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Effects of Electron Beam Irradiation on the Structural Properties of PVA/PAM/CMC Ternary Polymer Blends

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Ternary miscible blends based on various ratios of poly(vinyl alcohol) (PVA), poly(acrylamide) (PAM) and carboxymethyl cellulose (CMC) were prepared by solution casting in the form of thin films. The structure-property behavior of the ternary PVA/PAM/CMC blends, before and after they had been exposed to various doses of electron beam irradiation, was investigated by FT-IR spectroscopy, SEM, XRD and stress-strain curves. The visual observation showed that the cast films of the individual polymers PVA, PAM, and CMC and their blends over a wide range of composition are clear and transparent indicating the miscibility of PVA/PAM/CMC ternary blends. The FT-IR analysis of pure polymers or their ternary blends before or after electron beam irradiation proved the formation of hydrogen bonding. In addition, it was found that the intensity of the different absorption bands depends on the ratio of PAM and CMC in the ternary blend. The XRD patterns showed that the peak position for the ternary blends decreases with increasing the ratio of CMC in the blend. However, the peak position for the ternary blend based on equal ratios of pure polymers was not affected by blending and was found in the same position as in the XRD pattern of pure PVA. The SEM micrographs give support to the visual observation indicating the complete miscibility of PVA/PAM/CMC ternary blends. The improvement in morphology leads to improvement in the tensile mechanical properties of the ternary polymer blends.

Keywords: ternary blends; electron beam irradiation; mechanical properties; scanning electron microscopy (SEM); x-ray diffraction (XRD)

1 Introduction

Multi-component polymer systems with more than two phases have properties, which cannot frequently be achieved by binary polymer systems. This is due to the advantage of an extra degree of freedom offered by the third component. With the rapidly growing application of multi-component of multiphase polymers, attention has been directed recently towards ternary polymer blends (1–3). In comparison with binary blends, ternary polymer systems can be viewed technologically as the next generation in multiphase polymers (4–7).

Research work on ternary blends was focused primarily on miscible polymers, in which a completely homogenous phase structure is possible.

Although, there are several hundred miscible binary polymer blends reported in the literature over the last decade, only few miscible ternary blends have been reported. In this regard, the ternary blend of poly (methyl methacrylate)/poly(epichlorohydrin)/poly (ethylene oxide) (PMMA-PECH-PEO) was investigated (5–8). In addition, the ternary polymer blends based on poly(vinylidene flouride)/poly(methyl methacrylate)/poly (ethylacrylate) and poly (vinylidene chloride-co-vinyl chloride)/poly (vinyl chloride)/poly (acrylonitrile-co-butadiene) were studied (9–12). Both of these systems use one of the ternary components, the poly(vinylidene chloride) in the former and the poly(acrylonitrile-co-butadiene) in the latter, to solubilization of the other two. Therefore, the present work was undertaken to study the effect of electron beam irradiation on the structural properties of miscible ternary blends based on the water soluble polymers PVA, PAM and CMC at different compositions. In addition, the effect of heating temperature on the structural properties was studied.

2 Experimental

2.1 Materials

The homopolymer PVA used in this study was of laboratory grade, purchased from Kuraray Chemical Company Ltd. (Japan). It was in the form of powder, partially hydrolyzed, and had an average molecular weight (Mw) of 74,000. The homopolymer PAM was of laboratory grade in the form of

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powder. It has an average (Mw) of 50,000, and was purchased from BDH Chemical Ltd., Pool, England. CMC used in this work was a commercial product obtained from Daicel Co. Ltd., Japan The degree of substitution of the CMC is 2.2

2.2 *Preparation of Ternary Polymer Blends*

Films of PVA/PAM/CMC ternary polymer blends were prepared by the solution casting technique. The PVA and PAM powder were dissolved in distilled water at ~90°C, while the CMC was dissolved in distilled water at room temperature. The polymer solutions were then mixed with continuous stirring until complete miscibility and subsequently, cast into glass dishes to form films with a thickness of ~0.2 mm. The cast films were dried at room temperature for 24 h and then placed in a vacuum oven at 80°C to remove residual water.

2.3 *Electron Beam Irradiation*

Irradiation was carried out in the electron accelerator facility (1.5 Mev and 25 kW) of the National Center for Radiation Research and Technology. The required doses were obtained by adjusting the electron beam parameters and conveyer speed.

2.4 *FT-IR Spectroscopic Analysis*

Infrared spectroscopic analysis was performed on a FT-IR spectrophotometer (model Mattson 100) made by Unicam (England), over the 500–4000 cm^{-1}range. The samples for IR analysis were first dried in a vacuum oven at 80°C for 2 h.

2.5 *Scanning Electron Microscopy*

Scanning electron microscopy (SEM) was used to examine the morphology of the fracture surfaces of the ternary polymer blends. The scanning electron micrographs were taken with a JSM-5400 instrument (Jeol, Japan). A sputter coater was used to pre-coat conductive gold onto the fracture surfaces before observing the microstructure at 30 kV.

2.6 *X-Ray Diffraction (XRD)*

XRD study was performed at room temperature by a Philips pw 1390 diffractometer (30 kV, 10 mA) with copper target irradiation at a scanning rate of 8 deg/min in a range of $2\theta = 4–90°$.

2.7 *Tensile Mechanical Testing*

Mechanical tests including break stress and strain were performed at room temperature using an Instron machine (Model 1195) employing a crosshead speed of 5 mm/min. Polymer blend samples were cut into dog-bone shapes of initial dimensions of 40 mm length and 4 mm width. The recorded value for each mechanical parameter is the average of five measurements.

