

Evaluation of polymers designed for radiation processing

Grażyna Przybytniak,
Andrzej Nowicki,
Krzysztof Mirkowski

Abstract. Five types of commercially available polyethylene (PE) and some selected blends with components supporting cross-linking were radiation cross-linked. Mechanical properties and gel fraction were determined upon electron beam irradiation to such a dose that induces about 60% gel fraction. It was confirmed that for easily cross-linked PEs strength at break usually was growing and for polyethylenes less susceptible to radiation cross-linking – was reduced. Similar dependence was found for elongation at break. It was confirmed that for polyethylenes demonstrating high strength at break the efficiency of radiation cross-linking is limited. Additionally, for selected polymeric materials, stress relaxation and accelerated thermal aging were estimated. In order to enhance cross-linking yield some blends with EVA copolymer (ethylene-vinyl acetate) were prepared. On the basis of the literature data, the influence of crystalline regions on cross-linking and mechanical properties was discussed as well.

Key words: polyethylene • radiation processing • cross-linking

Introduction

Nowadays, significant part of the products made from polymeric materials is radiation cross-linked what results in a considerable improvement of their quality and durability. Such a treatment leads to the beneficial changes in some of their properties, e.g. heat resistance, tensile strength, cold flow, chemical resistance, etc. [1, 2]. Among industrial radiation processing, the most commonly used technique is cross-linking of thermoplastics. Radiation cross-linked polyethylene is a fundamental material for many wire and cable insulations, for heat shrinkable tubes and tapes, for piping for warm water supply, for foamed materials and for some mould parts (end caps, electronic component, machinery and automotive parts, etc.) [4]. Future development of radiation processing is predicted because the expectation of plastic industry increases every year due to many emerging applications of polymeric materials. Outstanding characteristic of some radiation cross-linked semicrystalline products results from improving their thermal, mechanical and chemical properties together with maintaining the degree of crystallinity on the same level upon processing, contrary to chemical treatment.

Polyethylene is a commonly radiation cross-linked thermoplastic. The morphology of polyethylene is an important factor determining radiation cross-linking [5]. Generally, it is accepted that cross-linking proceeds only in amorphous phase and on lamellar surfaces. Such an interpretation assumes existence of transient regions characterized by a linear gradient of density in model systems [3].

G. Przybytniak✉, A. Nowicki, K. Mirkowski
Department of Radiation Chemistry and Technology,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22 5041094, Fax: +48 22 8111532,
E-mail: przybyt@ichtj.waw.pl

Received: 22 September 2008
Accepted: 5 March 2009

At low absorption doses only amorphous phase is cross-linked, whereas at medium doses interchain bonds are formed also on the lamellar surfaces and between particular lamellae that leads to the loss of elasticity [11]. At high doses, transient domains are formed as a result of amorphization of the structure, therefore the content of intermediate zone increases [3].

It is widely accepted that free radical processes contribute to polyethylene cross-linking. Hydrogen atoms are predominantly released from second ordered carbon atoms. However, in manufacturing process, the chain branching is introduced to the linear macromolecules together with the formation of trans-vinylene and vinyl groups. According to Singh, unsaturated vinylene groups play an important role in radiation-induced cross-linking, especially via cationic mechanism [12]. One can expect that cross-linking of LDPE (0.91–0.93 g/cm³) is more effective than HDPE (0.941–0.965 g/cm³), roughly speaking due to greater content of amorphous phase. However, many investigations confirmed findings that for high absorption doses gel fraction prevails over percentage of amorphous component [10]. Thus, some authors concluded that cross-linking in crystalline regions is also probable. Such a statement supports observations that for model compounds of PE cross-linking in crystals is possible and it seems that the yield of the process is about 3.6 times smaller than in amorphous regions [13]. On the basis of NMR measurements, Whittaker [14] presented the opinion that radiation-induced defects in crystalline regions initiates cross-linking at these sites. Contrary to these opinions, Pattel and Keller claimed that the length of carbon-carbon bond is too short, ca. 1.54 Å, to be created between macromolecules situated in the crystal lattice since the distance between the adjacent chains is near 4.1 Å [9].

