Structural Properties of γ-Irradiated Poly(vinyl alcohol)/Poly(ethylene glycol) Polymer Blends

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ABSTRACT: The effect of various doses of γ radiation on the structural properties of water-soluble polymer blends based on poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) has been investigated. Although the aqueous solutions of individual PVA and PEG homopolymers were homogeneous and clear, films transparent to visual observation were only formed by solution casting of pure PVA and those blends containing low ratios of PEG up to 30%. The structure-property behavior of this range of blends before and after γ irradiation was investigated by light reflectance and UV absorbance, differential scanning calorimetry (DSC), IR spectroscopy, and tensile mechanical testing. The DSC thermograms of PVA/PEG blends, before or after γ irradiation, showed a solely endothermic peak over the temperature range 40–140°C, which may have arisen from the melting of the PEG component or from the glass transition of PVA/PEG as a miscible blend in accordance with those calculated on the basis of the theoretical Fox equation. Also, these thermograms did not clearly show any transition that arised from the pure PVA component. However, the improvement in tensile mechanical properties of PVA/PEG blends, the reflectance, and the optical absorption measurements support the idea of improved miscibility after γ irradiation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 167–176, 2004

Key words: poly(vinyl alcohol)/poly(ethylene glycol) blends; γ irradiation; miscibility; DSC

INTRODUCTION

Blending different homopolymers is an attractive method in the still-developing field of polymer chemistry for obtaining new products with industrially promising applications. These new products will eventually possess some of the important properties of each component. The importance of miscibility in polymer blends is attributed to the demand for products with advanced properties with good mechanical, thermal, and morphological properties. The research work in this field has been devoted to finding systems that are complementary, attracting one another by polarity or reactive groups, rather than finding polymer–polymer systems that are similar in common solvent. In this regard, the structure-property behavior of γ-irradiated polystyrene/poly(methyl methacrylate) miscible blends was previously investigated by different techniques using benzene as a common solvent.[1] The thermal analysis showed that this blend possesses a single glass transition temperature (T_g) and it decreases with increasing irradiation dose. Also, it was found that the presence of polystyrene in this blend affords protection against γ radiation and improves its thermal stability.

Poly(vinyl alcohol) (PVA) is an attractive nontoxic polymer with wide industrial applications due to its high hydrophilic properties, water solubility, and most importantly good film forming by solution casting. Despite these properties, it has been reported to be immiscible or partially miscible with most polymers, even with acrylic polymers.[2–4] For this reason, we wanted to find miscible polymer blends based on PVA and to illustrate the effect of high-energy radiation on the structure-property behavior of these blends. In this regard, PVA/carboxymethyl cellulose (CMC) water-soluble polymer blends were used as sorbents for dye wastes.[5] For this purpose, the PVA/CMC blend was converted to be completely insoluble in water by radiation grafting of a styrene monomer. Other authors improved the instability of the PVA/nylon-4 polymer blend for dialysis by esterfication of PVA with formic acid, which was used as a common casting solution.[6] They reported that this method is easier than chemical, γ radiation crosslinking, or high-temperature treatment. Also, other authors investigated the effects on the formation of conjugated double bonds in the thermal degradation of PVA blends with poly(vinyl chloride) using UV absorption and IR spectroscopy.[7]

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Poly(ethylene glycol) (PEG) is also a hydrophilic, nontoxic, water-soluble polymer and has a wide range of applications, mostly in cosmetic industries. This is because it dose not cause damage when it comes in contact with the skin or lips.[8] Also, previous studies showed that an acid-resistant membrane could be made from PVA and PEG.[9]

In a previous work, the miscibility of PVA/polyacrylamide (PAM) blends before and after γ irradiation was investigated by differential scanning calorimetry (DSC), thermogravimetric analysis, scanning electron microscopy, and mechanical testing.[10] The results showed that PVA/PAM is a miscible blend with a single T_g. Also, the results revealed that γ irradiation causes crosslinking and improves thermal stability. The present work investigates the effect of γ irradiation on the structural properties of polymer blends based on PVA with another water-soluble polyhydroxyl polymer. The blends before and after γ irradiation were characterized by different techniques.

EXPERIMENTAL

Materials

The homopolymer PVA used in this study was of laboratory grade, purchased from Laboratory Rasayan, Cairo, Egypt. It was in the form of powder, partially hydrolyzed, and had an average molecular weight (M_w) of 125,000 g mol^{-1}. The homopolymer PEG was of laboratory grade and had an average M_w of 4000 and was purchased from Fluka Chemical Co. (Germany). All homopolymers were used without further purification.

Preparation of polymer blends

Films of PVA/PEG blends were prepared by the solution casting technique. The PVA powder was dissolved in distilled water at 95°C while the PEG was dissolved in distilled water at room temperature. The polymer solutions were then mixed with continuous stirring until complete miscibility and were subsequently cast onto 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.