3 Results and Discussion

3.1 *IR Spectroscopic Analysis*

The FT-IR analysis was used to illustrate the change in the structure because of blending. Figures 1–3 show the IR spectra at room temperature and different temperatures of thin films of the pure polymers PVA, PAM and CMC before and after the exposure to a dose of 50 kGy of accelerated electrons. The polymer films were kept in a variable temperature controlled cell (cryostat) to obtain the IR spectra at different temperature. In this procedure, the room temperature IR spectrum inside the cryostat was recorded and then the sample was heated gradually. As shown in Figure 1(A), the room temperature IR spectrum of unirradiated PVA showed the absorption band due to the C=O stretching of the ester group at ~1720 cm^{-1}, in accordance with previous reports (13). Also, the absorption bands due to O-H stretching associated with the hydrolyzed PVA polymer can be observed at ~3340 cm^{-1}. The absorption band, which arises from C-H stretching of almost all organic compounds, can be observed at 2910 cm^{-1}. After heating, the

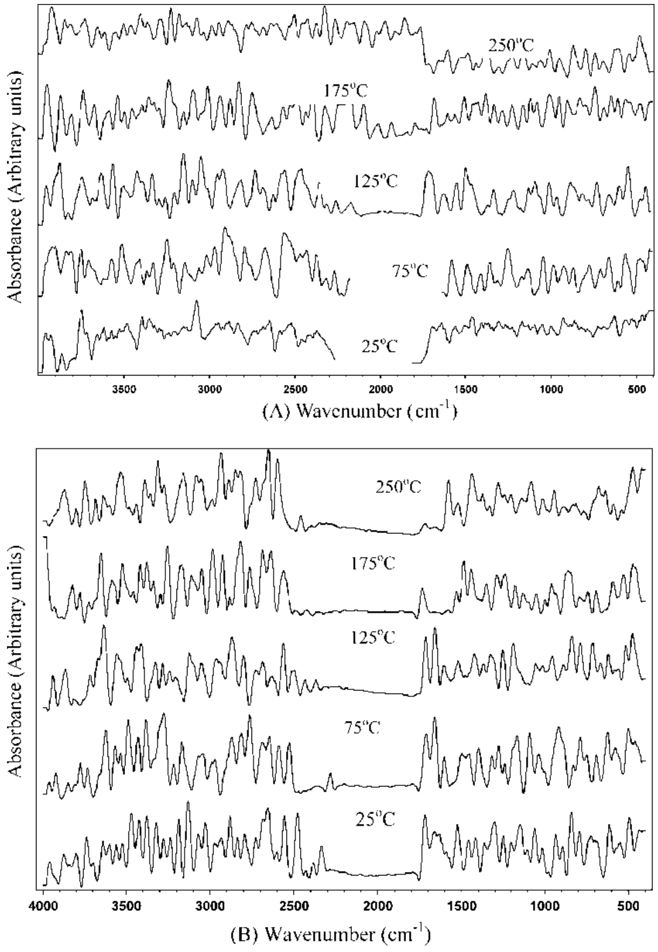

Fig. 1. IR spectra of thin films of pure PVA before (A) and after electron beam irradiation to a dose of 50 kGy (B). The IR spectra were recorded before and after heating to various temperatures.

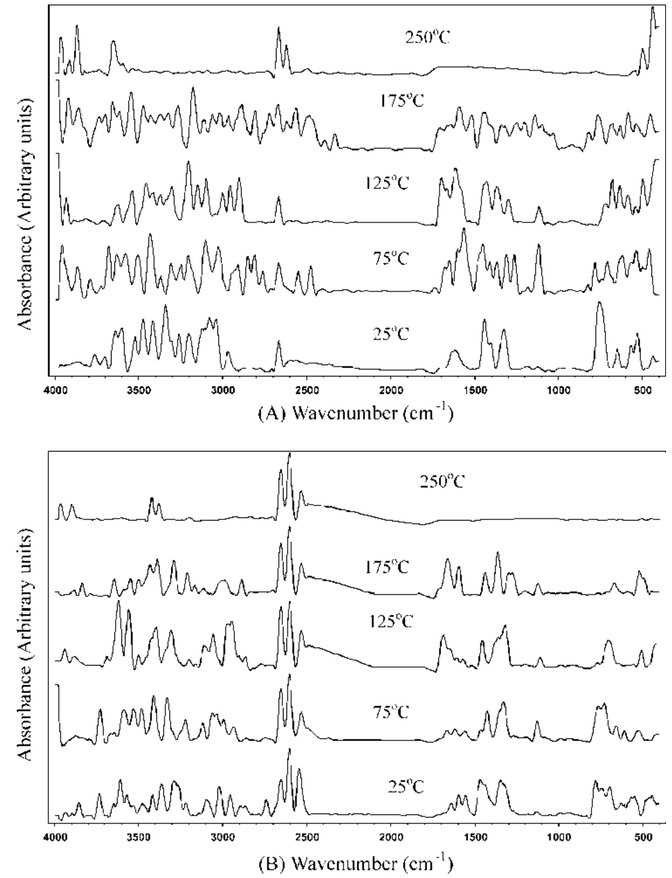

Fig. 2. IR spectra of thin films of pure PAM before (A) and after electron beam irradiation to a dose of 50 kGy (B). The IR spectra were recorded before and after heating to various temperatures.

intensity of most of the IR bands was decreased and shifted towards higher wave numbers. It is interesting to observe that when unirradiated PVA was heated within the temperature range 75–100°C, the IR bands (1500–1740 cm^{-1}) were greatly changed. Within this temperature range, i.e. the region of the glass transition of PVA, the C=O stretching band disappeared. However, the intensity of the stretching band due to CH at 2910 cm^{-1} was increased. Upon increasing the temperature up to 250°C, there is a distortion in the intensity of the absorption bands.