The discrepancies between the content of gel fraction and the amorphous phase might be also explained on the basis of the analysis of complex structure of PE. The crystallites are embedded in disorder regions and the nature of phases could not be defined strictly. It seems that a fraction of crystallites might be trapped by a network of cross-linked amorphous phase and during extraction with organic solvents a part of residues is not released to the solution. The interface also might play an important role as the developed boundary zone supports processes between chains.

The considerations concerning various aspects of cross-linking lead to the conclusions that proportion between ordered and disordered domains determines

final effect of the processes, however the relationship is complex. Content of crystalline regions determines to some degree density of the material, the parameter that is always revealed in the manufacturer characteristic of commercial products. The other features influencing cross-linking, e.g. branches per 1000 mers, their length, content of antioxidants or stabilizers and their types, usually are concealed by the producers. Therefore, the optimization of substrates designed for radiation modification has to be always followed by the initial studies. A structure of polymers influences yield and types of cross link, i.e. H-link (formed upon the combination of two second ordered alkyl radicals) or Y-link (produced between the vinyl terminal group and the secondary alkyl radicals induced by radiation). Some investigations confirmed that flexible and mobile chains mainly cross-linked with H type, but the rigid one predominantly formed Y bonds [16].

Selection of commercial PEs for radiation processing is supposed to rely not only on technological parameters, but on the ability to cross-linking induced by ionizing radiation as well. In reported studies five various types of PEs of properties fulfilling requirements necessary for the production of heat shrinkable tubes and tapes were investigated in order to estimate their efficiency to radiation cross-linking. Additionally, the studies on modification of cross-linking efficiency by blending of the selected PE with components that easily create interchain bonds were performed. The relationship between the ability to cross-linking and the mechanical properties of particular polyethylenes is discussed.

Experimental

Samples of several commercially available polyethylenes (PEs) examined in this study were prepared by extrusion of tapes (of thickness about 0.10 mm and width 10 cm) in an extruder PLV-151 Brabender. Characteristic of the samples (including melt flow index, MFI and density) is presented in Table 1. MFI provides an estimate of the average molecular weight of the polymer and its branching. On the other hand, density of the polymers might be in correlation with crystallinity of the materials.

Some blends were prepared by blending Borstar LE8707 with two EVA copolymers or Bralen RB03-23 (Table 2). EVA of the trade name Elvax 460 (18% VA, MFI 2.5 g/10 min, density 0.94 g/cm³) and Elvax 40W (40% VA, MFI 52 g/10 min, density 0.96 g/cm³) were

Table 1. List of studied polyethylenes

No.	Trade name	Producer	Type of PE	MFI 210°C/5 kg (g/10 min)	Density** (g/cm ³)
1	Lupolen 2012*	BASF	LDPE	2.9	0.936
2	Bralen RB03-23	Slovnaft TVK	LDPE	2.1	0.919
3	Hiplex TR418*	HIP-Petrochemija	MDPE+HMWPE ¹	1.2	0.950
4	Borstar FB1350	Borealis	LDPE+HDPE	1.1	0.935
5	Borstar LE8707*	Borealis	LLDPE ²	4.9	0.923

* PE containing 2.0–2.5% carbon black.

** Data from producer sheets.

¹ MDPE – middle density PE, HMWPE – high molecular weight PE.

² LLDPE – linear low density PE.

