

Thermal Degradation of Electron Beam Crosslinked Polyethylene and (Ethylene–Vinylacetate) Blends in Hot Water

S. Hassanpour, F. Khoylou, E. Jabbarzadeh

Gamma Irradiation Center, Atomic Energy Organization of Iran, P.O. Box 11365-8486, Tehran, I. R. Iran

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ABSTRACT: Low-density polyethylene and (ethylene–vinylacetate) blends in pure form were exposed to electron beam radiation at doses between (80–150) kGy, at room temperature, in air. Postirradiation thermal aging was done through immersing the samples in hot water at 95°C. Mechanical properties and changes in chemical structure were determined after 1500 h. Accelerated oven aging test was carried out on thin films after immersing them in hot water for 1000 h. Heat aging treatment showed that the blends have a convenient thermal stability compared to polyethylene. Although elongation at break and tensile strength de-

creased after heat aging procedure, obviously, this reduction was lower in blended samples than that of pure PE. In all samples, hydroxyl and transvinylene unsaturated end groups were formed during heat aging in hot water. Formation of these groups was less in blends at doses between 80–100 kGy, but was higher at 150 kGy than pure polyethylene. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2346–2352, 2003

Key words: crosslinking; degradation

INTRODUCTION

Over the last decay, plastic pipes have been found in ever-increasing use for hot water installation. Flexibility, great length, and easier handling of the plastic materials are decisive advantages in comparison with metal or nonplastic materials. Because of low thermal resistance, uncrosslinked polyethylene cannot be used in hot water pipes. Improvement in thermal stability, creep resistance, and long life service will be obtained by crosslinking. Desirable degree of crosslinking in hot water pipes is about 70%. Although most factories produce crosslinked PE pipe by chemical methods, radiation crosslinking in comparison with chemical crosslinking offers some distinct advantages: (1) radiation crosslinking is carried out without addition of initiator; (2) the process is very fast, clean, and can be controlled precisely; and (3) the reaction is carried out at lower temperature in comparison with chemical operation.

In this method the risk of precuring during production of pipe and the obligatory use of specific process is eliminated.^{1–6}

Low-density polyethylene is one of the most important plastics. Many scientists have studied their crosslinking behavior, structure, and properties.^{7,8} Polyethylene could be easily crosslinked without any

additives. It shows a quite desirable low-chain scission in comparison with other polyolefines. Crosslinking mainly occurs in the amorphous phase of polyethylene.^{7–10} Radiation crosslinking makes the polyethylene hard and split easily at low temperatures. Ethylene vinyl acetate, which is a rubber-like copolymer, has been used to overcome this weakness of polyethylene. Ethylene vinyl acetate increases radiation crosslinking yielding and flexibility of polyethylene and prevents its splitting.^{11,12} The effect of electron beam radiation on the electrical and mechanical properties of polyethylene and ethylene vinyl acetate in the presence of various types of sensitizer have been reported.^{1,13–15}

Thermo-oxidative degradation is serious in the range of 80–120°C. Thus, in designing of hot water pipes, thermal stability of polymer, resistance of the antioxidants, and other additives to extraction into hot water is important.¹⁶

In this work thermal stability of irradiated low-density polyethylene and (polyethylene–vinyl acetate) blends in hot water has been investigated. The effect of antioxidants and other additives on radiation crosslinking and the stability of them during heat aging in hot water will be presented in the next article.

EXPERIMENTAL

Materials

LDPE (0075 pipe grade with a melt flow index of 0.7 g/10 min) was supplied from Bandar Emam petro-

Correspondence to: E. Jabbarzadeh (mjabbarzadeh@seal.neda.net.ir).

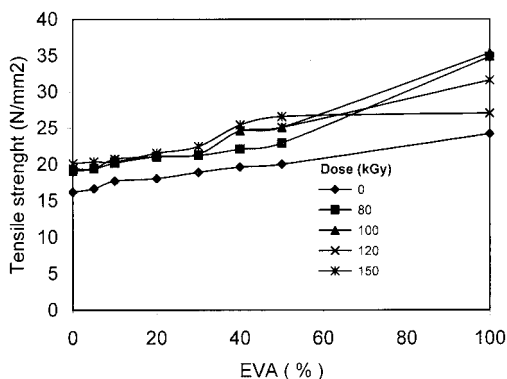


Figure 1 Variation of tensile strengths of LDPE blends as a function of different amounts of EVA at various irradiation doses.

chemical Co., Iran. EVA, with 18% vinyl acetate content and melt flow Index of 1.85 g/10 min, was prepared from Hyundai petrochemical Co., Korea.

