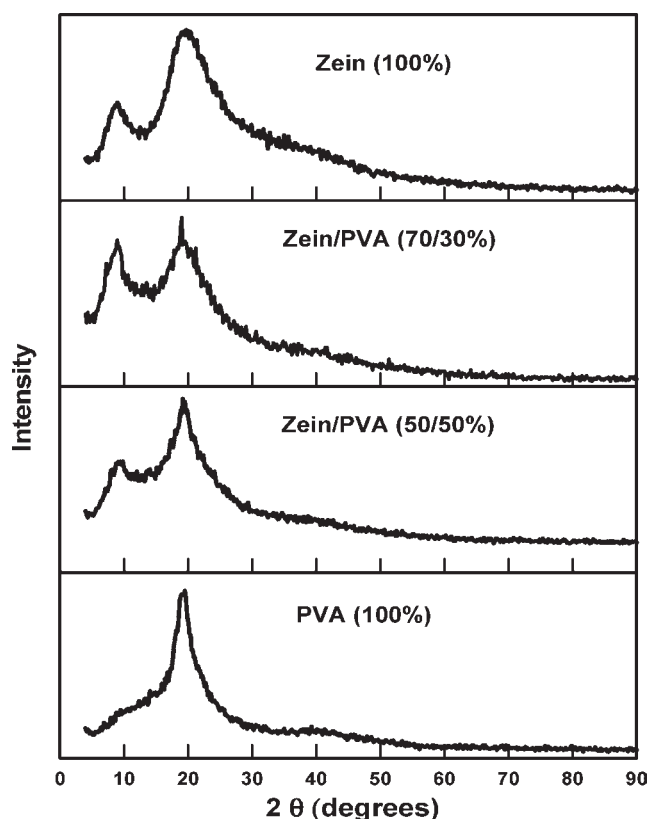


Figure 7. XRD patterns of unirradiated zein, PVA polymers and their blends at different ratios.

copolymers of blends with AAc showed a higher distribution of PVA polymer in zein matrix as shown in **Figure 6**. The grafted branches of AAc in both zein and PVA chains reduced the interfacial tension between the phases in blends and consequently improved the distribution of PVA phase in the zein matrix. In this sense, the SEM micrographs also showed that the phase pattern was decreased with increasing AAc ratio in the grafting solutions.

XRD Analysis. The XRD analysis was performed to clarify the change in crystalline structure of zein due to the blending with PVA and graft copolymerization with AAc. The XRD patterns of unirradiated zein, PVA and their blends of different ratios are shown in **Figure 7**. **Figure 8** shows the XRD patterns of the blend

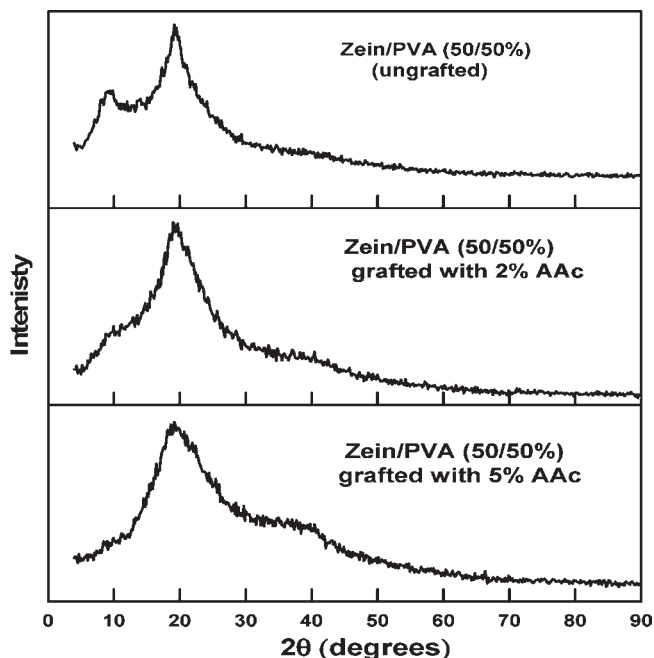


Figure 8. XRD patterns of zein/PVA (50/50%) graft copolymerized blend with different ratio of AAC.

composed of equal ratios of zein and PVA, before and after graft copolymerization with different ratios of AAC monomer. It can be seen that the position of maximum peak is slightly shifted to lower values by adding PVA. Also, the second peak in zein films at 2θ decreased with an increasing PVA ratio in the blend. These shift and decrease in peaks indicate that the orientation of molecules was modified in zein by addition of PVA. This change may be due to the presence of two parts in zein molecules: (i) polar part that can be attracted to polar groups of PVA (hydroxyl residues); (ii) formation of intermolecular hydrogen bonding higher than intramolecular hydrogen bonding. **Figure 8** also shows the effect of the grafting process on the XRD pattern structure of zein/PVA. It can be seen that the peak at $2\theta = 15.808$ in zein/PVA polymeric blend disappeared in grafted blends. In addition, a shifted position and a decreased intensity of other peaks occurred due to the grafting process, inducing a higher chain orientation level in zein molecules and more amorphous fractions from grafted AAC.