As shown in Figure 1(B), for the irradiated and heated PVA to different temperatures the bands due to C=O stretching disappeared indicating the occurrence of crosslinking.

As shown in Figure 2(A), the IR spectrum of unirradiated PAM polymer, showed absorption bands at 3350, 3203, 1670, and 1616 cm^{-1}, which are ascribed to the asymmetric and symmetric NH_2 stretching vibration, amide (ν C=O + ν CN), and amide (δ NH + ν CN), respectively (11, 12). Upon heating to 125°C, there is a great change involving most of the absorption bands, particularly the band due to C=O. Further heating up to 250°C, the band due to C=O disappeared. The IR spectra of irradiated and heated PAM showed similar behavior as shown in Figure 2(B).

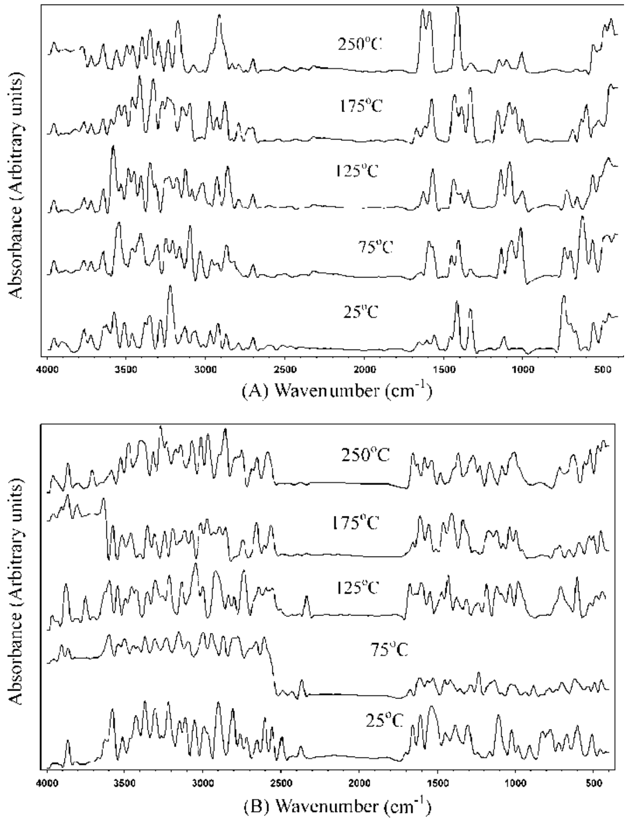

Fig. 3. IR spectra of thin films of pure CMC before (A) and after electron beam irradiation to a dose of 50 kGy (B). The IR spectra were recorded before and after heating to various temperatures.

The IR spectra of unirradiated CMC (Figure 3A) showed the characteristic absorption bands due to C-H stretching at ~2900 cm^{-1} and the bands due to O-H stretching at ~3500 cm^{-1}. While, the stretching absorption bands due to the C=O of the ester groups cannot be detected in the IR spectra of unirradiated and heated CMC due to the hindered effect, the IR spectra of irradiated CMC and heated CMC showed this band at ~1700 cm^{-1} due to the occurrence of oxidative degradation as shown in Figure 3(B).

Figures 4 and 5 show the IR spectra of ternary polymer blends composed of constant ratio of PVA (40%) and different ratios of PAM and CMC heated to different temperatures, before and after electron beam irradiation to a dose of 50 kGy. Based on these spectra, few points may be indicated: (1) the intensity of C-H stretching decreases with decreasing the ratio of CMC polymer as shown in Figure 5(A) going systematically with blend ratio. In addition, this finding holds true for intensity for the absorption band due to C=O stretching (2). In the IR spectra of pure polymers or their blends, the binding is through hydrogen bonding, in which all the spectra showed a sharp absorption bands around 3300 cm^{-1} (3). While the IR spectra of irradiated blends containing 20% PAM was clearly shown (Figure 4B), the IR spectra of the irradiated blend containing 40% PAM does not show