Sample preparation

LDPE/EVA blends at ratios of 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100, which have been represented with code names (L0, L95, L9, L8, L7, L6, L5, L4, E0) were prepared. The constituents were first drum mixed and then the mixture was fed into a laboratory extruder (Axon ab Co.). The L/D ratio of the screw was 20 within a 150–170°C temperature profile.

The homogenous extrudate was ground in a Retschmuhle cutting mill. Sheets with the thickness of 2 mm were prepared in a hydraulic Collin Press at 150°C and then were cooled in water. Specimens for irradiation and mechanical testing were cut from the sheets. The films for IR test were prepared with the thickness of 0.15 mm.

Irradiation was carried out in air condition using a Rhodotron type electron beam accelerator at acceleration voltage of 5 MeV. The dose rate was 50 kGy/pass. Irradiation dose was selected in the range of 80–250 kGy.

Mechanical properties

Tensile test was carried out on dumbbell-shaped specimens using the Instron tensile machine model Zwick 1425 with a crosshead speed of 50 mm/min. Ultimate tensile strength and the elongation at break were determined for unirradiated and irradiated samples.

Thermal properties

To study the thermal aging property, irradiated samples were placed in a hot water bath for 1500 h. The loss of elongation at break was measured as a function

of EVA concentration at different irradiation doses. Accelerated thermal aging test was studied for irradiated thin films at 150 kGy after 1000 h thermal aging in hot water, in an oven at 140°C with air inflation. The changes in chemical structure were monitored for different periods of time with the maximum of 2 h.

Fourier transform infrared spectroscopy

FTIR analysis was performed with a Bruker IFS- 45 Fourier transform infrared spectrometer. The absorptivity of bands at 1895 cm^{-1} , 1716 cm^{-1} , 3365 cm^{-1} , and 962 cm^{-1} were used to monitor relevant chemical changes during the thermal aging in hot water and in accelerated conditions.

Gel content

Gel content was determined by the method of soxhelt extraction with xylene for 12 h. The remaining samples were dried in a vacuum oven at 70°C for 24 h.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 illustrates the variations of tensile strength (T_s) as a function of EVA percentage at various irradiation doses. It was shown that the tensile strength of LDPE improved with the addition of EVA content in all unirradiated samples. Tensile strength of all samples increased after irradiation. In pure EVA, T_s was the highest at radiation doses up to 100 kGy, but when applied dose of radiation reached 120–150 kGy, T_s dropped gradually. It was reported^{12,17} that to get the optimum mechanical properties of EVA, the irradiation dose should not exceed 150 kGy, which is approximately equal to the critical dose obtained in our experiments. It can be explained that due to inductive effect of the ester groups in EVA, the alpha hydrogen

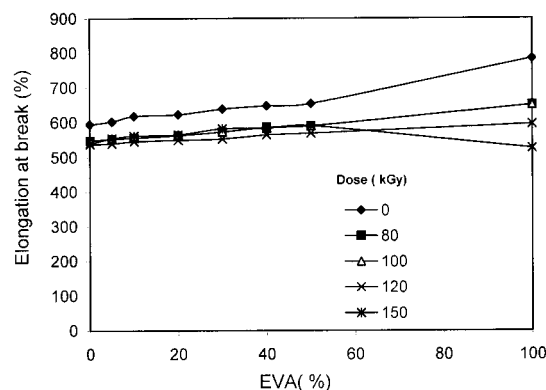


Figure 2 Variation of elongation at break of LDPE blends as a function of different amounts of EVA at various irradiation doses.

