Radiation Physics and Chemistry 94 (2014) 31–35

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Evidence of structural order recovery in LDPE based copolymers prepared by gamma irradiation

L.M. Ferreira [a,*], J.P. Leal [a,b], M.H. Casimiro [c], C. Cruz [a], J.J.H. Lancastre [a], A.N. Falcão [a]

[a] Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade Técnica de Lisboa, E.N. 10, 2686-953 Sacavém, Portugal
[b] Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[c] REQUINTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

HIGHLIGHTS

- LDPE based copolymers for catalytic processes were prepared by γ irradiation.
- Materials structural stability was evaluated based on its crystallinity evolution.
- Grafting degree and radiation dose of preparation were fundamental parameters.
- DSC and FTIR analysis were used for materials characterization.
- Partial structural order recovery was observed in high grafted films.

ARTICLE INFO

Article history:
Received 14 December 2012
Accepted 28 June 2013
Available online 25 July 2013

Keywords:
Graft copolymers
Gamma radiation
Polymers for bioapplications
Membranes for catalytic processes

ABSTRACT

PE-g-HEMA films prepared by the mutual gamma irradiation method were prepared to be used as catalyst support in catalytic membrane reactors (CMR). These copolymeric films showed good structural stability, even the high grafted ones, with a consistent correlation between their grafting degree and crystallinity. However, it was observed that above a certain radiation dose threshold, the structural changes induced in polyethylene (PE) backbone do not depend only on the extend of poly(HEMA) graft but also in what seems to be the reorganization of the amorphous regions in the PE matrix. The recovery of some crystallinity (up to 8%) in the copolymeric films was attested by DSC data. FTIR analysis confirmed this observation, revealing a slight increase in intensity and definition of the characteristic peak indicator of high crystalline regions in PE. This process seems to result from a radiation protective effect on copolymers matrix carried out by grafted poly(HEMA) which give to PE the ability to recover some of the lost structural order.

1. Introduction

Some polymers (*e.g.* PS and PVA) have been successfully used as backbone for radiation grafting of different monomers aiming its final application as polymeric catalytic membranes (Casimiro et al., 2012; Nunes and Peinemann, 2010; Shah and Ritchie, 2005). Special attention has been given to the optimization of catalytic membrane reactors, mainly active membrane and pervaporation reactors, for fine-chemical and environmental applications, for the production of medical active molecules, food additives and biofuels (Ozdemir et al., 2006). This technology demands the use of high stable membranes which includes: good mechanical strength, thermal stability, homogeneous porous distribution and good resistance to mechanical and pressure stress (Vankelecom, 2002).

In the case of polymeric membranes prepared by ionizing radiation techniques the changes/damages resulting from their exposure to ionizing radiation, even in crosslinking type polymers, may constrain their use due the risk of their structural disintegration resulting from work conditions. Given the capability of radiation to promote changes in the core structure of the materials, their crystallinity acquires a special importance in the evaluation of their structural cohesion and functionality, once the selectivity of the polymeric membranes is inversely dependent on its degree of amorphicity (Ozdemir et al., 2006).

For graft copolymers prepared by this route the evolution of the copolymer backbone crystallinity acquires an added importance once it depends on two main factors: radiation effects and graft reaction. Crosslinking processes and molecular deformations caused by these two agents can be mechanically limiting,

* Corresponding author. Tel.: +351 21 9946066; fax: +351 21 9946285.
E-mail addresses: ferreira@ctn.ist.utl.pt, lmferreira66@gmail.com (L.M. Ferreira).

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.06.031

impairing the functional performance of the new material. Therefore, it is necessary to obtain additional confidence of their structural stability and organization as a guarantee of the chemical success of the system.

The melting enthalpy of a polymeric material is related with the energy required to break the intermolecular bonds, and can be used to evaluate its crystallinity. Thus, polymer chains are more ordered, i.e., more crystalline, have stronger intermolecular bonds and in greater number, and therefore, higher temperatures and enthalpies of fusion. Consequently these materials are structural and mechanically more stable and “robust”.