γ Irradiation

Irradiation to the required doses was carried out in a ^{60}Co γ cell (made in Russia) at the National Center for Radiation Research and Technology, Cairo, Egypt. Irradiation was carried out under atmosphere at a dose rate 6.92 kGy/h.

Optical absorbance and reflectance measurements

Optical absorbance measurements were carried out before and after γ radiation in the wavelength range 200–500 nm using a UV/visible spectrophotometer (Unicam 8625 Series). A microcolor unit equipped with a data station made by Dr. Bruno Lange (Germany) was used for reflectance measurements. The L^*, a^*, and b^* system used in this method is based on sensory perception, developed by Judd-Hunter and standardized in 1976 (DIN 6174, CIE-LAB 1976). In this system, the L^* intercept specifies the dark–white axis, in which the integers zero and 100 represent the standard dark and white colors, respectively. The intercepts a^* and b^* specify the green–red and blue–yellow axes. The positive values of a^* and b^* represent the red and yellow components, while the negative values of a^* and b^* represent the green and blue color components, respectively.

Spectroscopic analysis

Infra red spectra of the film samples were obtained by using an ATI Mattson Genesis spectrophotometer made by Unicom (England).

DSC

The DSC thermograms were carried out on a Perkin–Elmer DSC-7 calorimeter. A heating rate of 10°C/mim was utilized under nitrogen atmosphere. The recorded glass transition temperature was taken as the temperature at which one half of the change in heat capacity had occurred.

Tensile mechanical properties

Mechanical tests including break stress and strain were performed at room temperature using an Instron machine (Model No. 1195) at a crosshead speed of 5 mm/min. Polymer blend samples were cut (dog-bone shape) to initial dimensions of 40 mm length and 4 mm width. The recorded value for each mechanical parameter is the average of five measurements.

RESULTS AND DISCUSSION

Although PEG is a water-soluble polymer with hydroxyl groups that give a clear and visually transparent solution, all attempts to form cast films failed. However, when PVA/PEG blend solutions with low PEG contents were casted, good films were obtained and appeared transparent to visual observation. In this regard, when the contents of PEG in the polymer blends were increased beyond 40%, phase separation was observed and the transparency no longer occured.

Reflectance properties and optical absorbance

PVA and PEG homopolymers are water-soluble polymers with, theoretically, the minimum number of functional groups required to achieve miscibility and the competition of hydrogen bonding. However, visual observation showed that the cast films of a wide range of composition were not transparent when associated with the appearance of phase separation, indicating the immiscibility of these blends. The transparent films were only obtained in the cases of PVA/PEG blends composed of any ratio of PEG up to 30%. In a previous work, a method was proposed to investigate the miscibility of polymer blends by reflectance measurements of passing light through the films.[10] The reflected light was analyzed to the different color components, as shown in Table I. It is interesting to see that the reflected beam of light from unirradiated pure PVA film possesses a proportion of red color components while those reflected from PVA/PEG blend films before and after γ irradiation showed proportions of the green color component. Also, unirradiated pure PVA films showed a relatively higher L^* value than unirradiated blend films. For the unirradiated films, the L^* value was found to decrease with increasing ratio of PEG components in the blend. Thus, in terms of transparency, the presence of PEG will eventually decrease the miscibility of PVA/PEG blends. On the other hand, the red color component ($+a^*$) of unirradiated PVA was totally changed to a green component ($-a^*$) after blending with PEG polymer. This quantity of green component was found to increase with increasing ratio of PEG and was accompanied with an increase in the quantities of blue color

component ($-b^*$). The combined effect of the decrement in L^* values and the increment in a^* and b^* values leads to a decrease in transparency, indicating the occurrence of partial miscibility. For PVA/PEG blends, the L^* and a^* values were found to slightly increase with increasing irradiation dose, suggesting improved miscibility upon exposure to γ radiation.

Transmission of light through the polymer decreases drastically when crystallization occurs. The correlation between turbidity and structure is extremely complicated; however, scattering arises from the fact that the ordering arising from crystallization produces alterations in the refractive index, if a given direction in the polymer is considered. This, in principle, can arise from variation in density and orientation. As shown above, the conversion of the red color component ($+a$) of the amorphous partially hydrolyzed PVA to green color components for PVA/PEG may be explained on the basis that the introduction of PEG, i.e., a crystalline part into the microstructure, will result in decreased transparency.

