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The Effect of Radiation-Induced Cross-linking on Loss of Chimassorb 944 from Polyethylene/Ethylene-Vinyl Acetate Blend in Hot Water

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A B S T R A C T

Loss of a high molecular weight hindered amine light stabilizer (HALS) from irradiated low density polyethylene-ethylene vinyl acetate blends (LDPE/EVA) in hot water has been investigated. The effects of Chimassorb 944 and two trifunctional monomers, triallyoxy-1,3,5-triazine and 2-ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate on LDPE/EVA properties after irradiation and on migration of stabilizer from the polymer base during thermal aging in hot water have been studied. The samples in both pure form and mixed with additives were exposed to electron beam radiation at doses between 50 and 150 kGy, at room temperature, in air. In order to study the thermal aging property, irradiated samples were placed in hot water bath at 95ºC for 1000 h and in an oven at 140ºC for several hours. Irradiated samples showed noticeable changes in mechanical properties. Long term heat stability of polymer blend was improved significantly by using of polyfunctional monomers. From the results of the thermal aging procedures, the HALS showed a convenient influence on the increasing of the polymer blend thermal stability at 95ºC. However in the accelerated condition, the value of oxidation induction time (OIT) decreased as a result of depletion of HALS from the polymer base during the immersion in hot water.

Key Words:

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INTRODUCTION

In recent years, various radiations like x-rays, gamma and ultraviolet rays, and electron beam (EB) have been used in the cross-linking of various polymers and curing of paints, adhesives, etc. [1].

Radiation cross-linking is done on the shaped polymer. Thus, it is a one-step process leading directly to the cross-linked structure. The enhancement in properties of radiation cross-linked polyethylene includes temperature stability, resistance to attack by chemicals and solvents, high mechanical strength, and superior electrical properties. Moreover, radiation processing improves mechanical properties of the blend samples. As it has been reported, tensile strength

and gel content of polyethylene/ethylene-vinyl acetate copolymer blends improved after electron beam irradiation [2,3]. The increase in tensile strength is due to existence of alpha hydrogen atoms with respect to $-COCH_3$ groups, which are more liable and even at low doses could easily be knocked during irradiation, leading to the formation of largely cross-linked structure [1].

Cross-linking and scission, which follow a free radical mechanism, are parallel and both are supposed to occur simultaneously during the irradiation of polyethylene and its blends. It was shown in the earlier paper that additional thermal oxidation degradation takes place in the irradiated polymer and its blends during their application at high temperature conditions [4]. Hence, most polymeric systems require the addition of stabilizers to provide protection during radiation processing and end use. The principal role of antioxidant is to transfer highly reactive alkyl, alkoxy, and alkyl peroxy radical into less reactive aromatic ones and simultaneously to lower the total level of free radicals by recombination.

In many applications such as pipes, not only the thermal stability of polymeric materials but also, the resistance of mixed antioxidants as well as other additives to extraction into water are crucial [5]. Low molecular weight stabilizers introduced into a polymer may be consumed during the polymer lifetime. The consumption and physical loss of stabilizers depend on the nature of the additives, the nature and geometry of the polymer samples, the environment, and the solubility of the stabilizers in the polymer.

The consumption of the stabilizers occurs during chemical reaction in the presence of light, heat, and radiation, while the physical loss of the stabilizers occurs by diffusion towards the polymer surface during exposure and subsequent removal from the surface by evaporation, washing-out or diffusion into the material in contact with the polymer. The consumption and loss of the stabilizers accelerates the aging of the polymer more than thermal-oxidation or photo-oxidation. Moreover, loss of the stabilizer from LDPE films is accompanied by degradation of the polymeric matrix. Thus, loss of the stabilizer simultaneously, promotes matrix degradation and it is accelerated by the same matrix degradation [6].

High molecular weight hindered amine light stabilizers (HALS) provide stability against photo-oxidation and protect materials from UV light damage

and they are often included in the polymer matrix.[7]. Also, it was reported that thermo-oxidative stability of polyethylene could be enhanced by addition of HALS stabilizer. They have high extraction resistance and cause long-term stabilization in the polymer. The stabilizing effect of HALS is generally attributed to free radical scavenging and to some extent to hydroperoxide decomposition [7].

