γ-Irradiation Effects on the Thermal and Structural Characteristics of Modified, Grafted Polypropylene

Magda M. I. Khalil,[1] Naeem M. El-Sawy,[2] Gamil A. El-Shobaky[3]

[1]*Radiation Physics Department, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt*
[2]*Polymer Chemistry Department, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt*
[3]*Physical Chemistry Department, National Research Center, Dokki, Cairo, Egypt*

ABSTRACT: The effects of both the degree of grafting and γ irradiation on the thermal stability and structural characteristic of polypropylene-*graft*-polyvinylpyrrolidone and polypropylene-*graft*-polyvinylpyrrolidone modified with α-cyano-δ-(2-thienyl) crotononitrile were investigated. The employed techniques were thermogravimetric analysis, differential thermogravimetry, and X-ray diffraction. The thermal stability of various polymeric substrates was investigated through the determination of the degradation temperature and activation energy of degradation. The effects of different parameters on the structural characteristics of different films were investigated through the determination of possible changes in the degree of ordering of the polymeric substrates. The results revealed that the thermal stability of the trunk polymer, grafted polymer, and polymer modified by α-cyano-δ-(2-thienyl) crotononitrile increased progressively with an increasing degree of grafting. The increase was, however, more pronounced for the sample undergoing the lowest degree of grafting. The activation energy of the thermal degradation process remained almost unchanged, and this indicated that the degradation processes of the different films followed almost the same mechanism. The γ irradiation at a dose of 60 kGy of the sulfur-treated polymeric films [i.e., the polymeric films treated with α-cyano-δ-(2-thienyl) crotononitrile] reduced their thermal stability. This conclusion was reached by the consideration of the changes observed in the pre-exponential factor of the Arrhenius equation due to different chemical and γ-irradiation treatments. The degree of ordering, evidenced by X-ray diffraction measurements of the trunk polymer, grafted polymer, and modified polymer, suffered a significant drop. This drop was much more pronounced for the sulfur-containing polymeric materials. The observed drop in the degree of ordering of the polymeric substrates was taken as a measure of the structure collapse due to a certain treatment (degree of grafting and sulfur inclusion). The γ irradiation of the sulfur-containing polymeric materials greatly increased their degree of ordering, which reached a value greater than that measured for the trunk polymer. Therefore, it was concluded that the thermal stability increased as the degree of ordering decreased. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 506–515, 2006

Key words: irradiation; structure; thermal properties; graft copolymers; polypropylene

INTRODUCTION

The radiation-induced grafting of polymers is a very efficient method for preparing membranes with good chemical and physical properties of the modified polymeric materials.[1–5] The modification of radiation grafting of *N*-vinyl-2-pyrrolidone (NVP) onto polypropylene (PP) or low-density polyethylene with α,δ-unsaturated nitrile has been investigated.[2,6] Grafted copolymers treated with some inorganic substrates and rare and transition elements have been studied with X-ray diffraction (XRD).[7–9] The thermal behavior of the copolymer of NVP with acrylamide has also been studied.[10] Furthermore, it has been shown in several studies that these polymeric systems exhibit interesting degradation kinetics.[11–13] The evaluation of the kinetics of the degradation mechanism has been widely discussed through thermogravimetric analysis (TGA) of PP.[14,15] Upon exposure to ionizing radiations, the energy absorbed by the polymeric material produces some active species such as radicals, thereby initiating various chemical reactions.[16] There are two fundamental processes resulting simultaneously from these reactions: (1) crosslinking, in which polymer chains are joined and a network is formed, and (2) degradation, in which the molecular weight of the polymer is reduced through chain scission.[17] An increase in the thermal degradation, accompanied by a decrease in the activation energy (E_a) of the thermal degradation process, has been reported.[18] In this study, the direct radiation grafting of NVP onto PP and the modification of the grafted copolymer with α-cyano-δ-(2-thienyl) crotononitrile (**2a**) were investigated by IR spectrophotometry and elemental analysis. Also, the grafted films and the grafted films modified with **2a** were examined with TGA. E_a was calculated for the grafted films, the modified, grafted films, and the irradiated, modified, grafted films to probe the thermal and chemical stability of the bonds and structure.

1	Grafting yield	3a
N1	6.8	S1
N2	17.5	S2
N3	25.9	S3
N4	41.3	S4
N5	52.9	S5
N6	64.1	S6
N7	95	S7
N8	120	S8
N9	149	S9

EXPERIMENTAL

Materials

As a polymer substrate, 35-μm-thick PP film (El-Nasr Co., Egypt) was used. NVP (99% pure; Merck, Germany) was used without further purification. Other chemicals were reagent grade and were used without further purification.

Graft polymerization

Strips of PP were washed with acetone, dried in a vacuum oven at 50°C, weighed, and immersed in a monomer–dimethylformamide solution in glass ampules. Ferric chloride (0.008%)[6] was added to the monomer–solvent mixture to reduce the homopolymerization process during irradiation. The glass ampules, which contained polymer and monomer–solvent mixtures, were deaerated through the bubbling of nitrogen gas for 5–7 min, sealed, and subjected to a ^{60}Co γ source at a dose rate of 1.6 Gy/s. The obtained grafted films were removed and washed thoroughly with hot distilled water and were soaked overnight in water to extract the residual monomer and homopolymer occluded in the films. The grafted films were then dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting (G) was determined by the percentage increase in the weight as follows:

$$G = [W_g - W_0 / W_0] \times 100 \tag{1}$$

where W_g and W_0 are the weights of the grafted and initial films, respectively.

Preparation of the grafted films modified with 2a

Colorless, grafted films (3 cm × 3 cm) were immersed in a solution prepared from **2a** (~5 g) and a few pellets of sodium hydroxide (~0.5 g) in ethanol (50 mL). The resulting mixtures were refluxed for 36 h. The colored films (brown to dark brown) were removed and washed with distilled water and ethanol; this was followed by drying over filter paper.

