Structure–Property Behavior of Gamma-Irradiated Poly(styrene) and Poly(methyl methacrylate) Miscible Blends

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ABSTRACT: Polymer blends based on various ratios of polystyrene (PS) and polymethyl methacrylate (PMMA) were exposed to different doses of gamma radiation up to 25 Mrad. The structure-property behavior of the polymer blends before and after they had been irradiated was investigated by DSC, TGA, and FTIR spectroscopy. The DSC scans of the glass transition temperature (T_{σ}) of the different polymer blends showed that the T_{g} was greatly decreased by increasing the ratio of the PMMA component in the polymer blends. Moreover, the T_g of PS/PMMA blends was found to decrease with increasing irradiation dose. The depression in T_g was noticeable in the case of blends rich in PMMA component. The TGA thermograms showed that the thermal stability of the unirradiated polymer blends decreases with increasing the ratios of PMMA component. Also, it was found that the presence of PS polymer in the blends affords protection against gamma radiation degradation and improves their thermal stability. However, exposing the polymer blends to high doses of gamma radiation caused oxidative degradation to PMMA components and decreased the thermal stability. The investigation of the kinetic parameters of the thermal decomposition reaction confirm the results of thermal stability. The FTIR analysis of the gamma-irradiated polymer blend films gives further support to the TGA data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 509-520, 1999

INTRODUCTION

Recent research and development of polymer materials has been directed to blending of different polymers to obtain new products having some of the desired properties of each component. Moreover, blending of different existing polymers is of considerable importance as an alternative to graft copolymerization and the very high cost to develop new homopolymers.

The physical and chemical properties of blends based on miscible polymers have been extensively investigated. Investigations of poly (styrene-*co*-4vinyl phenyldimethylsiland) and poly (*n*-butyl methacrylate) blends by DSC and FTIR spectroscopy showed that miscible blends were formed only for the copolymers containing 9-34 mol % of the latter polymer.¹ The thermal conductivity, heat capacity, and density of poly(vinyl chloride)/ poly caprolactone blends were greatly affected by the proportions of the blend components.²

The viscosity, stability, and transparency of blends containing starch and poly(vinyl alcohol) were significantly improved by using poly(vinyl alcohol) having butyl, octyl, and dodecyl end groups as well as using oxidized starch.³ Investigations by ultrasonic and rheological techniques indicate the possible miscibility of poly (ethylene oxide)/polyacrylic acid and poly(ethylene oxide)/ poly(vinyl pyrrolidone) blends and the immiscibil-

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ity of poly(ethylene oxide)/poly(vinyl alcohol) blends.⁴ Studies carried out by X-ray diffraction and Raman analysis and by measurements of mechanical properties indicate that there is an interaction between cellulose and chitosan molecules in their blend films.⁵

The widely investigated polymer blends in the literature so far have mostly reported on chemical and physical interactions between the polymer components; however, a few authors examined the effect of high-energy radiation on the properties of polymer blends. In this regard, the effect of electron beam irradiation on the gelation behavior of a series of poly(styrene) and poly(vinyl methyl ether) blends has been studied.⁶ The gel fraction was determined as a function of dose, blend composition, and morphology. The results indicate that poly(styrene) does not offer any protection from radiation crosslinking in the miscible blends. Also, the addition of a small amount of PVME to pure PS greatly increased the gel content, suggesting that a significant amount of grafting is occurring between the blend components. Moreover, a study has been made on the effect of gamma radiation crosslinking on the phase behavior of deuterated PS/PVME blends.⁷ It was reported that a significant amount of grafting occurred between the blend components. The gamma-ray-induced degradation of poly(styreneco-methyl methacrylate) and blends of polystyrene and poly(methyl methacrylate) was investigated by UV, FTIR spectroscopy, and viscosity measurements.⁸ A protective effect due to the polystyrene component was observed in case of degradation of the copolymer, but it was not observed for the blends. Micohardness testing was used to detect crosslinking in polystyrene/poly(methyl methacrylate) blends induced by gamma irradiation (1-75 Mrad) and electron beam irradiation (1 to 30 Mrad).9 Irradiation was found to produce crosslinking behavior in the specimens, and the crosslinking degree is related to the type of irradiation and dose and to the miscibility of PS and PMMA in the blend.