The miscibility of PVA/PEG polymer blends containing 20 and 30% PEG, before and after exposure to various doses of γ radiation, was further investigated by UV/visible spectroscopy. Figure 1 shows the UV/visible spectra of pure PVA and PVA blends containing 20 and 30% PEG before and after exposure to a dose of 100 kGy of γ radiation as an example. The spectra showed a broad absorption band at about 285 nm, whereas no detectable bands were observed along the visible range. The position of these bands was slightly changed with increasing irradiation dose. However, the intensity was found to increase with increasing irradiation dose as shown in Figure 2, in accordance with previous reports.[11] Also, Hass et. al[12] observed absorption bands in the region of 220–320 nm for irradiated PVA and attributed these bands to the presence of carbonyl groups, in which saturated aldehydes usually give absorption bands in the region 275–290 nm.[13] The existence of aldehydes rather than ketones was also confirmed by gas chromatography studies of the thermal degradation of PVA.[14]

On the basis of light reflectance and UV absorbance results, a few points may be noted: (1) The increase in PEG contents in the unirradiated blends decreases the miscibility and hence the transparency (L^*). On the other hand, unirradiated polymer blends containing 20 and 30% PEG give approximately equal UV absorbance (Fig. 2); however, they show higher absorbance than that observed by unirradiated PVA homopolymer. (2) The increase in irradiation dose was found to improve the transparency of polymer blends on the basis of reflectance measurements, indicating improvement in miscibility. In this regard, the highest improvement in miscibility was observed in the case of the PVA(80)/PEG(20) blend in which the L^* value was increased by a value of 5.2. The intensity of UV

TABLE I
Reflectance Component of Films of Pure PVA and Polymer Blends with Different Ratios of PVA and PEG before and after Exposure to Various Doses of γ Radiation

Polymer blend composition (%)	Irradiation dose (kGy)	Color components		
		L^*	a^*	b^*
PVA (100 %)	0	95.1	+2.3	−13.8
	50	94.2	+3.0	−10.7
	100	91.9	+6.0	−6.2
	200	89.9	+6.4	−1.4
PVA/PEG (90/10)	0	90.8	−2.6	−15.1
	50	93.0	−2.8	−15.0
	100	94.2	−3.6	−13.1
	200	91.6	−3.6	−12.5
PVA/PEG (80/20)	0	86.8	−2.9	−14.4
	50	91.6	−2.8	−14.2
	100	92.0	−3.3	−13.6
	200	88.8	−4.2	−11.5
PVA/PEG (70/30)	0	83.6	−3.7	−13.4
	50	86.2	−4.2	−10.2
	100	87.7	−4.3	−9.0
	200	86.9	−3.9	−10.9
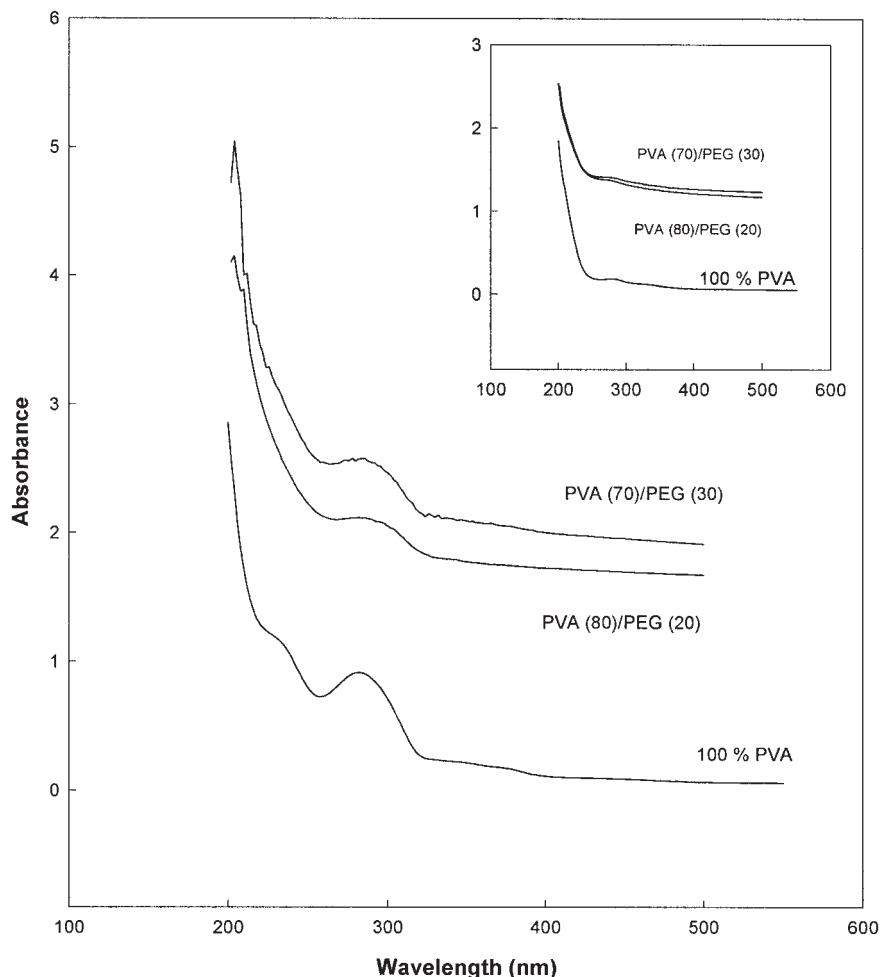
Figure 1   UV/visible spectra of pure PVA and PVA/PEG blends at different compositions before (top) and after exposure to a dose of 100 kGy γ radiation.

