Study of Structural and Thermal Properties of Electron Beam Irradiated Polymethylmethacrylate/Bisphenol-A-Polycarbonate Blends

M. M. Magida

Department of Radiation Chemistry, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

ABSTRACT: Polymethylmethacrylate (PMMA) and bisphenol-A-polycarbonate (PC) polymer blends are prepared by solution casting technique using tetrahydrofuran as a solvent. The structural properties of the polymer blends before and after they had been irradiated to electron beam accelerator was investigated by color strength, scanning electron microscopy (SEM), and FTIR spectroscopy. The thermal properties such as TGA and DSC were investigated. The TGA thermograms showed that the thermal stability of the unirradiated polymer blends PMMA/PC increases with increasing the ratios of PC component in the blend. Also, it was found that the presence of PC polymer in the blend affords protection against radiation degradation and improves their thermal stability. The DSC scans show a single T_g intermediate between PMMA and PC indicate the existence of specific interactions between PMMA and PC polymers in the blend. An intimate blends are reflected by substantial shifts in the frequencies of the PMMA and PC C=O vibration obtained by FTIR. SEM confirms the homogeneity of the blend. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3184–3190, 2012

Key words: electron beam; polycarbonate; thermal

INTRODUCTION

Polymer blends have always been considered to be interesting combinations for obtaining new high-performance polymeric materials without synthesizing fully new polymers especially when the properties of the two or more polymers are synergistically combined. By blending one may be able to achieve useful combinations of each material into a single product. In addition, one can expect a continuous range of properties simply by variation of blend composition. Furthermore, polymers with high glass-transition temperatures are attractive for industrial polymer science because of strong economic rewards that may arise from their potential applications. For example, polymethylmethacrylate (PMMA) is a transparent polymeric material possessing many desirable properties, such as light weight, high light transmittance, chemical resistance, colorlessness, resistance to weathering corrosion, and good insulating properties.[1] Also, polycarbonate (PC) is one of the toughest engineering thermoplastic. Its properties such as consistent clarity, excellent impact strength, dimensional stability, creep resistance, and heat resistance. Blends of PMMA and PC have received considerable attention[2–4] because of their potential application as gas separation membrane, pearl material, substrate of the optical data storage discs, packaging material, etc.[5]

Phase behavior of this blend system has been extensively investigated by various researchers[6–10] and it was found to depend on the method of preparation. For example, homogeneous blends of PMMA and PC were obtained by casting at an elevated temperature (47°C) from THF solution.[11] While partially miscible or complete immiscible blends are obtained by melt mixing.[11,12] However, these mixtures are thermodynamically unstable and undergo phase separation on heating at temperatures between 150 and 200°C.[7,10] Different types of chemical reaction between two polymers have been hypothesized to explain the formation of homogeneous PMMA/PC blends at temperature higher than 220°C.[13,14]

A number of articles[7,17–20] have described methods for preparing homogeneous blends of PMMA and PC. Tetrahydrofuran (THF) was used as solvent in most cases for making single-phase PMMA/PC blends. Chiou et al.[10] showed that melt processed blends of PMMA and PC have two distinct phases. Nishimoto et al.[21] presented evidence that the solvent preparation methods used result to that the two polymers PMMA and PC become kinetically trapped in homogeneous.

This work was undertaken to investigate the effect of electron irradiation on the structural properties and thermal stability of PMMA/PC polymer blends

which were obtained by casting at an elevated temperature (47°C) by using THF as a solvent.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Polymethylmethacrylate PMMA used in this study was of laboratory-grade chemicals purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. PMMA was a low molecular weight homopolymer in the form of powder and has inherent viscosity of 0.2 and Tm of 180°C. Polybisphenol-A-carbonate PC was in the form of crystals obtained from Bayer Middle East Egypt Company. PC under investigation is commercially available under the name Macrolon amorphous polymer Type 31001 Farbe Nature and Partie 55806 S.

A laboratory grade of tetrahydofuran (THF) obtained from Fluka-Germany was used in the preparation of PMMA/PC blends. THF was chosen because in this solvent, single phase of PMMA/PC blends can be made.