Poly(styrene) and poly(methyl methacrylate) form an important and unique pair of polymers in that they are chemically different; however, they display compatibility over different composition ranges at room temperature. The structure-property behavior of gamma-irradiated miscible blends containing different ratios of poly(styrene) and poly(methyl methacrylate) is the purpose of this study. The irradiated blends are characterized by different techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and FTIR spectroscopy.

EXPERIMENTAL

Materials

The polymers poly(styrene) and poly(methyl methacrylate) used in this study were of laboratory-grade chemicals purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. The poly(styrene) homopolymer was in the form of pellets, has an average molecular weight (\bar{M}_w) of 280,000, density of 1.047 g/cm², and melting point of ~ 237°C. The poly(methyl methacrylate was a low molecular-weight homopolymer in the form of powder and has an inherent viscosity of 0.2 and T_m of 180°C. A pure-grade benzene was used as a cosolvent for the polymers.

Preparation of Polymer Blends

Films of polystyrene (PS)/polymethyl methacrylate (PMMA) blends were prepared by the casting solution technique. Solutions of PS and PMMA in benzene were first prepared at various polymer compositions (polymer wt/solvent wt = 1/9). The polymer solutions were then mixed with continuous stirring until complete miscibility, and subsequently cast onto glass dishes to form transparent films with a thickness of ~ 0.2 mm. The cast films were dried under ambient conditions for 24 h and then placed in a vacuum oven at 80°C to remove residual solvent.

Gamma Irradiation

Irradiation to the required doses was carried out with a ⁶⁰Co gamma source (made in India) at the National Center for Radiation Research and Technology, Cairo, Egypt. The polymer blend films were exposed to gamma irradiation in air at a dose rate of 0.45 Mrad/h.

Thermogravimetic Analysis (TGA)

The TGA studies were carried out on a Shimadzu-30 (TGA-30) at a heating rate of 10°C/min in air over a temperature range from room temperature up to 500°C. The primary TGA thermograms were used to determine the different kinetic parameters such as activation energy and order of thermal decomposition reaction.



Figure 1 DSC scans of the glass transition temperature (T_g) of unirradiated PMMA/PS polymer blends and the same blends after they had exposed to 5, 20, 25 Mrad of gamma radiation.

IR Analysis

A FTIR Spectrophotometer model Mattson 100, made by Unicam, was used over the range $500-4000 \text{ cm}^{-1}$. For quantitative analysis, the resolution was set at 16 cm⁻¹.

Differential Scanning Calorimetry (DSC)

The DSC thermograms were performed using a Perkin-Elmer DSC-7 calorimeter. A heating rate

of 10°C/min was utilized under nitrogen atmosphere. The recorded glass transition temperature was taken as the temperature at which onehalf of the change in heat capacity ΔC_p has occurred.

RESULTS AND DISCUSSION

This work has been carried out to examine the behavior of miscible blends of a radiation-sensitive polymer (PMMA) and a radiation-resistant polymer (PS) towards gamma irradiation. In the present investigation, different binary blends having various proportions of PS were prepared and exposed to gamma irradiation in air to different dose levels.

Glass Transition Temperature (T_{ρ})

Figure 1 shows the DSC scans of the glass transition temperature of different unirradiated PMMA/PS blends and the same blends after they had been exposed to gamma radiation doses of 15, 20, and 25 Mrad. Table I presents the calculated glass transition temperature values of the different polymer blends before and after exposure to different doses of gamma radiation. It is apparent from this series of DSC scans that the relationship between the composition (wt % PS) and the glass transition temperature (T_g) of the polymer blends is not linear. Also, the glass transition temperatures of the polymer blends are much lower than those of pure PS or PMMA polymers. However, the glass transition temperature of the blends decreases with increasing PMMA content in the polymer blend. Moreover, it may be concluded that the entire range of the studied polymer compositions are compatible and miscible, because a single glass transition temperature was observed, although PS and PMMA have close

Table I Glass Transition Temperature (T_g) of Different PS/PMMA Polymer Blends Irradiated to Different Doses of Gamma Radiation

	Glass Transition Temperature (T_g)					
Polymer Blend	Irradiation Dose (Mrad)					
Composition	Unirradiated	15	20	25		
100% PS	86.9	82.8	83.0	82.8		
70% PS/30% PMMA	82.3	74.8	78.3	72.6		
50% PS/50% PMMA	81.5	79.0	81.7	74.5		
30% PS/70% PMMA	78.0	71.2	73.2	71.7		