Table 2. Blends of Borstar LE8707 with various components. MFI of the blends were determined under the following conditions: 190°C, 2.16 kg (g/10 min)

Components (MFI)	Blend-0	Blend-1	Blend-2	Blend-3	Blend-4
	Content of vinyl acetate (%)				
	–	3	6	3	–
Borstar LE8707	100	83.5	66.6	92.5	80
Elvax 460	–	16.5	33.3	–	–
Elvax 40W*	–	–	–	7.5	–
Bralen RB03-23	–	–	–	–	20
MFI	0.78	1.00	1.36	0.91	0.64

* Homogeneity of the Elvax 40W blend containing 6% vinyl acetate was insufficient thus the composite was excluded from further investigations.

purchased in DuPont Industrial Polymers. Blends with 3 and 6 wt.% of vinyl acetate content were prepared in a Brabender mixer at 180°C and at a rotor speed of 60 rpm, and subsequently compressed between two metal plates cooling with water.

The samples were irradiated to various absorption doses using an electron accelerator Elektronika of electron energy 10 MeV in air atmosphere at ambient temperature. The absorption doses were delivered to the studied materials in portions of 28 kGy per single pass.

Gel fraction of the irradiated samples was determined in accordance with the ASTM D2765 procedure. The samples were exposed to refluxing xylenes for 8 h. The residue was dried in a vacuum oven at 105–115°C to constant weight. Average values of gel fraction were determined on the basis of 3 independent measurements.

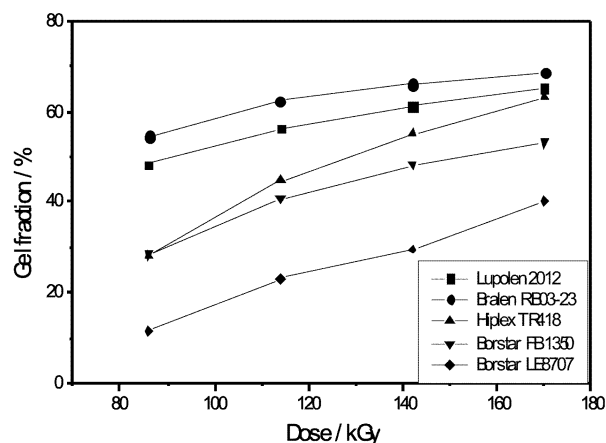
The mechanical testing of polymer samples, tensile strength and elongation at break were measured on dumbbell specimens according to ISO 527 in an Instron 5565 universal apparatus for mechanical testing at a speed of 100 mm/min. All measurements were performed at ambient temperature. Stress relaxation of the tapes was performed in an environmental chamber 319–409 (Instron 5565) at 160°C for 10 min. Accelerated aging of irradiated tapes was also carried out in the environmental chamber at 136°C for 168 h. The mechanical measurements were performed before and after aging.

Melt flow index (MFI) was measured with a Zwick 4105 apparatus under nonstandard conditions as Hipler TR418 and Borstar FB1350 show measurable fluidity just at a load of 5 kg (Table 1). Drastic reduction in MFI for irradiated PEs is observed even for small absorption doses. Generally no flow, was found at 50 kGy or more. MFIs of the blends are presented in Table 2.

Results and discussion

Figure 1 shows the results of average gel fraction as a function of integrated doses. It can be observed that the gel fraction increases significantly with increasing doses, however the relationship strongly depends on the type of PE.

In the range of absorption doses 0–170 kGy gel fraction reaches 60% only for three types of PEs: Bralen RB03-23 at 100 kGy, Lupolen 2012 at ca. 113 kGy, and Hipler TR418 for 155 kGy. For both types of Borstars, the 60% gel fraction might be achieved above 210 kGy. The

**Fig. 1.** Gel fraction vs. absorption doses for various types of commercial PEs.

yield of cross-linking for linear low density PE (Borstar LE8707) shows a noticeable decrease if compared with other types of polyethylenes at similar doses. The same phenomenon was found by Hutzler *et al.* [6]. Low efficiency of cross-linking in LLDPE is usually related to the absence of unsaturation.

