

Radiation-induced crosslinking of UHMWPE in the presence of co-agents: chemical and mechanical characterisation

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Abstract

Radiation-induced crosslinking has been shown to have a beneficial effect on the wear resistance of ultra high molecular weight polyethylene (UHMWPE). Since we postulate that crosslinking takes place through reactions involving terminal double bonds, unsaturated additives were added to UHMWPE in this study to enhance crosslinking. UHMWPE specimens soaked in 1,7-octadiene, methylacetylene and ethylene, respectively, were irradiated with electron beam to different doses in single or multiple passages. FTIR spectroscopy was used for the chemical characterisation of the crosslinked polymer. Tensile tests were performed with all samples in order to monitor changes in the mechanical properties.

Gel fraction measurements proved that crosslinking took place in all the irradiated samples, but 1,7-octadiene turned out to be the most effective additive for the present purpose, exhibiting a good efficiency in enhancing crosslinking. The FTIR analyses showed that consumption of vinyl double bonds is proportional to the irradiation dose, with an efficiency which increases with increasing their initial concentration, confirming the hypothesis of the involvement of these groups in the crosslinking process. In the case of UHMWPE with 1,7-octadiene irradiated to high doses in multiple passages, the results of the tensile tests indicated a significant decrease in both elongation at break (up to 65%) and ultimate stress (up to 25%). A possible explanation of the diminished strength of the crosslinked material has also been proposed.

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1. Introduction

Excellent properties in terms of wear, fatigue and fracture resistance have made ultra high molecular weight polyethylene (UHMWPE) the material of choice in a number of applications in which low frictional coefficients and high abrasion resistance are required. Among them, the replacement of damaged articulating cartilages in total joint replacement surgery is, at the present time, the most important [1–3]. Despite the outstanding success of this procedure, failures for aseptic loosening or rupture of the component after few years of implantation are still quite frequent [4,5].

In the last years, it has been demonstrated that most of the dramatic failures were to be ascribed to the oxidative degradation of polyethylene induced by sterilisation with gamma radiation in air [1,6]. Nevertheless, even for not oxidised polyethylene, wear is still a major concern, since

abrasion leads to the formation of debris, which in turn induce an inflammatory response, causing loosening of the implant [7].

An intimate knowledge of the processes involved into UHMWPE abrasion, would allow a substantial reduction of wear, with an increase in the average survivorship of the implant and lower social and economic costs, and create the possibility of implantation in young patients.

Abrasion is a complex and multifactorial process and it is strongly affected by the finish of the abrading surface and by the physical and chemical properties of the abraded material [8].

In previous studies, the generation of wear particles in acetabular components has been associated with the local accumulation of plastic strain under multiaxial loading conditions [9,10], while in tibial components the fatigue and fracture mechanisms have been directly related to the plastic flow parameters of UHMWPE, such as the yield stress and ultimate stress [11].

On the other hand, studies showed that crosslinking of UHMWPE with electron beam or γ rays is highly effective against wear [1,12–14], increasing the molecular mass, though

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decreasing other mechanical properties, as ultimate stress and elongation to failure [12]. In particular, better wear resistance of crosslinked UHMWPE compared with non-crosslinked UHMWPE was demonstrated when molecular mass is the key parameter governing the abrasion process, thus for smooth abrading counterfaces [15], such as those generally involved in a prosthetic coupling.

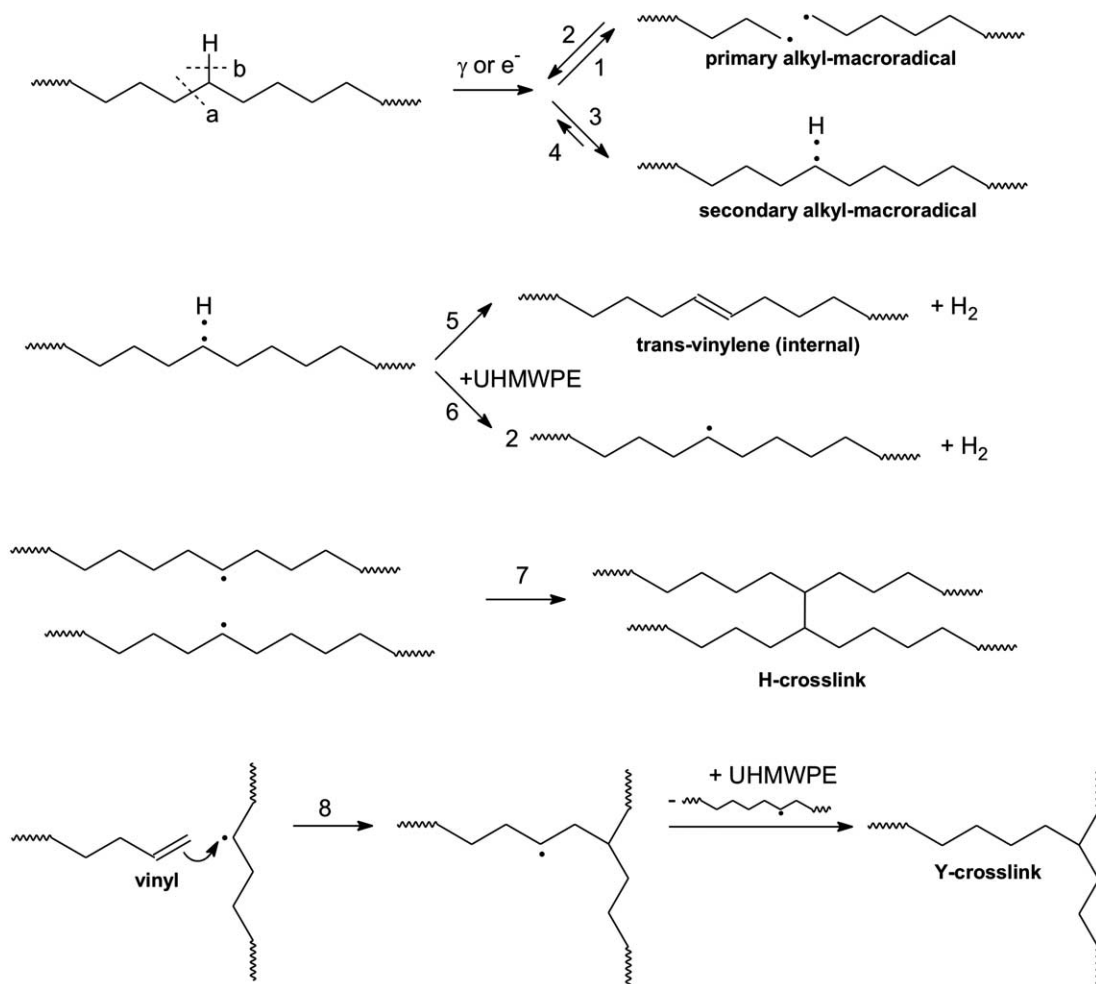
1.1. Mechanisms of interaction of high energy radiation with UHMWPE and chemistry of crosslinking