TABLE I
Elongation at Break (%) of the Irradiated Samples after 1500 h Thermal Aging in Hot water

Samples	Dose 80			Dose 100			Dose 120			Dose 150		
	0 h	1500 h	% loss	0 h	1500 h	% loss	0 h	1500 h	% loss	0 h	1500 h	% loss
L0	550	270	51	548	193	65	538	353	34	540	420	22
L95	560	519	7	553	513	7	540	486.7	10	555	435	21
L95	570	524	8	556	522	6	546	491	10	562	441	20
L8	577	540	6	563	530	6	550	493	10	565.5	487	14
L7	581	550.7	5	573	531	7	553	501	9	582.6	502	14
L6	590	568	4	586	546	7	564.9	524	7	583	510	13
L5	592	570	4	590	565	4	569	543	5	591	534	10
E0	664	600	10	651			596			527	480	9

atoms in respect to $-\text{OCOCH}_3$ group are more liable. Therefore, even at lower doses, they could easily be knocked out during irradiation, leading to the formation of largely crosslinked structure. At higher irradiation doses the crosslinked structure breaks down to form a small network structure, making the tensile strength decrease quickly. In the case of PE, the tensile strength changes marginally with the change of gel content due to the lack of the above structural feature. Also, both crosslinking and chain scission take place simultaneously over the whole range of irradiation doses.⁶ Figure 2 shows the variations of elongation at break (E_b) for the samples at different irradiation doses. Unirradiated blends with high content of EVA show high value of E_b . In all irradiated samples E_b decreases due to the formation of three dimensional network structure. E_b is lowest in EVA at 150 kGy.

The effects of thermal aging on mechanical properties

The thermal aging properties were determined by heating the irradiated samples in hot water at 95°C for 1500 h. The loss of E_b and T_s as a result of thermal aging were measured, and the values are shown in Tables I–II, respectively. It can be recognized that L0 has the maximum loss of E_b and T_s at all doses. Moreover, for L0, loss of E_b and T_s reduced with the increase of radiation dose. The blended samples show lower loss of E_b and T_s in comparison with pure poly-

ethylene. Loss of E_b in blended samples at 150 kGy is more than other doses. Consequently, although the amounts of oxygen in water is low, but heat aging at 95°C, causes thermo-oxidative degradation of samples during long time immersion in hot water. Also, it is noticeable that the thermal stability of L0 increased with the higher radiation doses, whereas in blended samples it decreased. Furthermore, it can be recognized that the thermal stability of PE improved with addition of EVA concentration.

FTIR study

The oxidation extent of polyethylene and its blends was followed by monitoring the increase in carbonyl, hydroxyl, and transvinylene unsaturated groups at the surface of the materials. During the thermal aging in hot water, the carbonyl groups are formed in the polyethylene chains. As depicted in Figure 3, the carbonyl absorbency of LDPE has been magnified after aging and with the increase of radiation dose. The increase of the carbonyl group due to aerial oxidation in the irradiated polyethylene samples has been reported by some other researchers.⁸ Because of high intensity of the peak in the region of 1737 cm^{-1} related to carbonyl groups in EVA, we could not detect these groups in blends. Figure 4(a)–(c) describes the variation of absorbency at 3365 cm^{-1} related to the existence of hydroxyl groups at different doses. An in-

TABLE II
Tensile Strength (N/mm²) of the Irradiated Samples after 1500 h Thermal Aging in Hot Water

Samples	80 kGy			100 kGy			120 kGy			150 kGy		
	0 h	500 h	% loss	0 h	1500 h	% loss	0 h	1500 h	% loss	0 h	1500 h	% loss
L0	19	10	45	19	10	47	19	12	39	20	15	25
L95	19	17	13	19	18	9	19	18	7	20	18	11
L9	20	17	16	21	18	14	21	18	11	20	19	7
L8	21	19	11	21	19	10	21	19	12	22	20	8
L7	21	19	9	21	20	8	21	21	4	22	21	7
L6	22	20	9	25	20	19	25	22	11	25	24	7
L5	23	21	9	25	23	10	25	23	9	27	24	9
E0	35	30	14	35			32			27	24	12