Chimassorb 944, which is a HALS stabilizer, is safe for medical usage as it does not dissolve or leach out in the aqueous medium primarily used for drug delivery through the syringes and are also recommended by the manufactures as the food medical grade [8]. In polymer blends exposed to ionizing radiation to modify the properties of the polymer, antioxidants have to satisfy some additional requirements, for example they should be stable in the radiation field or should not interfere with the cross-linking process. There is much less information on the effects of irradiation and subsequent service temperature on Chimassorb 944 and many additives like polyfunctional monomers which are presented in LDPE/EVA.

The objectives were to identify the effect of ionising radiation and post irradiation thermal treatment on consumption and loss of Chimassorb 944 from LDPE/EVA in the presence of polyfunctional monomers to develop LDPE/EVA compounds that upon electron beam irradiation yield materials with better mechanical properties and service temperature. For this purpose the influence of triallyoxy-1,3,5-triazine and 2-ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate on migration of Chimassorb 944 from irradiated LDPE/EVA blend in hot water has been investigated.

EXPERIMENTAL

The LDPE was a commercial resin with melt flow index of 0.7 g/10 min (0075, Bandar Emam Petrochemical Co., Iran). EVA with 18% vinyl acetate content and melt flow Index 1.8 g/10 min was prepared from Hyundi Petrochemical Co., Korea. The hindered amine light stabilizer, Chimassorb 944 is kindly donated by Ciba Gigy. Two polyfunctional monomers 2,4,6-triallyoxy-1,3,5-triazine (Aldrich) and 2-ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate (Merck) were used as cross-

Table 1. The base formulation of the samples.

Code*	A1(%)	M1(%)	M2(%)
E2	-	-	-
E3	0.25	-	-
E4	0.25	2	-
E5	0.25	-	2

(*) base formulation (LD/EVA 70/30 w/w %) ; A1: Chimassorb 944; M1: 2,4,6-trially-oxy-1,3,5-triazine ; M2: 2- ethyl 2-(hydroxymethyl)1,3- propandiol trimethacrylate.

linking agent. The sample compositions are presented in Table 1.

LDEP/EVA blend at ratio of 70/30 has been chosen due to its better thermal stability [4]. The constituents were first dry mixed, then the mixture was fed into an extruder with L/D=20 (Axon ab). The homogenous extrudate was grinded in a Rechmoul grounder. Plates with 0.5 mm thickness were prepared by a Collin press at 160ºC then, cooled with water. Specimens for irradiation and mechanical testing were cut from the plates.

The films for IR test were prepared in 0.15 mm thickness. Irradiation was carried out in air 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 between 50-150 kGy. The fraction of insoluble gel produced by cross-linking was determined by the extraction in xylene, according to ASTM D-2765.

Tensile measurements were carried out by means of a tensile machine model Zwick 1425. The changes in hydroxyl index (A3365/A1895) were followed. The absorbances at 3365 cm^{-1} and 1895 cm^{-1} are attributed to hydroxyl and reference groups, respectively. FTIR analysis was performed with a Bruker IFS-45 fourier transform infrared spectrometer. Oxidation induction time (OIT) measurements were carried out using a differential scanning calorimetry (DSC) Mettler-TC10A thermal analyzer under oxygen gas at 200°C.

Thermal Aging Procedures

The irradiated samples were aged in hot water at 95°C for 1000 h. The changes in chemical and mechanical structures were done in different time intervals. In order to estimate the thermo-stability of the samples after hot water aging, they were placed in a circulating air oven at 140°C for several hours [5]. The changes in chemical structure were monitored for different periods of time.
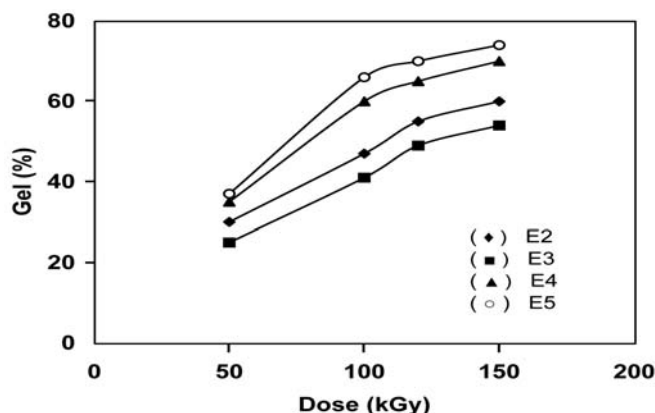

Figure 1. The effect of radiation dose on gel formation.

