Thermal Decomposition Behavior of γ-Irradiated Poly(vinyl acetate)/Poly(methyl methacrylate) Miscible Blends

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ABSTRACT: Miscible polymer blends based on various ratios of poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) were prepared in film form by the solution casting technique using benzene as a common solvent. The thermal decomposition behavior of these blends and their individual homopolymers before and after γ-irradiation at various doses (50–250 kGy) was investigated. The thermogravimetric analysis technique was utilized to determine the temperatures at which the maximum value of the rate of reaction (T_{max}) occurs and the kinetic parameters of the thermal decomposition. The rate of reaction curves of the individual homopolymers or their blends before or after γ-irradiation displayed similar trends in which the T_{max} corresponding to all polymers was found to exist in the same position but with different values. These findings and the visual observations of the blend solutions and the transparency of the films gave support to the complete miscibility of these blends. Three transitions were observed along the reaction rate versus temperature curves; the first was around 100–200°C with no defined T_{max}, which may arise from the evaporation of the solvent. The second T_{max} was in the 340–380°C range, which depended on the polymer blend and the γ-irradiation condition. A third transition was seen in the rate of reaction curves only for pure PVAc and its blends with PMMA with ratios up to 50%, regardless of γ-irradiation. We concluded that γ-irradiation improved the thermal stability of PVAc/PMMA blends, even though the PMMA polymer was degradable by γ irradiation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1773–1780, 2006

Key words: poly(vinyl acetate); poly(methyl methacrylate); blends; thermal stability; γ radiation

INTRODUCTION

Changes in the chemical and physical properties of polymers caused by high-energy radiation have received particular attention.[1–9] This is because high-energy radiation can induce chain scission and/or crosslinking. In recent years there has been increasing interest in blending different homopolymers to obtain new products that have some of the properties of each component. The demand for compatible blends may constitute one of the most attractive trends in the field of polymer processing.[10–12] We are interested in studying the effect of high-energy radiation on the structure–property behavior of polymer blends. In this regard, the miscibility of poly(vinyl alcohol)/polyacrylamide blends, prepared by the solution casting technique, before and after γ-irradiation was investigated.[13] The results of the different analytical methods showed that these blends are completely miscible over a wide range of compositions and indicate the occurrence of crosslinking upon exposure to a dose of 100 kGy of γ-radiation. In addition, the effect of γ-irradiation on the structural properties of limited miscibility poly(vinyl alcohol)/poly(ethylene glycol) blends was studied.[14] The different analyses and measurements showed that the miscibility was improved after γ-irradiation.

Poly(methyl methacrylate) (PMMA) is a radiation degradable type polymer that does not form a network structure under irradiation conditions, in which the reported G (S) value, which is the number of breaks for 100 eV of energy absorbed (chain scission), for chain scission is 1.22–3.5.[15] In contrast, poly(vinyl acetate) (PVAc) is a semicrystalline polymer and differs from PMMA in that the acetate group is attached through C—O bonding. PVAc and PMMA have been shown to form miscible blends at a wide range of compositions, and they appeared transparent to visual observation. This is because both homopolymers have minimum functional groups to achieve miscibility. Therefore, the present work was undertaken to investigate the kinetics of the thermal decomposition before

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and after exposure to various doses of γ-radiation utilizing the thermogravimetric analysis (TGA) technique.

EXPERIMENTAL

Materials

The PVAc and PMMA polymers used in this study were laboratory grade chemicals purchased from Aldrich Chemical Co. (Milwaukee, WI), and they used as received. The PVAc was a high molecular weight homopolymer in pellet form with a glass-transition temperature (T_g) of 30°C and a solubility parameter of 9.35. The PMMA was a low molecular weight homopolymer in powder form with an inherent viscosity of 0.2 and a melting temperature (T_m) of 180°C. Pure grade benzene was used as a cosolvent for the homopolymers.

Preparation of PVAc/PMMA blends

Films of PVAc/PMMA blends were prepared by the solution casting technique. Solutions of PVAc and PMMA in benzene were first prepared at various polymer compositions (polymer wt/solvent = 1/9). The polymer solutions were then mixed with continuous stirring until complete miscibility was achieved, and they were subsequently cast onto melamine dishes to form transparent films with a thickness of about 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 solvent.