Compound	G (%)	C (%)	H (%)	N (%)	S (%)
1	25.9	76.00	13.42	2.02	0.00
	52.9	73.30	12.50	4.05	0.00
3a	25.9	76.88	12.64	1.70	1.26
	52.9	72.44	11.31	4.24	1.93

Preparation of 2a

To a mixture of benzene (20 mL), acetic acid (0.01 mol), and ammonium acetate (0.01 mol) were added acetyl thiophene, acetyl pyridine, or acetophenone (0.01 mol) and malononitrile (0.01 mol). The mixture was heated for 10–15 min and then left overnight. The solid product that formed upon the addition of 20 mL of ethanol was collected by filtration, washed with water, and then crystallized from a proper solvent. PP grafted with NVP (N series) and the N series modified with **2a** (S series) are listed in Table I.

Polypropylene-*graft*-polyvinylpyrrolidone (PP-*g*-PVP or **1**) modified with **2a** (**3a**) was formed as yellow, needle crystals (1.48 g, 85%).

mp: 88–90°C (from ethanol). ν_{max} (cm^{-1}, KBr): 2210, 2220 cm^{-1}. δ_H: 8.24–8.05 (dd, 2H, thienyl), 7.24–7.31 (t, 1H, thienyl), 2.68 (S, 3H, CH$_3$). ANAL. Calcd for C$_9$H$_6$N$_2$S: C, 62.03%; H, 3.47%; N, 16.07%; S, 18.40%. Found: C, 61.77%; H, 3.40%; N, 15.89%; S, 18.1%.

The elemental analysis of the grafted polymer (**1**) and its modified form (**3a**) is in Table II. Compound **3a** was believed to be produced through the Michael addition of an active methylene in **1** to an ethylene double bond as shown in Scheme 1.

Apparatus

Fourier transform infrared (FTIR)

IR spectra were measured for the trunk PP films, the grafted PP films, and the modified, grafted PP films with a Shimadzu (Japan) 5000 FTIR spectrometer.
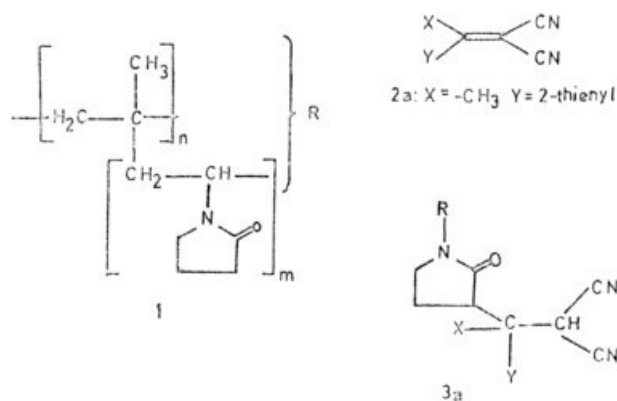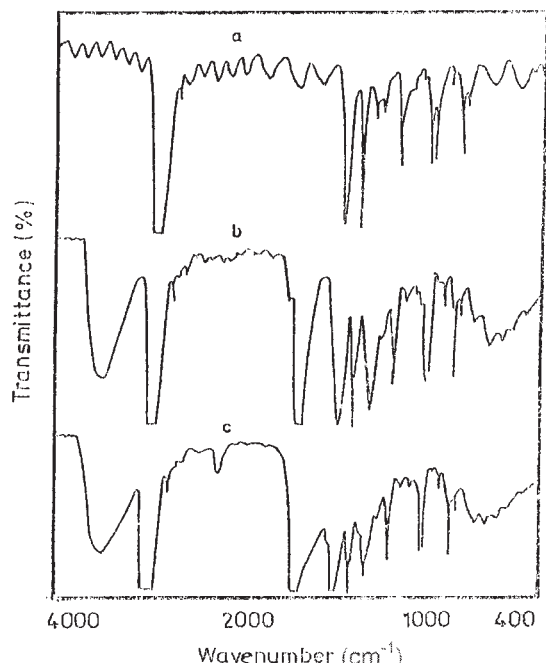

Scheme 1

Figure 1 IR spectra of (a) the original PP, (b) PP-*g*-PVP, and (c) **3a**, all with the same degree of grafting (25.9 wt %).

XRD

The XRD scanning was performed with a Shimadzu XD-D1; the target was copper (wavelength = 1.5405 Å) with an applied voltage of 40 kV and an anode current of 30 mA. The pattern was recorded at a scanning rate of 8°/min and an angle (2θ) of 6–30° with a divergence slit of 1°, a scatter slit of 1°, and a receiving slit of 0.3 mm; these operating conditions were sustained throughout the examination.

The recorded X-ray data for the investigated films were collected, adjusted, and arranged with an Excel computer-programmed system. This programmed system permitted us to draw different X-ray diffractograms of various films.

Thermal analysis

The TGA studies were carried out with a Shimadzu 5-TGA-50 at a heating rate of 10°C/min under a nitrogen atmosphere flowing at a rate of 20 mL/min from room temperature up to 600°C. The obtained primary TGA thermograms were used to determine the kinetic parameters.

Kinetic analysis[11]

The expression for the thermal decomposition of a homogeneous system has the following general form:

$$d\alpha(t)/dt = k(T)f[\alpha(t)] \tag{2}$$

where α is the reaction extent of the component of the sample being degraded. It is defined as $\alpha(t) = [w_0 - w(t)]/(w_0 - w_\infty)$, where w_0, $w(t)$, and w_∞ are the weights of the sample before the degradation, at time t, and after complete degradation, respectively. $k(T)$ is the rate coefficient that usually follows the Arrhenius equation. The differential conversion function, $f(\alpha)$, can present various functional forms, but its most commonly used form for solid-state reactions is $f(\alpha) = (1 - \alpha)^n$, where n is the reaction order, which is assumed to remain constant during the reaction.[19]

At a certain heating rate, $\beta = dT/dt$, we have

$$d\alpha/(1 - \alpha)^n = A/\beta \exp(-E_a/RT)dT \tag{3}$$

A large number of pyrolysis processes can be represented as first-order reactions;[20] in particular, the degradation of a series of unoxidized and oxidized starches was suggested to be first-order in a sample weight reaction.[21] The assumption of first-order kinetics for the thermal degradation of the grafted polymer and the modified, grafted polymer has also been adopted in this work. Therefore, we assume that $n = 1$ for the remainder of this article. Under this assumption, the integration of eq. (2) leads to

