

Improved Thermal Stability of Radiation Degradative Poly(methyl methacrylate) by Blending with Poly(ethylene glycol)

S. ALI AL-GAHTANY¹, D. MOHAMED ALSHANGITI^{2,*}, M. MADANI² and M. MOHAMADY GHOBASHY³

¹Faculty of Science, University of Jeddah, Jeddah, Saudi Arabia

²Faculty of Science and Humanities-Jubail, Imama Abdulrahman Bin Faisal University, Jubail, Saudi Arabia

³Radiation Research of Polymer Chemistry Department, National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority, P.O. Box 29, Nasr City, Cairo, Egypt

*Corresponding author: E-mail: dalshangite@iau.edu.sa

Received: 7 December 2019;

Accepted: 1 April 2020;

Published online: 27 June 2020;

AJC-19936

A blend polymer consists of poly(methyl methacrylate) (PMMA) and poly(ethylene glycol) (PEG) in four ratios 20:0, 18:2, 16:4 and 14:6. The blend polymer (PMMA/PEG) was characterized by using differential scanning calorimetry (DSC), TGA and FTIR. FTIR analysis proved that the lack of miscibility and interactions between PMMA (hydrophobic) and PEG (hydrophilic) were not due to hydrogen bonding but gamma irradiation at doses up to 20 kGy. Furthermore, DSC thermograms of the blend polymers display a positive deviation during the glass transition temperature (T_g) of PMMA due to gamma irradiation-induced PEG crosslinking, decreasing the molecular motion and chain relaxation between the two polymers. Blends that are not irradiated show negative T_g deviation from the corresponding values due to plasticization of PEG. Furthermore, the melting point (T_m) of PMMA increased with an increase in PEG, which acts as a filler at high temperatures.

Keywords: Thermal stability, Blend polymer, Gamma irradiation, Miscibility.

INTRODUCTION

Polymer blends involve mixing two or more polymers for combining the characteristics of individual polymers for easily tailoring their properties. Compatibilizing the phases in the blends provides it certain functional properties. Numerous polymer blend systems were reported through the development synthesis, microstructure and property characterization [1]. Furthermore, these functional polymer blend systems help to enhance the application spectrum of polymers.

Polymers that have high T_g are desirable materials in the industries. For example, poly(methyl methacrylate) (PMMA) is transparent and exhibits corrosion, high temperature, good electric insulation and weather and chemical resistance [2]. PMMA is useful because of these properties, but because of its poor mechanical properties, its application in the optical-electronics field is limited [3]. Furthermore, PMMA degrades on exposure to radiation [4]. PMMA that can form hydrogen bonds with other polymers having functional groups (inter-

polymer interactions) are of great value because of its T_g [5,6]. The effect of interpolymer interaction strength is reflected on the T_g and blend miscibility, classifying PMMA into three polymer blend classes: i) very weak, (ii) relatively weak and (3) strong interactions [7].

Irradiating polymeric materials converts them into valuable products with wide application potential [8-11]. The miscibility between two polymers is higher if gamma radiated rather than unirradiated [12]. New polymers with high thermal and radiation stability were achieved through blends formation. Typically, blending of two polymers with different radiations behaviours effectively improves radiation stability. For example, blending a radiated crosslinkable polymer with a radiation degradative polymer provides a protective effect on the degradative polymer, for example, PMMA/PEO system. PMMA is a typical radiation degradative polymer, whereas PEO is a radiation crosslinkable polymer [13]. Furthermore, a similar protective effect was observed in PMMA/PVDF blend. An explanation for this observation is radiation-induced crosslinking, which

restricts the chain mobility of radiation degradative polymer [14,15]. Radiation in cross-linking improves the thermal properties of polymers [16]. Previous studies [17,18] suggested that the T_g value of PMMA improved after copolymerization with hydrophilic polymer, exhibiting hydrogen bonding interactions between the two polymers. The T_g values of copolymers are generally higher than those of corresponding polymer blends because hydrogen-bonded copolymers are heterogeneous [19,20]. The blending of different polymers could improve the thermal and mechanical properties of the resultant polymer, irrespective of whether they are miscible, immiscible or partially miscible [21].