The investigations were performed with the intention of obtaining easily cross-linked, black PE that is usually more environmental resistant (especially for UV exposition) than non-coloring one. It was taken into account that the studied Lupolen 2012 has not been produced any longer and MFI of Hipler TR418 as well as Borstar FB1350 might be too low for some stages of polymer processing (e.g. tape extrusion).

The mechanical properties of irradiated plastics at ambient temperature depend significantly on the type of PEs (Fig. 2). Usually, in the materials demonstrating higher strength at break the content of crystalline phase is larger. It was found that Hipler TR418 characterizes the highest strength at break before irradiation, near 35 MPa, what results from the structure of components: one of them of middle density (MDPE) and the second one of long macromolecules (HMWPE) (Table 1). Borstar FB1350 also shows relatively favorable mechanical properties due to HDPE constituent, whereas Borstar LE8707 is an elastic material of significant elongation at break, reaching 1100%.

The polymers were irradiated to such a dose that allows to achieve a level of gel fraction ca. 60%. After exposure to ionizing radiation, the deterioration of both strength and elongation at break were confirmed for two types of polyethylene, Hipler TR418 and Borstar

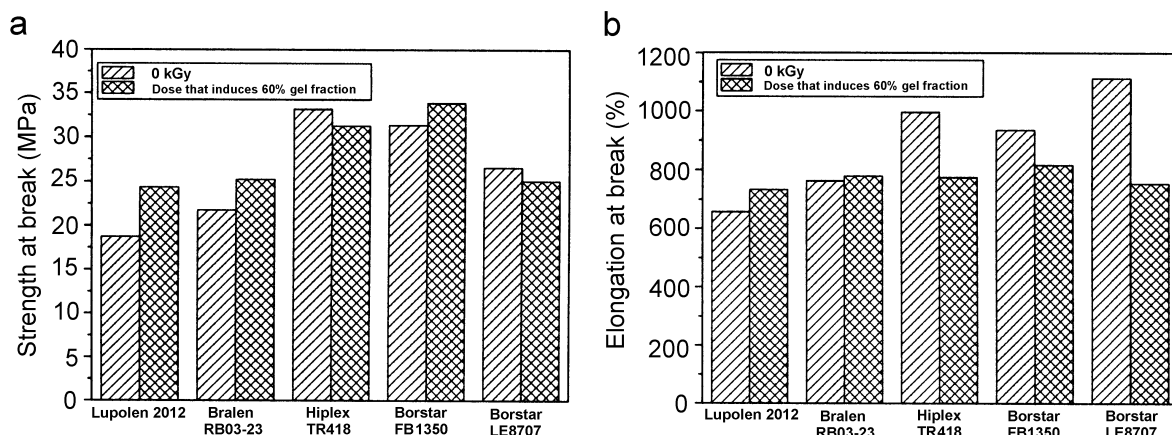


Fig. 2. Strength at break (a) and elongation at break (b) for radiation cross-linked PEs showing 60% gel fraction upon irradiation with the following doses: 113 kGy – Lupolen 2012; 100 kGy – Bralen RB03-23; 155 kGy – Hiplex TR418; 210 kGy – Borstar FB1350; 225 kGy – Borstar LE8707.

LE8707. For other studied polymers, an increase in strength at break was observed. Elongation at break to some extent grows only for plastics that undergo radiation cross-linking with high efficiency, i.e. for Lupolen 2012 and Bralen RB03-23.

For some applications, e.g. wrapping, Borstar LE8707, showing high elongation at break, might be used if only mechanical strength would be enhanced by cross-linking. However, in order to achieve gel fraction of about 60% for Borstar LE8707, the polymer ought to be irradiated to 225 kGy. Such a high absorption dose might result in drastic reduction of mechanical properties, especially elongation. Therefore, two smaller doses, 165 and 193 kGy, corresponding to 40% and 50% gel content, respectively, were applied. Subsequently, the mechanical characteristic of the samples was carried out after each step of the following procedure: exposition to ionizing radiation, thermal relaxation at 160°C for 10 min, and aging at 136°C for 168 h (Fig. 3). Thermal relaxation was studied in order to determine features of the material upon shrinkage, whereas the accelerated aging provided information concerning Borstar utility and weathering resistance.