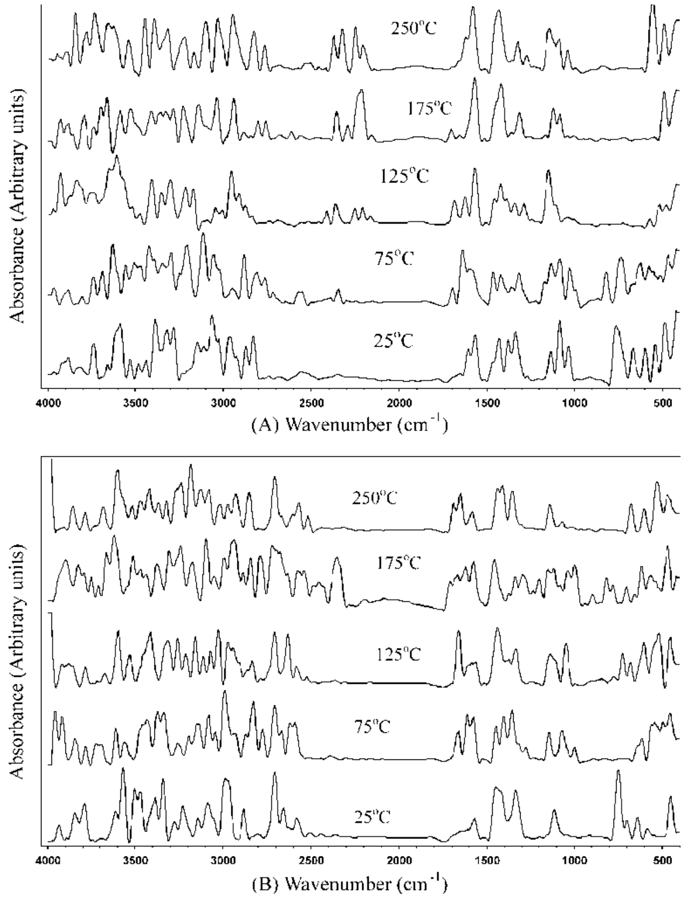

Fig. 4. IR spectra of thin films of ternary blend based on different ratios of PVA (40%), PAM (20%) and CMC (40%), before (A) and after electron beam irradiation to a dose of 50 kGy (B). The IR spectra were recorded before and after heating to various temperatures.

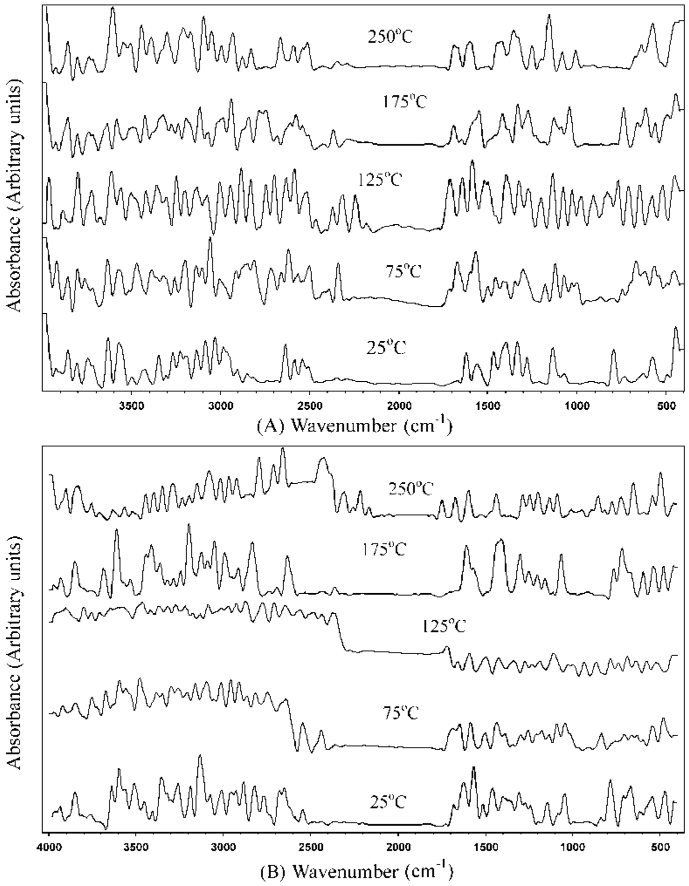

Fig. 5. IR spectra of thin films of ternary blend based on different ratios of PVA (40%), PAM (20%) and CMC (40%), before (A) and after electron beam irradiation to a dose of 50 kGy (B). The IR spectra were recorded before and after heating to various temperatures.

this band (4). The effect of heating on the structural changes of pure polymers or the ternary blends, either before or after electron beam irradiation, is similar.

3.2 *XRD Analysis of PVA/PAM/CMC Ternary Blends*

Figures 6 and 7 show XRD patterns for pure polymers and their ternary blends before and electron beam irradiation to a dose of 50 kGy. Also, Table 1 summarizes the results of the XRD analysis for these polymeric materials. For unirradiated polymers (Figure 6(A)), the (001) Bragg reflection for pure PVA is broad with a higher 2θ than those for pure PAM and CMC, indicating large crystallinity. However, the spacing "d" in the case of pure unirradiated CMC and PAM is higher than in the case of pure unirradiated PVA with higher intensity. After electron beam irradiation, the position of the XRD peaks was found to decrease for all pure polymers indicating the distortion of the crystalline structure.

For unirradiated PVA/PAM/CMC ternary blends (Figure 7(A)), the peak position was found to decrease with decreasing the ratio of PAM polymer in the blend and with increasing the ratio of CMC polymer. However, the peak position for the ternary blend containing equal ratios of polymers was not affected and displayed the Bragg reflection (001) identical to that of pure PVA. Also, the spacing "d" and the intensity of the XRD peaks are in accordance with 2θ values indicating complete miscibility. While, the peak position for the ternary blend containing equal ratios of polymers was not affected after electron beam irradiation, the peak position of the other blends was largely decreased. However, the peak intensity and broadness was largely increased after electron beam irradiation.