Looking for an adequate copolymeric substrate for membrane catalytic processes directed to the production of bioactive molecules, films of PE-*g*-HEMA were prepared by the mutual gamma irradiation method (Stannet, 1990). Low density PE was used as backbone of the copolymer due to its well-known high mechanical resistance to gamma radiation and crosslinking behavior as a consequence of its predominant amorphous structure (Geetha et al., 1988). The use of HEMA as graft monomer is due to its ability to improve the hydrophilicity of the materials endowing them with organic and aqueous media compatibility. On the other hand the presence of terminal OH groups and carbonyl groups in poly(HEMA) branches further ensures the possibility of post-functionalization of the copolymer according to the demands of catalysts immobilization (Ferreira et al., 1998). HEMA also has a natural biocompatibility which can be relevant in biocatalysis applications.

These materials were evaluated relatively to their crystallinity evolution, according to the degree of grafting and the respective radiation dose of preparation. This study was performed through thermal analysis techniques (TGA and DSC) and confirmed by FTIR spectroscopy.

2. Experimental

2.1. Materials

PE-*g*-HEMA copolymeric films were prepared by γ irradiation at a dose rate (*DR*) of 0.3 kGy h^{-1}, of pre-weighed strips of bioriented LDPE film (ρ=0.920 g.cm^{-3}; d=15 μm), without stabilizers (for food use approved), immersed in a solution of $[HEMA]_i$=15% (V/V in methanol). All irradiations took place in the absence of air using sealed glass ampoules as containers. Absorbed doses of preparation ranged from 3 to 12 kGy. After irradiation, grafted films were Soxhlet extracted with MeOH during 4 h to remove the residual monomer and homopolymer and, finally dried in vacuum (10^{-3} mbar) at 40 °C until constant weight. For each absorbed dose 6 samples were prepared. Grafting yield was determined by the percentage increase in weight as follows:

$$\text{Grafting yield}(\%) = [(W_g - W_o)/W_o]100 \quad (1)$$

where W_o and W_g represent the weights of the initial and grafted polymers, respectively.

According to this methodology 6 groups of samples were prepared with the following specifications:

Group 1: t_{irrad}=10 h, D_{abs}=3.0 kGy, Grafting yield=14 ± 2.3%; *Group* 2: t_{irrad}=20 h, D_{abs}=6.0 kGy, Grafting yield=130 ± 5.2%; *Group* 3: t_{irrad}=25 h, D_{abs}=7.5 kGy, Grafting yield=246 ± 8.2%; *Group* 4: t_{irrad}=30 h, D_{abs}=9.0 kGy, Grafting yield=400 ± 10.4%; *Group* 5: t_{irrad}=35 h, D_{abs}=10.5 kGy, Grafting yield=165 ± 4.3%; *Group* 6: t_{irrad}=40 h, D_{abs}=12.0 kGy, Grafting yield=163 ± 3.3%.

Poly(HEMA) was obtained from a 9 kGy irradiation (in the absence of air; *DR*=0.3 kGy h^{-1}) of an $[HEMA]_i$=15% (V/V in methanol) solution. Irradiation experiments were carried out at the Portuguese ^{60}Co Facility (UTR) located at the Nuclear and Technological Campus (IST/UTL) in Loures/Lisbon. Detailed procedure about the preparation of these copolymeric materials can be found elsewhere (Ferreira et al., 2005, 2006).

2.2. Samples' characterization

2.2.1. Thermal analysis

Thermal properties of non-irradiated and irradiated LDPE films and PE-*g*-HEMA copolymeric films were evaluated on DuPont Instruments equipment (TGA—model 951; DSC—model 910). Analyses were performed at 10 °C/min in nitrogen atmosphere covering the temperature range from 25 to 550 °C on the 6 samples of each group.

The degree of crystallinity of samples was determined from the respective melting enthalpy by using the following expression:

$$X_c(\%) = \frac{\Delta_f H}{\Delta_0 H} 100 \quad (2)$$

where $\Delta_f H$ represents the enthalpy of fusion of the polymeric sample measured by DSC analysis and$\Delta_0 H$ is the enthalpy of fusion for the polymer “completely” crystalline (Poly et al., 2004). For LDPE, the $\Delta_0 H$ tabled value considered was 290 J g^{-1} (Wunderlich, 1990; Mark, 1999).

2.2.2. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were collected using two FTIR spectrometers, from Brucker (Tensor 27 CSL) and from PerkinElmer (1600 series). All spectra were obtained at room temperature, at a resolution of 4 cm^{-1} (20 scans for each sample), from 4000 to 400 cm^{-1}. Spectra of dry particles of poly(HEMA) were obtained in KBr discs, and the spectra of the films were recorded directly from them.