The thermal relaxation partly restores mechanical properties: strength at break for the sample irradiated

with a dose of 165 kGy exceeds the value found for non-irradiated polymer, 27.4 and 26.6 MPa, respectively. For this sample, upon short annealing, elongation grows of about 200% in comparison to irradiated Borstar LE8707. On the other hand, accelerated aging at 136°C significantly diminishes positive effect of the relaxation. The consequences are less significant for the samples irradiated to higher dose, i.e. to 193 kGy. It seems that an increase in cross-linking supports thermal resistance of the material. In general, upon irradiation, the thermal relaxation and aging, scatter of the results characterizing mechanical properties diminishes.

Commercially available plastics might contain many additives: stabilizers, antioxidants, plasticizers, antistatic agents, retardants, etc. Usually, some of them are consumed during irradiation with low doses [15]. Therefore, when radiation cross-linked material undergoes thermal aging, a level of the degradation is independent of the initial concentration and nature of protecting agents, as usually they decay just during irradiation. It is generally accepted that antioxidants and stabilizers inhibit to some extent radical reactions, and consequently cross-linking. The later process develops predominantly in amorphous region, i.e. in the phase where applied additives are included as during formation of crystallites,

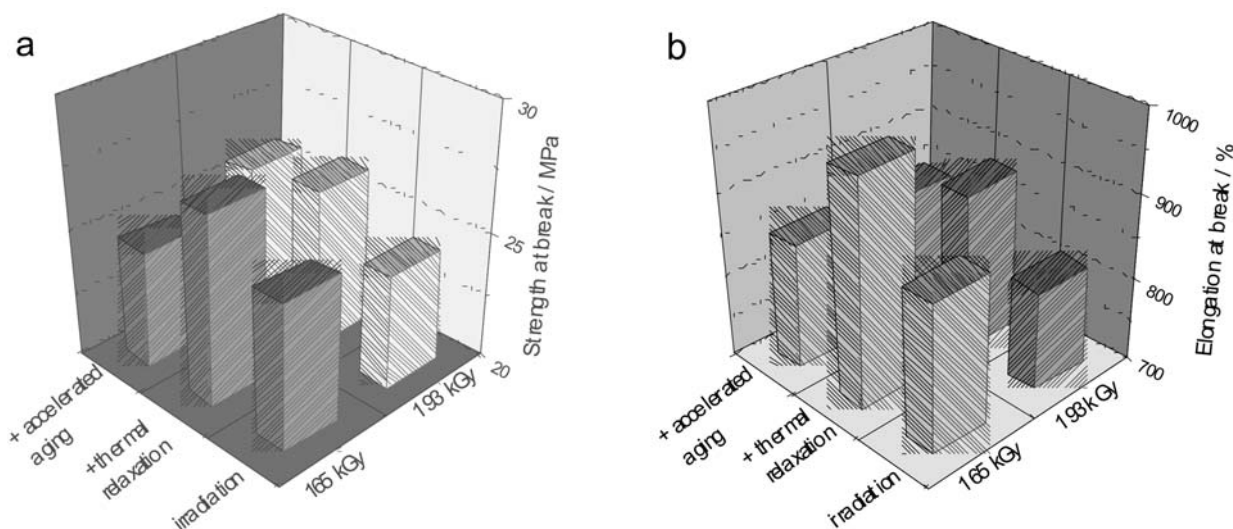


Fig. 3. Strength at break (a) and elongation at break (b) for Borstar LE8707 after irradiation, thermal relaxation and accelerated aging.