Experimental techniques

Blend preparation

Thin films of PMMA, PC and their blends PMMA/PC were prepared with the following PMMA/PC concentrations: 100/0, 75/25, 50/50, 25/75, 0/100 (wt/wt %) by casting solution. Tetrahydrofuran (THF) was used as solvent for all blend compositions. Solutions of PMMA/ PC blend in THF were heated to a temperature from 50–60°C to obtain complete solubility. All solutions were cast onto glass plates and covered with Petri dishes for slow evaporation overnight. Then the films were placed inside a vacuum for the removal of excess solvent.

Electron beam irradiation

The equipment used for electron irradiation was an electron accelerator (USA) operating at 1.5 MeV. The samples were put on a mobile plate in the electron accelerator and the selected doses were 25, 75, and 125 kGy.

Color measurements

A microcolor unit attached to a data station manufactured by Brano Lange (Germany) was used for color strength measurements. The $L*$, $a*$, $b*$ intercepts used in this system are based on the CIE color triangle (Commision International De E′ Claire units x, y, and z). In this system, the $L*$ value specifies the dark-white axis, $a*$ the green-red axis, and $b*$ the blue–yellow axis. It should be noted that the system used for the measurements of color interceptions essentially depends on the fact that any color including white (but not black) can be matched by mixing different proportions of blue–violet, green, and red colors. These colors are called the additive primaries. In this system, the $L*$ intercept specifies the dark–white axis. The values of $a*$ and $b*$ represent the red and blue color components, while the negative values of $a*$ and $b*$ represent the green and yellow color components, respectively.

Thermogravimetric analysis

The thermogravimetric analysis (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 600°C. The weight loss was recorded for multilayer unit and blends upon heating from room temperature up to 600°C in the presence of flowing nitrogen gas and employing a constant rate of heating.

Differential scanning calorimetry

DSC studies of PMMA/PC polymer blends were performed by using (Perkin- Elmer DSC- 7 station). A heating rate of 10°C/min was utilized under nitrogen atmosphere over the temperature range from 0 to 300°C.

IR analysis

A FTIR spectrophotometer model Mattson 100, made by Unicam, was used over the range 500–4000 cm^{-1}.

Scanning electron microscope

The surface morphology indicated by scanning electron microscopy (SEM) technique, Jeol (Japan) took the micrographs with a JSA-5400 instrument. A sputter coater was used to precoat conductive gold onto the fracture surfaces before observing the micrographs at 30 kV.

RESULTS AND DISCUSSION

Various degrees of miscibility are possible in polymer blends ranging from complete miscibility to phase separation.[22] Miscibility is a function of the interaction of polymer molecules in the blend and can be detected using various methods.[23] The properties of polymer blends are always governed by the miscibility of the components.[24] The structural behavior of the miscibility was tested by color strength, FTIR, and SEM.

Color Intercepts of Films of Pure PMMA and PC
Polymers and Their Blends at Different Compositions
before and after Exposure to Electron Beam Irradiation
to a Dose 125 kGy

Polymer blend composition %	Irradiation dose (kGy)	Color interceptions		
		L^*	a^*	b^*
100% PC	0	93.6	+11.8	−13.5
	125	91.9	+11.6	−12.3
PC/PMMA (75/25)	0	92.7	+11.4	−12.9
	125	91.8	+10.4	−10.6
PC/PMMA (50/50)	0	92.3	+10.6	−10.1
	125	90.5	+10.4	−9.3
PC/PMMA (25/75)	0	92.4	+12.2	−13.8
	125	90.3	+10.9	−11.1
100% PMMA	0	92.6	+11.9	−14.2
	125	90.1	+11.3	−14

L^*, value specifies the dark-white axis; a^*, The green-red axis; b^*, The blue–yellow axis.

Miscibility of PMMA/PC blends

An attempt was made to examine the miscibility by an experimental method based on the measurement of analyzed reflected beam of light to different color interceptions after passing through the blend films as shown in Table I. Table I shows color intercepts of films of pure PMMA and PC polymers and their blends at different compositions before and after exposure to electron beam irradiation to a dose 125kGy. It was shown that, the transparency in terms of L^* of the unirradiated PMMA/PC blends is between those of pure PMMA and PC films and slightly decreases with increasing the ratio of PMMA component in the blend. However, it is clear that the films of PMMA/ PC at any composition are transparent based on the L^* values which is very close to those of the individual polymer. The transparency of individual PMMA and PC films or their binary blends was found to decrease slightly after those films had been exposed to electron irradiation as for example, at a dose 125 kGy. Based on the transparency L^*, it may be concluded that PMMA/ PC blends are miscible at any composition.