γ Irradiation

Irradiation at the required doses was carried out in a ₆₀Co γ cell at the National Center for Radiation Research and Technology (Cairo, Egypt) under an air atmosphere at a dose rate of 7.0 kGy h⁻¹.

TGA

The TGA thermograms were carried out on a Shimadzu-50 instrument (Kyoto, Japan) at a heating rate of 10°C/min under flowing nitrogen (20 mL/min) from room temperature to 500°C. The primary TGA thermograms were used to determine the kinetic parameters such as the activation energy and order of thermal decomposition.

RESULTS AND DISCUSSION

The average dissociation energies for PVAc and PMMA homopolymers were 420.1 and 414.0 kJ/mol based on the dissociation energy reported for the different covalent bonds forming the polymer mole-

cules.[16] In addition, Van Krevelen developed a correlation for the temperature of half-decomposition ($T_{d1/2}$), which is defined as the temperature at which the loss of weight during pyrolysis reaches 50% of its final value (at a constant rate of temperature rise).[17] In this correlation $T_{d1/2}$ is approximated in terms of the ratio of the molar thermal decomposition function ($Y_{d1/2}$) divided by the molecular weight (M) per repeat units: $T_{d1/2} = Y_{d1/2}/M$. It should be noted that $Y_{d1/2}$ is estimated by using group contributions and is expressed in Kelvin kilograms/mole; and, because M is in grams/mole, a conversion factor of 1000 much be used to obtain $T_{d1/2}$ in Kelvins. On the basis of this correlation, the calculated $T_{d1/2}$ values for PVAc and PMMA were found to be 273.5 and 332.0°C, respectively.[18] This difference in thermal stability is related to the structure of polymers. Whereas the acetate groups in PVAc are attached through C—O bonding, the acrylate groups in PMMA are attached through C—C, which possesses a relatively lower dissociation energy than the C—O bond. These theoretical calculations indicate that PVAc is thermally more stable than PMMA and the blending of these homopolymers at any ratio will eventually produce a product with lower thermal stability than PVAc.

TGA is widely used to investigate the thermal decomposition of polymers and to determine the kinetic parameters of the thermal decomposition such as the activation energy and order of reaction. These parameters can be used to obtain a better understanding of the thermal stability. In the present work, the weight loss was recorded for the different blends upon heating from room temperature up to 500°C in the presence of flowing nitrogen gas and employing a constant rate of heating.

Initial TGA thermograms and weight loss

Figure 1 shows the initial TGA thermograms of PVAc and PMMA homopolymers and their polymer blends at various ratios before and after γ-irradiation with a 150-kGy dose as examples for such thermograms. The percentage weight loss at different temperatures for all polymer blends before and after γ-irradiation at various doses is summarized in Table I. It can be seen that the unirradiated homopolymers or polymer blends are stable up to ~150°C, and nearly no loss in weight was observed. Up to a heating temperature of 200°C, the unirradiated PMMA homopolymer displayed higher thermal stability with less weight loss than unirradiated PVAc or PVAc/PMMA blends at different compositions. In addition, at such heating temperatures the thermal stability of unirradiated PVAc/PMMA blends decreased with an increasing ratio of PMMA polymer in the blend. Different thermal decomposition behavior was seen within the heating temperature range of 300–500°C, in which unirra-
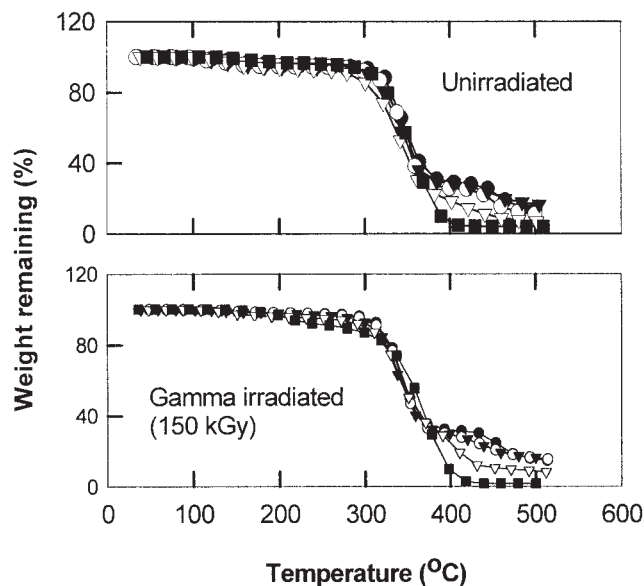
Figure 1 Primary TGA thermograms of unirradiated PVAc and PMMA homopolymers and their polymer blends at various ratios before and after γ irradiation with a dose of 150 kGy: (●) 100% PVAc, (■) 80/20 PVAc/PMMA, (▲) 50/50 PVAc/PMMA, (○) 20/80 PVAc/PMMA, and (□) 100% PMMA.