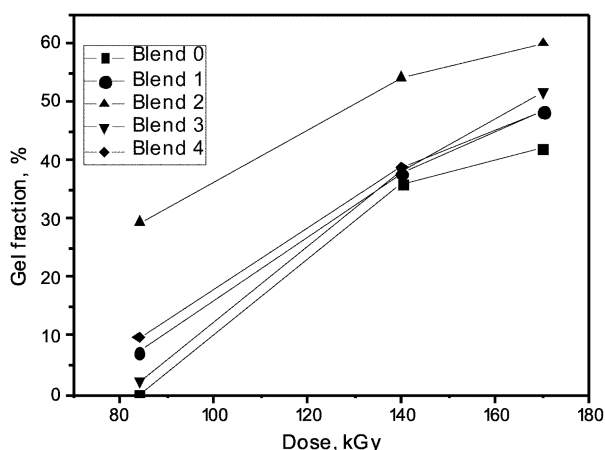


Fig. 4. Gel fraction of the blends vs. absorption doses.

doped substances are pushed out to the intercrystalline space. Therefore, their concentration in ordered phase is insignificant and they cumulate in amorphous regions. The exposition to ionizing radiation, particularly on high doses, results in conversion of the additives to inactive species. Consequently, the response of the polyethylene on thermal degradation predominantly results from structural changes initiated by ionizing radiation, but not from the action of antioxidants and stabilizers. Thus, the more cross-linked Borstar LE8707 (193 kGy, gel fraction 50%) shows upon aging higher strength at break than the less cross-linked one (165 kGy, gel fraction 40%).

Intramolecular heterogeneity distribution is significantly different in linear low density PE than in LDPE. There is a relatively small number of short-chain branching in LLDPE and a neglected amount of double bonds in main chains. Therefore, some mechanical properties of linear PE are enhanced, but simultaneously the ability towards cross-linking decreases.

In order to study the possibility of increasing the efficiency of cross-linking, some blends with the components that are more susceptible to the formation of intermolecular network were prepared. Thus, in the next stage of our studies, Borstar LE8707 having good enough initial mechanical properties was modified with the components that potentially are able to enhance the tendency to cross-linking [7]. Two EVA copolymers and Bralen RB03-23 were used as the agents influencing the structure of Borstar LE8707 (Table 2). Figure 4 shows the gel fraction of blends as a function of absorption doses.

It results from Fig. 4, that sensitivity to irradiation of the blends 1 and 3 is almost the same as that of the Blend-0 (Borstar LE8707), while the blend containing 20% of Bralen (Blend-4) is essentially less sensitive to radiation. A considerable increase in gel fraction was confirmed for Blend-2 that contains 33.3% of EVA (6% vinyl acetate). It seems that incorporation of the components supports cross-linking of Borstar LE8707. The other important factor determining benefits in applications of the radiation treatment is preservation/improvement of mechanical properties. Unfortunately, significant reduction in strength and elongation at break were found for all blends, both before and after irradiation. Table 3 reveals an example of the data obtained for one of the blends.

Table 3. Comparison of the mechanical properties of Borstar LE8707 and its blend with Bralen RB03-23

Dose (kGy)	Strength at break (MPa)		Elongation at break (%)	
	Blend-0	Blend-5	Blend-0	Blend-5
0	26.56	20.16	1113	883
165	25.71	22.06	877	758
193	24.37	20.63	818	688