		ΔC_p (J/g.deg.)					
Composition	Unirradiated	15 Mrad	20 Mrad	25 Mrad			
100% PS	0.24	0.29	0.32	0.22			
70% PS/30% PMMA	0.14	0.24	0.27	0.20			
50% PS/50% PMMA	0.27	0.16	0.30	0.26			
30% PS/70% PMMA	0.12	0.082	0.13	0.12			

Table II Heat Capacity (ΔC_p) at the Glass Transition Temperature of Different PS/PMMA Polymer Blends Exposed to Different Doses of Gamma Radiation

glass transition temperatures. On the other hand, the visual observation showed that all the blend solutions were clear; neither macroscopic phase separation nor the appearance of precipitates were observed. The cast films are transparent and clear over the entire composition range for PMMA/PS blends. It should also be noted that the heat capacity ΔC_p values as shown in Table II are composition dependent. As the PMMA content increases to 30%, the ΔC_p at the T_g of the blend decreases, and then increases as the PMMA content was increased to 50%. Further increase in PMMA content in the blend is accompanied with a sudden decrease in ΔC_p .

The decrease in glass transition temperature observed with increasing PMMA content in the different blends may be interpreted on the basis of the capability of PMMA to form hydrogen bonding with the neighboring PMMA polymer. As the concentration of hydrogen bonding was increased, it was reasoned that the volume shrinkage would increase. Also, it can be seen that there is a depression in T_g associated with increasing irradiation dose, regardless of the variation of PS ratios in the different blends. These changes in T_g towards gamma irradiation may be attributed to degradation of the PMMA phase; however, the presence of the PS polymer in higher contents protect the blends against radiation degradation.

Thermal Decomposition Behavior

Figures 2–4 show the initial TGA thermograms of unirradiated polymer blends containing different ratios of PMMA and PS and the same blends after they had been exposed to gamma radiation doses



Figure 2 TGA thermograms of unirradiated PMMA/PS polymer blends.



Figure 3 TGA thermograms of different PMMA/PS polymer blends irradiated to 5 Mrad.



Figure 4 TGA thermograms of different PMMA/PS polymer blends irradiated to 20 Mrad.

of 5 and 20 Mrads. Table III summarizes the percentage weight loss at different decomposition temperatures for the unirradiated and irradiated PS/PMMA polymer blends taken from the TGA thermograms. It can be seen that the unirradiated pure PS and PMMA polymers lose about 5% of weight at 280 and 200°C, respectively. This behavior indicates that the initial decomposition

reaction for PS begins at a slightly higher temperature than for PMMA. By increasing the heating temperature from 280 to 340°C, the loss in weight of the PS was found to be about half the loss in weight of the PMMA. Thus, it may be concluded that the unirradiated PS polymer is more stable against thermal decomposition than the unirradiated PMMA over the entire range of studied temperatures. On the other hand, the thermal stability of unirradiated PS/PMMA blends at any composition is lower than those of pure components. However, unirradiated polymer blends rich in PS content displayed a relatively high thermal stability on the basis of % weight loss.

The thermal stability of any polymer material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The calculated dissociation energy for the different covalent bonds C—H, C—C, C—O, C—O, and C—C in the literature were found to be 98, 81, 87, 174, and 145 kcal/mol, respectively.¹⁰ Based on these values, it can be calculated that the average complete dissociation energy of PS is about 101.5 kcal/mol and 99.1 kcal/mol for PMMA. The lower complete dissociation energy of PMMA compared to PS polymer is certainly due to the lack of the C—C bonds of aromatic nuclei in the PMMA molecule. Therefore, it can be concluded that the presence of the PMMA polymer in