Differential scanning calorimetry (DSC) is the most common method used to establish polymer miscibility, making the blends homogeneous and strongly miscible. This blend exhibits only one T_g , which is between the T_g 's of both blend components and closely related to the blend composition. The miscibility of intermolecular interactions between two polymer chains produce hydrogen bond, ionic bond and dipole-dipole interactions [22]. Some researchers [23] found that PMMA undergoes degradation on exposure to gamma radiation. Chipara [24] reported that irradiation changes the T_g of polymers where cross-linking increases during degradation and decreases during depolymerization or chain scission.

This article explains that gamma radiation alters the thermal stability of PMMA and the content of PEGs through a series of change in melting and glass temperatures in terms the heat capacity and enthalpy, measured using differential scanning calorimetry. According to the results, DSC is a simple and flexible method of characterizing the blend polymer (PMMA/PEG). The effects of immiscibility on thermal properties were experimentally measured, as gamma radiation predominantly induces crosslinks rather than degradation in PEG network matrices. Thermal properties of all unirradiated and irradiated blend polymers (PMMA/PEG) have been examined with DSC. This study states that the immiscibility of two polymers in the blend affects its thermal properties and the inter H-bond was absent. FTIR showed that blend polymer (PMMA/PEG) lack miscibility due to the absence of H-bond between PMMA and PEG. Therefore, this study investigated the thermal properties of PMMA.

EXPERIMENTAL

All the chemicals used were of analytical purity. The poly (methyl methacrylate) (PMMA) employed in this work was a commercial sample with a supplied as a monomer (99%) by Sigma-Aldrich Chemical Company. Spontaneous thermal initiation of methyl methacrylate monomer converts to the linear polymer of poly(methyl methacrylate) due to self-polymerization [25,26]. Chloroform (Sigma-Aldrich, 99.5% purity) was used as solvent. PEG4000 was obtained from CLARIANT (Sulzbach, Germany). All the reagents were analytical grades and used without further purification.

Gamma radiation source: Specimens were irradiated at 2.05 KGy/h with gamma radiation at the ^{60}Co Indian irradiation facility. The irradiation facility was designed by the Egyptian Atomic Energy Authority of Cairo's National Center for Radiation Research and Technology.

Preparation of blend polymer (PMMA-PEG) film by gamma irradiation: The blend was prepared according to the known procedure described elsewhere [27]. PMMA (2 g) was dissolved in 20 mL of purified chloroform. Thin films at different concentrations of PEG-4000 were used at room temperature for investigation. PEG/PMMA mixtures of four different concentrations were used, namely 0/20, 2/18, 4/16 and 6/14 w/w%. After stirring and sonication, four samples were transferred into glass tubes and degassed with nitrogen. Subsequently, they were exposed to 20 kGy of ^{60}Co γ -rays in a gamma cell at a dose rate of 2.05 KGy/h at room temperature. After irradiation, four mixtures of PMMA-PEG were casted on petri dishes and allowed to dry at room temperature; a dry atmosphere was ensured for evaporating the solvent to form transparent films and then finally stored in a desiccator. Irradiated blend polymers of PMMA/PEG with different PEG contents are well known degradative polymers [28,29].

Characterizations: The probable of chemical interaction between PEG ad PMMA was measured using Attenuated total reflectance-Fourier transform infrared ATR-FTIR spectroscopy Vertex 70 FTIR spectrometer equipped with HYPERION™ series microscope, BrukerOptik GmbH, Ettlingen, Germany, over the 4000-400 cm^{-1} range, at a resolution of 4 cm^{-1} . Software OPUS 6.0 (BRUKER) was used for data processing, which was baseline corrected by the rubber band method with CO_2 bands excluded. Thermal analysis was performed using a DSC (Q2000) from TA Instruments, New Castle, DE, USA. The glass-transition temperature (T_g) and melting temperature (T_m) of the polymer blend was calculated by heating rate 10 $^\circ\text{C}/\text{min}$. All measurements were conducted under a nitrogen atmosphere. The cell was calibrated using an indium standard; the weight of the sample was 5-10 mg. Thermal analysis was performed using a TGA from (TA Instruments, New Castle, DE, USA). The TGA features a top-loading balance, furnaces provide the highest available cooling speed. Conversely, heating up to 600 $^\circ\text{C}$ with heating rate 10 $^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