3.3 *Scanning Electron Microscopy*

Figure 8 shows the SEM micrographs of the unirradiated pure polymers. It is clear that the fracture surface differs from one polymer to another. As shown in Figure 8(A), the fracture surface of pure PVA is very smooth, showing a limited number of small particles dispersed along the micrographs. A different morphology can be seen for CMC homopolymers (Figure 8(C)), in which the surface is not smooth and full of cavities. After electron beam irradiation, the morphology

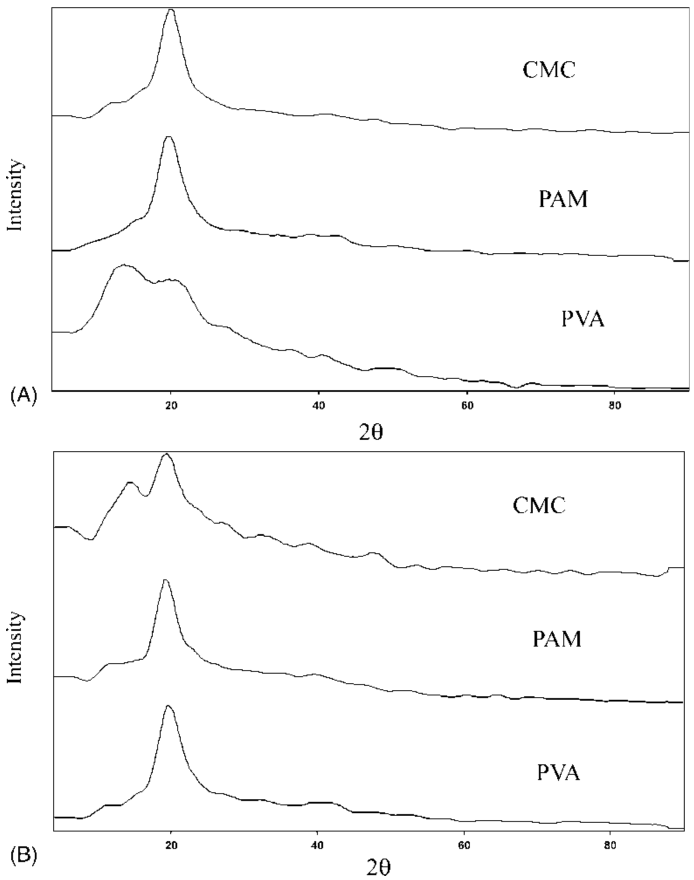

Fig. 6. XRD Spectra of pure polymers. (A) Unirradiated, (B) exposed to a dose of 50 kGy of accelerated electrons.

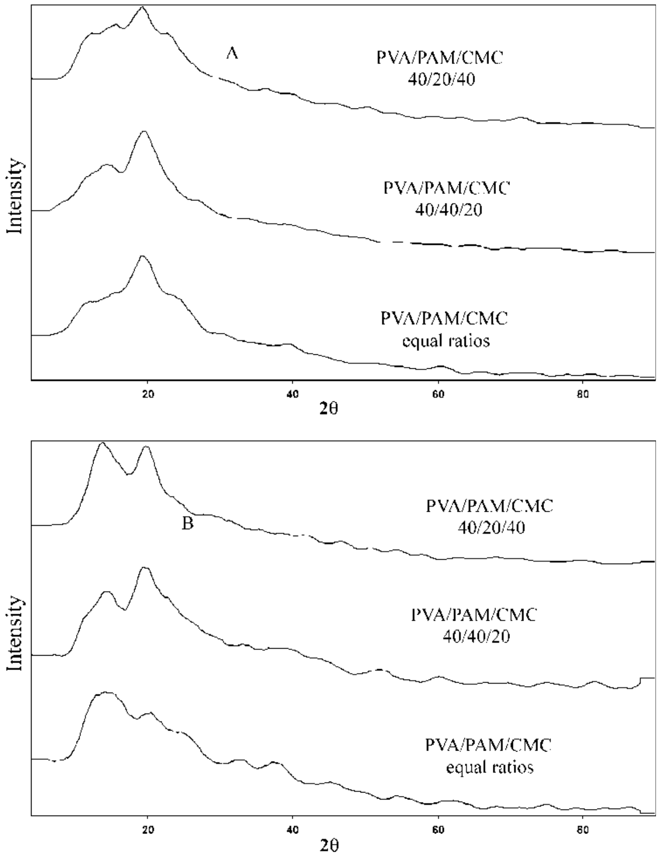

Fig. 7. XRD Spectra of ternary polymer blends at various compositions. (A) Unirradiated, (B) exposed to a dose of 50 kGy of accelerated electrons.

was changed in which the fracture surface of PVA seems more compact and the small particles still exists indicating the occurrence of crosslinking (Figure 9(A)). On the other hand, the occurrence of oxidative degradation to CMC is clear, in which the formation of cracks is the predominate feature and the surface became continuous (Figure 9(C)).

The fracture surface of the cast of PVA/PAM/CMC blends was examined by SEM to verify the miscibility

Table 1. Summary of XRD patterns of pure PVA, PAM and CMC polymer and their ternary blends of various ratios before and after electron beam irradiation to a dose of 50 kGy

Blend composition (%)	Irradiation	2*θ* (degree)	d (A°)	Intensity (kcps)
PVA	Unirradiated	20.40	4.35	0.392
	Irradiated	19.72	4.50	0.248
PAM	Unirradiated	19.40	4.58	0.568
	Irradiated	19.55	4.54	0.690
CMC	Unirradiated	18.43	4.80	0.105
	Irradiated	19.55	4.54	0.185
PVA/PAM/CMC (40/40/20)	Unirradiated	19.89	4.46	0.213
	Irradiated	18.87	4.70	0.163
PVA/PAM/CMC (40/20/40)	Unirradiated	19.04	4.66	0.223
	Irradiated	19.89	4.46	0.310
PVA/PAM/CMC (33/330/33)	Unirradiated	20.40	4.35	0.163
	Irradiated	20.40	4.35	0.318