Interaction of high energy radiation with UHMWPE leads to the scission of C–C (Scheme 1, reaction 1) and C–H (reaction 3) bonds, giving H radicals and primary and secondary macroradicals [6]. Only secondary macroradicals can be detected [16,17], then it is assumed that in the solid state primary macroradicals undergo recombination following reaction 2.

Secondary macroradicals give hydrogen elimination via intra (reaction 5) or inter-molecular mechanisms (reaction 6), forming *trans* (Fig. 1) and *cis*-vinylene internal double bonds both in the amorphous and in the crystalline phase.

Formation of H-shaped crosslinks (hereafter H-crosslinks) between two secondary macroradicals (reaction 7) has been suggested in some studies [12] to explain crosslinking of the polymer caused by irradiation. Although thermodynamically feasible at room temperature, the reaction is highly unlikely due to steric hindrance, when UHMWPE is in the solid state [6]. Models of the crystalline phase of UHMWPE show that the minimum distance between two C atoms is 5.6 Å, thus much higher than the mean C–C bond length (1.54 Å) [18]. Therefore, the formation of H-crosslinks is sterically hindered in the crystalline phase. In addition, the ratio between the kinetic constants of disproportion and coupling for a secondary butyl radical, in the liquid state, at room temperature, is about 1.5, increasing by one order of magnitude for the same radical in the solid state [19]. Studies by Zhu et al. on HDPE [20] demonstrated that the yields of H-crosslinks significantly increases only above the melting temperature. Moreover, the presence of H-crosslinks in polyethylene irradiated in the solid state has been ruled out in previous NMR studies [21,22].

Vinyl double bonds are consumed during irradiation [23,24] as they react with secondary macroradicals according to reaction 8, which leads to the formation of Y-shaped branching



Scheme 1.

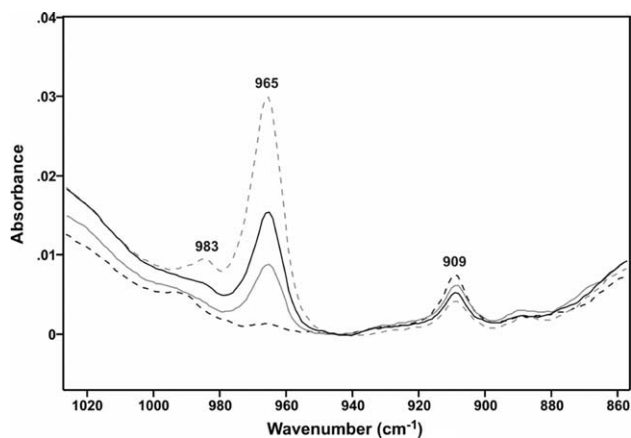


Fig. 1. FTIR spectra of unsoaked UHMWPE irradiated to 0 (---), 25 (—), 50 (—) and 100 (- - -) kGy.

(hereafter Y-crosslink) [25,26]. Reaction 8 is exothermic, with $\Delta G \approx -50$ kJ/mol at room temperature [27], and it is sterically feasible, being similar to the radical polymerisation of 1-butene.

Since UHMWPE contains in the amorphous phase more than one vinyl end group per chain [6], the reaction of the first vinyl unit results in branching, while the following ones lead to crosslinking. Therefore, the crosslinking degree is dependent on the amount of pendent double bonds in the polymer and on the absorbed dose.

Since the amount of pendent double bonds cannot be increased during UHMWPE synthesis, the effectiveness of crosslinking may be improved by diffusing into the polymer crosslinking additives containing reactive double or triple bonds. Studies showing the evidence for the formation of polyene crosslinks when polyethylenes are gamma-irradiated in the presence of acetylene have already been reported [18].

In the present work, UHMWPE diffused with methylacetylene, ethylene or 1,7-octadiene was exposed to increasing doses of electron beam. We expected that ethylene could turn secondary macroradicals into primary, more reactive and mobile, while 1,7-octadiene and methylacetylene formed new vinyl or vinylidene end groups, which can in turn react with secondary macroradicals and give crosslinking.

Starting from the hypothesis that crosslinking takes place through the reaction of pendent double bonds with the macroradicals formed upon irradiation, the goal of the study is to demonstrate that addition of suitable reactive additives to UHMWPE prior to irradiation leads to an enhancement of crosslinking.

2. Experimental

2.1. Material

A compression molded slab of medical grade UHMWPE (Gur 1020, Poly Hi Solidur, Vreden Germany), with a molecular mass higher than 4×10^6 amu and a density of 0.93 g/cm³, was microtomed in 180 μ m thick films

(PolyCuts Microtome, Reichert–Jung), in air and at room temperature [28].

2.2. FTIR spectroscopy

A FTIR System 2000 (Perkin–Elmer Instruments) spectrometer was used. All spectra were run in the transmission mode with a 4 cm⁻¹ resolution and 32 scans per spectrum. The peak at 2020 cm⁻¹, a combination band associated with the twisting of CH₂ [29], was used as an internal standard, since it can be regarded as unaffected by minor changes in the polymer structure. At the peak at 2020 cm⁻¹, all the spectra were normalised at an absorption of 0.05, correlating to a film thickness of ca. 100 μ m.

The double bond and methyl concentration was calculated from the respective absorption bands using the molar absorptivity proposed by De Kock and Hol (Table 1) [30]. Due to the overlapping of the strong absorption of the methylene bending (1368 cm⁻¹) to the methyl bending signal (1378 cm⁻¹), changes in the methyl concentration were calculated after subtraction of a reference spectrum.