IR spectroscopic analysis

The FTIR analysis was used to illustrate the change in the structure because of blending. Figure 1 shows the IR spectra of unirradiated thin films of 100%PMMA, 100%PC, and PMMA/PC polymer blends of different ratios, and the same polymers after they had been exposed to 125 kGy. For pure PMMA, as with almost all organic compounds, an absorption band can be seen at 2972 cm^{-1}, arising from C—H stretching. A very distinctive absorption band can be observed at 1733 cm^{-1}, which is due to the C=O of the ester group of PMMA. Moreover, a

strong absorption band is seen at 1176 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. On the other hand, for pure PC 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 two benzene rings of PC can be confirmed from the wide absorption band due to —CH— stretching which falls near 3047 cm^{-1}. Also, shows absorption bands 1783 cm^{-1} due to C=O (carbonate) stretch, 1601 cm^{-1} due to C=C (benzene) ring stretch, 1497 cm^{-1} due to C=C (benzene) ring stretch, 1201 cm^{-1} due to O—C—O (carbonate) a symmetrical stretch and 830 cm^{-1} due to C—H (benzene) out of plane bending.

The IR spectra of the polymer blend containing different ratios of PMMA and PC show the absorption bands characteristic of both PMMA and PC polymers.

In Figure 1 spectra A and B are for pure PMMA before and after electron irradiation at 125 kGy, respectively. It was found that, in FTIR spectrum of PMMA before and after irradiation there is a slightly change between A and B spectra in which the carbonyl group of B spectrum is shifted by ∼ 6 cm^{-1} due to oxidative degradation of PMMA. On the other hand, spectra E and F are for pure PC before and after irradiation respectively. Comparing spectra F and E there are no new peaks in spectrum F. This shows that there is no serious degradation of the PC main chain. This could be attributed to the stability of
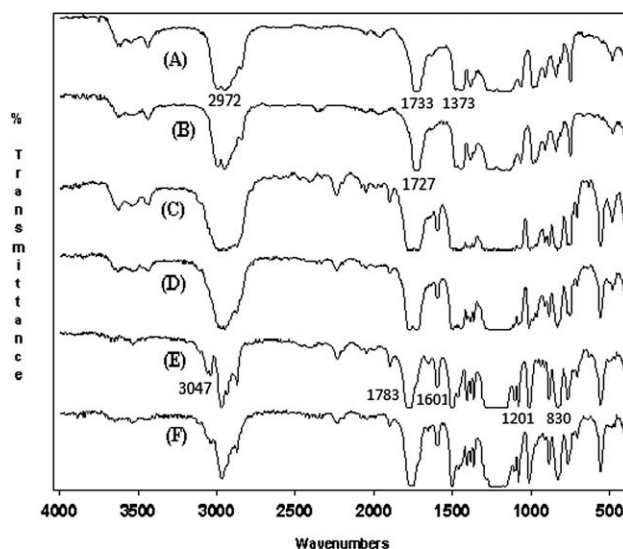

Figure 1 IR spectra of different unirradiated 100%PMMA, 100%PC, and blends of equal ratios and the same polymers after they had been exposed to 125 kGy. (A) Unirradiated pure PMMA (B) Irradiated pure PMMA. (C) Unirradiated 50% PMMA/50%PC blend. (D) Irradiated 50% PMMA/50%PC blend. (E) Unirradiated pure PC. (F) Irradiated pure PC.

PC against radiation degradation. Moreover, spectra of polymer blend PMMA/PC (50/50) before and after irradiation are C and D, respectively. It can be concluded that, the specific characteristic bands of PC in the blend which exposed to 125 kGy were not greatly affected. Finally, it may be concluded that, the presence of PC in the polymer blend protects PMMA polymer against radiation degradation. On the other hand, the miscibility between PMMA and PC can be considered to be a result of n-Π complex formation between free electrons of the ester groups in the PMMA and Π electrons of the aromatic rings of the PC. This indicates specific interactions between PMMA and PC phases.