DSC Measurements. The DSC technique is one of the convenient methods for investigating the compatibility of polymer blends; therefore it was used to investigate the compatibility between zein and PVA in their blends based on the glass transitions (T_g) and crystalline melting temperatures (T_m). **Figure 9** shows the DSC thermograms for unirradiated zein, PVA polymers and their blends of different ratios. The different DSC parameters derived from the DSC thermograms were also summarized in **Table 3**. It can be seen that the DSC thermograms for all the samples showed two endothermic peaks due to T_g and T_m for both pure polymers or their blends. The reported T_g value for pure zein occurred at 170–180 °C and decreased to approximately 60–80 °C in zein films plasticized by polyols (e.g., glycerol) (31). The blending of zein with hydrophilic polymers can also reduce the T_g of the resulting composite material (32,33). From **Table 3**, it can be seen that T_g for plasticized zein and PVA polymers were 65 and 43 °C, respectively. However, the DSC thermograms of zein/PVA showed a single T_g neither of zein or PVA indicating the compatibility within the blends. It was found also that the T_m and ΔH increases with an increase of PVA ratio in the polymeric blend.

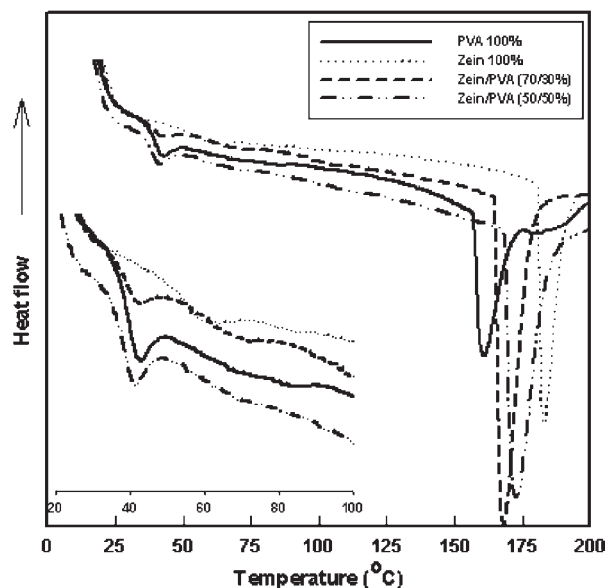


Figure 9. DSC thermograms of unirradiated zein, PVA polymers and their blends of different ratios gamma irradiated at a dose of 20 kGy. The inset is for the polymers within the low temperature scale.

Table 3. DSC Zein, PVA and Their Graft Copolymerized Blends of Different Ratios before and after with Different Ratios of Acrylic Acid Monomer (AAC)

blend composition (%)	T_g (°C)	T_m (°C)	ΔH^a (J/g)
zein/PVA (100/0)	65.0	183.0	1.2
zein/PVA (0/100)	43.0	161.0	31.3
zein/PVA (70/30)	42.5	172.6	69.4
zein/PVA (50/50)	41.6	168.0	71.0
zein/PVA (50/50) graft copolymer with 2% AAC	57.0	167.0	42.7
zein/PVA (50/50) graft copolymer with 5% AAC	66.0	162.0	39.0

^a Heat of fusion.

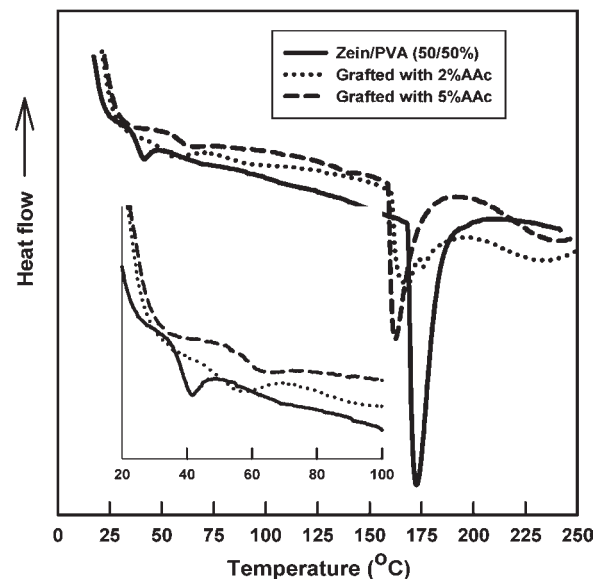


Figure 10. DSC thermograms of unirradiated zein/PVA (50/50%) blend before and after gamma-radiation graft copolymerization with different ratios of AAC monomer. The inset is for the polymers within the low temperature scale.

Figure 10 shows the DSC thermograms for the blend composed of equal ratios of zein and PVA before and after graft copolymerization with different ratios of AAC under the effect of gamma

irradiation. It is clear that the DSC thermograms showed a single T_g indicating the effect of grafting of AAc on the compatibility within the blends. However, it can be seen that the T_g of the blend increased with an increasing ratio of grafted AAc. This increase in T_g value is probably due to a higher restriction in chain mobility resulting from the presence of PAAc chains between zein and PVA chains. The decrease of T_m could be due to the destruction of the crystalline phases in the blend upon grafting. In conclusion, gamma irradiation and graft copolymerization enhanced the compatibility and improves the film formation as shown in the mechanical testing and DSC studies.

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