3. Results and Discussion

The thermal behavior of these copolymeric films has already been partly evaluated in previous work related to their possible use as biomaterial (Ferreira et al., 2005, 2006). However, the work undertaken attempting to extend the use of this material in a new application, has revealed new data about the structural evolution of these materials with the respective radiation dose of preparation and final grafting degree. As previously stated, catalytic membrane reactors demand the use of high stable membranes with properties in which the membrane material crystallinity is directive.

Fig. 1 shows TGA (a) and DSC (b) thermograms of LDPE film, poly(HEMA) and PE-*g*-HEMA films with different grafting yields representative of the 6 groups of copolymers prepared and analyzed. It can be observed that with increasing grafting yield the thermal behavior of copolymers increasingly approaches that of poly(HEMA), departing from that characteristic of a pure LDPE film. The profile of thermogravimetric curves of high grafted PE-*g*-HEMA films, 246 ± 8.2% (7.5 kGy) and 400 ± 10.4% (9 kGy), shows virtually no traces of the thermal identity of the LDPE matrix, being very close to that shown by poly(HEMA). This behavior is accompanied by an accentuated decrease of melting enthalpy and corresponding loss of crystallinity in the samples prepared with radiation doses up to 9 kGy, relatively to non-irradiated LDPE film. These facts, which seem to result directly from the high degree of grafting and from radiation induced crosslinking effect, are indicative of a large structural disorder in the copolymers matrix.

Nevertheless, above 400 °C, the thermal behavior of all grafted films approaches that of the LDPE backbone, suggesting that the copolymeric material still keeps part of the LDPE structure identity. This fact is supported by thermal stability data obtained by DSC analysis (see Table 1). It can be observed that the