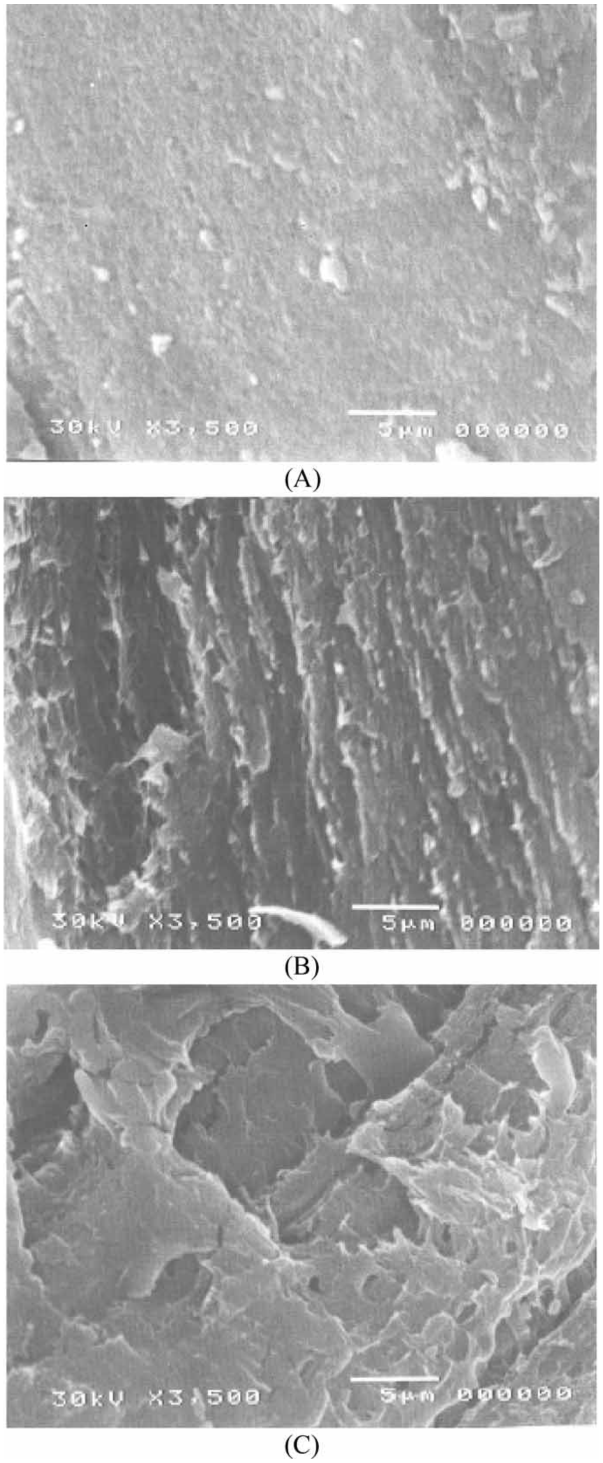

Fig. 8. SEM micrographs of unirradiated pure polymers. (A) PVA, (B) PAM, (C) CMC.

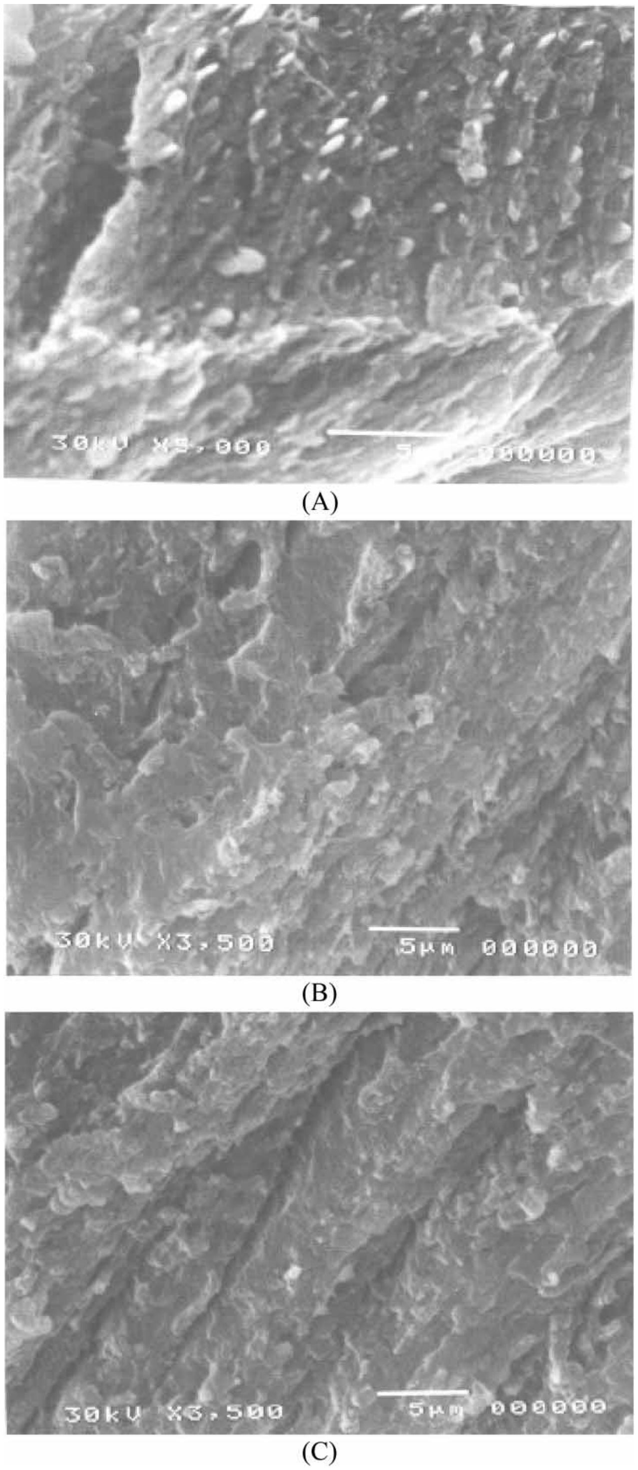

Fig. 9. SEM micrographs of electron beam irradiated pure polymers. (A) PVA, (B) PAM, (C) CMC.