RESULTS AND DISCUSSION

Gel Fraction

The electron beam produces excited chemical species and free radicals. The free radicals then may undergo chain scission, cross-linking, and recombination of broken chains depending on the structure of polymers. The increased gel fraction indicates a cross-linking reaction.

Figure 1 shows that in the range of doses between (50-150) kGy gel fraction increases for all samples. In E2 and E3 because of the absence of the polyfunctional monomers, the lower amount of gel has been obtained. E3 has the lowest amount of gel percent than E2. This is due to the fact that existence of stabilizer in E3 prevents radical formation during irradiation and consequently reduces formation of network structure.

Generally, polyfunctional monomers are used in radiation cross-linking to obtain optimum properties and reduce the radiation dose level to reach the required cross-linking density. The reactivity of these monomers depends on various factors like their number of double bonds, shape, and size [9]. It can be seen that the significant cross-linking yield which is obtained for E4 and E5 at lower doses in comparison with E3, have good congruency with the above theory.

For E5, at 120 kGy, the gel content is about 70%, which is approximately equal to what had been reported for cross-linked PE in pipe [5], while the effective cross-linking reaction occurs at 250 kGy for pure samples in the previous work [4]. The slight difference in the cross-linking efficiency of E4 and E5 is related to the polyfunctional monomers structure incorporated in these
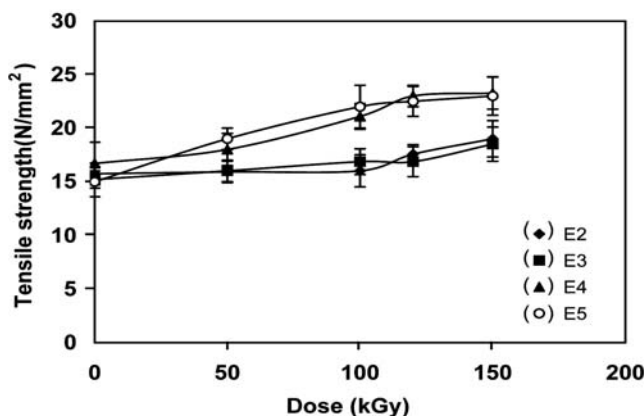
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Figure 2. Tensile strength of the samples vs. radiation dose.

Figure 3. Loss percent of elongation-at-break of the samples vs. radiation dose.

samples. It seems that in E5, polyfunctional monomer which has a branch-like structure with three methacrylate groups helps easy cross-linking mechanism with LDPE/EVA through these methacrylated moieties. In the case of E4 because of cyclic structure of polyfunctional monomer the molecule becomes bulkier, thus causing a difficult situation to easily diffuse into the polymer backbone.

Mechanical Properties

Figure 2 shows the effect of additives on the mechanical properties of irradiated samples. The tensile strength (Ts) of the specimens is plotted against different total doses. The tensile strength increases with increase of radiation dose for all samples. E2 and E3 have lower Ts than the others due to the lower gel content. E4 and E5 exhibited the highest Ts values that are nearly the same. Figure 3 demonstrates the elongation-at-break after irradiation; it decreases with increasing of radiation doses. E4 and E5 show lower elongation-at-break in comparison with E3. It can be explained that in E4 and E5 addition of polyfunctional monomers promotes rapid free radical propagation reaction leading to formation of network structures through grafting via their double bonds. These network structures results in higher Ts and lower elongation-at-break.