diated PVAc/PMMA blends possess higher thermal stability than pure homopolymers. As shown from Figure 1, the temperatures of the $T_{d1/2}$ for unirradiated PVAc, PMMA, 80/20 PVAc/PMMA, 50/50 PVAc/PMMA, and 20/80 PVAc/PMMA occurred at 354, 354, 384, 348, and 342°C, respectively. However, the $T_{d1/2}$ for the same polymers and polymer blends after exposure to a dose of 150 kGy of γ-irradiation occurred at 352, 348, 348, 351, and 363°C, respectively.

On the basis of the percentage weight loss and the experimentally calculated $T_{d1/2}$, a few points may be outlined. The major loss in weight (20–70%) for the unirradiated polymers occurs within the range of 320–370°C, whereas for the polymers γ-irradiated with a dose of 150 kGy it occurs within 338–385°C. This behavior may indicate that γ-irradiated polymers possess a relatively higher thermal stability than the unirradiated polymers, regardless of the polymer blend composition. In general, the differences between the theoretical $T_{d1/2}$ based on the Krevelen correlation and the experimental $T_{d1/2}$ could be due to the dissolution and film casting from polymer blend solutions. Although the percentage weight loss over the entire heating temperature range is in agreement with the theoretical calculations of the average dissociation energy, there is a contradiction between the $T_{d1/2}$ calculated theoretically and that found experimentally. This contradiction may be attributed to the fact that the Krevelen correlations are based on group contributions, but they are not strictly additive because they incorporate some of the environmental effects playing a role in determining the thermal stability.[18] The rel-

TABLE I
Weight Loss (%) at Different Decomposition Temperatures of PVAc and PMMA Homopolymers and Their Blends at Different Ratios Before and After γ-Irradiation

Polymer blend composition (%)	Irradiation dose (kGy)	Weight loss (%)				
		200°C	300°C	350°C	400°C	500°C
PVAc (100)	Unirradiated	4.7	6.3	39.1	70.8	86.2
	50	2.2	4.2	42.3	68.1	84.0
	150	1.9	4.9	49.7	68.1	84.5
	250	2.3	4.4	44.0	67.5	84.4
PVAc/PMMA						
80/20	Unirradiated	5.1	7.8	47.4	74.4	89.0
	50	3.2	3.2	44.5	69.5	85.9
	150	1.9	6.2	53.0	70.9	83.8
	250	1.7	5.3	42.9	70.7	83.8
50/50	Unirradiated	5.7	8.1	55.4	71.3	83.2
	50	3.6	8.0	54.3	73.0	87.9
	150	1.9	5.5	49.7	79.4	83.2
	250	2.1	15.7	54.7	79.4	93.2
20/80	Unirradiated	6.0	14.4	60.3	81.5	93.1
	50	4.3	8.4	52.5	77.2	89.6
	150	3.9	9.9	49.6	75.4	91.4
	250	2.9	8.8	49.0	68.9	89.6
PMMA (100)	Unirradiated	2.9	7.1	42.9	93.8	95.9
	50	4.0	14.2	88.3	88.3	92.7
	150	3.3	13.1	90.1	90.1	98.4
	250	2.8	18.2	88.8	88.8	97.0
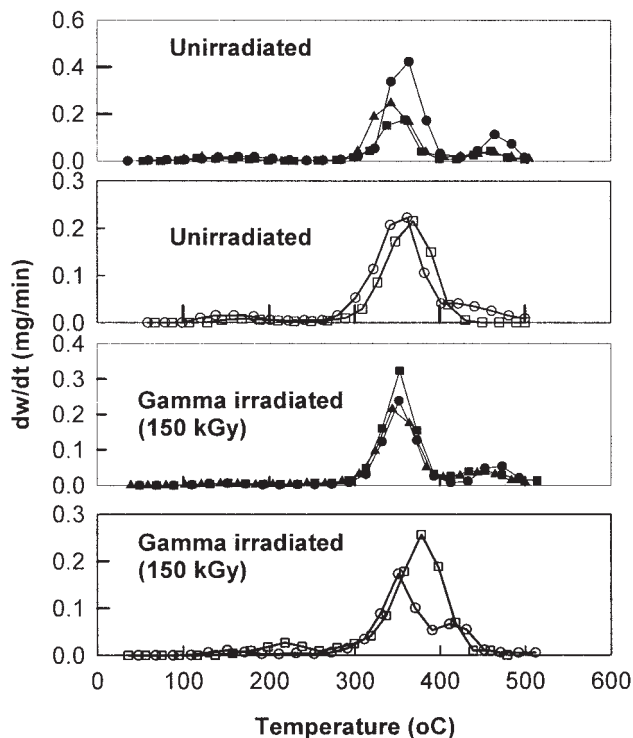
Figure 2 The rate of reaction (dw/dt) versus the temperature for unirradiated PVAc and PMMA homopolymers and their polymer blends at various ratios before and after γ irradiation with a dose of 150 kGy: (●) 100% PVAc, (■) 80/20 PVAc/PMMA, (▲) 50/50 PVAc/PMMA, (○) 20/80 PVAc/PMMA, and (□) 100% PMMA.