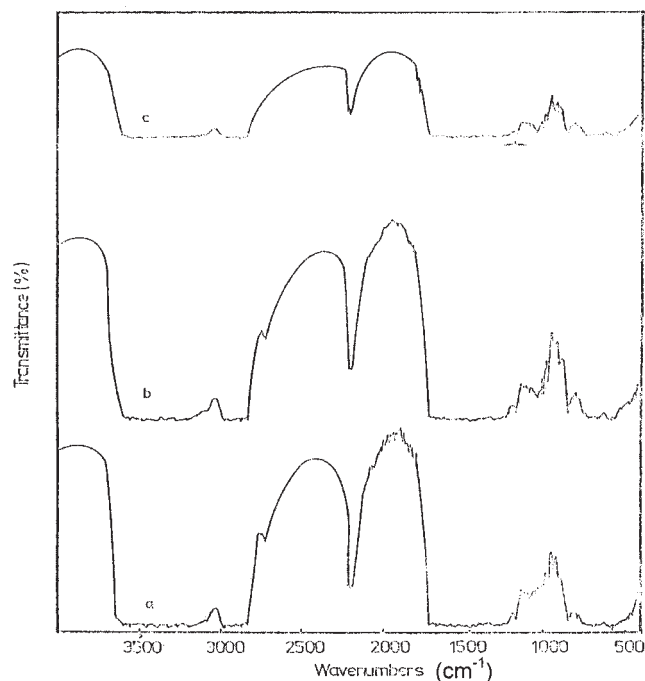$$\ln(1 - \alpha) = -A/\beta \int_{T_o}^{T} \exp(E_a/RT)dT \tag{4}$$

Figure 2 IR spectra of (a) **3a** without irradiation, (b) **3a** with 60 kGy of irradiation, and (c) **3a** with 120 kGy of irradiation, all with the same degree of grafting (120 wt %).
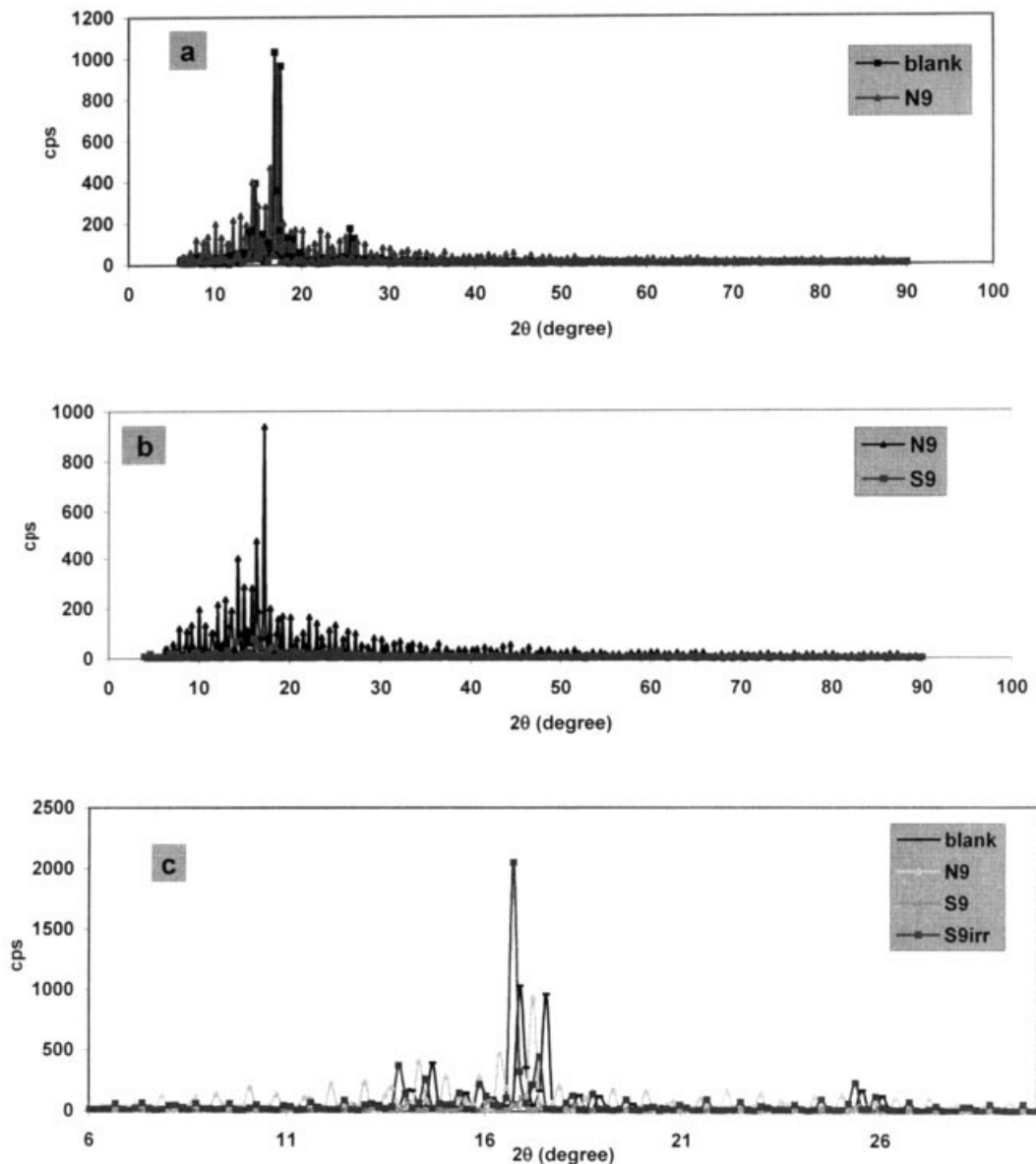
Figure 3 X-ray diffractograms of the films: (a) the effect of grafting, (b) the effect of sulfur inclusion on the grafted samples, and (c) the effect of sulfur inclusion and irradiation on the grafted samples.

The temperature integral does not have an exact form. Several approximations for the integral function lead to several methods for the evaluation of the thermokinetic parameters A and E_a from a single thermogravimetric experiment carried out at a given heating rate.