		Weight Loss (%)						
Polymer Blend Composition	Irradiation Dose (Mrad)	200 (°C)	240 (°C)	260 (°C)	280 (°C)	300 (°C)	320 (°C)	340 (°C)
PS(100%)	0 5	$\begin{array}{c} 2.6 \\ 1.7 \end{array}$	$\begin{array}{c} 3.0\\ 2.1 \end{array}$	$3.8 \\ 2.3$	$5.3 \\ 2.6$	$\begin{array}{c} 12.4\\ 4.4\end{array}$	$\begin{array}{c} 27.1\\ 9.0\end{array}$	47.8 18.9
PS(70%)/PMMA(30%)	20 0 5	2.0 2.7 3.9	$2.8 \\ 5.4 \\ 7.6$	$\begin{array}{c} 3.7\\11.8\\8 \end{array}$	$8.8 \\ 27.0 \\ 11.2$	$22.4 \\ 42.3 \\ 14.4$	42.0 80.2 17.9	63.7 94.6 22.6
PS(50%)/PMMA(50%)	20 0	$\begin{array}{c} 3.9\\ 4.3\end{array}$	$7.5 \\ 11.3$	$11.8 \\ 22.5$	$11.2 \\ 19.7 \\ 34.1$	37.7 47.7	64.5 81.7	86.0 95.5
	5 20	4.5 5.0	14.6 19.6	16.1 27.9	18.1 41.9	20.0 67.0	22.9 90.5	28.3 97.8
PS(30%)/PMMA(70%)	0 5 20	5.0 5.4 6.7	19.6 19.5 15.2	24.9 24.4 23.0	24.9 29.8 41.2	60.1 36.1 66.1	84.7 42.9 88.5	96.0 51.2 97.0
PMMA(100%)	0 5	5.4 6.0	6.1 9.5	7.6 10.4	10.7 11.1	$22.2 \\ 14.7$	43.5 18.9	74.1 26.7
	20	13.1	13.1	18.9	29.9	43.9	58.2	71.3

 Table III
 Weight Loss (%) at Different Decomposition Temperatures for Different Polymer Blends of

 Various Ratios of PS and PMMA Irradiated to Different Doses of Gamma Radiation



Figure 5 Representative curves of the rate of reaction (dw/dt) against 1/T for unirradiated PMMA/PS polymer blends.

larger contents in the polymer blends cannot improve the thermal stability. Thus, the respective thermal stability obtained by experimental TGA thermograms of the various PMMA/PS blends before exposure to gamma radiation can be explained on the basis of these theoretical calculations of average dissociation energy of polymer molecules.

For the 5-Mrad gamma-irradiated PS/PMMA polymer blends, it can be observed that with increasing PS contents, the thermal stability increases over the entire temperature range. The interaction of radiation with polystyrene has been reported to produce two types of radical intermediates.¹¹ The G(X) values are between 0.02 and 0.054, while G(S) has been reported to be below 0.02. On the other hand, PMMA is the most common example of a nongelling polymer that does not form a three-dimensional network structure under irradiation conditions. The reported G(S)

value for chain scission of PMMA under the effect of gamma radiation ranged from 1.22 to 3.5. Therefore, it can be concluded that PS offers some sort of protection against radiation degradation of PMMA component inside the blends. Irradiation of the PS/PMMA polymer blends to higher gamma doses seems to decrease the thermal stability of the different polymer blends to higher extents. This behavior may be attributed to the oxidative degradation of PMMA polymer at higher doses of gamma radiation and the occurrence of radiation crosslinking of PMMA polymer at relatively lower doses.

The thermal behavior of the PS/PMMA polymer blends either unirradiated or exposed to gamma radiation cannot be confirmed unless the kinetics of the thermal decomposition reactions are determined.

Thermogravimetric analysis (TGA) is widely used to investigate the thermal decomposition of polymers and to determine the kinetic parameters such as activation energy and order of reaction. These parameters can be used to give a better understanding of the thermal stability of polymers. Different methods were postulated to determine these kinetic parameters based on the measurement of the rate of conversion¹² and on the heating rate.^{13,14}

In the present work, a method based on the rate of conversion proposed by Anderson and Freeman was utilized.¹⁵ This procedure has the advantage of being operationally simpler and is more advantageous in those cases where changes in mechanism are involved. Furthermore, the energy of activation and order of reaction may be evaluated from a single experimental TGA curve. In this method, the quantities $\Delta \log(dw/dt)$ and $\Delta \log w$ corresponding to a constant small difference of 1/T over the entire course of the initial TGA curve were first determined. The relationship that correlates these quantities is given by the following equation:

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

where dw/dt is the rate of thermal decomposition reaction, w the reactant weight, R gas constant, E^* the activation energy, and n the order of reaction. When $\Delta \log(dw/dt)$ is plotted against $\Delta \log w$, it gives a straight line of slope n and the interception gives the activation energy E^* .