FTIR analysis: The interaction between PMMA and PEG was investigated using FTIR spectroscopy. Fig. 1 shows the FTIR spectra of pure components of neat PMMA and their corresponding blends, such as PMMA/6%PEG. The carbonyl peak positions of the blend and neat PMMA were almost the same with a sharp transmittance peak at 1724 cm^{-1} , which indicated the absence of the carbonyl-hydroxyl interaction. Thus, the FTIR analysis proved that no chemical interactions occurred between PMMA (hydrophobic) and PEG (hydrophilic). The interaction between PMMA and PEG was not a simple hydrogen bonding [30,31]. A slight shift in the peak of carbonyl groups noted at 1715 cm^{-1} (Fig. 1d) for PMMA is due to crosslinkings with PEG caused by gamma radiation. Thus, gamma irradiation induces miscibility between two immiscible polymers.

Impact of gamma irradiation and PEG content in the thermal stability of PMMA: Unirradiated blend samples (PMMA/PEG) with different PEG compositions from 0 to 6 wt% were investigated by using DSC thermogram to prove variations in both T_m and T_g of PMMA based on variation of

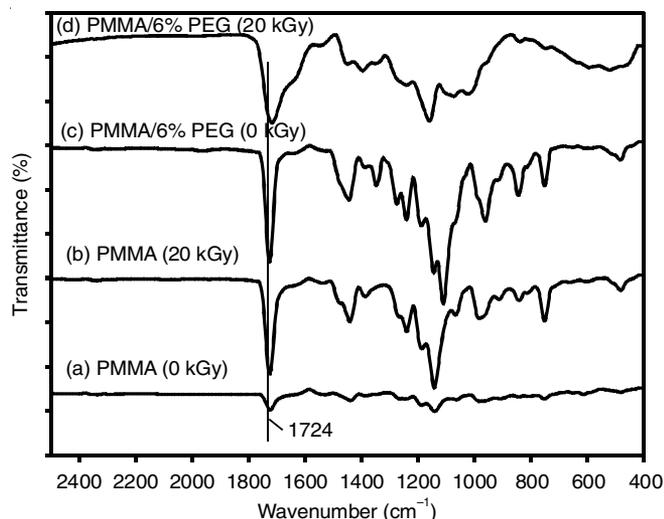


Fig. 1. FT-IR spectra of the irradiated and unirradiated neat PMMA and PMMA/6 wt% PEG films measured in ATR mode