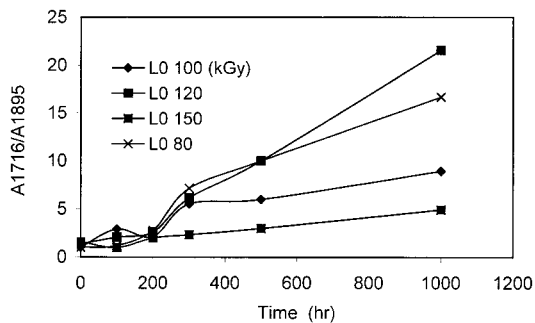


Figure 3 The effect of thermal aging in hot water on carbonyl formation in pure LDPE at different irradiation doses.

crease of hydroxyl absorbency for all samples was observed during thermal aging in hot water, whereas absorbency at the 3365 region was higher for L0. Moreover, the hydroxyl absorbency declined with higher vinyl acetate content for samples irradiated at 80–100 kGy [Fig. 4(a)–(b)]. Hydroxyl absorbency of L6 and L5 at 150 kGy, was quite higher than that of L0 [Fig. 4 (c)]. In Figure 5(a)–(c) the formation of transvinylene unsaturated groups at the region of 962 cm^{-1} is shown. At 80 and 100 kGy, L0 shows higher increase in absorbency of 962 cm^{-1} than L5 and L6 after thermal aging [Fig. 5(a)–(b)]. In contrast, at high radiation doses (150 kGy), L0 had less transvinylene group than blends [Fig. 5(c)]. It can be explained that with the increase of vinyl acetate content, the mobility of the α -hydrogen atom increases and then they split off

easily upon irradiation, so the number of macroradicals increases with the increase of vinyl acetate content. At high radiation doses there are many macroradicals that easily react with oxygen to produce peroxy radicals.⁶

Irradiated samples at 150 kGy that were aged for 1000 h in hot water were put in an oven at 140°C with inflating air. Figure 6 indicates that the absorbency at 3365 cm^{-1} gradually increases with higher amount of EVA content during accelerated thermal aging. Figure 7 shows the variation of absorbency in 962 cm^{-1} . It is clear that the absorbency in this region increases with the increase of vinyl acetate content. At higher temperatures and higher amount of oxygen when the applied dose is 150 kGy, degradation reaction accelerates and the extent of oxidation of blended samples increases significantly. Figure 8(a)–(c) illustrates the FTIR spectra of some of the selected samples, L0 and L5, to show the changes after irradiation and thermal aging procedure for unirradiated samples, for the samples, which were put in hot water for 1000 h after being irradiated at 150 kGy and for the specimens, which were aged in oven at 140°C, respectively.

Gel content

Figure 9 shows the changes of gel content in samples, which were irradiated in the range of doses between 80–250 kGy. The gel fraction increased regularly with the augment of radiation dose. High value of the gel