In order to study the extractability and stability of the additives, the specimens were placed in hot water for 1000 h. The changes of tensile strength and elongation-at-break for irradiated samples during thermal aging in hot water are illustrated in Figures 4a-4c and 5. Generally due to the low concentration of oxygen in hot water, thermo-oxidative degradation is insignificant
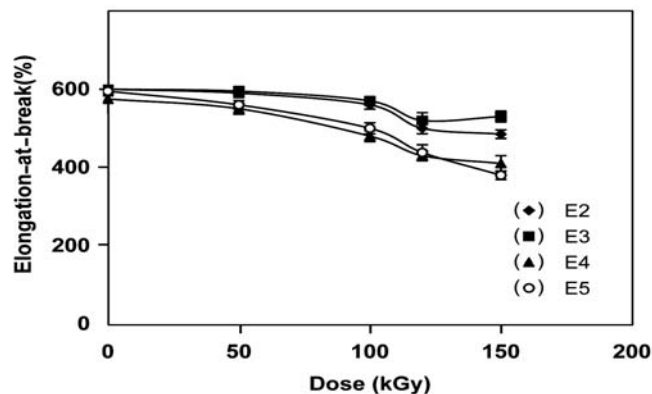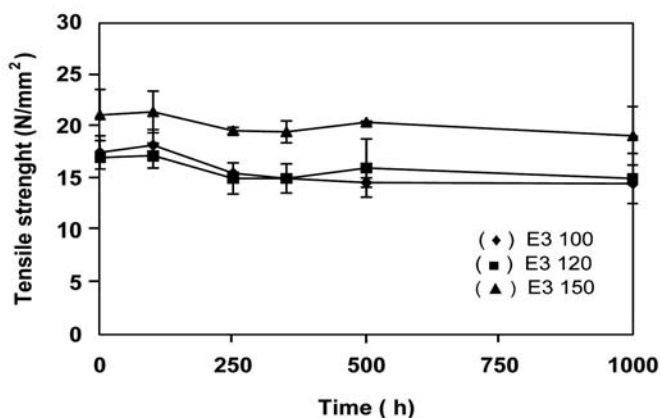
thus, the small changes of Ts and elongation-at-break is observed.

In Figure 4a the tensile strength of E3 at all doses declines during prolonged immersion in hot water. However, the tensile strength of E4 at 150 kGy in Figure 4b shows stable behaviour during prolonged periods in hot water. It can be inferred that existence of higher gel content in E4 impedes migration of the HALS to the contact medium.
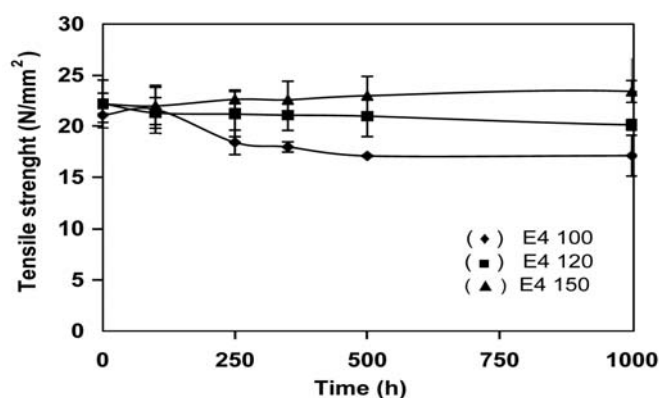
It should be mentioned that at the first stages, post cross-linking reactions occurs due to the presence of free radicals when air irradiated polymer exposed to high temperature conditions. The cross-linked structures affect on the segmental mobility of the polymer chains, resulted decrease in diffusion of the stabilizer out of the polymer matrix. The prolonged heat aging procedure resulted increase in the mobility of the polymer chains which cause loss of the stabilizer from the samples. However, loss of the stabilizer from the samples with high percent of gel content is less. It can be easily viewed in Figures 4a and 4b that the higher applied doses lead to higher thermal stability in E3 and E4.