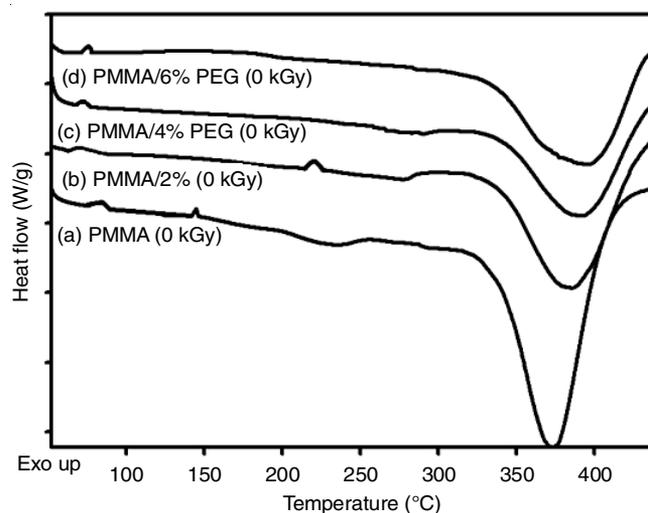


Fig. 2. DSC thermogram of series PEG/PMMA blends Un irradiated

PEG composition. During thermal initiation, methyl methacrylate monomer forms a linear polymer of PMMA are held for various times at several sub- T_g and annealing temperatures (T_{ann}), the results are analyzed in the context. Fig. 2a shows DSC thermogram results of neat PMMA (0 kGy), with a single T_g at 77.62 °C, $C_p = 0.0306$ mW and exothermic crystalline temperature (T_c) = 145.44 °C. The endothermic temperature at 234 °C may be attributed to the 'annealing peak', which always appears above T_c and T_g and below T_m depending on annealing conditions [32,33]. The highest endothermic T_m of PMMA was observed from 310 to 420 °C at a T_{max} of 373 °C and calculated enthalpy change (ΔH) of 607 J/g. DSC thermogram can show the thermal history of PMMA. Thermal history peaks shifted at 2 wt% of PEG (Fig. 2b-c) and the T_g shift from 77.62 °C to 72.82 °C, 72.75 °C and 72.66 °C indicated that PEG acts as a plasticizer [34]. Furthermore, Fig. 2b shows that the exothermic T_c is 218 °C and the endothermic T_{ann} is 278.25 °C. Moreover, a large shift was observed in T_m because of 2 wt% PEG (Fig. 2b), the T_m was 385.85 °C. Therefore, the high melting temperatures of PMMA are responsible for excellent retention of network caused by PEG plasticization, which acts as a filler at high temperatures. At high temperatures, the PEG network decomposed and the unzipping process and carbon ash act as fillers, increasing the T_m and the same explanation holds for T_c and T_{ann} . The typical peaks of T_c and T_{ann} were observed in the curves of 'a' and 'b' but not in the curves 'c' and 'd' for 4 and 6 wt% of PEG, respectively. From both curves c and d, the T_m shifted to high temperatures of 392 °C and 395 °C with ΔH 326.90 and 461.25 J/g for 4 and 6 wt% of PEG, respectively. The T_m of PMMA increased an increase in PEG content, which proves that PEG acts as a filler at high temperatures.

DSC (Fig. 3a) results demonstrated that blank PMMA irradiated with 20 kGy decreased T_g to 75.80 °C, C_p to 0.390 mW and T_c to 142.35 °C. These parameters decreased due to gamma ray-induced PMMA degradation. Qi *et al.* [35] found the same results and stated that the decreased T_g of PMMA is attributed to the molecular motion and chain relaxation below glass transition caused by gamma radiation. Moreover, these

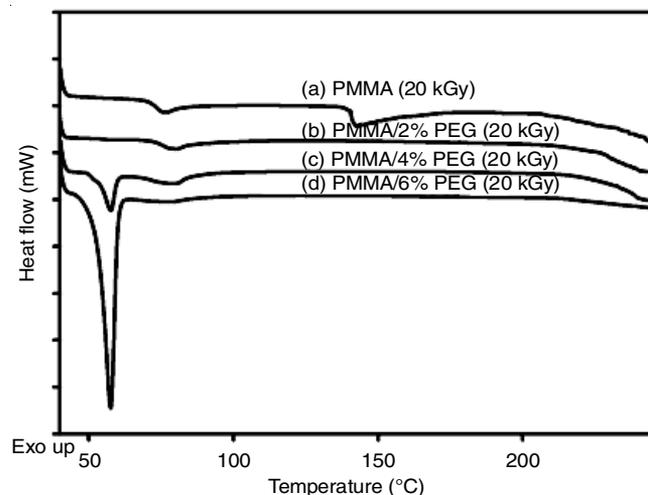


Fig. 3. TGs curves for (PMMA/PEG) irradiated by 20 kGy gamma rays

results are in agreement with those of Tatro *et al.* [36] irradiating blank PMMA with 20 kGy increased the endothermic T_m to 392 °C and ΔH was 155.3 J/g (Fig. 4a). Thus at high temperatures, macro-radicals are formed due to crosslinking, with H atoms as crosslinking precursors.