The application of the Anderson and Freeman method to the polymer blends under investigation



Figure 6 Representative curves of the rate of reaction (dw/dt) against 1/T for different PMMA/PS polymer blends irradiated to 5 Mrad.

can be described in the following steps: (1) the rate of conversion or the rate of reaction dw/dt or the derivative of thermogravimetric analysis curve DTGA (taken from the primary TGA thermograms every 2 min and the corresponding residual mass are plotted against the reciprocal of the absolute temperature 1/T for the unirradiated polymer blends and those irradiated to various doses of gamma radiation, as shown in Figures 5–7. In these curves the rate of reaction is only shown because the residual weights have been already shown in Figures 2-4. Also, it should be noted that the numerical values on the rate of reaction axis were not shown because all curves starting from zero point. (2) The quantities $\Delta \log dw/dt$ and $\Delta \log w$ were taken at equal intervals of 1/T of 5×10^{-5} K⁻¹ from these curves. It can be seen that these type of curves display a similar trends; however, the temperatures at which the maximum value of the rate of reaction occurs differs from one polymer blend to

another, depending on the relative ratios of PS and PMMA components, as shown in Table IV. Also, it can be observed that the temperature of the maximum value of the rate of thermal decomposition of unirradiated pure 100% PMMA increases gradually with increasing PS ratio in the polymer blends. The corresponding temperatures of the polymer blends were found to increase when the blends had been exposed to 5 Mrad and afterwards tend to decrease at 20 Mrad.

Thermal Decomposition Kinetics of Unirradiated Polymer Blends

When $\Delta \log dw/dt$ was plotted against $\Delta \log w$ for the unirradiated pure PMMA and PS polymer and unirradiated polymer blends containing different ratio of PMMA and PS over the entire studied temperature scale, the data points fall on



Figure 7 Representative curves of the rate of reaction (dw/dt) against 1/T for different PMMA/PS polymer blends irradiated to 20 Mrad.

	Temperature of Maximum Rate of Reaction (°C)				
Polymer Blend	TT · 1· / 1	5 MD			
Composition	Unirradiated	5 MR	20 MR		
100% PMMA	310	415	317		
70% PMMA/30% PS	320	417	301		
50% PMMA/50% PS	330	420	310		
30% PMMA/70% PS	350	420	320		
100% PS	362	401	341		

Table IVTemperatures of the MaximumValues of the Rate of Conversion ofUnirradiated and Irradiated Polymer BlendsHaving Different Ratios of PS and PMMA

a straight line. Therefore, and on the basis of the Anderson and Freeman expression, the thermal decomposition reaction depends on the residual mass and follows first-order reaction kinetics, as shown in Figures 8 and 9. It should be noted that the slopes on some of these figures do not show unity because they have been drawn on regular paper. However, if the data points were plotted on a logarithmic paper, they would show unity. The calculated activation energies and the order of



Figure 8 Anderson and Freeman plots of $\Delta \log dw/dt$ against $\Delta \log w$ for the thermal decomposition of unirradiated pure 100% PMMA and polymer blends containing 30 and 50% PS.



Figure 9 Anderson and Freeman plots of $\Delta \log dw/dt$ against $\Delta \log w$ for the thermal decomposition of unirradiated polymer blend containing 70% PS and 100% PMMA.

reaction for the thermal decomposition of unirradiated PS/PMMA blends are summarized in Table V. It can be seen that the PMMA polymer showed the highest thermal stability, higher than those of the pure PS polymer and its blends. However, a break in the line representing $\Delta \log dw/dt$ vs. $\Delta \log w$ for PS/PMMA at equal ratios can be observed, as shown in Figure 8. This elbow may be attributed to the occurrence of phase separation between PS and PMMA components inside the blend.

Thermal Decomposition Kinetics of Irradiated Polymer Blends

When the above polymer blends were exposed to gamma radiation doses of 5 and 20 Mrad, the results of the application of the method used differs from one polymer blend to another. For thermal decomposition reaction of pure 100% PMMA irradiated to 5 and 20 Mrad, the kinetic analysis indicates temperature dependency, as shown in Figure 10. Also, the thermal decomposition reaction of polymer blend containing 30% PS and 70% PMMA and irradiated to 5 Mrad indicates temperature dependency as shown in Figure 11. When the same blend was irradiated to 20 Mrad, it displayed a temperature dependency within the