absorbance at 285 nm is in accordance with these findings, in which the PVA(80)/PEG(20) blend irradiated to 100 kGy gives higher absorbance than the PVA(70)/PEG(30) blend at the same irradiation dose. (3) It seems increasing the irradiation dose to 200 kGy causes a retarding effect on the miscibility, in which the L^* values were found to decrease due to the occurrence of oxidation degradation (chain scission).

IR spectroscopic analysis

The IR spectra of thin films of pure PVA and polymer blends containing different compositions of PVA and PEG before and after exposure to a dose of 100 kGy of γ radiation are shown in Figures 3 and 4 as examples. An absorption band due to C=O stretching of the ester group of the unirradiated partially hydrolyzed PVA can be seen at ~1740 cm^{-1} in accordance with previous reports[15]. Also, the absorption bands due to O–H stretching associated with the hydrolyzed PVA polymer can be observed at about 3340 cm^{-1}. The

absorption band which arises from C–H stretching of almost all organic compounds can be observed at 2910 cm^{-1}.

The IR spectra of unirradiated PVA/PEG blends showed nearly the same characteristic bands as seen in Figure 3 for pure PVA polymer. It is known that the existence of hydrogen bonding changes the position of the absorption band due to O–H stretching from 3600 cm^{-1} for compounds of less extensive hydrogen bonding to ~3330 cm^{-1} for those with extensive hydrogen bonding. It is clear that both IR spectra for pure PVA or PVA/PEG blends showed the existence of extensive hydrogen bonding in the range 3000–3500 cm^{-1}. However, it seems that the polymer blends possess relatively higher extents of hydrogen bonding than pure PVA.

To make a relation between the ratios of PVA and PEG in the different blends and the effect of γ radiation on these blends, the intensity of the different bands was calculated quantitatively as shown in Table II. It can be seen that the change in intensity of the
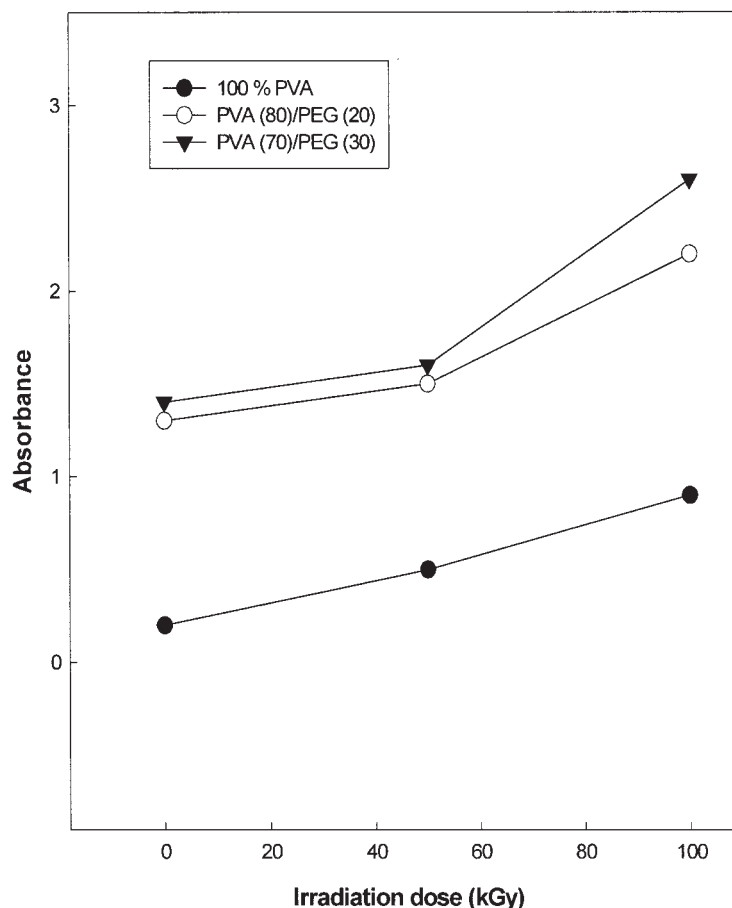
Figure 2 Absorbance intensity at wavelength 285 nm as a function of irradiation dose for pure PVA and PVA/PEG polymer blends at different compositions.