Structure morphology by SEM

Figure 2 shows SEM micrographs of fracture surfaces of unirradiated pure PMMA, PC and polymer blend PMMA/PC composed of equal ratios (50/50) and the same polymers irradiated to 125 kGy. In Figure 2(A) for pure PC, a large area of the fracture surface is relatively smooth and featureless. On the other hand, it seems that electron irradiation improves the homogeneity of the surface of pure PC as shown in Figure 2(B). In Figure 2(E) for pure PMMA, SEM showed a nonhomogeneous surfaces with continuous matrix and there is a sign of little cavities. The fracture surface of the
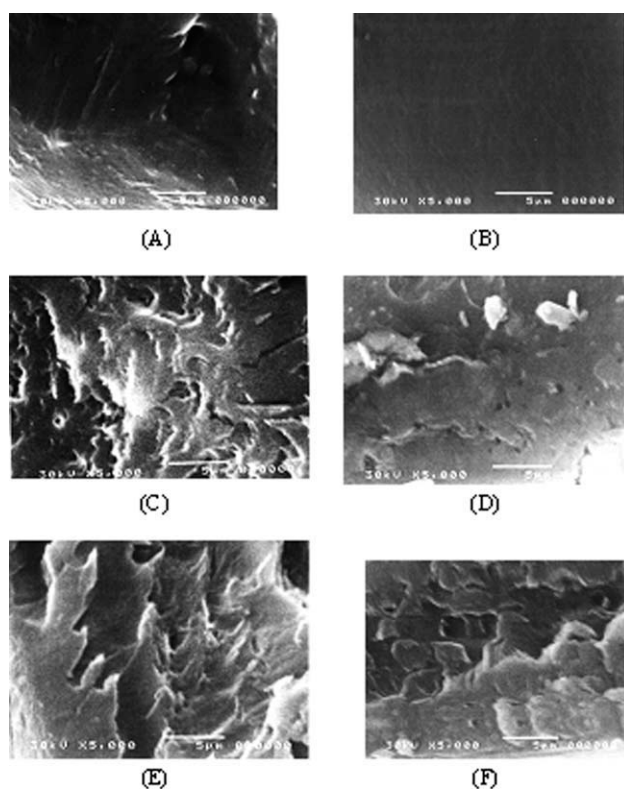
Figure 2 SEM micrographs of the fracture surfaces of (A) unirradiated PC (B) irradiated PC, (C) unirradiated blend 50%PMMA/50%PC, (D) irradiated blend 50%PMMA/50%PC, (E) unirradiated PMMA, (F) irradiated PMMA to 125 kGy.
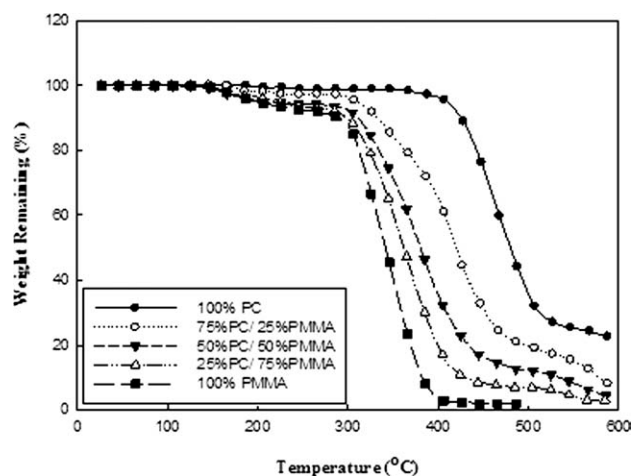
Figure 3 TGA thermograms of unirradiated PMMA/PC polymer blends.

irradiated pure PMMA becomes rough and brittle suggesting occurrence of oxidative degradation as shown in Figure 2(F). The SEM micrographs of unirradiated PMMA/PC polymer blend with ratio (50/50), reveals the formation of an interpenetrating network or cocontinuous two-phase structure as shown in Figure 2(C). This indicates that, there is partial miscibility between the two polymers. Moreover, SEM micrograph of irradiated PMMA/PC (50/50) showed smooth continuous surface with indication of increasing the interfacial adhesion between the two phases suggesting the formation of crosslinking as shown in Figure 2(D). These findings indicate that the improvement in compatibility is greater in case of using electron irradiation.