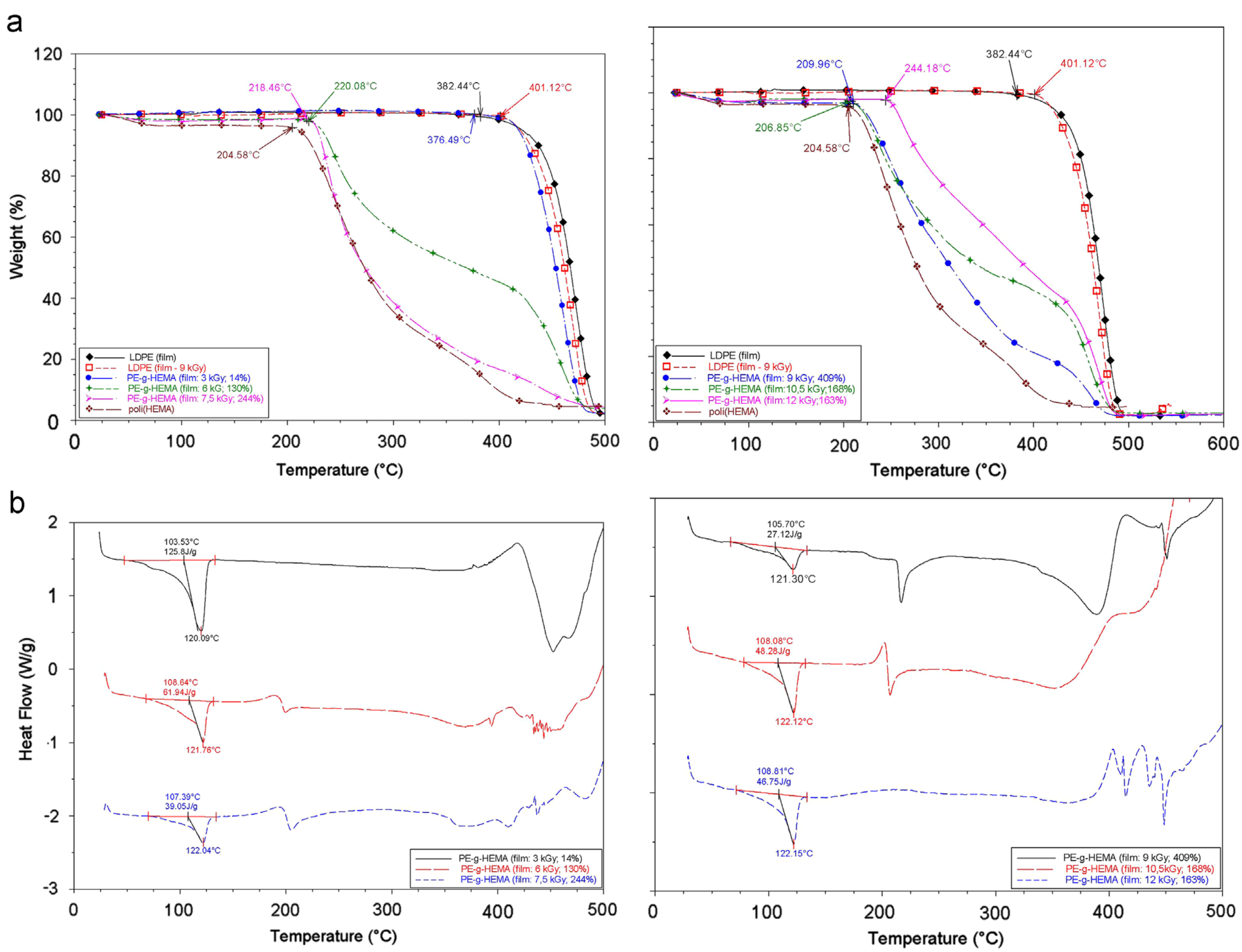

Fig. 1. TGA (a) and DSC (b) thermograms of LDPE film, poly(HEMA) and PE-g-HEMA films with different grafting yields, obtained by gamma irradiation in absence of air (DR=0.3 kGy h^{-1}, $[HEMA]_i$=15% (V/V in MeOH)).

Table 1
Temperature of thermal degradation (T_{deg}) and fusion (T_f), enthalpy of fusion ($\Delta_f H$) and degree of crystallinity (X_c) obtained for LDPE and PE-g-HEMA films prepared with different radiation doses.

Material		*Grafting* (%)	T_{deg} (°C)	T_f (°C)	$\Delta_f H$ (J g^{-1})	X_c (%)
LDPE	Non-irradiated	–	382 ± 1.12	102 ± 2.43	136 ± 1.6	47 ± 0.8
	Irradiated (9 kGy)	–	401 ± 1.57	105 ± 1.73	133 ± 2.1	46 ± 0.9
PE-g-HEMA	3.0 kGy	14 ± 2.3	377 ± 1.61	104 ± 1.18	126 ± 1.3	43 ± 0.6
	6.0 kGy	130 ± 5.2	220 ± 2.39	109 ± 1.37	62 ± 2.3	21 ± 1.2
	7.5 kGy	246 ± 8.2	216 ± 2.83	107 ± 1.49	39 ± 3.4	13 ± 1.7
	9.0 kGy	400 ± 10.4	210 ± 4.77	106 ± 1.65	27 ± 4.1	9 ± 1.7
	10.5 kGy	165 ± 4.3	207 ± 2.57	108 ± 2.21	48 ± 2.4	17 ± 1.2
	12.0 kGy	163 ± 9.3	244 ± 1.04	109 ± 1.61	46 ± 2.2	16 ± 0.8

endothermic transition temperature does not depart considerably from that of pure irradiated LDPE, irrespective of grafting yield (ΔT_{max}≈4.00 °C). As already suggested by authors (Ferreira et al., 2005, 2006), it seems that the grafted poly(HEMA) acts as a protective shield of the LDPE backbone, somehow preventing the degree of structural damages (not so pronounced) in the copolymer matrix.

Considering now the films prepared with doses above 9.0 kGy, with 10.5 and 12.0 kGy respectively, one observes a decrease in the samples grafting degree, suggesting a decrease in the grafted coating layer of poly(HEMA) with increasing radiation dose of preparation. Authors have already referred to this effect as *Abrasive Effect of Radiation* (Ferreira et al., 2007). This decrease in samples grafting degree is accompanied by an increase in respective melting enthalpy, to which correspond a crystallinity recover of up to near 18% (see Fig. 2). The increase in $\Delta_f H$ with radiation dose, contrary to what was found in bibliography (Bovey, 1958; Burlant and Hoffman, 1960; Makhlis, 1975; Davenas et al. 2002), could be explained by the partial rearrangement of the polyethylene matrix chains, somewhat more preserved from the effects of gamma radiation. Thus, the recovery of crystallinity degree observed in these PE-g-HEMA samples seems to be therefore consequence of some structural order recovery in the copolymers matrix.