When PEG was introduced to form a PMMA/PEG blend through irradiation with 20 kGy, T_g increases to 80.62 °C based on the PEG content corresponding to PMMA, which may be due to gamma irradiation-induced crosslinking effect of PEG in the blends [37]. Furthermore, adding PEG increased T_g to 79.30 °C and 97.34 °C with 4 and 6 wt% of PEG, respectively, when PEG was crosslinked through gamma radiation and was not acting as a plasticizer. Although no chemical interactions were observed between PEG and PMMA matrixes based on ATR/FTIR charts, DSC detected that PEGs affect the chain mobility of PMMA. Therefore, PEG is valuable for influencing the T_g (Fig. 2b-d). Similar behaviour was noted with a non-interacting system of poly(vinyl acetate)/poly(methyl acrylate) by Song *et al.* [38]. The endothermic T_m of PEG at 57.88 °C, 57.56 °C and 57.58 °C with ΔH values of 0.036, 8.03 and 66.20 (J/g), respectively, can be explained by the increase in crystalline

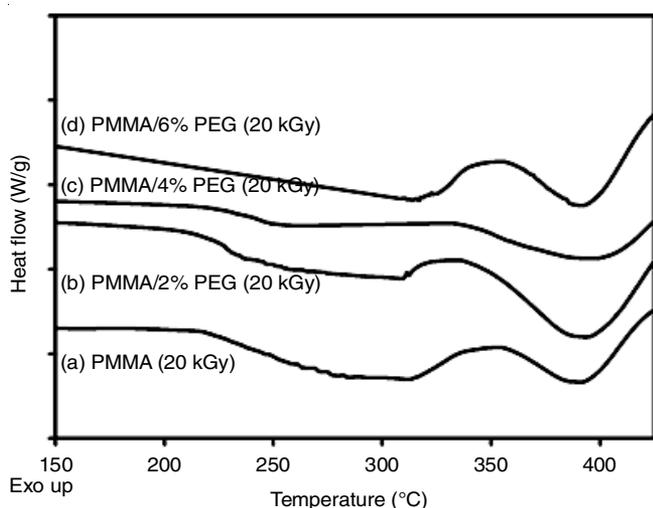
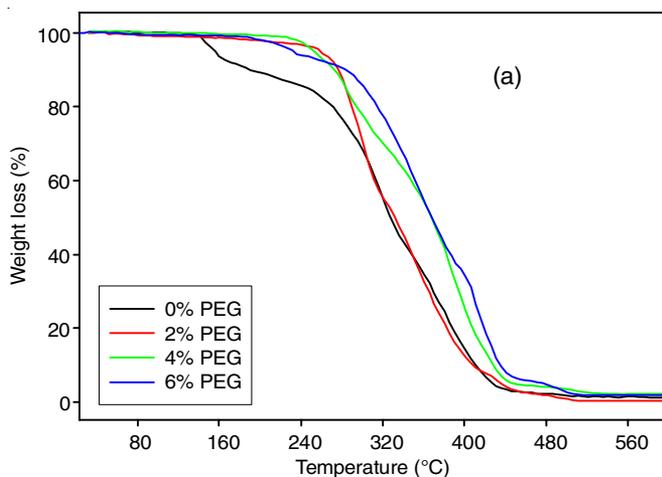


Fig. 4. TMS curves for (PMMA/PEG) irradiated by 20 kGy gamma rays

areas with increase in the PEG content from 2 to 4 and 6 wt%. Crystallinity and T_m of PMMA networks increase with an increase in PEG content [39]. The endothermic T_{ms} of blend polymers PMMA with a PEG content of 2, 4, and 6 wt% were 393.47 °C, 394 °C and 397.25 °C with ΔH of 141, 147 and 176 (J/g), respectively. These parameters confirmed that the predominant mechanism in PMMA formation is crosslinked.

Thermogravimetric curves (Fig. 5a) show that the thermal stability of PMMA improves after gamma ray-induced blending with PEG. Furthermore, energy of activation (E_a) during the main decomposition stage of the blended irradiated samples was determined by using TGA according to the Horowitz and Metzger method [40]. Thus, a force-pressure relationship is shown in Fig. 5b, which gives a straight line with a slope equal to the unit.