within the systems before and after electron beam irradiation as shown in Figures 10 and 11. It can be seen that the blending results in a decrease in the particle size of all the polymers within the matrix of the blends and the rough and dendric structure of CMC no longer occurs. In addition, there is a reduction in the domain size, due to the compatibility of the different components in the blends. However, it can be observed that the compatibility within the blends containing lower ratios of CMC is higher than the blends with higher contents of CMC (Figure 10(A)). After electron beam

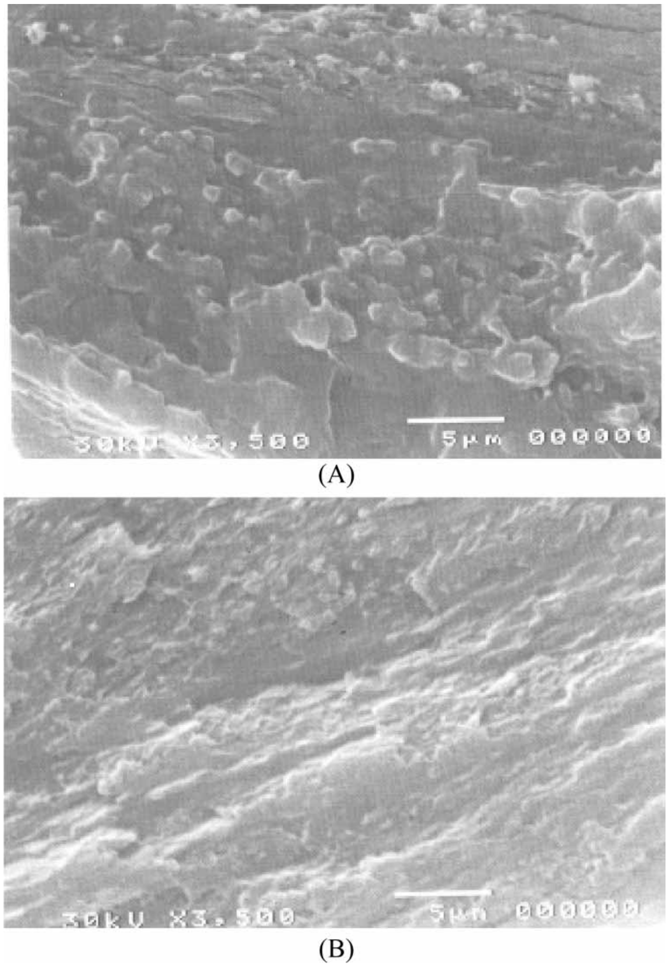

Fig. 10. SEM micrographs of the ternary blend PVA/PAM/CMC (40/40/20) before and after electron beam irradiated. (A) unirradiated, (B) 50 kGy.

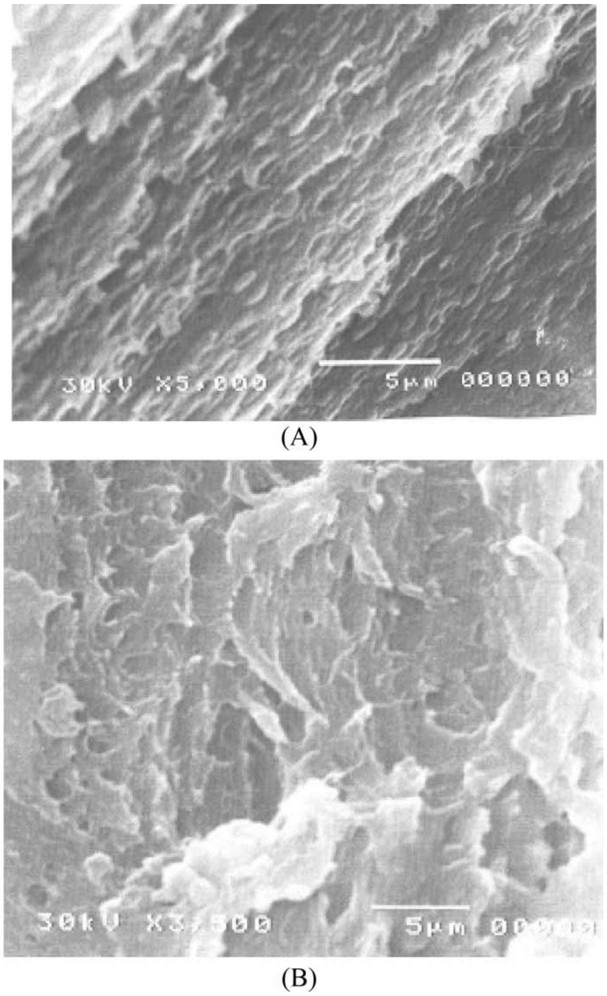

Fig. 11. SEM of the ternary blend PVA/PAM/CMC (40/20/40) before and after electron beam irradiation (A) unirradiated, (B) 50 kGy.

irradiation, the fracture surface was improved, in which the formed radicals enhances the bonding between the different polymer components. However, the effect of electron beam irradiation on the structure of the blends containing higher ratios of CMC is clear, in which the surface was completely changed with the appearance of whiteness and cavities (Figure 11(B)).