In the Broido method, one assumes $(-E_a/RT) \approx (T_m/T)^2(-E_a/RT)$, where T_m is the temperature of the maximum degradation rate (i.e., the temperature range of the analysis was close to T_m).[20] Then, eq. (3) can be rewritten as follows:

$$\ln(1 - \alpha) = -(A/\beta)(RT_m^2/E)\exp(-E_a/RT) \quad (5)$$

or

$$\ln[-\ln(1 - \alpha)] = (-E_a/RT) + \text{Constant} \quad (6)$$

In this method, a straight line should be obtained upon the plotting of $\ln[-\ln(1 - \alpha)]$ versus $1/T$ with a slope of $-E_a/R$ and an intercept of $(A/\beta)(RT_m^2/E)$.

In this work, we used the Broido method to determine the different thermokinetic parameters for the various films.
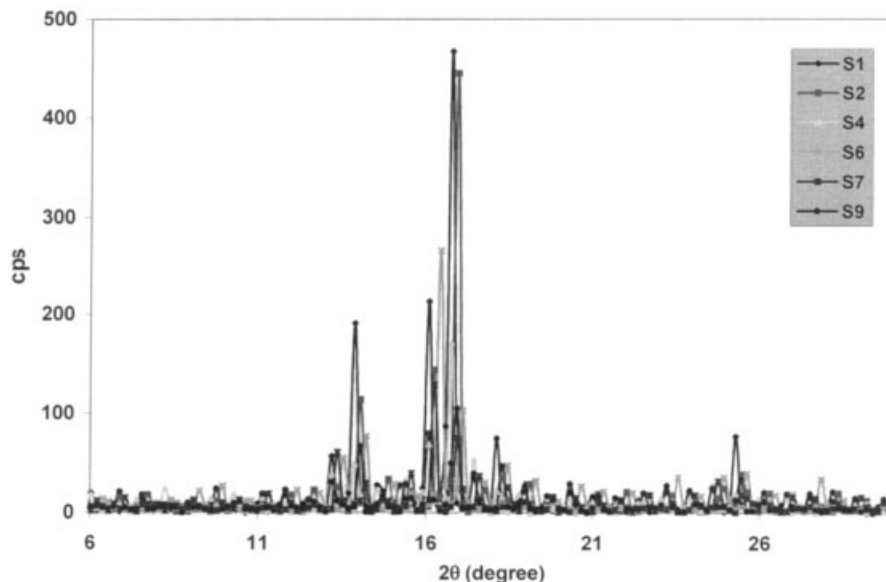
Figure 4 X-ray diffractograms showing the effect of sulfur inclusion on the grafting ratios of the films.

RESULTS AND DISCUSSION

IR spectroscopy investigation of various films

IR spectroscopy investigation of the grafted and modified copolymers

Figure 1 shows the IR spectra of the original PP, PP-*g*-PVP, and **3a**, all with the same degree of grafting (25.9 wt %). In Figure 1(a), bands appearing at 2840–2800, 1440, and 1380 cm^{-1} are characteristic of the PP structure. However, for PP grafted with NVP [Fig. 1(b)], the bands appearing at 3429 and 1659 cm^{-1} can be attributed to ν(OH) of water contamination and ν(C=O) of the amide group, respectively. The intensity of the band at 1659 cm^{-1} increases with the grafting yield.

NVP can be viewed as a species containing three active sites: a vinyl group, a carbonyl group, and an active methylene function. These sites were reduced to two sites only after grafting. The remaining two sites, a carbonyl group and a methylene function, showed variety in their reactivity. The amide carbonyl group showed no reactivity toward the nucleophilic reagent, and this may have been due to the lowest reactivity in the amide carbonyl group or the chain steric effect. This finding prompted us to investigate the reactivity of the α-methylene function.

Compound **2a** undergoes a Michael addition reaction to give **3a** (cf. Scheme 1), which is established not only by the IR spectra but also on the basis of the elemental analysis results for the modified graft reactions. The presence of sulfur (**3a**) can be seen from a comparison of the data with those of grafted membrane **1** in Table I. Table I also shows that the modified, grafted films (**3a**) increased the amount of sulfur and nitrogen according to the degree of grafting.

The modified, grafted copolymer films [**3a**; Fig. 1(c)] showed the presence of cyano groups at 2195–2191 cm^{-1}, which were absent in PP-*g*-PVP [Fig. 1(b)].

IR spectroscopy investigation of the unirradiated, modified, grafted copolymers and the irradiated, modified, grafted copolymers

Figure 2 shows the IR spectra for the modified, grafted copolymer (**3a**) without irradiation, for **3a** irradiated with 60 kGy, and for **3a** irradiated with 120 kGy, all with the same degree of grafting (120 wt %). The modified, grafted copolymer films (**3a**) revealed the presence of a cyano group at 2195–2191 cm^{1}. The intensity of the band with respect to a cyano group decreased with exposure to γ rays to an extent proportional to the employed dose of γ rays. The observed decrease in the intensity of the band of a cyano group due to irradiation at a dose of 60 kGy could be attributed to some degradation through the chains of the polymeric substrate. However, a significant decrease in the intensity of this band due to the treatment with 120 kGy of γ rays can be attributed to some decomposition of the modified compound (**2a**) via the polymeric material.

Effects of grafting, sulfur inclusion, and γ irradiation on the ordering of the different films