In Figure 4c, the changes in tensile strength of E5 after 1000 h in hot water are shown. The samples, which were irradiated at 100 and 120 kGy are more stable in hot water for prolonged periods than those irradiated at 150 kGy.
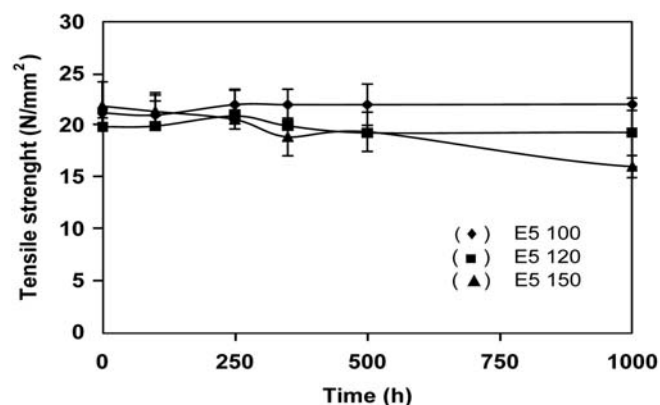
Figure 5 represents the variation of elongation-at-break during aging in hot water for the irradiated samples at 150 kGy. It is shown that elongation-at-break decreases slowly for E3. In spite of E4 that shows a constant pattern, elongation-at-break for E5 falls rapidly. Obviously, the changes in Ts at different doses of irradi-

(a)

(b)

(c)

Figure 4. Variation of tensile strength of the irradiated samples during thermal aging in hot water (a) E3, (b)E4, and (c) E5.

Figure 5. Variation of elongation-at-break of the irradiated samples at 150 kGy during thermal aging in hot water.

limit significant oxygen migration to the sample. Less oxygen availability would naturally lead to less oxidative degradation [10].

It is clear from Figures 4c and 5 that increasing of radiation dose to 150 kGy leads to reduction in tensile strength and elongation-at-break in E5 during heat treatment in hot water. It can be concluded that at high radiation dose chain scission takes place along with cross-linking to form a small network structure. Reduction in mechanical properties in E5 during thermal aging is a result of chain scission and formation of small network structures at 150 kGy. Lower thermal stability of E5 at high radiation dose is due to the presence of tri-functional methacrylate monomer (M2). Studies show that thermal stability of methacrylate is lower than acrylate monomers when they cure under EB irradiation [11].

FTIR Study

In order to investigate the changes in chemical structure, the changes at 3365 cm^{-1} region were followed during the thermal aging of irradiated samples. It can be seen in Figure 6 that hydroxyl group is formed during thermal aging. The rapid increase of hydroxyl group was observed at early times of aging, but it dropped at longer heat aging times. It can be explained that, when air-irradiated polyethylene is immersed in hot water after irradiation, cross-linking and scission, which follow a free radical mechanism, both occur simultaneously. The mobility of trapped radicals increases by heat and they easily react with oxygen to produce hydroxyl group. The reduction of hydroxyl group seems to occur because the oxidation products are converted to other com-

ated samples are not significant. The lower rate of degradation of irradiated samples is due to the high dose rates of electron beam irradiation which lead to formation of high concentration of free radicals during the exposure and much higher recombination reaction. In addition, the much shortened irradiation duration would
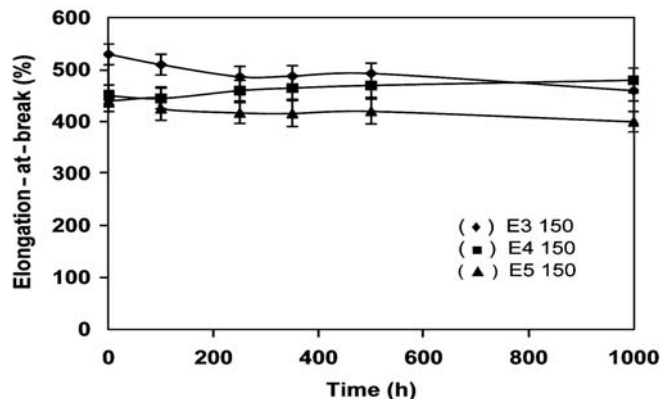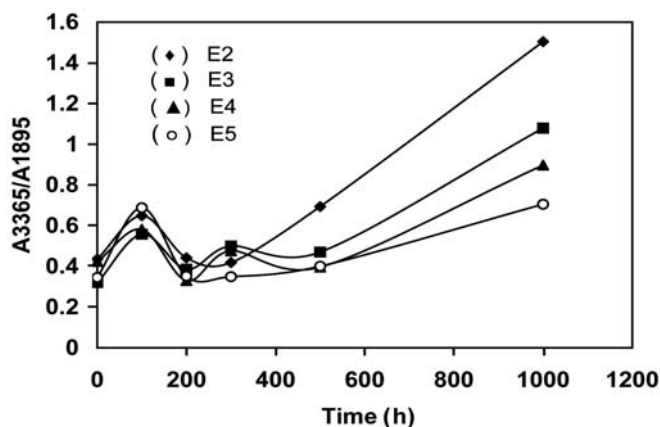
Figure 6. Formation of hydroxyl group of the irradiated samples at 120 kGy during thermal aging in hot water.