Thermal decomposition behavior

From the theoretical point, polycarbonate (PC) possesses the highest thermal stability over polymethylmethacrylate (PMMA), whereas PMMA possesses
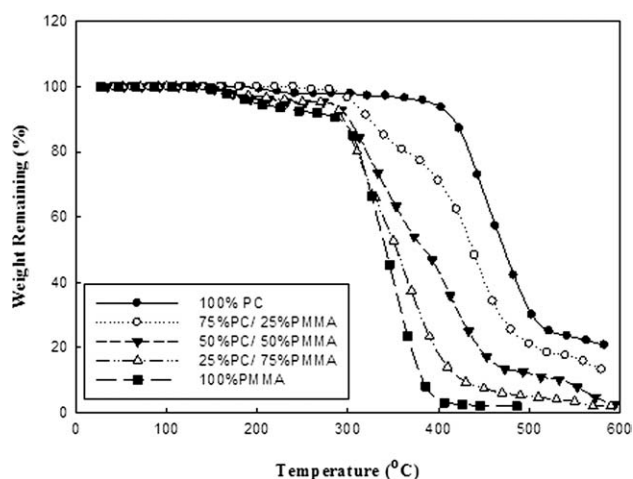
Figure 4 TGA thermograms of different PMMA/PC polymer blends irradiated at 25 kGy.
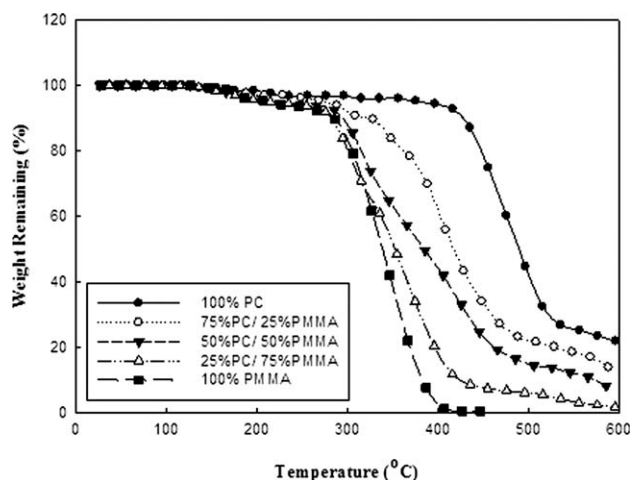
Figure 5 TGA thermograms of different PMMA/PC polymer blends irradiated at 75 kGy.

the lowest thermal stability based on the reported dissociation energy of the different covalent bonds forming the polymer molecules. The average complete dissociation energy for PC and PMMA was calculated to be 103.9 and 99.1 Kcal/mol, respectively. Figures 3–6 show the thermal decomposition behavior of unirradiated pure PMMA, PC, and their blend PMMA/PC having different ratios before and after they had been exposed to different doses of electron irradiation. Table II summarizes the percentage weight loss at different decomposition temperatures for the unirradiated and irradiated pure PMMA, PC, and their blend PMMA/PC taken from the TGA thermograms. It can be observed that there is a marked increase in the thermal stability of the unirradiated PMMA/PC polymer blends with increasing the ratio of PC in the blend as shown in Figure 3 and Table II. The increase in the thermal stability of the PMMA/PC blend is attributed to the
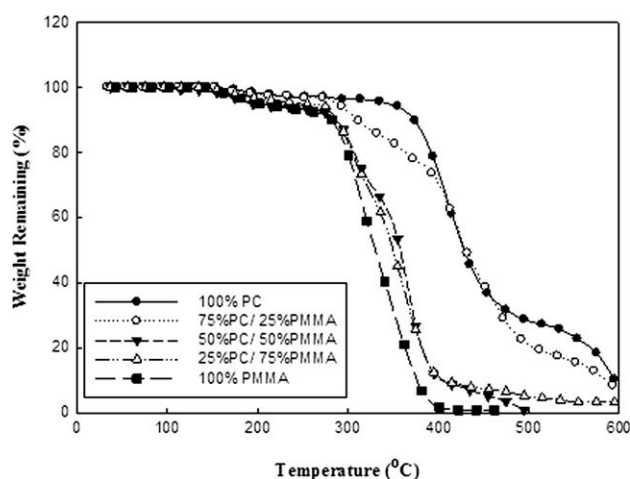
TABLE II
Weight Loss (%) at Different Decomposition Temperatures for Different Polymer Blends of Various Ratios of PMMA and PC Unirradiated and Irradiated at Different Doses of Electron Beam Irradiation