In the original UHMWPE, vinyl double bonds only were detected by FTIR spectroscopy and their amount was estimated from the 909 cm⁻¹ absorption band in ca. 20 units per chain (based on the average MM=4.000.000 amu).

2.3. Diffusion

Six UHMWPE films per each set of samples were placed in sealed glass vials (diameter 2 cm) and evacuated for 48 h at 1.5 Pa, in order to eliminate the dissolved oxygen. Then, they were exposed to ethylene or methylacetylene at the pressure of 100 kPa, for 7 days at room temperature. In the case of 1,7-octadiene, the vials were filled with the liquid reactant and kept at 60 °C in a thermostated oil bath for 10 days. The time for complete saturation of the specimens was approximately estimated by means of the diffusion coefficients reported in the literature for similar molecules [31].

2.4. Electron beam irradiation

Vials containing the films soaked in ethylene, methylacetylene and 1,7-octadiene were exposed to electron beam with doses of 25, 50 and 100 kGy. Reference unsoaked specimens were irradiated under nitrogen to the same doses.

Table 1
FTIR absorption and extinction coefficients of unsaturated and methyl groups in polyethylene

Group	Absorption (Wavenumber in cm ⁻¹)	Molar absorptivity (l cm ⁻¹ mol ⁻¹)
Vinylidene	888	129
Vinyl	909	123
<i>trans</i> -Vinylene	965	168
<i>trans-trans</i> -Vinylene	983	168
Methyl	1378	18.3

E-beam irradiation was performed with a 10 MeV accelerator (Bioster, Seriate, Italy), operating at 25 kW power, with a dose rate of 6×10^4 kGy/h, at room temperature.

48 h after irradiation, the samples were analysed with FTIR spectroscopy. Then, the films were evacuated to remove the unreacted diffusant (12 h at 1.5 Pa) and further analysed by FTIR.

Samples soaked in 1,7-octadiene and irradiated to 25, 50 and 100 kGy were analysed after removal of the unreacted

reagent by extraction with boiling cyclohexane under reflux for 12 h and then irradiated again with increasing doses of electron beam (50, 100, 150, 200 kGy).

2.5. Solubility

The solubility of each set of samples was determined by a solvent extraction. A known amount of sample (ca. 50 mg) was

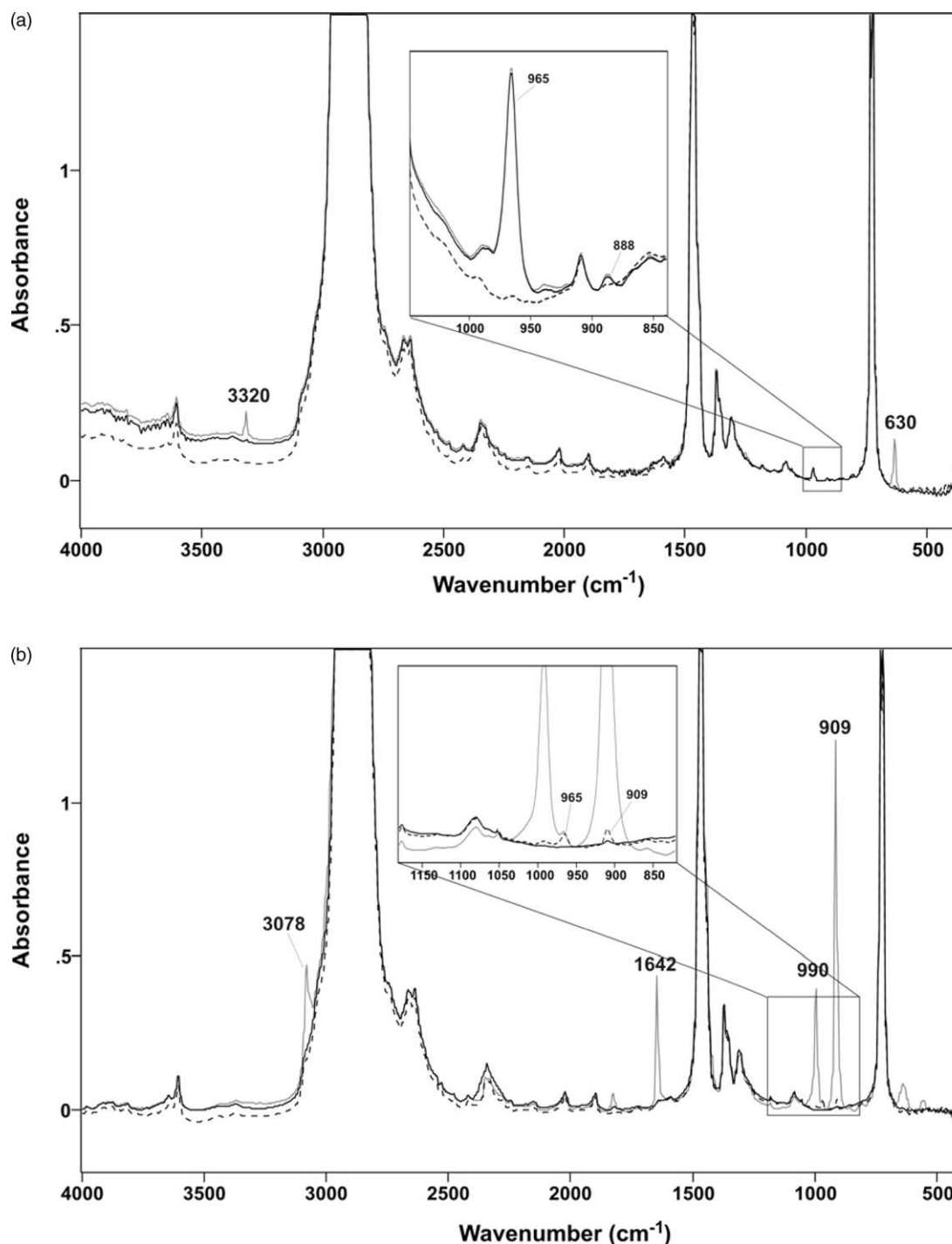


Fig. 2. (a) FTIR spectra of UHMWPE films: reference, not irradiated (---), soaked with methylacetylene and irradiated to 100 kGy (—) soaked with methylacetylene, irradiated to 100 kGy and evacuated (- - -). (b) FTIR spectra of UHMWPE films: reference, not irradiated (—), soaked with 1,7-octadiene and irradiated to 100 kGy (---) soaked with 1,7-octadiene, irradiated to 100 kGy and evacuated (- - -).