Figure 7. Variation of hydroxyl group of the irradiated samples at 100 kGy during accelerated thermal oven aging.

pounds by heat.

During prolonged heat aging hydroxyl groups increased in all samples. Incorporation of stabilizer and polyfunctional monomer to the polymer matrix results in decrease in hydroxyl group formation, and it is the lowest for E5 at 120 kGy. In E2 formation of hydroxyl group is higher due to the lack of polyfunctional monomer and stabilizer.

It seems that the superior efficiency of the HALS is related to production of nitroxyl radical similar to the mechanism in the presence of UV light and heat. HALS nitroxyl radicals are able to react with the polymer matrix, meaning that a certain amount of non-extractable compound can be formed. The fast conversion from piperidine moieties to nitroxyl radicals can readily occur in the presence of hydroperoxides [6,12].

In order to study both migration of the stabilizer and thermal stability of polyfunctional monomers, all irradiated samples, after 1000 h thermal aging in hot water, were put in the oven at 140°C. By studying the thermal stability of the samples after long time of exposure to hot water, an opinion can be formed as whether the antioxidant remains in the samples or not [5].

In Figure 7 it can be seen that the hydroxyl groups of E2 increase rapidly and it is damaged after short time of heating. Figures 7 and 8 indicate that at 100 and 120 kGy E5 has the best thermal stability due to the lowest hydroxyl group formation. In E3 it seems that migration of stabilizer is the highest due to the lowest gel content in this sample.

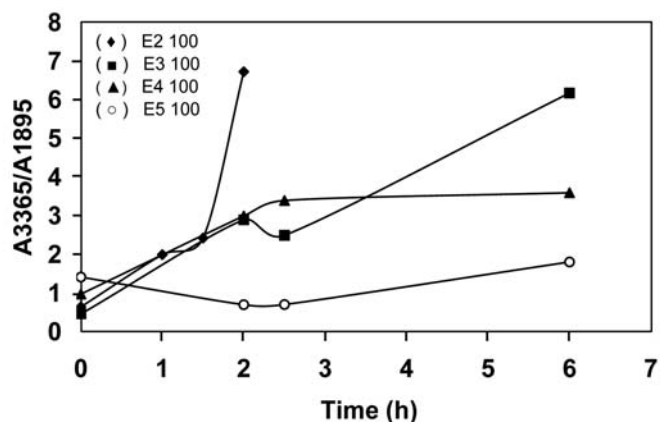It has been reported that polyfunctional monomers

increase the radical-radical reaction termination and hence decrease the extent of scission reaction and oxidation. It is expected that more highly cross-linked structures would have less oxygen permeability [11]. Comparing Figures 6 and 8 indicates that when the temperature is increased from 95°C to 140°C the hydroxyl Index sharply increases.