These observations suggest that poly(HEMA) actually carries an effective protective effect on the polymeric matrix in PE-g-HEMA copolymers. The origin of this effect could be attributed to its amorphous nature. According to Geetha et al. (1988) how bigger the extent of amorphous regions in a polymer, greater is its mechanical resistance to radiation. Detailed analysis of the thermal behavior of poly(HEMA) revealed its amorphous nature although keeping a good structural cohesion, which shall be responsible for the stability observed in the material. Thus, even being a degradative polymer type face to gamma radiation poly(HEMA) appears not only to successfully prevent the energy impact from radiation (although with the cost of their own degradation), but also give to LDPE some ability to recover part of the lost structural order.

Infrared analysis was based on the identification of the main vibrations absorption bands associated to functional groups present in polyethylene and poly(HEMA) molecules and on its evolution with grafting degree *vs.* radiation dose. In Fig. 3 one observes that the main absorption peaks characteristics of methacrylic polymers, identified in poly(HEMA) spectra, appear in the copolymeric films with increasing intensity, accompanying the increase in their grafting degree. The IR absorption peaks and bands characteristics of methacrylic polymers identified in poly(HEMA) and PE-g-HEMA are: (i) a peak near 750 cm^{-1}, due to the rotation of the –CH2 group (dislocated relatively to that observed in LDPE);

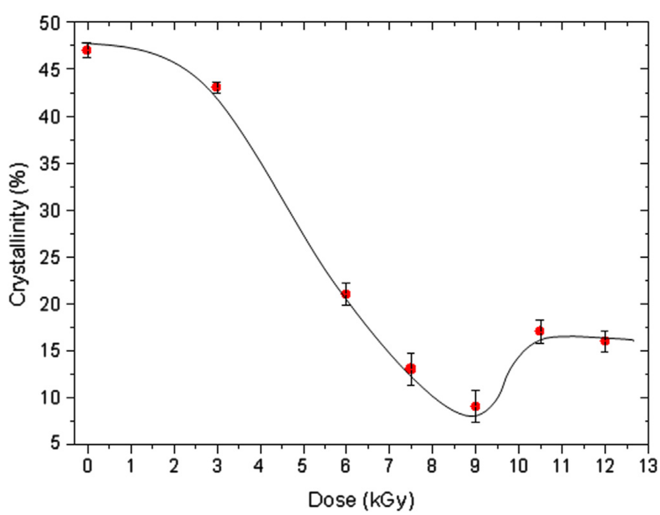

Fig. 2. Evolution of the degree of crystallinity of the PE-g-HEMA films with the respective radiation dose of preparation.

(ii) two bands between 1200 and 1050 cm^{-1}, associated with the elongation of the C–O bond; (iii) a strong band near 1725 cm^{-1} corresponding to the elongation of the carbonyl group, C=O; and, (iv) a flattened broadband and slightly defined between 3600 and 3200 cm^{-1}, corresponding to the elongation of O–H bond in an environment in which the hydroxyl groups are involved in hydrogen bridge links between neighboring groups (Sadtler, 1980). The large band between 3600 and 3200 cm^{-1}, practically incipient in the copolymers with lower degree of graft, gains expression with the increasing degree of grafting of the samples. This suggests the occurrence of hydrogen bonding between hydroxyl groups neighbors, the number of which increases with the degree of grafting (the hydrogen bonding may also occur between the hydroxyl groups of grafted poly(HEMA) and water molecules absorbed from the atmosphere, during samples analysis). The *Abrasive Effect of Radiation* for high doses of preparation (10.5 and 12.0 kGy) is also detected in the respective spectra, expressed by the attenuation of these characteristics peaks.

Concerning pure LDPE film and its “IR fingerprint” in PE-g-HEMA spectra it can be seen that its spectra exhibit the major vibrational absorption bands characteristic of polyethylene: (i) near 2900 cm^{-1} and 1470 cm^{-1} due to stretching and distortion, respectively, of the C–H bond (characteristics of alkenes); (ii) close to 1375 cm^{-1}, corresponding to the deformation of the terminal connections of $–CH_3$ in polyethylene molecules, and, (iii) a doublet in the region of 730–700 cm^{-1}, associated with the rotational movement of the $–CH_2$. This doublet is indicative of the presence of regions of higher crystallinity (crystalline ethylene units) in polyethylene. For a predominantly amorphous polyethylene, only one band appears in this region of the spectrum (Sadtler, 1980).