As explained in previous studies [41], in this method, the relation between $\ln[\ln((W_0 - W_f)/(W_t - W_f))]$ and q is plotted, which gives a straight line with a slope equal to $E_a \times 10^3/RT_s^2$. This slope can be used to calculate the activation energy value. Herein, W_0 , W_f and W_t are the initial, final and sample weights, respectively, at time t and R is the gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). And $\theta = T_t - T_s$, where T_s is the temperature at which the value of $[(W_t - W_f)/(W_0 - W_f)] = 1/e$.



The thermal activation energy values of all prepared samples are listed in Table-1, which indicate that char residue % increased with increase in the PEG content of the blend, which confirms that at a high temperature, the PEG network decomposed, leading to an unzipping process and carbon ash formation, which acts as a filler, increasing char residue %. Regarding E_a values, pure PMMA has a higher E_a value than other samples; this is in agreement with DSC results, which indicates that pure PMMA is a crystalline polymer. Samples with 2 and 4 wt% of PEG have drastically reduced E_a values, which is caused by the plasticization effect of PEG in the blend. When the content of PEG is high (6 wt%), the E_a value increases to 45.52 kJ/mol. This occurs because at a high temperature, the PEG network decomposes, leading to an unzipping process and carbon ash formation, acts as a filler, increasing the E_a value.

Sample	Char residue at 600 °C (%)	Activation energies (E_a , kJ/mol)
0% PEG	1.17	50.3
2% PEG	0.19	41.2
4% PEG	2.06	39.2
6% PEG	1.96	45.5

Conclusion

The blend polymer (PMMA and PEG) lacks miscibility, with hydrophobic and hydrophilic domains. DSC thermograms indicated that gamma irradiation induced an interaction between PEG and PMMA. Furthermore, it showed that PEG could act as a plasticizer at low temperatures and as a filler at high temperatures for unirradiated blend samples. The effect of gamma irradiation on miscibility was indicated by a significant increase in T_g and T_m . Furthermore, PEG crosslinks induced by radiation of 20 kGy cannot act as a plasticiser as do irradiated blend samples. The results indicate that miscibility might improve with gamma radiation exposure due to crosslinking of one of two polymers, in which increase the thermal stability irrespective of immiscibility of the two given polymers (PMMA/PEG). Thus, the predominant effect of gamma radiation is crosslink formation

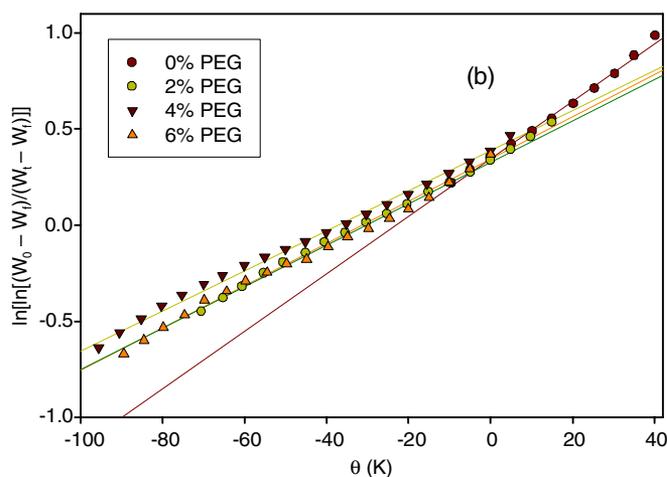


Fig. 5. (a) TGA curves (b) Plot of $\ln[\ln((W_0 - W_f)/(W_t - W_f))]$ and θ for PMMA-PEG blend