Blend Composition	Irradiation Dose (Mrad)	Activation Energy (E^*) (Kcal/mol)
100% PMMA	unirradiated	40.3 (1st order)
	5	17.9 (zero order)
	20	5.2 (zero order)
70% PMMA/30% PS	unirradiated	17.3 (1st order)
	5	4.6 (zero order)
	20	14.1 (zero order) and 31.1 (1st order)
50% PMMA/50% PS	unirradiated	25.2 (1st order)
	5	22.9 (1st order)
	20	10.6 (zero order) and 25.6 (1st order)
30% PMMA/70% PS	unirradiated	32.9 (1st order)
	5	20.6 (1st order)
	20	17.6 (zero order) and 33.9 (1st order)
100% PS	unirradiated	30.2 (1st order)
	5	32.9 (1st order)
	20	39.3 (1st order)

Table VKinetic Parameters of the Thermal Decomposition Reaction of Gamma-IrradiatedPolymer Blends Based on PMMA and PS

low temperature scale and a first-order reaction within the high temperature scale, as shown in Table V. Polymer blends containing different ratios of PS from 50% and up to 100% and irradiated to 5 Mrad showed a thermal decomposition reaction dependent on residual mass and follows first-order reaction kinetics within the full temperature range, as shown in Table V. At high radiation doses of 20 Mrad, these polymer blends



Figure 10 Temperature dependency plots of the rate of reaction (dw/dt) for pure PMMA polymer irradiated to 5 Mrad and 20 Mrad.

showed a zero-order reaction within the low temperature scale and first-order reaction over the high temperature scale, as shown in Table V.

On the basis of the kinetic analysis of the thermal decomposition of gamma-irradiated PS/ PMMA blends, two points may be addressed: (1) the thermal stability of pure PMMA polymer was found to decrease with increasing irradiation dose, whereas the thermal stability of pure PS polymer was found to increase with increasing irradiation doses. This behavior can be attributed to the relative sensitivity of these polymers towards gamma radiation in which PMMA undergoes oxidative degradation under the effect of



Figure 11 Temperature-dependency plots of the rate of reaction (dw/dt) for polymer blend composed of 30% PS and 70% PMMA irradiated to 5 Mrad.



Figure 12 IR spectra of different unirradiated 100% PMMA, 100% PS, and blends of equal ratios and the same polymers after they had been exposed to 20 Mrad.

gamma irradiation. (2) The thermal decomposition reaction of polymer blends containing different ratios of PS AND PMMA previously exposed to high doses of 20 Mrad seems to go through a two-step mechanism within the low and high temperature scales. Nevertheless, the presence of PS polymer at various ratios offers protection to the PMMA polymer against oxidative degradation because the activation energies of such blends are higher than those of the pure PMMA polymer.

IR Spectroscopic Analysis

Figure 12 shows the IR spectra of unirradiated thin films of 100% PMMA, 100% PS, and PMMA/PS polymer blends of equal ratios, and the same polymers after they had been exposed to 20 Mrad. For pure PMMA, as with almost all organic compounds, an absorption band can be seen at 2950 cm⁻¹, arising from C—H stretching. A very distinctive absorption band can be observed at 1743 cm⁻¹, which is due to the C=O of the ester group of PMMA. Moreover, a strong absorption band is seen at 1187 cm⁻¹, which is due to C—O stretching of the ester group. The methyl groups of PMMA can be confirmed by the appearance of the stretching absorption band at 1373 cm⁻¹ in the fingerprint region of the IR spectrum.

For pure PS polymer, the IR spectrum also shows an absorption band around 3000 cm^{-1} due

to the C—H stretching of organic compounds. The presence of the benzene ring of PS can be confirmed from two regions; the wide absorption band due to —CH— stretching, which falls near 3023 cm^{-1} , and the absorption band characteristic for the conjugation giving rise to a series of four peaks around 1670 cm⁻¹. The IR spectra of the polymer blends containing different ratios of PMMA and PS show the absorption band characteristic of both PMMA and PS.

To give a relation between the respective ratios of PMMA and PS in the different blends, the intensity of the different specific bands was calculated quantitatively, as shown in Table VI, taking in consideration the thickness of the samples.

It can be seen that the change in intensity of the specific characteristic bands of PS does not go systematically with increasing its ratio in the polymer blends. In this regard, the increase in intensity of the aryl-CH band with increasing the ratio of PS from 0 to 30% or from 30 to 50% or from 50 to 70% were found to be 10, 17.4, 28.6, and 49.1%, respectively. However, theoretically, they should be 30, 50, and 70%, as in the prepared polymer blends. The same holds true with respect to the aryl -C=C band. These contradictions may be attributed to the overlapping of these absorption bands with those of the close bands of the methyl group of PMMA polymer. On the other hand, the increase in the intensities of the specific absorption bands of PMMA polymer seem to fit approximately with ratios in the polymer blends except for the --CH₃ groups.