The role played by grafting, sulfur inclusion (**3a**), and γ irradiation at a dose of 60 kGy in the degree of ordering of polymeric substrates was investigated with XRD.
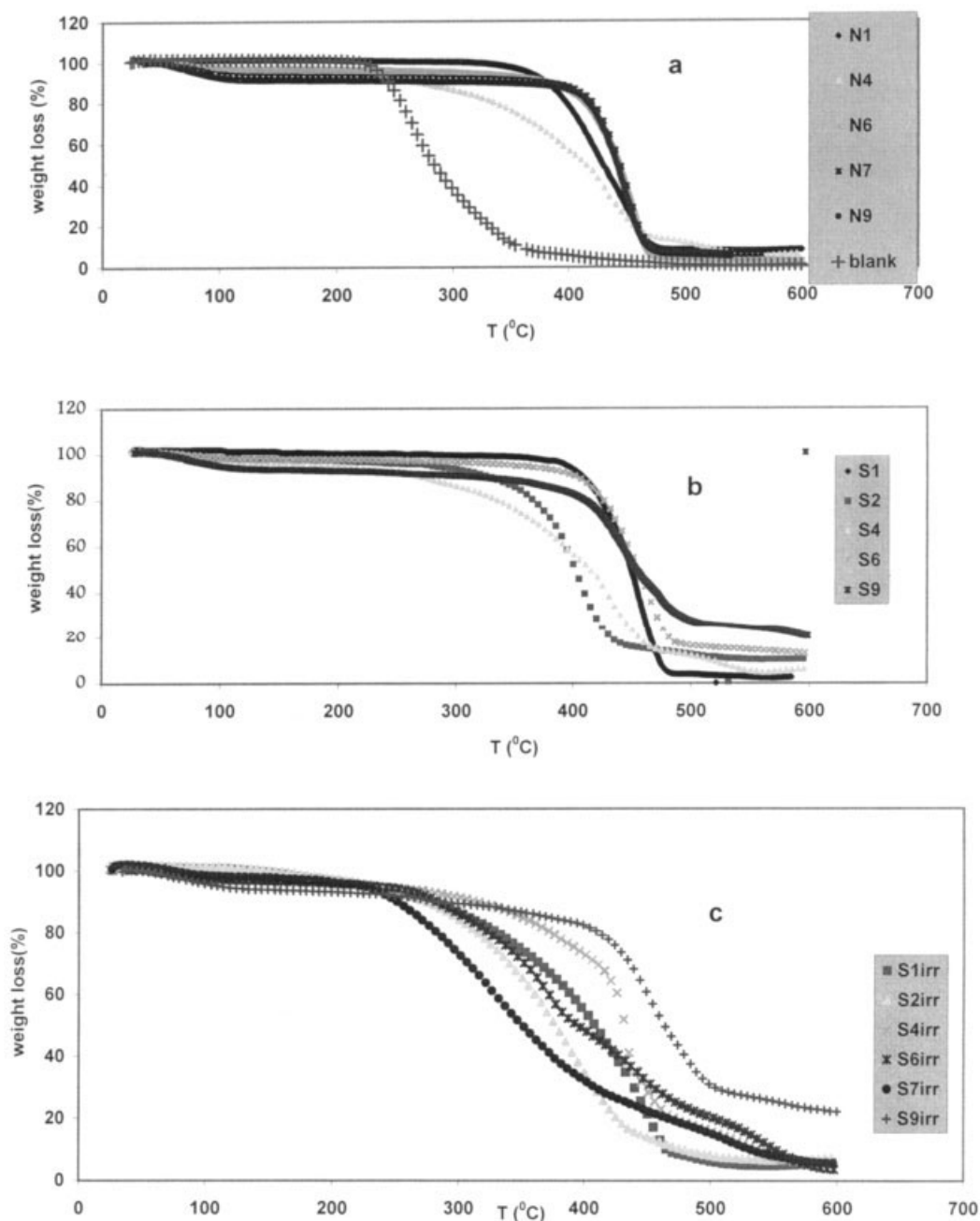
Figure 5 TGA curves of various films: (a) PP-*g*-PVP, (b) **3a**, and (c) irradiated **3a**.

Figure 3(a) depicts the X-ray diffractograms of the trunk PP film and the film undergoing the maximum degree of grafting (N₉). The grafting process induced a measurable decrease in the degree of ordering of the semicrystalline film. This finding might reflect some kind of structural collapse due to the formation of polyvinylpyrrolidone.

Figure 3(b) shows the effects of inclusion sulfur-containing substrates (**3a**, S₉) on the degree of ordering of the polymeric film. The X-ray diffractograms of both the highly grafted film (N₉) and the film treated with the sulfur-containing substrate were determined.

The inclusion of the sulfur-containing substrate in the grafted film brought about a drastic decrease in the degree of ordering of the semicrystalline polymeric film. This finding indicates a noticeable collapse of the structure of the polymeric film.

Figure 3(c) shows the X-ray diffractograms of different treated polymeric films. These figures collectively summarize the effects of grafting, modified grafting with the sulfur-containing polymer, and γ irradiation on the degree of ordering of these films. The γ irradiation of the sulfur-treated film (S₉) increased considerably the degree of ordering of the
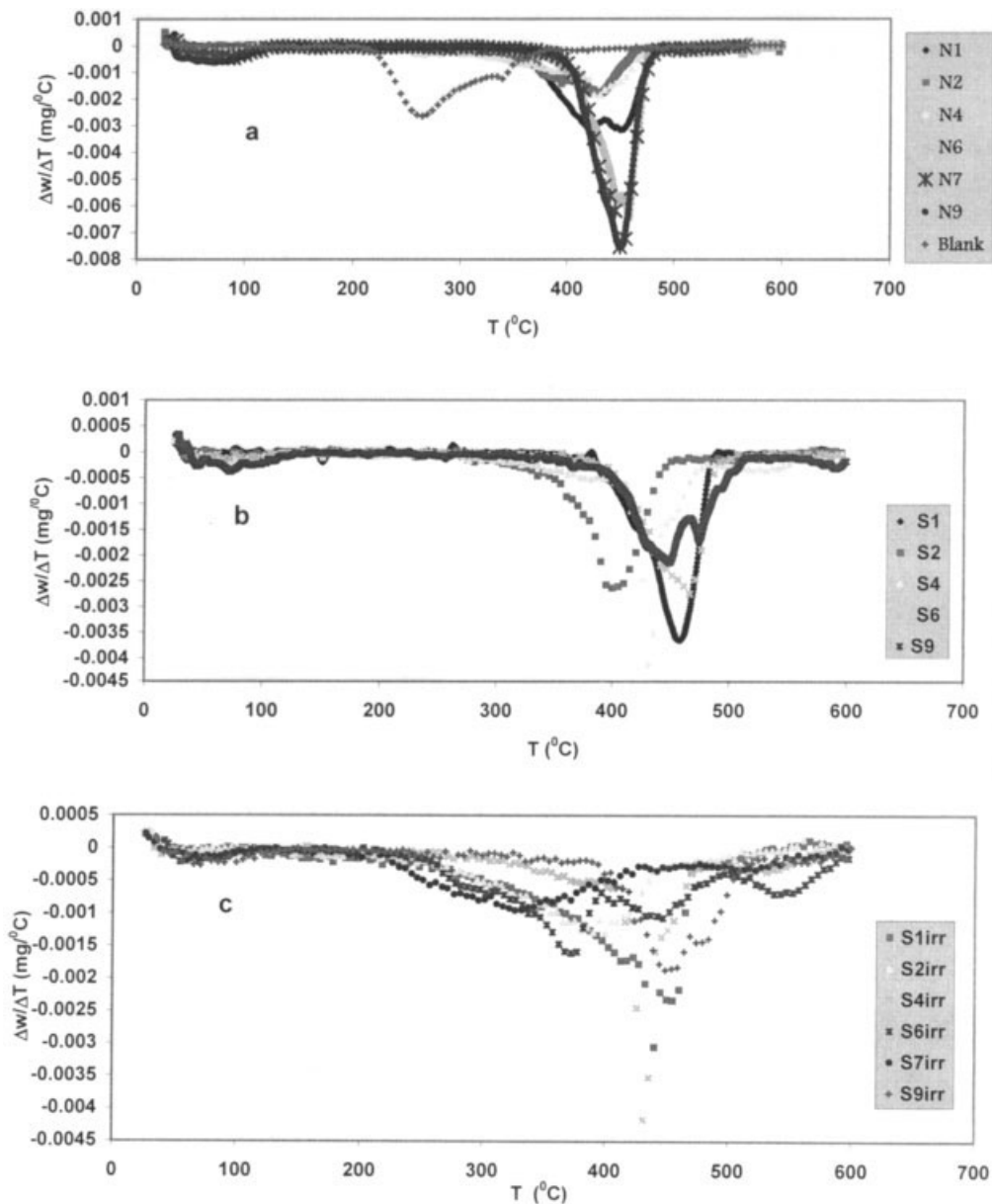
Figure 6 DTG curves of various films: (a) PP-g-PVP, (b) **3a**, and (c) irradiated **3a** ($\Delta w / \Delta T$ is the grafting rate).