Polymer blend composition	Irradiation dose (kGy)	Weight loss (%)			
		200°C	300°C	400°C	500°C
100%PMMA	0	5.5	15	97	–
	25	4.24	16.53	94	99.16
	75	4.55	20.78	98.71	–
	125	5.05	21.99	98.32	–
(75%/ 25%) (PMMA/PC)	0	3.88	11.63	82.95	93.03
	25	3.34	20	86	95.34
	75	4.35	16.15	79.51	93.79
	125	3.27	13.73	87.59	94.78
(50%/50%) (PMMA/PC)	0	5.1	8.29	67.52	87.9
	25	3.91	7.04	53.13	87.5
	75	4.14	14.49	57.94	85.52
	125	5.18	12.94	87.94	99.16
(25%/75%) (PMMA/PC)	0	1.82	4.55	39.1	80.91
	25	0	3.51	28	78.95
	75	3.11	9.31	44.19	78.3
	125	1.94	5.81	26.46	77.42
100%PC	0	0.56	1.11	4.42	67.96
	25	0.72	2.15	6.43	70
	75	1.63	3.26	5.7	55.29
	125	1.48	3.68	21.33	71.33

presence of aromatic rings in PC and also the high dissociation energy of pure PC. This may suggest the occurrence of a chemical interaction between the two polymers in the blend, which is capable of improving the thermal stability of the blend.

Table II shows that the main weight loss is noted in the temperature range between 300 and 400°C and a small weight loss is between 400 and 500°C. The same trend is observed on exposing the pure polymers and their blend to electron irradiation as shown in Figures 4–6 and Table II. So the thermal stability of irradiated pure polymers and PMMA/PC blend with all ratios is higher than that of unirradiated ones. Thus it can be concluded that PC offers some sort of protection against radiation degradation of PMMA component due to PC being aromatic with low lying electronic energy states (Π electrons) can absorb the effect of electron irradiation reducing degradation.[25] On the other hand, the miscibility between PMMA and PC can be considered to be a result of n-Π complex formation between free electrons of the ester groups in the PMMA and Π electrons of the aromatic rings of the PC. This indicates specific interactions between PMMA and PC phases.

Differential scanning calorimetry

DSC thermograms as-cast PMMA, PC, and their blends before and after they had been exposed to electron irradiation at a dose 125 kGy are shown in

Figure 6 TGA thermograms of different PMMA/PC polymer blends irradiated at 125 kGy.

Figure 7. PC shows an endothermic peak at $\sim 240^{\circ}C$ corresponding to its melting point whereas PMMA exhibits no such peak due to the glassy nature of PMMA. As the PMMA content increases, melting peak shows broadening suggesting the variation of heat fusion with the PMMA content. In the polymer blend 75%PMMA/25% PC there is no clear signature of melting peak due to the higher PMMA content. So, it is evident that the crystallinity of PMMA/ PC blend decreases with increasing PMMA content. This is very much on expected line in view of the glassy nature of PMMA. Figure 8 shows the T_{g}s of PMMA, PC, and their blends before and after they had been exposed to electron irradiation at a dose 125 kGy in order to check the miscibility of the blends. The unirradiated and irradiated polymer blends having the ratio 25%PMMA/75%PC show single glass transition temperature with a T_g slightly less than the glass transition temperature of pure PC and higher than the T_g of PMMA. On the other hand, the unirradiated and irradiated polymer blends having the ratios 50%PMMA/50%PC and 75%PMMA/25%PC showing that, there are two distinct T_{g}s which is in broad agreement with the find-