immersed in boiling *p*-xylene for 6 h, then the residue was dried under dynamic vacuum (1.5 Pa) to a constant weight. Experiments were carried out in duplicate. The gel ratio was calculated by the following equation:

$$\text{Gel ratio (\%)} = \frac{\text{extracted sample weight (g)}}{\text{sample weight (g)}} \times 100$$

2.6. Tension tests

Tensile tests were performed on all samples with an Adamek Lhomargy DY22 machine, with a crosshead speed of 10 mm/min at room temperature. Type V dogbone specimens were punched out from 180 μm thick films, according to ASTM D638-00. Experiments were carried out in triplicate. The results were plotted in terms of engineering stress vs. % of elongation.

3. Results

3.1. FTIR analysis

Fig. 1 reports the FTIR spectra of the reference unsoaked UHMWPE irradiated in nitrogen to 0, 25, 50 and 100 kGy, respectively. The *trans*-vinylene absorption band appears at 965 cm^{-1} on the spectra of irradiated UHMWPE and its intensity increases with the absorbed dose. At high irradiation dose, also conjugated *trans-trans*-vinylene absorption at 983 cm^{-1} can be detected. Furthermore, a decrease is observed in the vinyl absorption at 909 cm^{-1} [30,32].

Fig. 2(a) and (b) shows the FTIR spectra of UHMWPE films soaked with methylacetylene and 1,7-octadiene, respectively, after 100 kGy of e-beam and following evacuation. Before evacuation, both spectra evidenced the presence of new absorption bands, not attributable to the original polymer. In Fig. 2(a), absorptions at 630 cm^{-1} ($\text{C}\equiv\text{C}$ stretching) and 3320 cm^{-1} (C-H methyl stretching) indicate the presence of diffused methylacetylene, while in Fig. 2(b), absorptions at 909, 990, 1642 and 3078 cm^{-1} , typical of the vinyl group of 1,7-octadiene are detected [32,33].

In both cases, the unreacted additives have been completely removed after evacuation and in Fig. 2(a) an increase in both

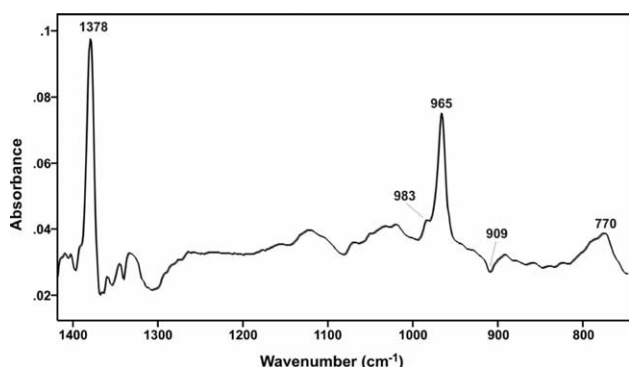


Fig. 3. Difference between the spectrum of a sample soaked in ethylene and irradiated to 50 kGy and that of original UHMWPE.

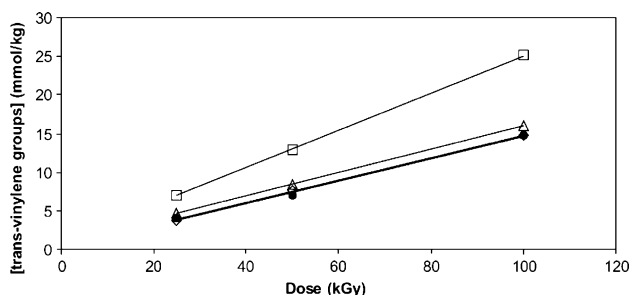


Fig. 4. *trans*-Vinylene concentration in the function of the absorbed dose. \diamond , 1,7 octadiene; \square , methylacetylene; \bullet , ethylene; \triangle , nitrogen.

vinylidene (888 cm^{-1}) and *trans*-vinylene (965 cm^{-1}) absorption can be observed, while in Fig. 2(b) an increase in the vinyl (909 cm^{-1}) and *trans*-vinylene (965 cm^{-1}) absorption is detected.

No additional absorption was observed in the spectra of samples treated with ethylene. The difference between the spectrum of a film soaked with ethylene and irradiated at 50 kGy and the spectrum of original UHMWPE is reported in Fig. 3. Appearance of a *trans*-vinylene absorption at 965 cm^{-1} and a decrease in the vinyl absorption at 909 cm^{-1} occur, as already observed in the original UHMWPE irradiated under nitrogen. In addition, methyl terminal groups (1378 cm^{-1}) and ethyl branching (770 cm^{-1}) [32] are detected.

The concentration profiles of *trans*-vinylene (965 cm^{-1}), vinyl (909 cm^{-1}) and vinylidene (888 cm^{-1}) double bonds and of methyl groups (1378 cm^{-1}), after evacuation and removal of the unreacted additives, are reported in the function of the absorbed dose in Figs. 4–7, respectively.

Samples soaked in 1,7-octadiene and irradiated contain a variable amount of vinyl end groups, depending on the absorbed dose (Fig. 5). These samples were irradiated for the second time at increasing e-beam doses. FTIR spectra show a decrease in the vinyl double bond absorption (Fig. 8(a)) and the formation of new *trans*-vinylene (Fig. 8(b)) and *trans-trans*-vinylene double bonds (Fig. 8(c)), the latter being measurable only at high absorbed doses.