film, which exceeded that of the trunk polymer. In other words, γ rays rearranged the structural units constituting the semicrystalline films, which reached a maximum degree of ordering, and also effected an increase in the crosslinking between the layers in the polymer matrix.

The effect of the inclusion of the sulfur-containing substrate in the films (**3a**) with different degrees of grafting on the degree of ordering of these films was also investigated via the measurement of their X-ray diffractograms (Fig. 4). These diffractograms show clearly that the decrease in the degree of ordering of these films was directly proportional to the grafting yield.

Thermal analysis of the different films

TGA and differential thermogravimetry (DTG) curves of the different films were determined

TGA and DTG curves for PP-g-PVP

Figures 5(a) and 6(a) depict the recorded TGA and DTG curves of different grafted films varying between 6.8 and 149 wt %. The degradation rate and T_m were determined from DTG curves, and the computed values are given in Table III. Most of the films showed a single T_m value. The blank and the film with the smallest grafting ratio (N_1) showed two T_m's (T_{m1} and

TABLE III
DTG Analysis of PP-g-PVP Films

Sample	T_{m1}	Degradation rate	T_{m2}	Degradation rate
Blank	264.2	0.002637	339	0.001235
N_1	423.4	0.003137	453.2	0.00313
N_2	429.6	0.001813		
N_4	430.6	0.001869		
N_6	457.9	0.006429		
N_7	449.9	0.007543		
N_9	450.4	0.006765		

TABLE V
DTG Analysis of 3a

Sample	T_{m1}	Degradation rate	T_{m2}	Degradation rate
S_{1irr}	440.1	0.003054		
S_{2irr}	400.4	0.001296		
S_{4irr}	431.3	0.04169		
S_{6irr}	377.2	0.001589		
S_{7irr}	326.3	0.000958		
S_{9irr}	449.1	0.00187		

T_{m2}). An inspection of Tables III–V shows that the thermal stability, as evidenced from the T_m values, increased progressively with an increasing grafting yield. The increase was, however, more pronounced for the sample with the minimum grafting yield. The increase in the grafting yield up to 149 wt % was accompanied by a progressive small increase in the thermal stability of the treated films. Therefore, it might be concluded from this finding that the grafting yield played a limited role in the increasing thermal stability of PP-g-PVP.

TGA and DTG curves of the modified, grafted polymer (3a)

Figures 5(b) and 6(b) depict the recorded TGA and DTG curves of different modified, grafted films with the inclusion of the sulfur-containing polymer (**3a**). The grafting rate and T_m were determined from the DTG curves, and the computed values are given in Table IV. This table shows that the inclusion of the sulfur-containing substrate in the N_1 sample (6.8 wt %) effected a measurable increase in the thermal stability of the treated film. The thermal stability generally increased with an increasing grafting yield with the sulfur-containing substrate, reaching a maximum limit at about 64 wt %. Then, it decreased with an increasing grafting yield above this limit. The observed significant change in the thermal stability of the modified, grafted films with the inclusion of the sulfur-containing substrate could be attributed to an effective increase in the structure of the modified films. The observed lim-

ited decrease in the thermal stability due to the grafting yield increasing up to 149 wt % with compound **2a** might be attributed to possible steric hindrance between the grafted chains and the sulfur-containing polymers.
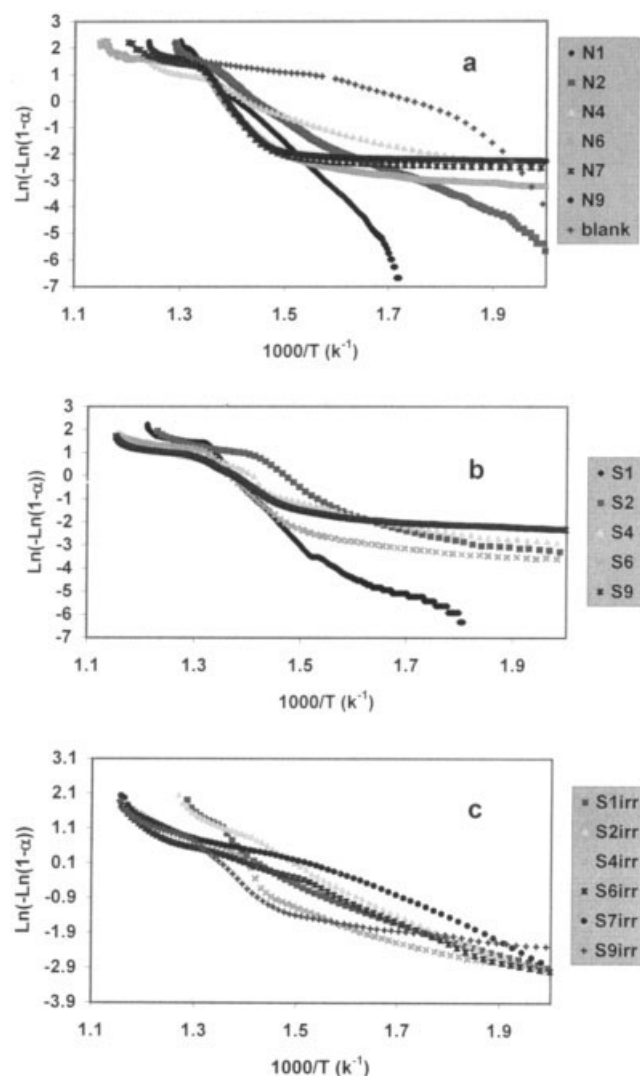
Figure 7 Arrhenius plots of various films: (a) PP-g-PVP, (b) **3a**, and (c) irradiated **3a**.