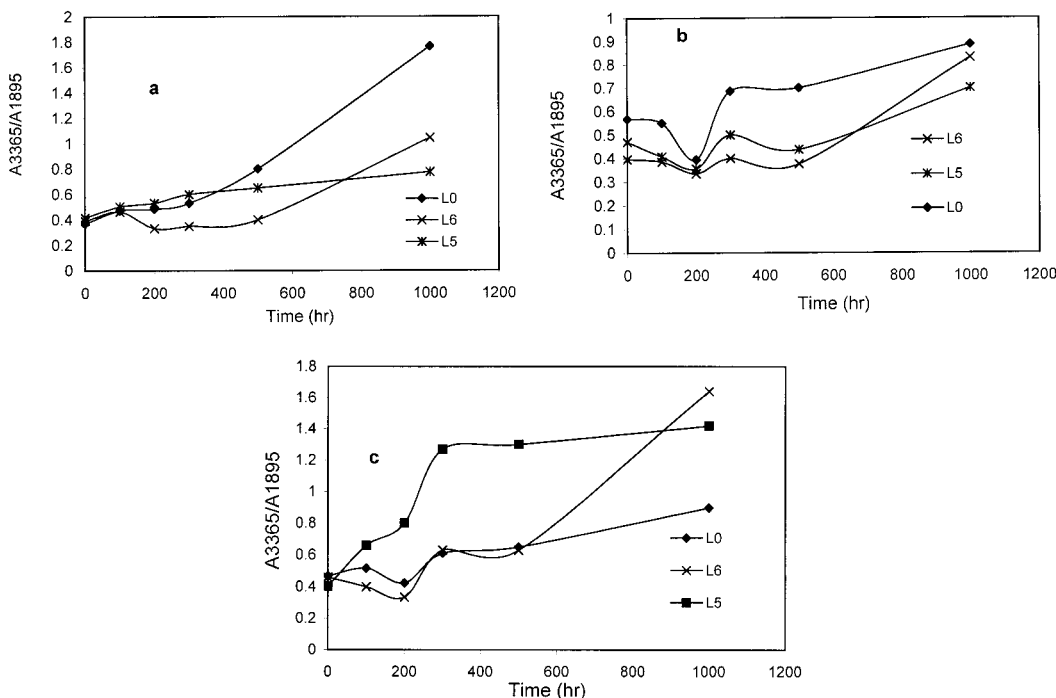


Figure 4 Formation of hydroxyl groups in irradiation samples during thermal aging in hot water at (a) 80 kGy, (b) 100 kGy, (c) 150 kGy.

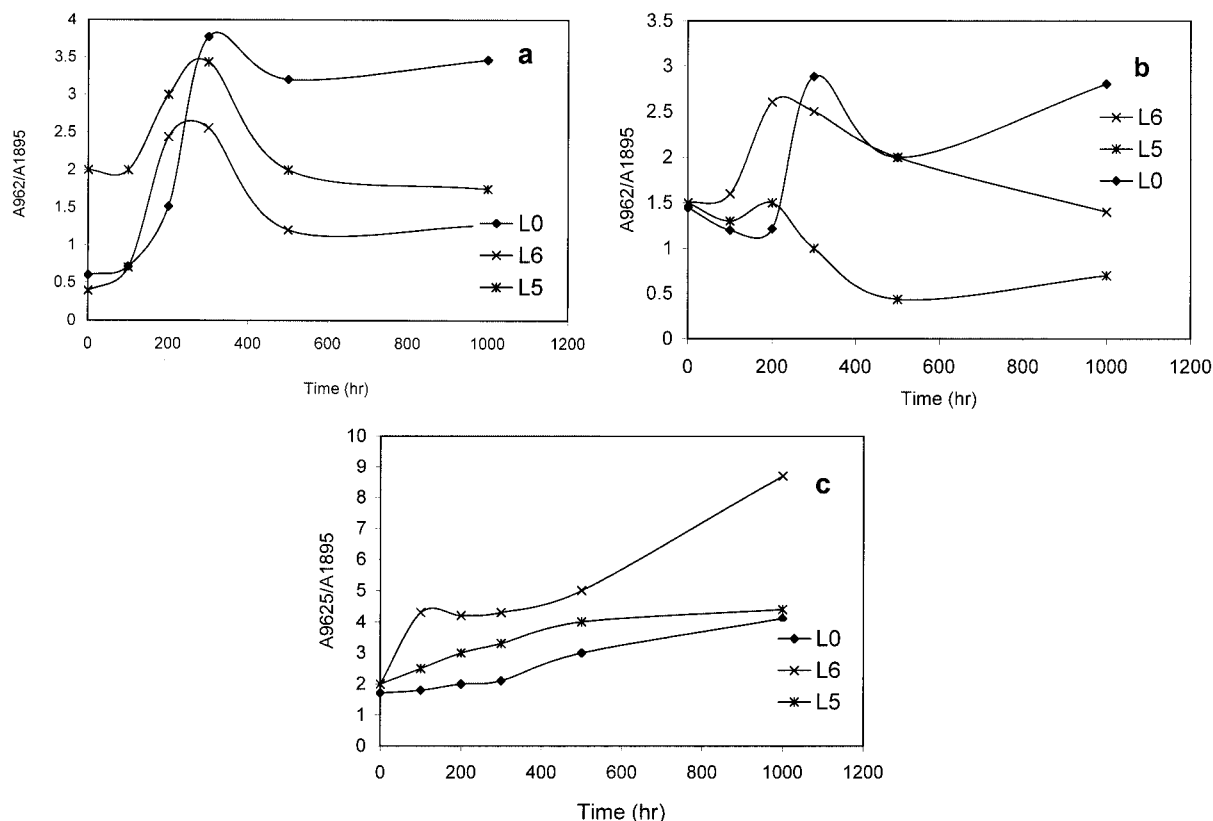


Figure 5 Formation of transvinylene bonds in irradiated samples during thermal aging in hot water at (a) 80 kGy, (b) 100 kGy, (c) 150 kGy.