γ-irradiated homopolymers and polymer blends to various doses are provided in Table II. Note that the rate of the thermal decomposition reaction of all polymers, whether before or after γ-irradiation, showed more than one maximum with increasing temperature. This behavior indicates that the thermal decomposition of these polymers passes through multiple stages, depending on the state of decomposition and not on the components. This is because PVAc and PMMA are miscible polymers having minimum functional groups required to achieve miscibility. Moreover, a visual observation showed that all solutions of PVAc/PMMA mixtures were clear at room temperature and highly stable. In addition, the films of PVAc/PMMA with different compositions appear transparent in a way similar to the films of pure components as determined from light absorbance measurements (not shown).

The rate of reaction curves for all unirradiated polymers showed a transition at around 100–200°C with no clear maximum, which is probably due to the evaporation of solvent. It can be seen that the second T_{max} tends to decrease with an increasing ratio of the PMMA component up to 50%, and then it tends to increase and reaches the highest value for pure PMMA. The lowest T_{max} was observed in the case of the blend containing equal ratios of PVAc and PMMA. This T_{max} is attributable to the decomposition of polymer blends to the lower molecular weight fragments.

ative thermal stability on the basis of the weight loss between PVAc and PMMA homopolymers before γ-irradiation can be explained by the fact that PMMA undergoes stepwise breakdown depolymerization starting at the chain ends, yielding monomer molecules. In contrast, PVAc may undergo random scission of bonds along the chain backbone. Upon exposure to γ-irradiation, the thermal stability of the different polymers will depend to a large extent on the products of radiochemical yields.
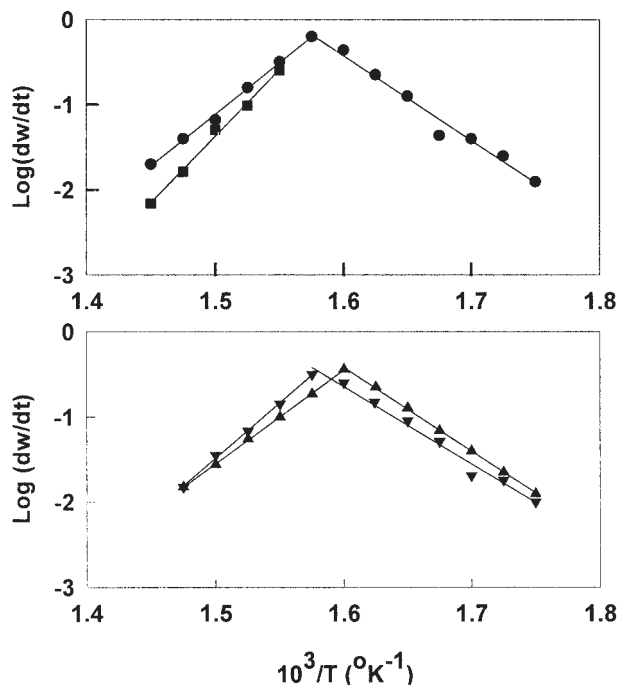
Temperatures of maximum rate of reaction