Summarizing

Each studied polyethylene reveals different characteristic upon irradiation. For a selected dose, Bralen RB03-23 shows the greatest gel fraction and noticeable improvement in mechanical properties. For this material, just at ca. 100 kGy the gel fraction achieves above 60%, whereas for other studied PEs this value is situated in the range of 20–50%. The polymer might be applied as a fundamental material for radiation processing. Unfortunately, there is no analogous of Bralen RB03-23 containing carbon black, what is recommended for many products subjected to radiation treatment. Borstars and Hiplex TR418 demonstrate poorer ability to cross-linking and better mechanical properties. For these materials, the yield of cross-linking might be improved by the implementation of easily cross-linked components, e.g. EVA or Bralen RB03-23, however in such a case the worsening of mechanical properties was confirmed thus the benefits of overall effect are doubtful. It seems that in the blends crystallization to some extent is impeded due to increasing content of amorphous components [8]. Therefore, during selection of polyethylene for particular products, two contradictory trends must be considered: LDPE of moderate mechanical properties undergoes cross-linking with high yield, whereas other types of PE, usually of better mechanical characteristic, are less susceptible to such a process. On the other hand, blends of the other types of polyethylene (e.g. LLDPE) with easily cross-linking constituents, usually demonstrate loss of the superior mechanical characteristic just upon the stage of blending due to limited miscibility between components and probable diminishing degree of crystallinity. In spite of the growing tendency to cross-linking, the final properties of blends are not as good as those of PE alone.

References

1. Berejka AJ (2007) Radiation response of industrial materials: dose-rate and morphology implications. *Nucl Instrum Methods Phys Res B* 261:86–89
2. Chmielewski AG, Haji-Saeid M, Ahmed S (2005) Progress in radiation processing of polymers. *Nucl Instrum Methods Phys Res B* 236:44–54
3. Chodak I (1995) Properties of crosslinked polyolefine-based materials. *Prog Polym Sci* 20:1165–1199
4. Gehring J, Zyball A (1995) Radiation cross linking of polymers – status, current issues, trends and challenges. *Radiat Phys Chem* 46:931–936
5. Gheysari D, Behjat A, Haji-Saeid M (2001) The effect of high-energy electron beam on mechanical and thermal properties of LDPE and HDPE. *Eur Polym J* 37:295–302

6. Hutzler BW, Machado LDB, Villavicencio A-LCH, Lugao AB (2000) Crystallization of irradiated polyethylene. *Radiat Phys Chem* 57:431–434
7. Mateev M, Karageorgiev S (1998) The effect of electron beam irradiation of EVA upon the gel-forming processes in LDPE-EVA films. *Radiat Phys Chem* 51:205–206
8. Moly KA, Radusch HJ, Androsch R, Bhagawan SS, Thomas S (2005) Nonisothermal crystallisation, melting behaviour and wide angle X-ray scattering investigations on linear low density polyethylene (LLDPE)/ethylene vinyl acetate (EVA) blends: effects of compatibilisation and dynamic crosslinking. *Eur Polym J* 41:1410–1419
9. Patel GN, Keller A (1975) Crystallinity and the effect of ionizing radiation in polyethylene. I. Crosslinking and the crystal core. *J Polym Sci: Polym Phys Ed* 13:303–321
10. Singh A, Lopata VJ, Kremers W, Sze YK (1996) Crosslinking of commercial polyethylenes by 10 MeV electrons. Atomic Energy of Canada Limited Report AECL-11259
11. Silverman J (1992) Radiation-induced and chemical crosslinking. In: Singh A, Silverman J (ed) *Radiation processing of polymers*. Hanser Publisher, Munich, pp 15–22
12. Singh A (1999) Irradiation of polyethylene: some aspects of crosslinking and oxidative degradation. *Radiat Phys Chem* 56:375–380
13. Sohma J, Chen Q, Wu XW, Scholtyssek G, Zachmann GH (1991) MAS NMR studies on cross links induced by irradiation to polyethylene. In: *Proc of 7th Tihany Symp on Radiation Chemistry*, pp 281–288
14. Whittaker A (1996) ¹H NMR studies of the radiation-induced crosslinking of poly(ethylene). *Radiat Phys Chem* 48:601–604
15. Zagorski ZP (2004) EB-crosslinking of elastomers, how does it compare with radiation crosslinking of other polymers? *Radiat Phys Chem* 71:261–265
16. Zhen SJ (2001) The effect of chain flexibility and chain mobility on radiation crosslinking of polymers. *Radiat Phys Chem* 60:445–451