TABLE IV
DTG Analysis of 3a

Sample	T_{m1}	Degradation rate	T_{m2}	Degradation rate
S_1	459	0.003645		
S_2	400	0.002633		
S_4	431.3	0.004169		
S_6	466.3	0.002746		
S_9	449.2	0.002135	474.9	0.00169

TABLE VI
E_a **and** β^* **of the PP-g-PVP Films**

Sample	Grafting yield (%)	E_a (kJ/mol)	β^*	Temp range (°C)
Blank	0	5.4	5.2	403.9–458.7
N_1	6.8	36.2	25.7	355.9–438.1
N_2	17.5	31.9	23.2	422.1–465.3
N_4	41.3	23.4	16.8	420.5–460.2
N_6	64.1	41.8	29.1	390.9–479.4
N_7	95	52.8	36.8	419.8–457
N_9	149	54.7	38.3	427.5–472.8

TABLE VIII
E_a **and** β^* **of the Irradiated, Modified, Grafted Films**

Sample	Grafting yield (%)	E_a (kJ/mol)	β^*	Temp range (°C)
S_{1irr}	6.8	11.9	8.5	342.7–403
S_{2irr}	17.5	12.7	9.5	254.4–385.3
S_{4irr}	41.3	11.7	7.7	356–421
S_{6irr}	64.1	12.6	9.2	277.2–392.1
S_{7irr}	95	11.4	8.9	276.5–372.1
S_{9irr}	149	26.9	18.4	429.2–479.1

TGA and DTG curves for the irradiated, modified, grafted, sulfur-containing polymeric substrate

Figures 5(c) and 6(c) depict the recorded TGA and DTG curves of different irradiated, modified, grafted films with the inclusion of the sulfur-containing polymer. The grafting rate and T_m were determined from DTG curves, and the computed values are given in Table V. The exposure of the modified, grafted films with compound **2a** to a dose of 60 kGy resulted in a drastic decrease in the thermal stability of the different irradiated films. The observed decrease in the thermal stability of the irradiated films could be attributed to a possible limited degradation of the films via the formation of degradable layers of the polymer matrix.

Determination of E_a of the different films

The values of E_a and the pre-exponential factor (β^*) were computed with the method suggested by Briodo.[20] Figure 7 shows an Arrhenius plot relating $\ln[-\ln(1 - \alpha)]$ as a function of $1/T$. The values of E_a were computed from the linear portions of different curves in different temperature ranges, and the data are given in Tables VI–VIII. An examination of these tables shows the following. First, the E_a values increased progressively with an increasing grafting yield for most of the investigated films. This finding is parallel to the observed increase in the thermal stability of these films. Second, E_a for the sulfur-containing grafted polymeric substrate underwent fluctuations, that is, both increases and decreases.

This finding did not support the observed increase in the thermal stability of the treated films (cf. Table III). Third, the irradiation of different films brought about a slight modification of the E_a values and a sudden increase in E_a for the sample of the highly grafted film (149 wt %, S_{9irr}). These results also did not support the observed changes in the thermal stability of these films.

This discrepancy, which reflected the heterogeneity of the different films, could be solved by the consideration of the observed change in the value of the pre-exponential term of the Arrhenius equation. This was done, and the computed values of this term are given in the last column of Tables VI–VIII. The values of this column show that β^* follows the same trend as E_a.

When E_a was plotted as a function of β^* for different films, straight lines were obtained in all cases (cf. Fig. 8). It can be clearly deduced from Figure 8 that the observed change in the E_a values of different treated films can be mainly attributed to a corresponding change in the value of the β^* term of the Arrhenius equation. In other words, the thermal degradation process of different films always follows the same mechanism.

CONCLUSIONS

The main conclusions that can be drawn from the results are as follows:

1. The thermal stability and structural characteristics of PP-g-PVP and its modified form (**3a**) were investigated with TGA, DTG, and XRD analyses.
2. The observed increase in the thermal stability of the different films was evidenced by fine TGA and DTG.
3. E_a of the thermal degradation processes was determined from TGA and DTG data with the Broido method.
4. The computed E_a values suggested that the degradation processes of the different films followed almost the same mechanism. The observed change in the E_a values due to different treatments resulted mainly from corresponding changes in the β^* values of the Arrhenius equation.
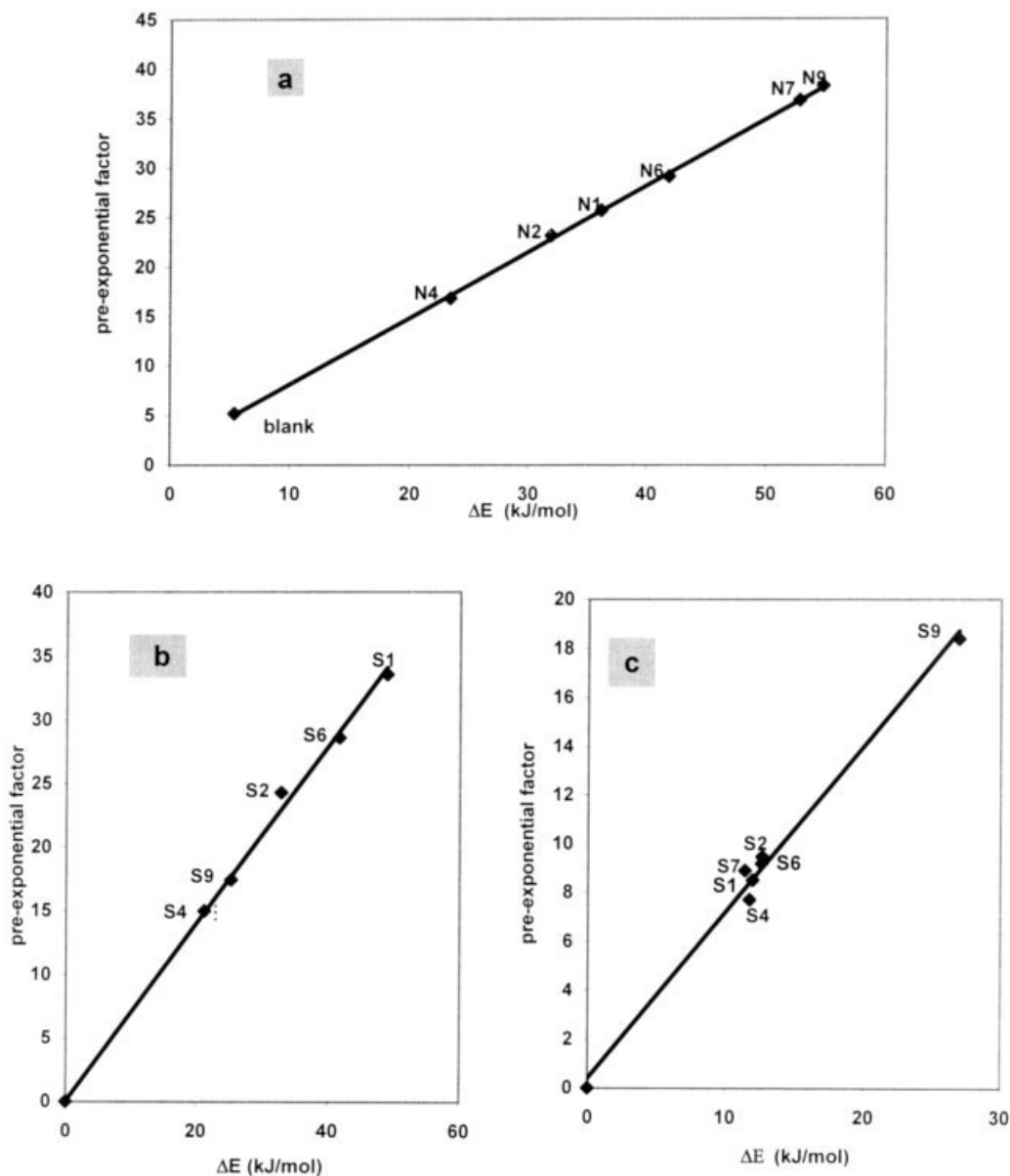
TABLE VII
E_a **and** β^* **of the Modified, Grafted Films**

Sample	Grafting yield (%)	E_a (kJ/mol)	β^*	Temp range (°C)
S_1	6.8	48.9	33.5	393.1–479
S_2	17.5	32.9	24.3	374.9–424.8
S_4	41.3	21.3	15	426–486.2
S_6	64.1	41.7	28.6	416.4–476.4
S_9	149	25.3	17.4	422.2–504.3

Figure 8 Relationship between the E_a and β^* values of various films: (a) PP-g-PVP, (b) **3a**, and (c) irradiated **3a**.

References

1. Fany, Y. E.; Lu, X. B.; Cheng, Q. J Appl Polym Sci 1998, 68, 83.
2. Al Sagheer, F. A.; El-Sawy, N. M. J Appl Polym Sci 2000, 76, 282.
3. Taher, N. H.; Hegaazy, E. A.; Dessouki, A. M.; El-Arnaouty, M. B. Radiat Phys Chem 1989, 33, 129.
4. Dessouki, A. M.; Taher, N. H.; El-Arnaouty, M. B. Polym Int 1998, 45, 67.
5. Taher, N. H.; Dessouki, A. M.; Khalil, F. H. Radiat Phys Chem 1990, 36, 785.
6. El-Sawy, N. M.; Elassar, A. A. Eur Polym J 1998, 34, 1073.
7. Zhang, Y. Q.; Lee, J. H.; Rhee, J. M.; Rhee, K. Y. Compos Sci Technol 2004, 64, 1383.
8. El-Sawy, N. M.; Fagal, G. A.; El-Shobaky, G. A. J Polym Sci Part A: Polym Chem 1993, 31, 3291.
9. El-Sawy, N. M. J Appl Polym Sci 1998, 67, 1449.
10. Kiatkamjornwong, S.; Suwanmala, P. J Appl Polym Sci 1998, 68, 91.
11. Mano, J. F.; Koniarova, D.; Reis, R. L. J Mater Sci: Mater Med 2003, 14, 127.
12. Demirgöz, D.; Elviraa, C.; Mano, J. F.; Cunha, A. M.; Piskin, E.; Reis, R. L. Polym Degrad Stab 2000, 70, 161.
13. Vaz, C. M.; Cunha, A. M.; Reis, R. L. Mater Res Innovations 2001, 4, 375.
14. Chan, J. H.; Balke, S. T. Polym Degrad Stab 1997, 57, 135.
15. Albano, C.; De Freitas, E. Polym Degrad Stab 1998, 61, 289.
16. Burillo, G.; Herrera-Franco, P.; Vazquez, M.; Adem, E. Radiat Phys Chem 2002, 63, 241.
17. Hassan, M. M.; Ali, A. E.-H.; Mahmoud, G. A.; Hegazy, E. A. J Appl Polym Sci 2005, 96, 1741.
18. Ashour, A. H.; El-Sawy, N. M.; Abdel Ghaffar, M. A.; El-Shobaky, G. A. J Appl Polym Sci 2005, 97, 867.
19. Hatakeyama, T.; Quinnnn, F. X. Thermal Analysis, Fundamentals and Applications to Polymer Science; Wiley: Chichester, England, 1994.
20. Broido, A. J Polym Sci Part A-2: Polym Phys 1969, 7, 1761.
21. Soliman, A. A.; El-Shinnawy, N. A.; Mobarak, F. Thermochim Acta 1997, 296, 149.