As noted, the effect of γ-irradiation on the thermal stability of PVAc/PMMA blends cannot be confirmed on the basis of the weight loss versus the heating temperature or the theoretical calculation and the experimental determination of the $T_{1/2}$. The rate of reaction (dw/dt) was plotted against the heating temperatures for the homopolymers and polymer blends before and after γ-irradiation with a dose of 150 kGy, which is shown in Figure 2 as an example. It can be seen that these types of curves generally display similar trends; however, the temperatures at which the maximum value (T_{max}) of the rate of reaction differ from one polymer to another. The T_{max} values of

TABLE II
Temperatures of Maximum Rate of Reaction for PVAc and PMMA Homopolymers and Their Blends at Different Ratios Before and After γ-Irradiation

Polymer blend composition (%)	Irradiation dose (kGy)	Temp. of max. rate of reaction (°C)	
		2nd Max.	3rd Max.
PVAc (100)	Unirradiated	364	465
	50	359	460
	150	352	473
	250	355	456
PVAc/PMMA			
80/20	Unirradiated	359	460
	50	359	460
	150	353	453
	250	359	439
50/50	Unirradiated	343	465
	50	362	461
	150	344	444
	250	246	—
20/80	Unirradiated	362	—
	50	357	—
	150	351	—
	250	343	—
PMMA (100)	Unirradiated	369	—
	50	323	—
	150	378	—
	250	374	—

Figure 3 The temperature dependency of the logarithm of the rate of reaction of the thermal decomposition of PVAc homopolymers (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.

It is interesting to note that a third T_{max} appeared around 450–500°C only in the case of unirradiated and irradiated PVAc/PMMA blends containing various ratios of PMMA up to 50%, as shown in Figure 2. The appearance of the T_{max} of all polymers at around the same temperature position may give further support to the miscibility of these blends. However, these T_{max} values are probably due to the complete thermal decomposition. Even though the unirradiated pure PMMA displayed a higher T_{max} of 369°C and the unirradiated pure PVAc showed a T_{max} of 364°C, their unirradiated blends showed a lower T_{max} and reached the lowest thermal stability for the blend at equal ratios.

As can be seen from Figure 2, the trends of the rate of reaction curves of the pure polymers or their blends were not changed after γ-irradiation. However, the T_{max} values of γ-irradiated pure polymers or their polymer blends with a dose of 150 kGy decreased, depending on the blend composition. Moreover, within the γ-irradiated polymer blends, the change in T_{max} as a function of the irradiation dose is the same as in the case of unirradiated polymers. The γ-irradiated PMMA polymer displayed a new T_{max}, which appeared as a shoulder to the main T_{max}.

## Kinetic parameters of thermal decomposition reaction

The thermal stability was further confirmed by determining the kinetics of the thermal decomposition re-

action. A method based on the rate of reaction modified by Anderson and Freeman[20] was utilized, in which the quantities $\Delta \log \dot{w} (dw/dt)$ and $\Delta \log$ corresponding to a constant small difference of $\Delta 1/T$ over the entire course of the initial TGA curves were first determined. The Anderson–Freeman equation, which relates these quantities, is

$$\Delta \log(dw/dt) = n\Delta \log \dot{w} - (E^*/2.303R)\Delta 1/T \quad (1)$$

where dw/dt is the rate of the thermal decomposition reaction (mg min^{-1}), $\dot{w}$ is the reactant mass (mg), R is the gas constant (J mol^{-1} k^{-1}), E^* is the activation energy (J mol^{-1}), and n is the order of the reaction. When $\Delta \log(dw/dt)$ is plotted against $\Delta \log \dot{w}$, it gives a straight line of slop n and the intercept gives the E^*. The procedure and applications of this method are described elsewhere.[19]