In the IR spectra of PE-g-HEMA copolymers a decrease of intensity and definition of this doublet with the increasing degree of graft in the copolymeric films up to a dose of preparation of 9.0 kGy is observed. This seems to result from the loss of crystallinity due to the effect of γ radiation and the graft of poly(HEMA). Nevertheless, for the higher doses of preparation, 10.5 and 12.0 kGy respectively, a slight increase can be seen in strength and definition of this characteristic doublet, evidencing the recovery of some crystallinity in the copolymeric films. These facts confirm the data obtained by thermal analysis.

The remaining characteristics bands of polyethylene are also present in the grafted copolymers and its definition and intensity also decreases with yield of graft increasing. The increase in the amount of poly(HEMA) grafted onto polyethylene leads

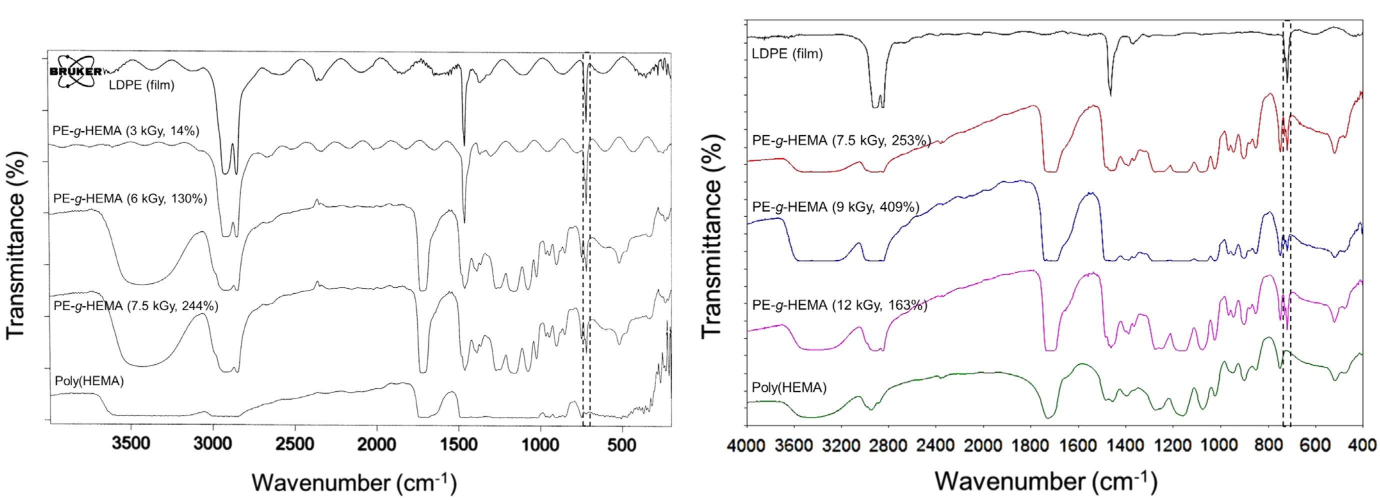

Fig. 3. IR spectra of LDPE film, poly(HEMA) and PE-g-HEMA films with different grafting yields, obtained by gamma irradiation in absence of air (DR=0.3 kGy h^{-1}, $[HEMA]_i$=15% (V/V in MeOH)).

to the attenuation of the vibrational bands of the copolymer matrix. These observations are once again coherent with obtained thermal data.

4. Conclusions

The structural analysis of PE-*g*-HEMA copolymeric films prepared by gamma irradiation, through thermal analysis and IR spectroscopy allowed to understand better the behavior and importance of the grafted poly(HEMA) branches in the structural stability observed in this copolymer. Results confirmed a density increment of the grafted coating mantle over PE with the radiation dose of preparation up to a maximum value, endowing from this point the PE matrix of a protective radiation "shield". This dense mantle seems to act not only preventing more severe structural damages but giving capacity to the PE matrix of some structural order recovery, with a consequent recuperation of structural stability. These facts suggest good perspectives for the application of PE-*g*-HEMA films in CMR.

XRD and mechanical studies on these materials are ongoing to obtain additional data about these important and unusual processes, which will be full discussed in a forthcoming paper.

Acknowledgments

The authors acknowledge the Fundação para a Ciência e a Tecnologia for financial support through the project PTDC/CTM-POL/114579/2009 and Grant SFRH/BPD/26961/2006.

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