content was obtained in all applied doses for L4 and L5, which have the highest concentration of EVA. The reason for superior crosslinking is due to increase of amorphous phase in blend samples. It was reported that radiation curing occurs mainly in the amorphous phase of the polymers.¹⁰ In the samples, which were irradiated at 250 kGy, gel content increased with the increasing of EVA percent in all compounds. In this method a high amount of gel fraction can be obtained at room temperature without changing the base for-

mulation. Contrarily, in the chemical method, achieving a high degree of crosslinking is dependent to the usage of a high percent of peroxide in the base formulation and to the elevation of temperature for curing, which both lead to chain scission in the polymers.^{18,19}

CONCLUSION

Irradiation of pure EVA at 80–100 kGy improved the mechanical properties of the polymer, but this prop-

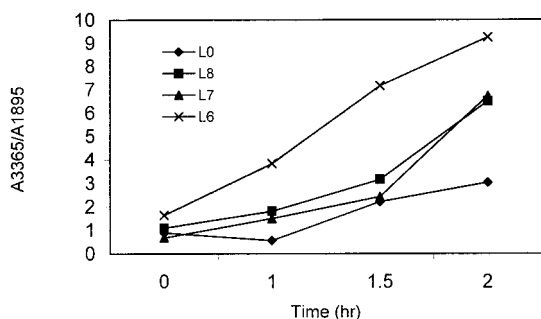


Figure 6 The effect of accelerated thermal oven aging at 140°C upon increase of hydroxyl groups in blend samples that were irradiated at 140 kGy and immersed in hot water for 1000 h.

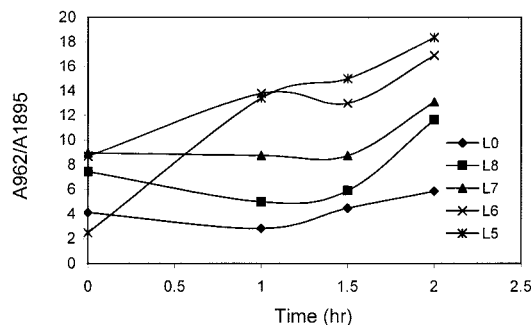


Figure 7 The effect of accelerated thermal oven aging at 140°C upon increase of transvinylene bonds in blend samples that were irradiated at 150 kGy and immersed in hot water for 1000 h.