When $\Delta \log(dw/dt)$ was plotted against $\Delta \log \dot{w}$ for the present materials before or after γ-irradiation and over the entire scale of heating temperatures, the data points in some cases completely verified the equation and fell on a straight line, giving a first-order reaction. In other cases, the data points did not fall on a straight line; hence, the thermal decomposition of these polymers does not depend on the residual mass, but instead depends on the temperature and follows a zero-order reaction. In this case, $\log(dw/dt)$ is plotted against $1/T$ and the slope is equal to $E^*/2.303R$, from which the activation energy can be calculated.
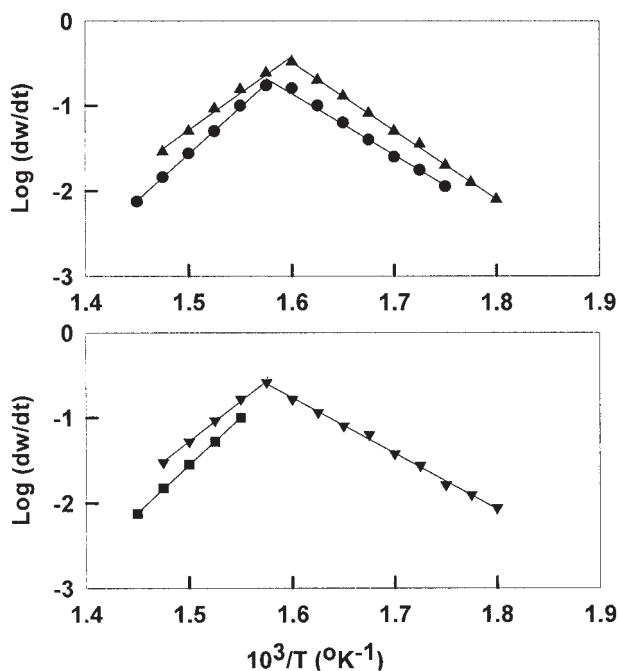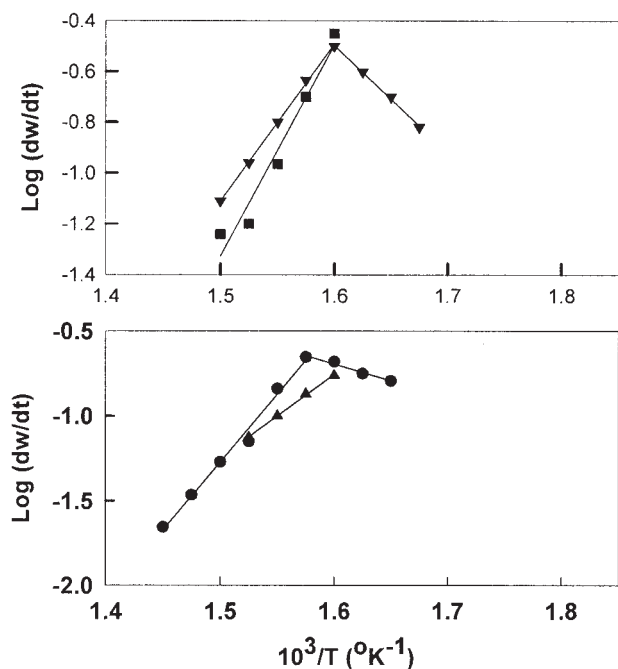

Figure 4 The temperature dependency of the logarithm of the rate of reaction of the thermal decomposition of 80/20 PVAc/PMMA (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.
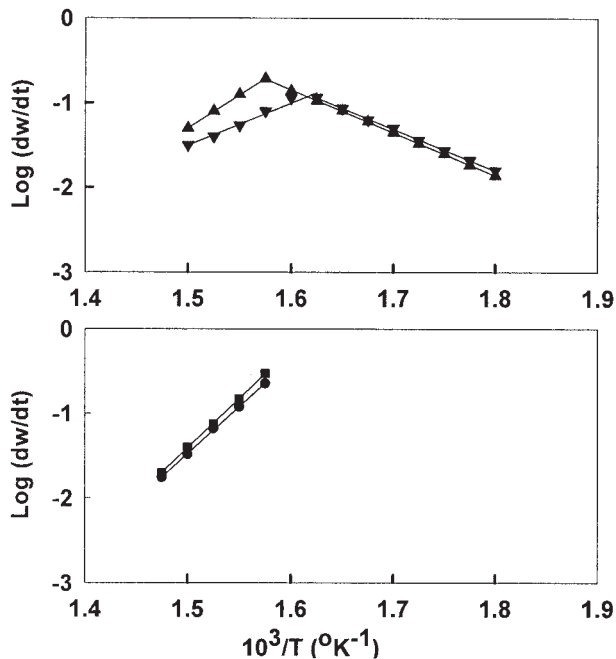
Figure 5 The temperature dependency of the logarithm of the rate of reaction of the thermal decomposition of 50/50 PVAc/PMMA (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.