rather than chain scission for PMMA compared with individual components. Additionally, thermogravimetric analysis confirmed that at a high temperature, the PEG network decomposes, leading to an unzipping process and carbon ash formation, which acts as a filler, increasing the E_a value.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- P. Jyotishkumar, S. Thomas and Y. Grohens, Polymer Blends: State of the Art, New Challenges, and Opportunities, In: Characterization of Polymer Blends, Wiley-VCH Verlag GmbH & Co. KGaA, pp 1-6 (2015)
- Y. Kita, K. Kishino and K. Nakagawa, *J. Appl. Polym. Sci.*, **63**, 363 (1997); [https://doi.org/10.1002/\(SICI\)1097-4628\(19970118\)63:3<363::AID-APP12>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1097-4628(19970118)63:3<363::AID-APP12>3.0.CO;2-1)
- T. Otsu, A. Matsumoto, T. Kubota and S. Mori, *Polym. Bull.*, **23**, 43 (1990); <https://doi.org/10.1007/BF00983962>
- J. Sun and X. Zhong, Studies on Radiation Stability of Polymers (IAEA-TECDOC-1062), International Atomic Energy Agency (IAEA) (1999).
- R. Chauhan and V. Choudhary, *J. Appl. Polym. Sci.*, **112**, 1088 (2009); <https://doi.org/10.1002/app.29493>
- H. Teng, K. Koike, D. Zhou, Z. Satoh, Y. Koike and Y. Okamoto, *J. Polym. Sci. A Polym. Chem.*, **47**, 315 (2009); <https://doi.org/10.1002/pola.23154>
- X. Lu and R.A. Weiss, *Macromolecules*, **25**, 3242 (1992); <https://doi.org/10.1021/ma00038a033>
- M.M. Ghobashy, *Ultrason. Sonochem.*, **37**, 529 (2017); <https://doi.org/10.1016/j.ultsonch.2017.02.014>
- M.M. Ghobashy, *Nanocomposites*, **3**, 42 (2017); <https://doi.org/10.1080/20550324.2017.1316600>
- M.M. Ghobashy *Int. J. Plast. Technol.*, **21**, 130 (2017); <https://doi.org/10.1007/s12588-017-9176-5>
- M.M. Ghobashy and M.A. Elhady, *Radiat. Phys. Chem.*, **134**, 47 (2017); <https://doi.org/10.1016/j.radphyschem.2017.01.021>
- M.M. Ghobashy and E. Khozemey, *Adv. Polym. Technol.*, **37**, 1249 (2016); <https://doi.org/10.1002/adv.21781>
- K. Miklesova and F. Szocs, *Eur. Polym. J.*, **28**, 553 (1992); [https://doi.org/10.1016/0014-3057\(92\)90132-L](https://doi.org/10.1016/0014-3057(92)90132-L)
- R.L. Clough and S.W. Shalaby, Radiation Effects on Polymers, Technology & Engineering, American Chemical Society, pp 633 (1991).
- J. Davenas, I. Stevenson, N. Celette, S. Cambon, J.L. Gardette, A. Rivaton and L. Vignoud, *Nucl. Instrum. Methods Phys. Res. B*, **191**, 653 (2002); [https://doi.org/10.1016/S0168-583X\(02\)00628-6](https://doi.org/10.1016/S0168-583X(02)00628-6)
- J.G. Drobny, Radiation Technology for Polymers, CRC Press: Boca Raton (2003).
- S.W. Kuo, H.C. Kao and F.C. Chang, *Polymer*, **44**, 6873 (2003); <https://doi.org/10.1016/j.polymer.2003.08.026>
- J.K. Chen, S.W. Kuo, H.C. Kao and F.C. Chang, *Polymer*, **46**, 2354 (2005); <https://doi.org/10.1016/j.polymer.2005.01.046>
- M.M. Coleman, Y. Xu and P.C. Painter, *Macromolecules*, **27**, 127 (1994); <https://doi.org/10.1021/ma00079a019>