3.4 Tensile Mechanical Properties

Improvement in miscibility leads to a change in morphology towards smaller dispersed domains, which in turn improves the mechanical properties. The mechanical testing showed that none of the pure polymers PVA, PAM, and CMC) and their ternary polymer blends at various compositions showed the stress–strain behavior of tough polymers with yielding properties. Figure 12 shows the break stress and strain of pure polymers and ternary polymer blends PVA/PAM/CMC, before and after electron beam irradiation to various doses. The higher break stress of the unirradiated ternary blends with respect to pure polymers can be attributed to the physical bonding, the intra and inter hydrogen bonding between the functional groups present in the three individual polymers. However, the unirradiated pure CMC polymer displayed the highest break stress, while pure PAM polymer showed the lowest break stress. Also, it can be seen that the ternary blends containing higher ratios of CMC polymer displayed higher break stress than the blends containing higher ratios of pure PAM.

The effect of electron beam irradiation on the tensile mechanical properties differs from one individual polymer to another and from ternary blend composition to another. While, the break stress of pure PVA and PAM was found to increase with increasing irradiation dose from 50 to 100 kGy, the break stress of pure CMC decreases with increasing irradiation dose. This behavior is understandable since ionizing radiation can induce chain–scission and crosslinking. The increase in break stress in the case of pure PVA and PAM is due to the occurrence of crosslinking. The

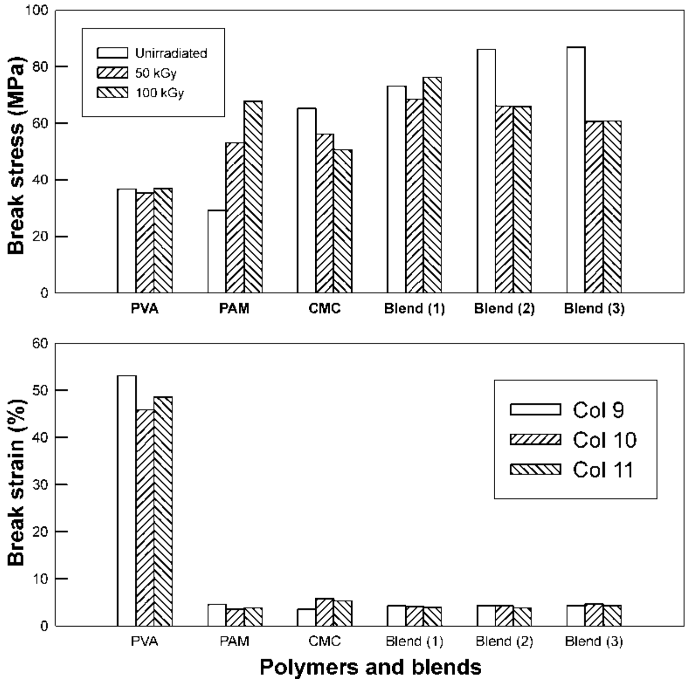

Fig. 12. Tensile strength properties of pure polymers and their blends at different ratios before and after gamma irradiation to various doses. Blend (1): PVA/PAM/CMC equal ratio from each polymer; Blend (2): PVA/PAM/CMC (40/20/40); Blend (3); PVA/PAM/CMC (40/40/20).

difference in sensitivity to electron beam irradiation of pure polymers is much clearer in the case of mechanical properties of the ternary blends composed of different ratios. While the stress at break was suddenly decreased for the blends containing higher ratios of CMC or PAM at a dose of 50 kGy, the break stress of ternary blends containing equal ratio tends to increase with increasing electron beam irradiation dose. This behavior may be explained based on the ratio of the crystalline part in the blend, in which PVA is a semi-crystalline polymer, while PAM and CMC are amorphous polymers. Also, these finding may be attributed to the break down of the hydrogen bonding between PVA, PAM and CMC from one side and the occurrence of oxidation degradation by electron beam irradiation from the other side (reduction of crystallinity).

Elongation at break of individual polymers is much higher than the ternary blends, regardless of the composition even after electron beam irradiation. However, the break strain of the ternary blends was not greatly affected by electron irradiation. The higher mechanical properties of the ternary blends compared to the individual polymers may be explained based on the improvement in miscibility. The improvement in miscibility may be explained based on the radicals formed on the macromolecules of PVA, PAM and CMC. These radicals initiate the formation of covalent bonds, copolymerization and crosslinking of these polymers. The radiation-induced chemical reactions of vinyl polymers include, in general, crosslinking, chain scission, small molecular elimination, internal or terminal double bond formation, and gas evolution was reported (14, 15).

4 Conclusions

The results presented in this work demonstrate the effect of EB irradiation on the structural properties of ternary polymer blends. On the basis of results obtained throughout this study, few points may be concluded. (1) The IR spectra of pure polymers or their blends showed the binding is through hydrogen bonding. (2) The peak position for unirradiated ternary blends was found to decrease with decreasing the ratio of PAM polymer in the blend and with increasing the ratio of CMC polymer. (3) The peak intensity and broadness was largely increased after EB irradiation. (4) The reduction in the domain size indicates clearly the compatibility of the different components in the blends. After EB irradiation, the compatibility within the blends containing lower ratios of CMC is higher than the blends with higher contents of CMC. (5) The stress at break was decreased for the blends containing higher ratios of CMC or PAM at a dose of 50 kGy.

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