Figures 3–6 plot the Anderson–Freeman equation (temperature dependency). Figures 7–9 show the Anderson–Freeman plots (residual mass dependency)
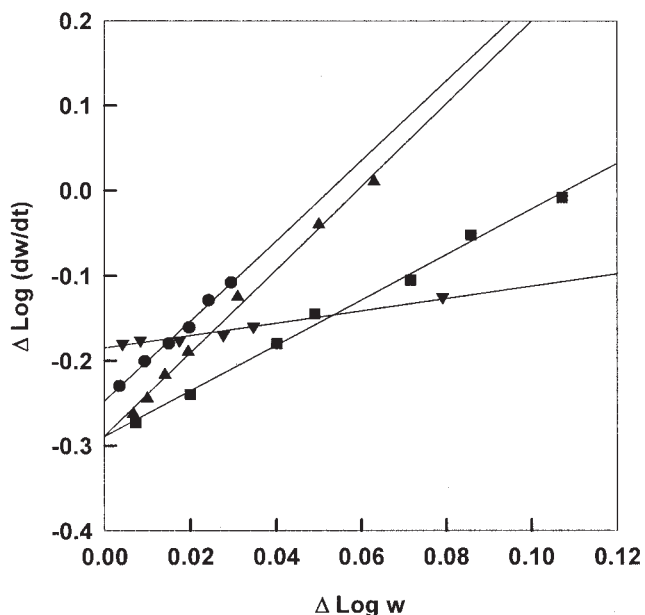

Figure 6 The temperature dependency of the logarithm of the rate of reaction of the thermal decomposition of 20/80 PVAc/PMMA (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.
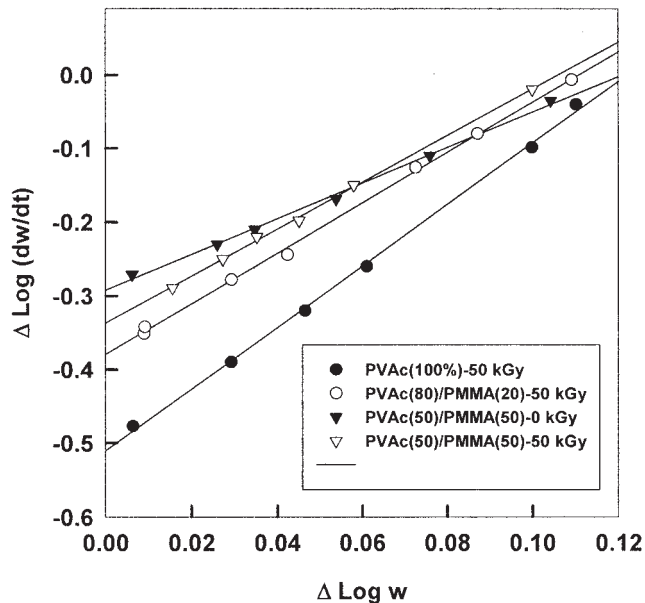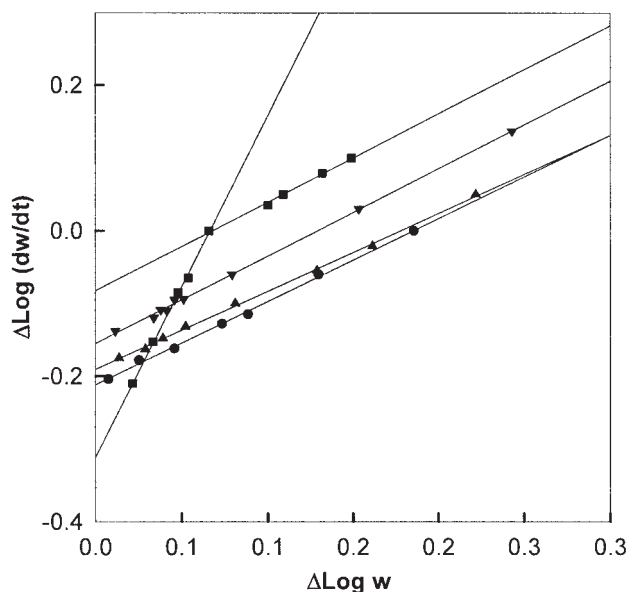