- S.W. Kuo, H. Xu, C.F. Huang and F.C. Chang, *J. Polym. Sci., B, Polym. Phys.*, **40**, 2313 (2002); <https://doi.org/10.1002/polb.10292>
- H. Xu, T.B. Norsten, O. Uzun, E. Jeoung and V.M. Rotello, *Chem. Commun.*, **41**, 5157 (2005); <https://doi.org/10.1039/b509572g>
- S.W. Kuo and H.T. Tsai, *Macromolecules*, **42**, 4701 (2009); <https://doi.org/10.1021/ma900640a>
- C. Albano, R. Perera and P. Silva, Revista Latinoamericana de Metalurgia y Materiales, **30**, 3 (2010).
- M.I. Chipara, *Physica B: Condens. Matter*, **263**, 234 (1997); [https://doi.org/10.1016/S0921-4526\(96\)00950-7](https://doi.org/10.1016/S0921-4526(96)00950-7)
- M. Stickler and G. Meyerhoff, *Polymer*, **22**, 928 (1981); [https://doi.org/10.1016/0032-3861\(81\)90270-6](https://doi.org/10.1016/0032-3861(81)90270-6)
- J. Lingnau and G. Meyerhoff, *Polymer*, **24**, 1473 (1983); [https://doi.org/10.1016/0032-3861\(83\)90233-1](https://doi.org/10.1016/0032-3861(83)90233-1)
- M.M. Ghobashy, A.M.A. Reheem and N.A. Mazied, *Int. Polym. Process.*, **32**, 174 (2017); <https://doi.org/10.3139/217.3258>
- R. Dorati, C. Colonna, M. Serra, I. Genta, T. Modena, F. Pavanetto, P. Perugini and B. Conti, *AAPS PharmSciTech*, **9**, 718 (2008); <https://doi.org/10.1208/s12249-008-9103-3>
- T. Zhongfeng, C. Youshuang, Q. Guangan, T. Bin, L. Hua, T. Xiaoxing and K. Xiangbo, *Nucl. Sci. Techniq.*, **24**, 36 (2013).
- N. Ise and I. Tabushi, An Introduction to Speciality Polymers Hardcover, Cambridge University Press: Cambridge (1983).
- J. Straka, P. Schmidt, J. Dybal, B. Schneider and J. Spiváček, *Polymer*, **36**, 1147 (1995); [https://doi.org/10.1016/0032-3861\(95\)93916-A](https://doi.org/10.1016/0032-3861(95)93916-A)
- T. Liu, *Eur. Polym. J.*, **39**, 1311 (2003); [https://doi.org/10.1016/S0014-3057\(03\)00017-X](https://doi.org/10.1016/S0014-3057(03)00017-X)
- J.J. Tribone, J.M. O'Reilly and J. Greener, *Macromolecules*, **19**, 1732 (1986); <https://doi.org/10.1021/ma00160a043>
- M.L. Sanyang, S.M. Sapuan, M. Jawaid, M.R. Ishak and J. Sahari, *Polymers*, **7**, 1106 (2015); <https://doi.org/10.3390/polym7061106>
- N. Qi, Z.Q. Chen and A. Uedono, *Radiat. Phys. Chem.*, **108**, 81 (2015); <https://doi.org/10.1016/j.radphyschem.2014.11.018>
- S.R. Tatro, L.M. Clayton, P.A. O'Rourke Muisener, A.M. Rao and J.P. Harmon, *Polymer*, **45**, 1971 (2004); <https://doi.org/10.1016/j.polymer.2004.01.012>
- S.L. Simon and J.K. Gillham, *J. Appl. Polym. Sci.*, **46**, 1245 (1992); <https://doi.org/10.1002/app.1992.070460714>
- M. Song, D.J. Hourston, H.M. Pollock and A. Hammiche, *Polymer*, **40**, 4763 (1999); [https://doi.org/10.1016/S0032-3861\(98\)00705-8](https://doi.org/10.1016/S0032-3861(98)00705-8)
- Y. Li, Q. Ma, C. Huang and G. Liu, *Mater. Sci.*, **19**, 147 (2013); <https://doi.org/10.5755/j01.ms.19.2.4430>
- H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963); <https://doi.org/10.1021/ac60203a013>
- D.M. Alshangiti and M. Madani, *Polym. Plast. Technol. Eng.*, **53**, 1385 (2014); <https://doi.org/10.1080/03602559.2014.909471>