specific characteristic bands of PVA goes systematically with increasing the ratio of PEG in the unirradiated polymer blend. In this regard, the decrease in the intensity of the absorption band due to C=O, specific for the acetate groups of the partially hydrolyzed PVA, with increasing the ratio of PEG from 0 to 20 or from 0 to 30%, was found to be 22.0 and 33%, respectively. However, theoretically, they should be 20 and 30%. The same holds true with respect to the C–O band. For the change in intensity of the absorption band due to O–H, it is difficult to reach an assessment because both components contain hydroxyl groups and extensive hydrogen bonding. However, the change in intensity of this group with increasing the ratio of PEG from 0 to 20 and from 0 to 30 was found to be ~16 and 59%, respectively. Also, the intensity of this band was found to decrease with increasing irradiation dose for both pure PVA and its blends with PEG. In the same time, the intensity due to C=O was found to increase with increasing irradiation dose due to the formation of aldehydes, in accordance with previous reports.[16,12]

DSC

The glass transition temperature (T_g) of polymers depends on the structure and cooperative mobility of the segments. This behavior is reflected in a single glass transition temperature in miscible blends. In the case of partially miscible blends, the glass transition temperature of the blend components remains separated, but the T_g's are shifted toward each other compared with pure components.[17] In completely immiscible polymer blends, T_g's remain largely unaltered. Therefore, DSC can be considered one of the practical methods for investigating the miscibility of polymer blends. In a study on the effect of PEG as a plasticizer for PVA and hydroxypropyl methacrylate homopolymers or their blend, it was reported that the T_g of PVA decreased with increasing content of PEG, indicating plasticization.[18] However, a shoulder was observed in the logarithmic decrement curve at around 50 to 60°C for systems with PEG content ≥30%. The presence of this shoulder was explained as being due to the presence of incompatibility in systems with high PEG contents and is consistent with the observation in the present work.
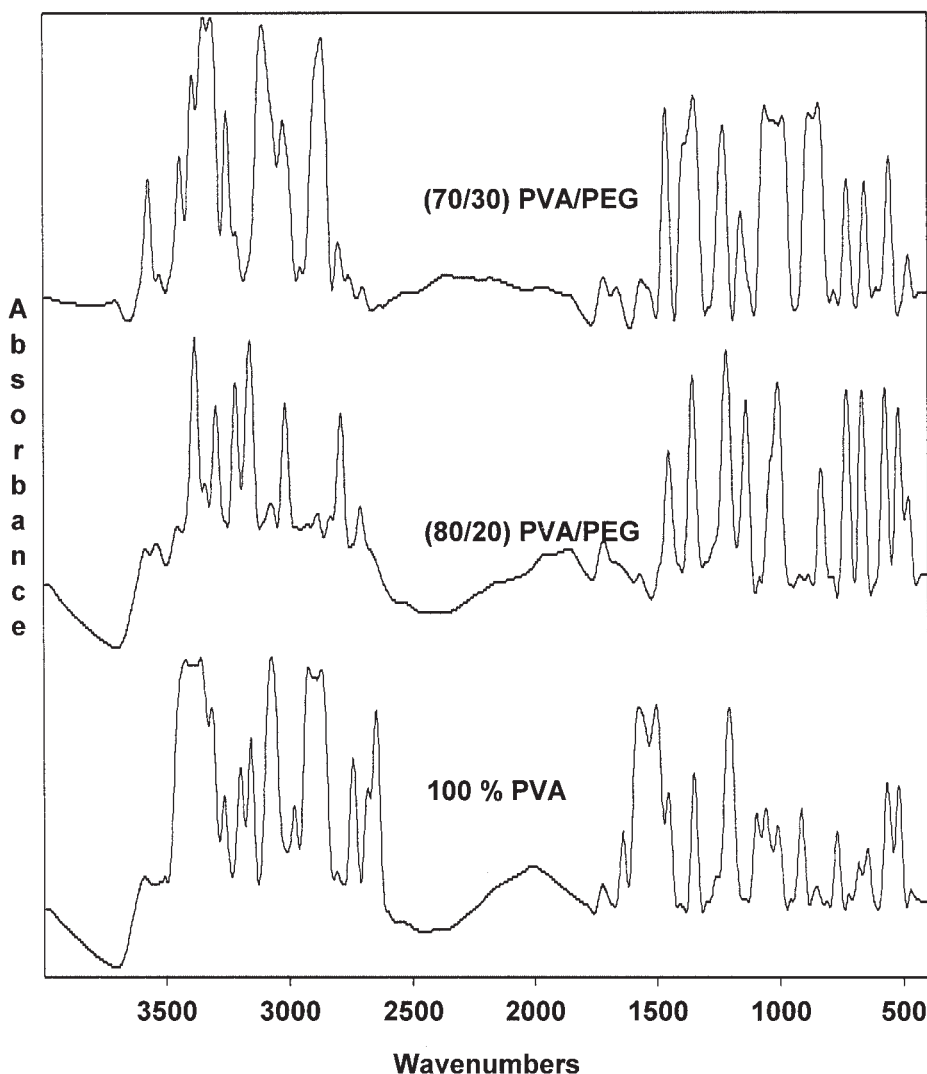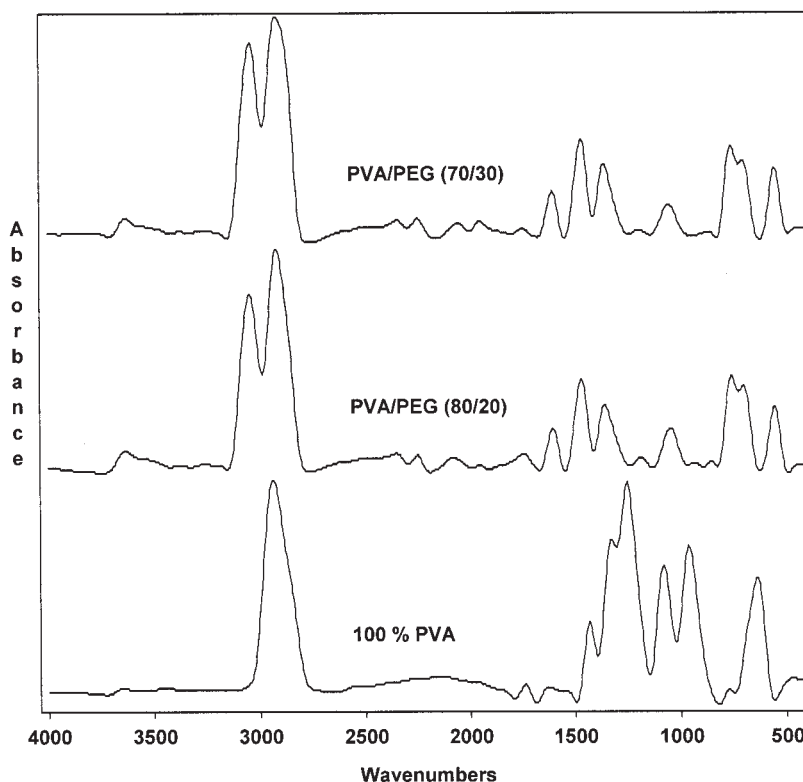
Figure 3   IR spectra of thin films of unirradiated pure PVA and PVA/PEG blends at different compositions.