Figure 7 Anderson–Freeman plots for the thermal decomposition of pure PVAc and its blends with PMMA at different ratios before and after γ-irradiation with a dose of 50 kGy.

for pure PVAc, PMMA, and PVAc/PMMA blends with different compositions before and after γ-irradiation with various doses. The calculated activation energies of the thermal decomposition reaction of all polymers and polymer blends are summarized in Table III. The data in Table III lead us to the following conclusions. First, pure PVAc and its blends with

Figure 8 Anderson–Freeman plots for the thermal decomposition of 20/80 PVAc/PMMA (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.

Figure 9 Anderson–Freeman plots for the thermal decomposition of pure PMMA homopolymers (●) before and after γ-irradiation with doses of (■) 50, (▲) 150, and (▼) 250 kGy.

PMMA before and after γ-irradiation undergo a zero-order thermal decomposition reaction within the high temperature range of 370–490°C, independently of the residual mass. However, the activation energy for the thermal decomposition of pure PMMA over the entire range of temperatures indicates a first-order reaction, in which the thermal decomposition depends on the residual mass. These findings may explain the difference in thermal decomposition mechanisms during the high range of heating temperatures, where PMMA undergoes systematic molecular decomposition to end with low molecular weight products. The thermal decomposition of unirradiated pure PVAc and the blend with 20% PMMA displays a zero-order reaction over the entire range of heating temperatures. Polymer blends of PVAc with increased ratios of PMMA up to 80% display a thermal decomposition reaction that is dependent on both the residual mass and the temperature.

Second, we observed that the activation energies for pure PVAc and PVAc/PMMA blends over the entire range of heating temperatures were suddenly increased at a dose of 50 kGy and then progressively decreased with increasing doses up to 250 kGy. The increased activation energy would suggest the occurrence of crosslinking at such doses, followed by oxidative degradation upon exposure to higher doses of γ radiation. The reported G (S) and G (X), which is the number of crosslinks formed for 100 eV of energy absorbed, for PVAc were 0.06–0.17 and 0.1–0.3, respectively.[15] The mechanisms associated with the chain scission of PMMA are postulated to occur through the formation of unsaturation sites, which are sensitive to radiation leading to carbon compounds. In contrast, crosslinking of PVAc occurs through the for-

TABLE III
Activation Energies of Thermal Decomposition Reactions of PVAc and PMMA
Homopolymers and Their Blends at Different Ratios Before and After γ-Irradiation

Polymer blend composition (%)	Irradiation dose (kGy)	Activation energy (kJ/mol)	
		280–370°C	370–490°C
PVAc (100)	Unirradiated	197.8 (0 order)	243.2 (0 order)
	50	391.5 (1st order)	308.3 (0 order)
	150	184.8 (0 order)	208.7 (0 order)
	250	182.7 (0 order)	261.0 (0 order)
PVAc/PMMA			
80/20	Unirradiated	147.5 (0 order)	202.4 (0 order)
	50	204.3 (1st order)	204.8 (0 order)
	150	156.3 (0 order)	177.5 (0 order)
	250	135.2 (0 order)	186.3 (0 order)
50/50	Unirradiated	289.0 (1st order)	204.9 (0 order)
	50	258.2 (1st order)	229.8 (0 order)
	150	93.1 (0 order)	147.6 (0 order)
	250	84.1 (0 order)	102.1 (0 order)
20/80	Unirradiated	191.5 (1st order)	100.1 (0 order)
	50	222.1 (1st order)	149.0 (0 order)
	150	137.9 (1st order)	102.3 (0 order)
	250	97.5 (1st order)	113.6 (0 order)
PMMA (100)	Unirradiated	162.0 (1st order)	
	50	151.7 (1st order)	
	150	144.4 (1st order)	
	250	117.8 (1st order)	

mation of free radicals on the backbone of the polymer, which subsequently unite to form a network structure.

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