3.2. Solubility

The original unirradiated UHMWPE exhibits a gel content of 55%. All the irradiated samples, even those treated with the minimum dose of e-beam, are completely insoluble in xylene at

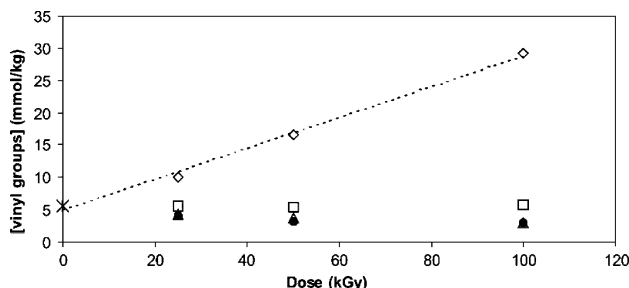


Fig. 5. Vinyl concentration in the function of the absorbed dose. \diamond , 1,7 octadiene; \square , methylacetylene; \bullet , ethylene; \triangle , nitrogen. \times , not irradiated.

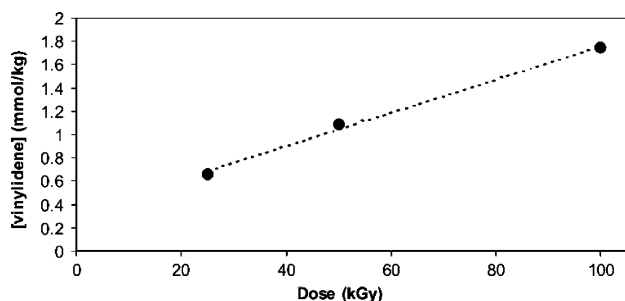


Fig. 6. Vinylidene concentration in the function of the absorbed dose for samples soaked in methylacetylene.

140 °C (undetectable weight loss). This indicates that crosslinking to a certain extent took place in all samples.

3.3. Tensile properties

The results of the tensile tests for the samples irradiated at 25, 50 and 100 kGy has been summarised in Table 2, together with the data from reference unirradiated UHMWPE specimens for comparison. An overall decrease in the ultimate tensile stress and elongation at break is observed with increasing the irradiation dose, independently on the specific additive. However, it must be pointed out that an increase in the tensile stress at the same percentage of elongation can be noted. Fig. 9 reports the stress–strain curves for the samples soaked in 1,7-octadiene and irradiated with multiple passages. Again, a significant decrease in the ultimate tensile stress and elongation to failure is recorded with increasing the irradiation dose.

4. Discussion

4.1. Ethylene

UHMWPE soaked in ethylene shows, after irradiation, the appearance of methyl terminal groups and short ethyl branching only, while no long branching (butyl or hexyl at 888–887 cm^{-1}) [32] can be detected (Figs. 3, 5 and 7). This result leads to the conclusion that secondary macroradicals formed by irradiation initiate a polymerisation process of the ethylene diffused in the amorphous phase (Scheme 2, reaction 9). Nevertheless, probably due to the low concentration of diffused ethylene, propagation does not occur and the process terminates immediately through hydrogen extraction

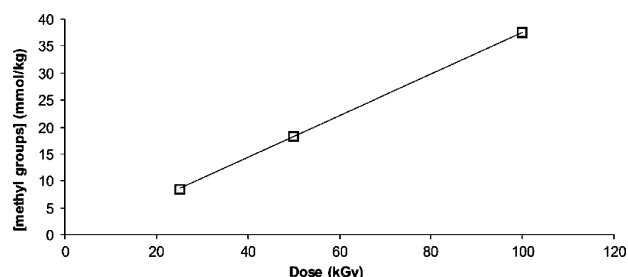


Fig. 7. Methyl concentration in the function of the absorbed dose for samples soaked in ethylene.

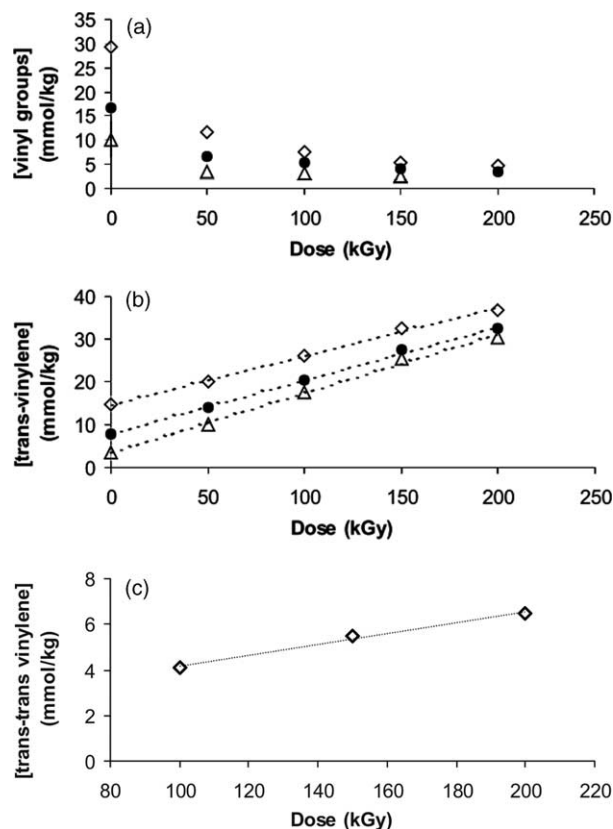


Fig. 8. Double bonds concentration in the function of the dose absorbed after the second e-beam irradiation for samples soaked in 1,7-octadiene and previously irradiated to \diamond , 100 kGy; \bullet , 50 kGy; \triangle , 25 kGy. (a) Vinyl end groups; (b) *trans*-vinylene internal unsaturation; (c) *trans-trans*-vinylene internal unsaturation.

from a surrounding UHMWPE molecule and formation of a secondary macroradical (reaction 10).

The high concentration of methyl terminal units (Fig. 7), formed through reaction 10, indicates that crosslinking via the formation of bridges between two macromolecular chain (reaction 11) is not favoured. Thus, the reaction of the two macroradicals involved in reaction 11 is less likely that reaction 10 under these conditions.

4.2. Methylacetylene

Samples soaked in methylacetylene show, after irradiation and removal of the unreacted additive, an increase in vinylidene (Figs. 2(a) and 6), and *trans*-vinylene double bonds (Figs. 2(a) and 4), the latter in amount higher than that expected according to reaction 5.