The IR spectra and the intensity of the different specific absorption bands of the same polymer blends after they had exposed to 5 Mrad and 20 Mrad are shown in Table VI. It can be observed that the intensity of absorption bands of the pure PS polymer decreases slightly with increasing the irradiation dose, suggesting the stability of this polymer against gamma radiation degradation. However, in the case of pure PMMA, the oxidative degradation is pronounced, and the decrease in the specific absorption bands is noticeable, particularly at high doses of gamma radiation. For polymer blends rich in PS polymer irradiated to 5 Mrad, the decrease in specific characteristic bands of PMMA is not as much as those having low contents of PS. Also, it is noted that the specific characteristic bands of PS in these blends exposed to this dose of gamma radiation were not greatly affected. Moreover, it is evident that the intensity of the characteristic absorption bands of PMMA component decreases with increasing ir-

		Intensity of Characteristic Bands					
Polymer Blend Composition	Irradiation Dose (Mrad)	C=0 (1735 cm ⁻¹)	C-0 (1187 cm ⁻¹)	Aryl C—H (3023 cm ⁻¹)	Aryl C=C (1496 cm^{-1})	$-CH_3$ (1388 cm ⁻¹)	
100% PS	Unirradiated			49.7	22.3	_	
	5	_	_	44.2	20.8	_	
	20	_	_	34.5	16.7	_	
70% PS/30% PMMA	Unirradiated	20.7	4.5	28.6	9.7	8.6	
	5	21.0	4.2	29.1	9.1	9.8	
	20	18.5	3.3	28.5	8.5	16.7	
50% PS/50% PMMA	Unirradiated	47.0	43.8	17.4	9.0	22.3	
	5	40.0	30.7	17.2	10.2	14.8	
	20	22.8	15.9	16.8	10.0	18.6	
30% PS/70% PMMA	Unirradiated	69.2	60.3	10.2	3.9	22.6	
	5	60.2	40.3	10.0	3.8	19.7	
	20	34.0	15.9	7.2	3.0	13.1	
100% PMMA	Unirradiated	93.1	75.6	_	_	28.9	
	5	70.1	52.4	_	_	14.3	
	20	25.8	31.4	_	—	22.9	

Table VIIntensity of the Characteristic Absorption Bands of the I Spectra of Gamma-IrradiatedPMMA/PSBlends

radiation dose to 20 Mrad and decreasing PS ratios in the polymer blends. Thus, it may be concluded that the presence of PS in the polymer blend protects PMMA polymer against radiation degradation at low doses.

CONCLUSIONS

The results presented in this work demonstrate the effect of gamma radiation on the glass transition temperature behavior and thermal decomposition behavior of polymer blends composed of a radiation-sensitive polymer (PMMA) and a radiation-resistant polymer (PS). PS/PMMA blends were shown to be highly compatible over a wide range of ratios, as seen by the visual observation. In addition, DSC scans of the glass transition temperature of a series of polymer blends containing various ratios of PMMA and PS indicated a single T_g over the studied compositions. Upon exposure of the PS/PMMA blends a further depression in T_g was observed, particularly with polymer blends rich in PMMA ratios. The drop in $T_{\rm g}$ occurring at high doses of 25 Mrad can be attributed to the degradation of the PMMA component. The relative rise in T_g temperatures of blends observed at 20 Mrad may be attributed to the occurrence of grafting between the blend com-

ponents. This state of affairs results in introducing restrictions on the molecular motion of chains, hence, increasing the T_g . TGA investigations showed that pure PS and PMMA polymers possess higher thermal stability than those of their blends. The derivative of the thermogravimetric analysis curves (DTGA) gives further support to this finding. By using these thermograms, it is difficult to make a conclusion concerning the thermal stability of PS/PMMA blends. Determination of the activation energy of the thermal decomposition may be the best method for studing the thermal stability. The calculation of activation energy showed that unirradiated PMMA polymer possesses a relatively higher thermal stability than that of pure PS. Moreover, the calculation of the activation energy and order of reaction for PS/PMMA blends exposed to 5 and 20 Mrad of gamma radiation indicated that PS offers protection against oxidative degradation to these blends. The quantitative IR analysis of the different PS/PMMA blends before and after gamma irradiation are in accordance with these results.

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