The T_g's of PVA and PEG have been reported to be 85 and -41°C, respectively,.[3,19] The familiar Fox equation (shown below) derived to predict the T_g of binary mixtures of complete miscible polymers was applied to the present blend supposing that PVA and PEG are compatible.[20]

$$1/T_g = M_1/T_{g1} + M_2/T_{g2}$$

T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the blend and individual polymers, respectively. M_1 and M_2 are the mass fraction of the individual polymers in the blend. Thus, the expected T_g values for the PVA/PEG blend at 90/10 and 80/20 according to the Fox equation were calculated to be ~66 and 50°C. Figures 5 and 6 show the DSC thermograms within the temperature range 40–140°C for PVA/PEG blends containing 10 and 20% PEG before and after γ irradiation to 50 and 100 kGy doses. As can be seen, an

endothermic peak appeared within the temperature range 45–57°C, and the maximum of these peaks was found to increase with irradiation dose. Also, no transitions were observed with increasing temperature up to 140°C in the DSC thermograms of either blend. These peaks may arise from the melting of the PEG component or from the glass transition of miscible blends, in which no transitions were detected within the temperature range of the glass transition of pure PVA polymer (~85°C). Since a hysteresis endothermic peak due to destroying some residual order is frequently observed in amorphous polymers such polystyrene, the endothermic peak observed in the DSC thermograms is also possibly associated with the glass transition of PVA/PEG blends.[19] The latter hypothesis and the nonexistence of glass transition for PVA may indicate that this endothermic peak is due to the glass transition of PVA/PEG blends rather than to the melting of the PEG component. These finding are in accor-

Figure 4 IR spectra of thin films of pure PVA and PVA/PEG blends at different compositions after exposure to a dose of 100 kGy γ irradiation.

dance with the calculations of glass transitions according to the Fox equation of miscible blends and the results of reflectance measurements. The increase in the glass transition temperatures of the blends with dose to reach that calculated from the Fox equation may indicate that γ irradiation improves the miscibility of PVA/PEG blends.