Vinylidene groups are formed through reaction 12 and 13 (Scheme 3) between UHMWPE and methylacetylene.

trans-Vinylene double bonds on the main chain (internal unsaturation) are formed through reaction 5 (Scheme 1), as it always happen to irradiated UHMWPE, but reaction 15 (Scheme 3) between UHMWPE and methylacetylene also occurs, and further pendent *trans*-vinylene are produced.

The concentration of pendent *trans*-vinylene (Table 3) has been estimated as follows:

Table 2
Summary of the tensile properties for samples irradiated to doses ranging between 0 and 100 kGy in the presence or absence of additives

	Dose (kGy)	Reference unirradiated	Irradiated in nitrogen	Irradiated in methylacetylene	Irradiated in ethylene	Irradiated in 1,7-octadiene
Ultimate tensile stress (MPa)	0	43.5 ± 1.2	–	–	–	–
	25	–	48.2 ± 1.4	44.3 ± 2.0	46.3 ± 1.7	48.5 ± 1.7
	50	–	47.0 ± 1.2	39.2 ± 1.8	42.4 ± 1.6	45.6 ± 1.6
	100	–	37.5 ± 2.3	35.0 ± 1.7	39.1 ± 1.8	41.3 ± 2.1
Elongation at break (%)	0	875 ± 17	–	–	–	–
	25	–	851 ± 21	798 ± 20	866 ± 17	781 ± 18
	50	–	810 ± 17	650 ± 18	741 ± 17	728 ± 18
	100	–	512 ± 30	525 ± 16	600 ± 19	663 ± 21
Tensile stress at 500% elongation	0	23.8 ± 1.3	–	–	–	–
	25	–	27.5 ± 1.2	25.6 ± 1.6	25.6 ± 1.5	28.1 ± 1.1
	50	–	28.9 ± 1.3	28.3 ± 1.4	26.7 ± 1.1	29.4 ± 1.0
	100	–	35.8 ± 1.6	32.9 ± 1.4	31.2 ± 1.2	30.5 ± 1.1

$[trans - vinylene]_{pendent}$

$$= [trans - vinylene]_{TOT} - [trans - vinylene]_{internal}$$

where $[trans - vinylene]_{TOT}$ was calculated from the 965 cm^{-1} absorption on the spectra of irradiated samples soaked in methylacetylene and $[trans - vinylene]_{internal}$ was assumed to be equal to that measured in the samples irradiated under nitrogen in the absence of additives, as the formation of internal vinylene upon irradiation does not seem to be affected by the presence of additives.

Jones et al. reported the formation of polyene crosslinks in polyethylene irradiated in the presence of acetylene [18], but in the present case conjugated double bonds (*trans-trans*-vinylene, 983 cm^{-1}) were almost undetectable. Then, it can be concluded that the polymerisation of methylacetylene, initiated by secondary macroradicals formed by irradiation, quickly terminates via chain transfer, as already discussed for ethylene, and that further additions to the resulting short branching (reaction 14) are unlikely.

The number of total pendent units is proportional to the absorbed dose, thus to the amount of free secondary macroradicals formed by irradiation (Table 3). Methylacetylene units react mostly according to reaction 15, more favoured than reaction 12 for sterical and thermodynamical effects, giving *trans*-vinylene unsaturation, which are ineffective for further crosslinking.

4.3. 1,7-Octadiene

Samples soaked in 1,7-octadiene show, after irradiation and removal of the unreacted additive, an increase in vinyl end groups (Figs. 2(b) and 5) due to the addition of the diene to UHMWPE, according to reaction 16 (Scheme 4). The high concentration of resulting vinyl groups indicates that, as in the other cases, the reaction of the new pendent units with macroalkyl radicals to form bridges (reaction 17) is, at this stage, unlikely.

The concentration of internal *trans*-vinylene increases proportionally with the absorbed dose, to the same extent than in additive-free UHMWPE irradiated under nitrogen (Figs. 2(b) and 4).

The overall concentration of new short branches formed upon irradiation in methylacetylene and 1,7-octadiene, respectively, is reported in Table 3.

The analysis of the new species formed in the presence of additives (100 kGy, 11–26 mmol/kg of reacted molecules, compared to 16 mmol/kg of internal unsaturation) indicates that in fact the addition of the additive competes with the hydrogen elimination, even if the latter is thermodynamically favoured [6]. The concentration of diffused methylacetylene, estimated from solubility data [31], was 0.27 mol/kg, while that of 1,7-octadiene, experimentally calculated from the FTIR absorption of the vinyl group, was 1.10 mol/kg.

Then, the ratio of the concentration of 1,7-octadiene to that of methylacetylene was approximately 4, while the average ratio of formed short branching is ca. 2. This indicates that the process depends substantially on the absorbed dose, i.e. on the amount of formed radicals, rather than on the additive concentration. A further confirmation comes from the high efficiency of the reaction of vinyl double bonds in the original UHMWPE even if their concentration is very low (ca. 5 mmol/kg). Therefore, a very high rate of transfer of the secondary macroradical must be assumed.

The concentration of radicals measured after irradiation with 25 kGy is about 10 mmol/kg [34]. The formation of alkyl radicals arises from the scission of a C–H bond and further migration of the H radical. It can be assumed, since