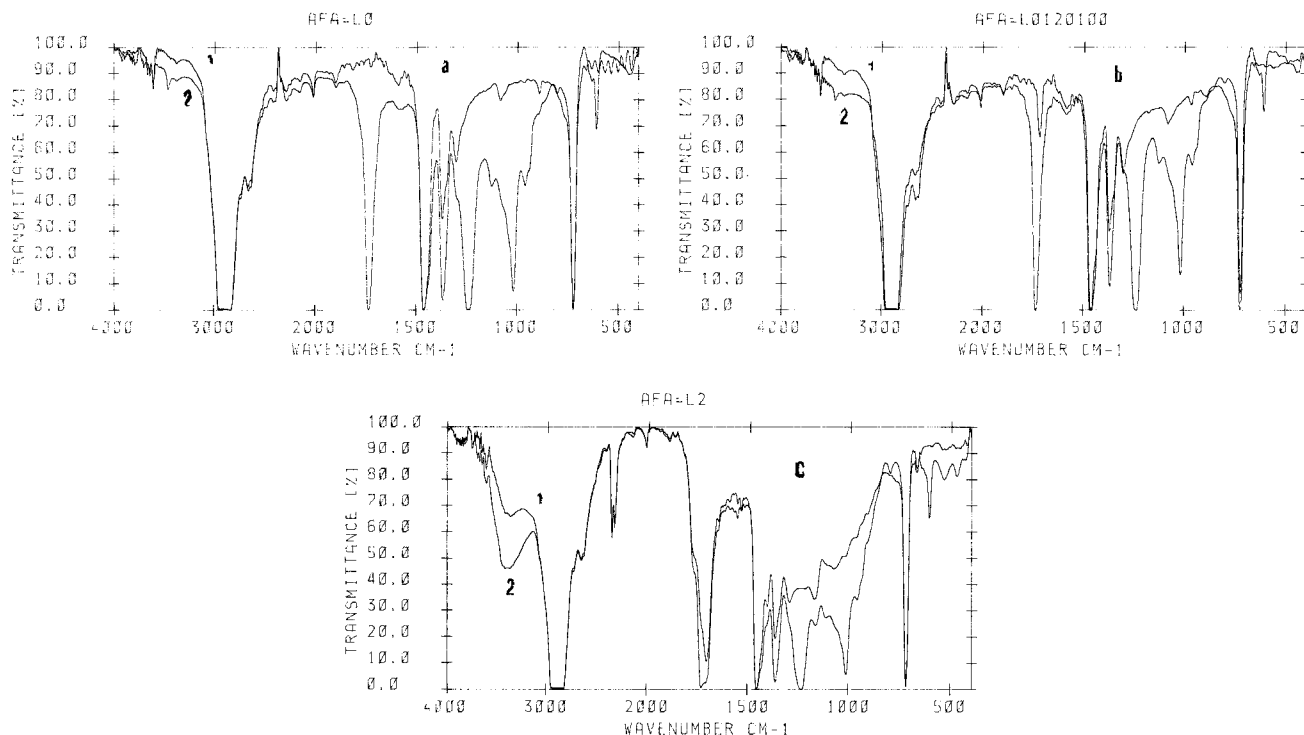


Figure 8 FTIR spectra of (1) L0 and (2) L5 (a) unirradiated samples, (b) after 150 kGy irradiation and 1000 h immersion in hot water, c) after 2 h accelerated thermal oven aging on samples, which were irradiated at 150 kGy and immersed in hot water for 1000 h.

erty dropped with the increasing of the radiation dose up to 150 kGy. Increasing different concentrations of EVA up to 50% to polyethylene improved the mechanical properties of polymer blends after irradiation at applied doses.

Thermal aging of irradiated polymer blends outlines that blends have a higher thermal stability in comparison with pure LDPE, and they retain their mechanical properties during a long time immersion in hot water, except for the blends, which were irradiated at 150 kGy.

Thermo-oxidative degradation takes place in irradiated samples during heat aging in hot water at 95°C. Carbonyl, hydroxyl, and transvinylene unsaturated groups are formed during thermal aging in hot water in irradiated polyethylene. In blended samples, the amounts of hydroxyl and transvinylene unsaturated groups are less in comparison with pure polyethylene at lower doses. At high radiation doses more degradation occurs in blended samples. Furthermore, the number of hydroxyl and transvinylene unsaturated groups multiplied with the higher amount of ethylene-vinyl acetate. These factual results were confirmed by the results obtained from accelerated thermal oven aging process for all the samples after 1000-h immersion in hot water.

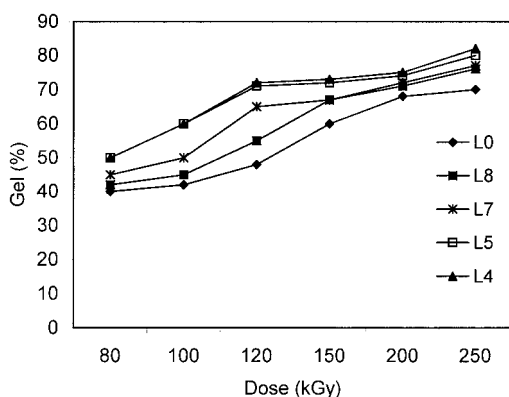


Figure 9 Effect of absorbed dose on gel content.

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