Figure 8 DSC thermograms of the glass transition temperature (T_g) of unirradiated PMMA/PC blends and the same blends after they had been exposed to 125 kGy of electron beam irradiation. (a) unirradiated 100%PC (b) irradiated 100%PC. (c) unirradiated 75%PC/25%PMMA (d) irradiated 75%PC/25%PMMA. (e) unirradiated 50%PC/50%PMMA (f) irradiated 50%PC/50%PMMA (g) unirradiated 25%PC/75%PMMA (h) irradiated 25%PC/75%PMMA (i) unirradiated 100%PMMA (j) irradiated 100%PMMA.
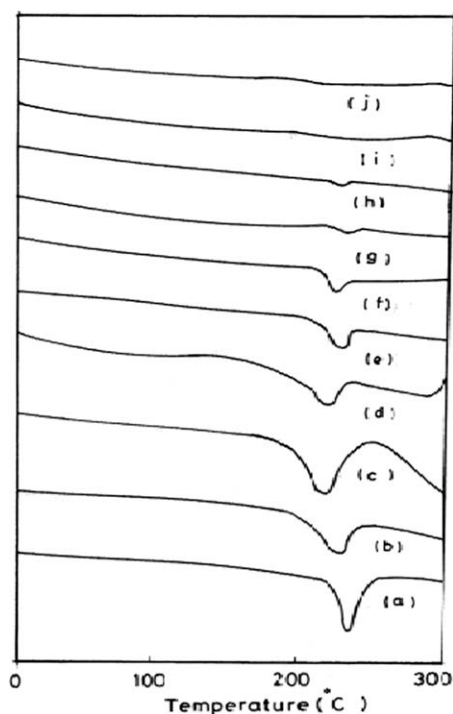

Figure 7 DSC thermograms of unirradiated PMMA/PC blends prepared using THF and the same blends after they had been exposed to 125 kGy of electron beam irradiation (a) unirradiated 100%PC (b) irradiated 100%PC (c) unirradiated 75%PC/25%PMMA (d) irradiated 75%PC/25%PMMA (e) unirradiated 50%PC/50%PMMA (f) irradiated 50%PC/50%PMMA (g) unirradiated 25%PC/75%PMMA (h) irradiated 25%PC/75%PMMA (i) unirradiated 100%PMMA (j) irradiated 100%PMMA as measured by endothermic melting peak in DSC thermograms.
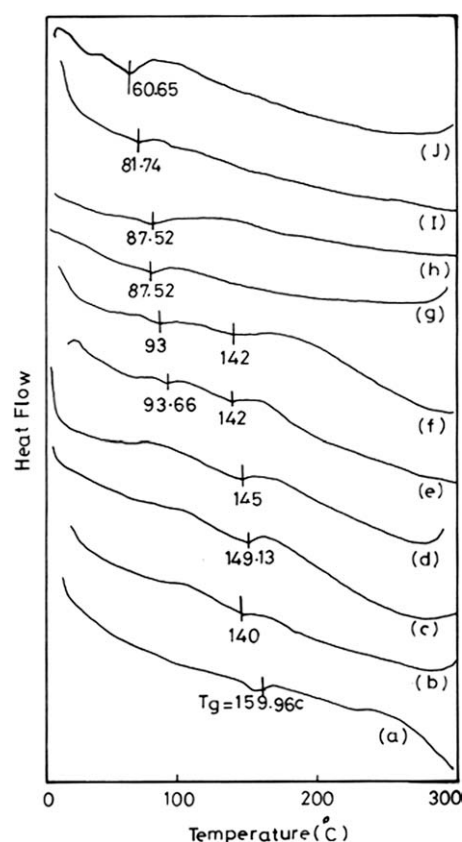
ings of Woo and Su[26] and Saldanha and Kyu.[7] The lower T_g can be easily attributed to PMMA-rich phase while the higher T_g due to PC-rich phase. These findings indicate the existence of specific interactions between PMMA and PC polymers in the blend.