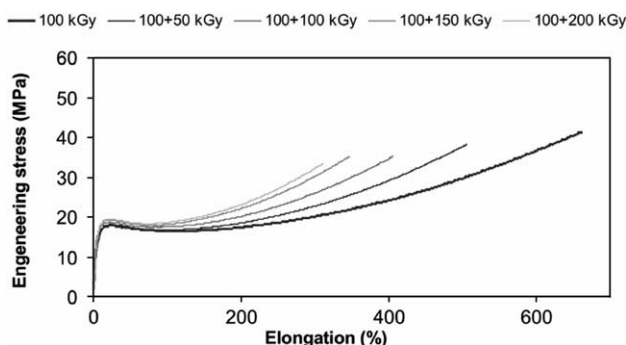
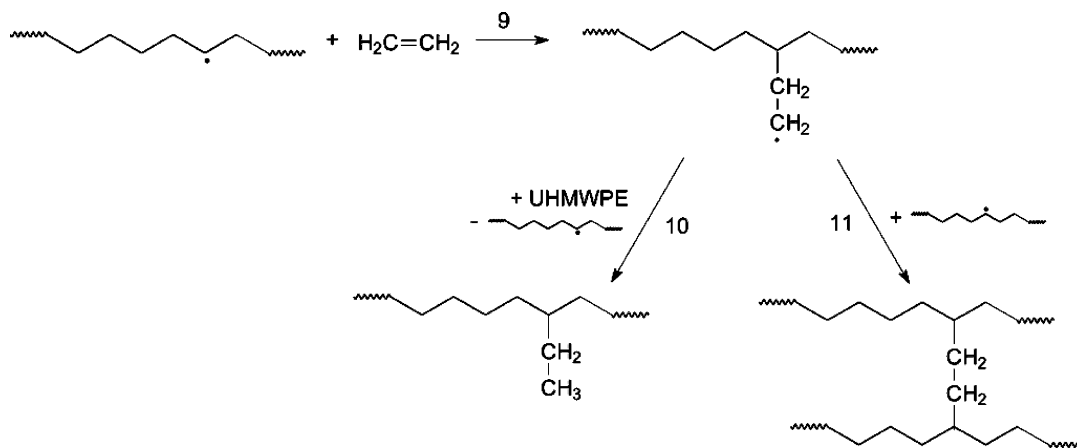
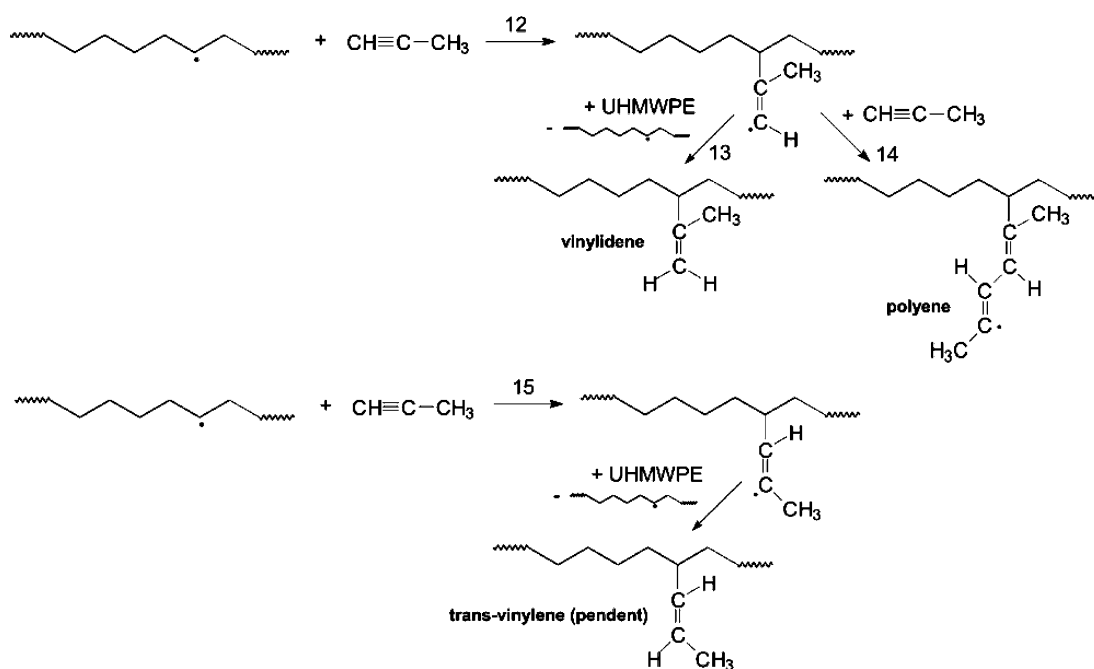


Fig. 9. Stress–strain curves for samples soaked in 1,7-octadiene and irradiated in multiple passages.



Scheme 2.



Scheme 3.

the crystallinity is about 50% that approximately half of the formed macroradicals are in the amorphous phase and half in the crystalline one.

In the crystalline phase, radicals have a longer lifetime. In the amorphous phase they react according to reaction 5 giving internal unsaturation. The presence of additives does not seem to affect the formation of internal unsaturation (Fig. 4). This indicates that to reaction 9, 12, 15 and 16 always follows an intermolecular extraction, with the formation of a secondary radical, which in turn will give further reactions.

4.4. 1,7-Octadiene—second irradiation

Samples soaked in 1,7-octadiene and irradiated for the second time at increasing e-beam doses show a decrease in vinyl double bonds (Fig. 8(a)) and the formation of new

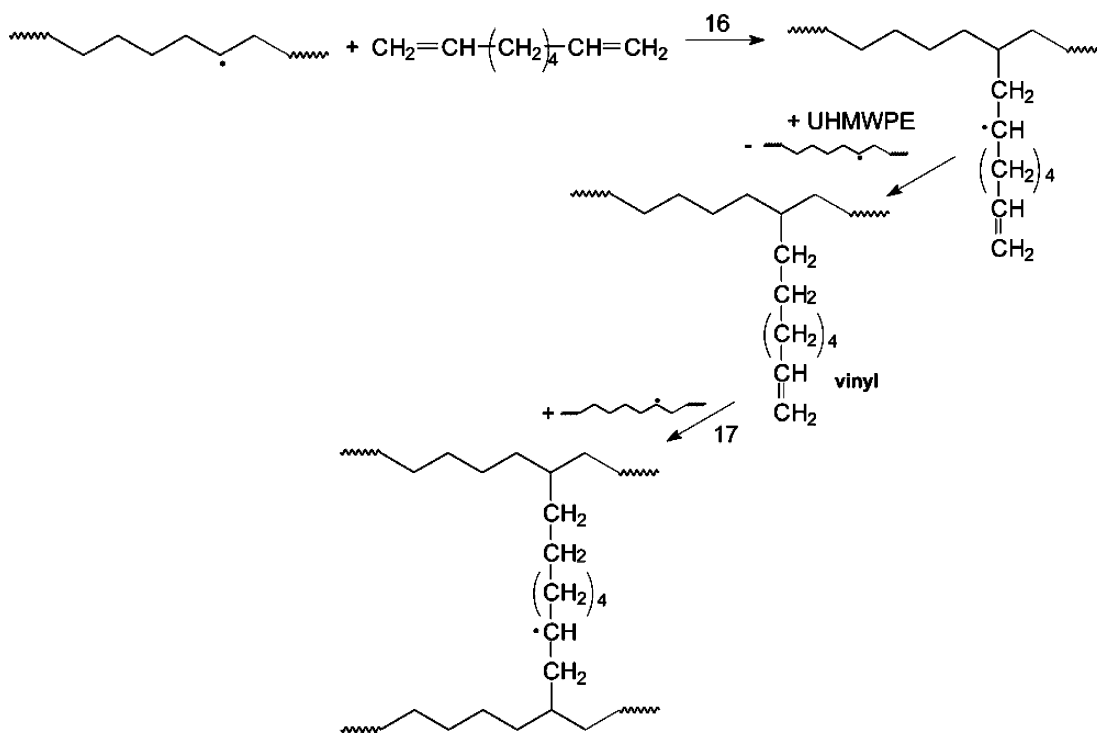
trans-vinylene (Fig. 8(b)) and *trans-trans*-vinylene double bonds (Fig. 8(c)).