TABLE II
Intensity of the Characteristic Absorption Bands of IR Spectra of Films of Pure PVA and Polymer Blends with Different Ratios of PVA and PEG before and after Exposure to Various Doses of γ Radiation

Polymer blend composition (%)	Irradiation dose (kGy)	Intensity of characteristic bands			
		OH	C=O	C–O	C–H
PVA (100 %)	0	53.4	55.4	44.2	47.3
	50	38.5	57.6	42.1	43.0
	100	29.9	60.3	38.0	37.2
PVA/PEG (80/20)	0	62.2	43.2	36.1	38.6
	50	41.3	59.4	43.9	35.3
	100	32.5	63.3	54.3	31.7
PVA/PEG (70/30)	0	85.1	37.2	29.0	33.9
	50	69.5	43.2	49.2	27.0
	100	38.7	48.0	43.3	21.3

Tensile mechanical properties

Improvement in miscibility leads to a change in morphology toward smaller dispersed domains, which in turn improves the mechanical properties. The mechanical testing showed that none of the pure PVA nor its blends with PEG showed the stress–strain behavior of tough polymers with yielding properties as shown in Table III. It is clear that the break stress or strain of unirradiated PVA is higher than that for PVA/PEG blends. Also, the stress and strain at the break point was found to decrease with increasing ratios of PEG in the blend. An overall trend indicates that the tensile mechanical properties of PVA/PEG blends improved as a result of γ irradiation up to a dose of 100 kGy. Moreover, it can be seen that the blend of PVA (70%)/PEG (30%) showed the stress–strain behavior of tough polymers with yielding and these yielding properties disappear at high doses of γ radiation.

The improved miscibility may be explained on the basis that the radicals formed on the macromolecules of PVA and PEG will eventually initiate covalent bonds to form copolymerization and crosslinking of PVA. 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.[21–23]
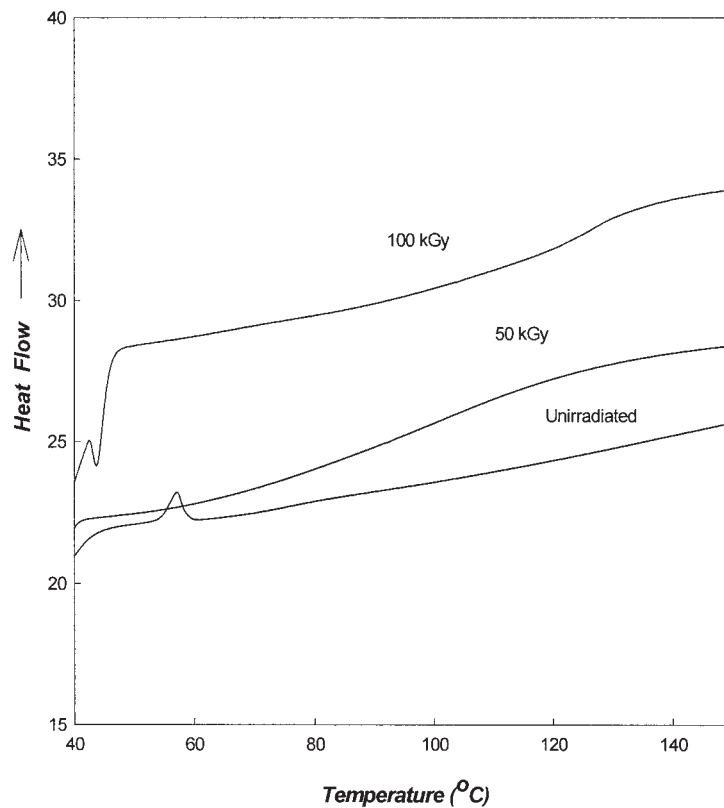
Figure 5   DSC thermograms of the PVA(90)/PEG(10) blend before and after γ irradiation to various doses.
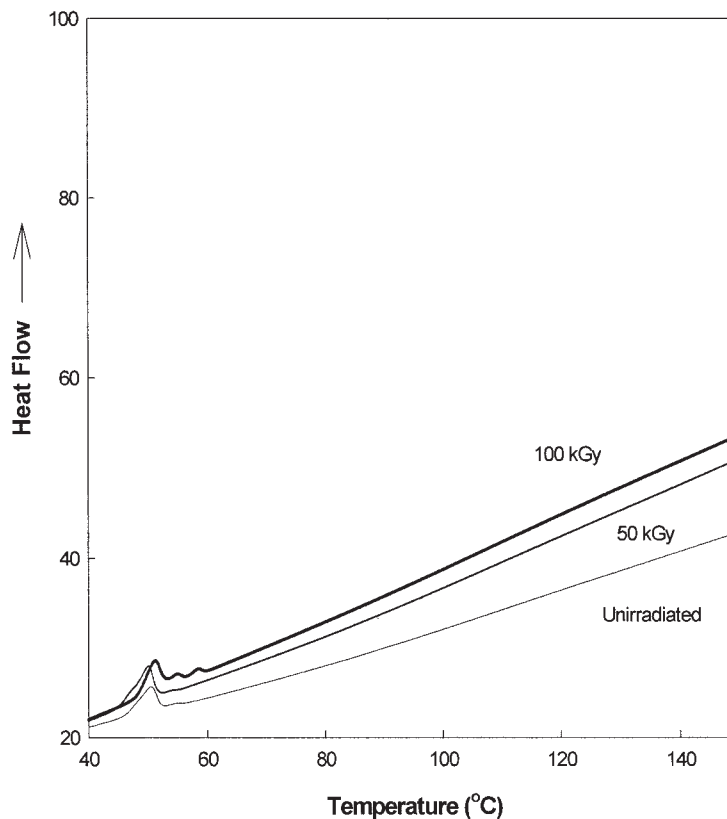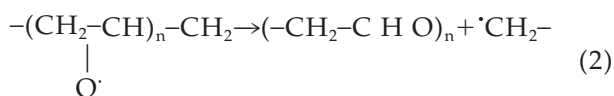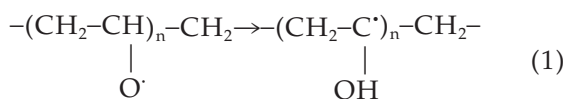