CONCLUSIONS

The results presented in this work demonstrate the effect of electron beam irradiation on the thermal decomposition behavior of polymer blends composed of a radiation-sensitive polymer (PMMA) and a radiation-resistant polymer (PC). PMMA/PC blends were shown to be highly compatible over a wide range of ratios, as seen by the visual observation. In addition, TGA investigations showed that pure PC polymer possesses higher thermal stability than those of pure PMMA and their blends over the entire range of applied temperatures. Moreover, it was noticed that the presence of PC polymer in the

blend affords protection against radiation degradation and improves their thermal stability. DSC scans of the glass transition temperatures of a series of polymer blends containing various ratios of PMMA and PC indicated a single T_g less than the glass transition temperature of pure PC and higher than the T_g of PMMA for the blend having the ratio 25%PMMA/75%PC. Also, DSC show two distinct T_gs the lower T_g can be easily attributed to PMMA-rich phase while the higher T_g due to PC-rich phase. IR analyses of different PMMA/PC polymer blends before and after they had been exposed to electron irradiation are in accordance with the results of TGA studies. Also, SEM micrographs of irradiated blends show an indication of interfacial adhesion and a smooth continuous surface. So, SEM micrographs give further supports of PC against the effect of electron irradiation as a tool for improving the compatibility which may be accounted for the occurrence of crosslinking. All these observations point towards the existence of specific interactions between the PMMA and PC phases in the blends.

References

1. Yuichi, K. J Appl Polym Sci 1997, 63, 363.
2. Agari, Y.; Ueda, A.; Omura, Y.; Naga, S. Polymer 1997, 38, 801.
3. Butzbach, G. D.; Wendroff, J. Polymer 1991, 32, 1155.
4. Rabenoy, M.; Hseih, D. T.; Garner, R. T.; Peiffer, D. G. J Chem Phys 1992, 97, 4505.
5. An, N.; Yang, Y.; Dong, L. Macromolecules 2007, 40, 306.
6. Kim, C. K.; Paul, D. R. Macromolecules 1992, 20, 3097.
7. Saldanha, M.; Kyu, T. Macromolecules 1987, 20, 2840.
8. Kyu, T.; Lim, D. S. J Polym Sci Part C: Polym Lett 1989, 27, 421.
9. Hung, C. C.; Carson, W. C.; Bohn, S. P. J Polym Sci Part B: Polym Phys 1994, 32, 141.
10. Chiou, T. S.; Barlow, J. W.; Paul, D. R. J Polym Sci Part B: Polym Phys 1987, 25, 1459.
11. Kim, W. N.; Burns, C. M. Macromolecules 1987, 20, 1876.
12. Montaudo, G.; Puglisi, C.; Samperi, F. J Polym Sci Part A: Polym Chem 1998, 36, 1873.
13. Ko, C.-C.; Kyu, T.; Smith, S. D. J Polym Sci Part B: Polym Phys 1995, 33, 517.
14. Debier, D.; Devaux, J.; Legras, R. J Polym Sci Part A: Polym Chem 1995, 33, 407.
15. Rincon, A.; McNeill, I. C. Polym Degrad Stab 1987, 18, 99.
16. Kyu, T. K.; Ko, C. C.; Lim, D. S.; Smith, D. S.; Noda, S. J Polym Sci Polym Phys Edn 1993, 31, 1641.
17. Kyu, T.; Saldanha, J. M. J Polym Sci Polym Lett Ed 1988, 26, 33.
18. Landry, C. J. T.; Henrichs, P. M. Macromolecules 1989, 22, 2157.
19. Kyu, T.; Saldanha, J. M. Macromolecules 1988, 21, 1021.
20. Kim, W. N.; Burns, C. M. J Appl Polym Sci 1990, 41, 1575.
21. Nishimota, M.; Keskkula, H.; Paul, D. R. Polymer 1991, 32, 272.
22. Paul, D. R.; Bucknall, C. B. In Polymer Blends, V.11; Paul, D. R.; Bucknall, C. B., Eds., Wiley-Interscience: New York, 2000.
23. Olabisi, O.; Robensen, L. M.; Shaw, M. T. Polymer-Polymer Miscibility; Academic Press: New York, 1979.
24. Fekete, E.; Foldes, E.; Damsits, F.; Pukaanszky, B. Polym Bull 2000, 44, 363.
25. Jingshen, W.; Yiu, W. M. J Mater Sci 1994, 29, 4510.
26. Woo, E. M., Su, C. C. Polymer 1996, 37, 4111.