Vinyl groups are consumed through the formation of crosslinks (reaction 17, Scheme 4), while *trans* and

Table 3

Total short branching formed after irradiation of samples soaked in methylacetylene and 1,7-octadiene

[Unsaturation] (mmol/kg)/dose (kGy)	0	25	50	100
<i>trans</i> -Vinylene in nitrogen	–	4.7	8.3	16.0
<i>trans</i> -Vinylene in methylacetylene	–	7.0	12.7	25.0
Pendent <i>trans</i> -vinylene ($\text{RCH}=\text{CH}-\text{CH}_3$) in methylacetylene	–	2.2	4.5	9.0
Side vinylidene ($\text{R}'\text{RC}=\text{CH}_2$) in methylacetylene	–	0.8	1.0	1.8
Total short branching in methylacetylene	–	3.0	5.5	10.8
Vinyl in nitrogen	5.5	4.3	3.7	3.0
Vinyl in 1,7-octadiene	–	10.0	16.5	29.3
Total short branching in 1,7-octadiene	–	5.7	12.8	26.3



trans-trans-vinylene are formed through the same path described above (reaction 5, Scheme 2).

4.5. Tensile properties

It is widely known that crosslinked UHMWPE exhibits a lower tensile strength and elongation at break than original UHMWPE [12].

In our case, all the irradiated samples exhibit a lower ultimate stress and elongation at break, compared to the unirradiated control, but they show a higher tensile stress at the same elongation (Table 2). This occurs because the presence of crosslinking between chains causes an increase in the force required to achieve the same elongation.

No significant differences are observed among samples soaked with different agents, confirming the hypothesis that, at this stage, the extent of crosslinking depends almost exclusively on the vinyl chain ends present in the original polymer.

Samples diffused with 1,7-octadiene and irradiated in two passages (Fig. 9) exhibit a further decrease in elongation to break and ultimate stress, which is proportional to the overall absorbed dose and then to the concentration of formed *trans*-vinylene. The tensile stress at the same elongation increases with increasing the irradiation dose, when a significant decrease of the vinyl double bonds indicates a higher degree of crosslinking (Table 4).

In the authors' opinion, a few chain scissions and small changes in crystallinity [12] arising from irradiation cannot explain such a significant variation in the tensile properties.

Irradiation of UHMWPE leads to the formation of a number of internal unsaturation (*trans*-vinylene), proportional to the absorbed dose. Some kinetic models of fracture indicate

a correlation between the logarithm of the time to failure and the activation energy of the omolitical scission of the polymeric bonds [35]. The energy associated to a C–C bond is 338 kJ/mol, while the energy required for the scission of a C–C bond in β to one or two vinylene double bonds is 292 or 250 kJ/mol, respectively.

Fig. 10 reports the concentration of *trans*-vinylene internal unsaturation versus ultimate elongation for samples irradiated in the presence or in the absence of 1,7-octadiene. In both cases, the decrease in the ultimate tensile stress and elongation at break appears to be proportional to the amount of vinylene double bonds formed upon irradiation. Furthermore, a lower elongation at break at the same vinylene content for the additivated specimens can be explained by taking in account that, in this case, a higher degree of crosslinking prevents free sliding of the polymer chains.

5. Conclusions

The results of this study confirm the hypothesis that crosslinking in irradiated UHMWPE takes place through

Table 4
Vinyl end groups content and tensile stress at the same elongation for samples irradiated with multiple passages in the presence of 1,7-octadiene

Dose (kGy) 100+...	Tensile stress (MPa) at 300% elongation	[Vinyl] (mmol/kg)
0	20.0	29.3
50	22.7	11.8
100	25.9	7.6
150	30.0	5.4
200	32.1	4.8

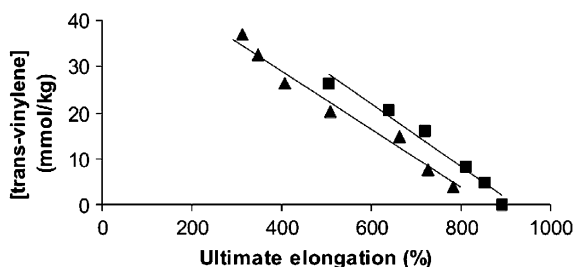


Fig. 10. *trans*-Vinylene internal unsaturation versus ultimate elongation for samples irradiated in nitrogen (■) or in the presence of 1,7-octadiene (▲).

the reaction between vinyl double bonds and secondary alkyl radicals formed upon irradiation. The addition of 1,7-octadiene, which provides additional vinyl double bonds to the polymer, has been shown to enhance the crosslinking efficiency. On the contrary, methylacetylene and ethylene, providing additional pendent vinylidene and primary radicals, respectively, did not show any improvement in crosslinking. This demonstrates that other pendent groups are not as effective as vinyl double bonds at forming crosslinking upon irradiation.

Moreover, an inverse relation was observed between the concentration of *trans*-vinylene unsaturation and elongation at break, suggesting that the formation of this kind of double bonds can be responsible for the observed decrease in some tensile properties.

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