Figure 6   DSC thermograms of the PVA(80)/PEG(20) blend before and after γ irradiation to various doses.

TABLE III
Tensile Mechanical Properties of PVA Homopolymers and Its Blends with PEG at Different Contents
before and after γ Irradiation at Various Doses

Polymer blend composition (%)	Irradiation dose (kGy)	Break stress (MPa)	Break strain (%)	Yield stress (MPa)	Yield strain (%)
PVA (100)	Unirradiated	5.35 ± 0.15	33.0 ± 2.2	None	None
	50	6.87 ± 0.22	28.2 ± 2.1	—	—
	100	8.47 ± 0.32	21.4 ± 3.2	—	—
	200	7.05 ± 0.18	26.2 ± 3.5	—	—
PVA/PEG (80/20)	Unirradiated	3.43 ± 0.14	14.3 ± 2.8	None	None
	50	4.09 ± 0.01	31.6 ± 2.7	—	—
	100	5.19 ± 0.15	35.3 ± 3.0	—	—
	200	3.77 ± 0.02	23.2 ± 2.1	—	—
PVA/PEG (70/30)	Unirradiated	3.38 ± 0.11	11.8 ± 2.3	None	None
	50	2.69 ± 0.13	20.5 ± 2.5	2.0 ±	13.6 ± 1.3
	100	2.59 ± 0.01	35.8 ± 3.2	3.4 ±	11.2 ± 0.7
	200	3.57 ± 0.03	19.4 ± 1.7	None	None

It has been proposed that the yield species of γ-irradiated PVA as alkoxy radicals decay by one of two processes, one of which leads to formation of α-carbon radicals and the other leads to the formation of alkyl radicals and an aldehyde, as shown below:[24]

$$-(CH_2-CH)_n-CH_2 \rightarrow (CH_2-C^\cdot)_n-CH_2- \quad (1)$$
$$\qquad\qquad | \qquad\qquad\qquad |$$
$$\qquad\qquad O^\cdot \qquad\qquad\qquad OH$$

$$-(CH_2-CH)_n-CH_2 \rightarrow (-CH_2-C\ H\ O)_n + {}^\cdot CH_2- \quad (2)$$
$$\qquad\qquad |$$
$$\qquad\qquad O^\cdot$$

The chain end alkyl radical formed in reaction 2 would readily undergo an abstraction reaction and form the α-carbon radical. These findings were also observed in the pulse radiolysis studies by Samskog et al.[16] and McMillan,[25] in which they identified the alkoxy radicals as the primary species produced in the radiolysis of low-molecular-weight secondary alcohols.

CONCLUSION

Even though blending of already-existing polymers is of special importance in the field of polymer chemistry, the noncompatibility still constitutes the major problem in obtaining new products with characteristic properties. In this regard, PVA/PEG blends have been shown to be of a limited compatibilty over the range of 0–30% PEG, as seen by visual observation and optical measurements. However, the results showed clearly that the tensile mechanical properties of unirradiated PVA/PEG blends are lower than those of pure PVA due to the brittle PEG component. Exposure of PVA/PEG blends composed of PEG ratio up to 30% to γ irradiation to

doses up to 100 kGy results in an improvement in the tensile mechanical properties of pure PVA and the PVA(80)/PEG(20) blend. While the break stress of the PVA(70)/PEG(30) blend was shown to slightly decrease upon exposure to γ radiation, the break strain was greatly increased with increasing irradiation dose up to 100 kGy and accompanied by the appearance of yielding properties. These findings may lead to the conclusion that exposure to γ radiation can be used as a technique to improve the miscibility of polymer blends. It is proposed that the free radicals formed during irradiation will be involved in the formation of covalent bonding along the boundaries of the polymers and, hence, improve the compatibility. The DSC thermograms of PVA/PEG before or after γ irradiation cannot be taken as an indication of the miscibility in this case, even though they did not show a separate glass transition of the PVA polymer. Meanwhile, these endothermic peaks may be taken as being due to the glass transition temperature of PVA/PEG blends rather than to the melting transition of PEG.

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