DSC Measurements

The isothermal DSC is a useful technique for determination of the thermo-oxidative stability of polymer. The oxidative induction time (OIT) is calculated from onset temperature. The first step in auto-oxidation reaction of polyethylene is the formation of free radicals. In the case of vinyl acetate copolymer the initial step in the degradation involves the formation of acetic acid and
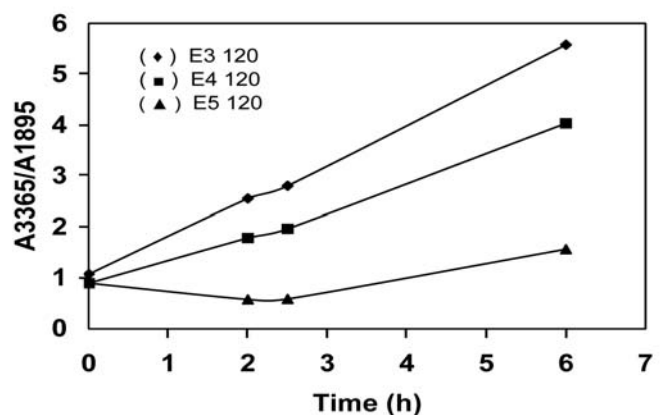

Figure 8. Variation of hydroxyl group of the irradiated samples at 120 kGy during accelerated thermal oven aging.
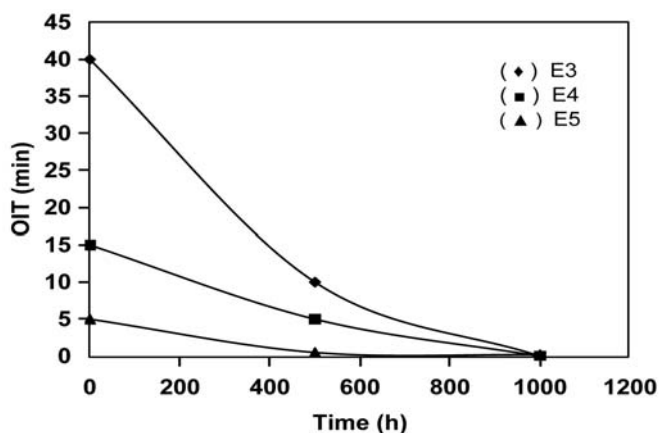
Figure 9. The changes in OIT of the irradiated samples during thermal aging in hot water (OIT for unirradiated E3, E4, and E5 are 40, 40, and 50, respectively).

breakdown of the main chain [13].

During the induction period free radicals are accumulated by the initiation reaction and by reaction of the existing radicals with oxygen. In the absence of inhibitors non-radical hydroperoxide decomposes, producing further free radicals accelerating their accumulation. In the unstabilized polymer, the induction period is short, especially at elevated temperatures [14]. The auto oxidation and degradation of polymer is retarded by addition of stabilizer.

Induction times as the function of heat aging time in hot water are shown in Figure 9. For all samples the induction time decreases with irradiation. It is most probably due to the depletion of the stabilizer by irradiation and change of its chemical composition. Also, it can be seen that the nature of cross-linking monomer plays an important role in the reactivity of the generated radicals.

The induction time of E5 is the highest and E3 has the lowest value of OIT after irradiation at 100 kGy. The value of OIT is influenced by the time of heating in hot water since it extremely decreases in the order: E5, E4, E3 after 500 h.

The smallest amount of induction time is obtained after 1000 h of heat aging time for all samples. It is most probably due to the depletion of A1 during heat aging in hot water for all samples. However, in the early stages of thermo-oxidative process the extent of gel fraction affects the rate of migration of the stabilizer from the polymer base.

It means that, segmental mobility of the polymer chains decrease due to the network structure, hence the loss of molecules of stabilizer from the polymer matrix decreases.

CONCLUSION

According to the results obtained, it can be concluded that addition of Chimassorb 944 enhanced thermal stability during immersion in hot water. But in accelerated conditions the value of oxidation induction time (OIT) shows that a amount of stabilizer decreases during immersion in hot water. However, the cross-linking monomers play an important role on decrease in the value of OIT during irradiation through the reactivity of the radicals with the stabilizer. It can be concluded that this kind of stabilizer cannot be used as an effective stabilizer in long time applications. Furthermore, its migration to hot water decreased as the gel content increased. Both used polyfunctional monomers enhanced gel fraction of the polymer. The promotion of cross-linking in E5 is due to its polyfunctional monomer structure. Highly cross-linked structure improves thermal stability of the polymer blends due to decrease in segmental mobility of the polymer chains which lead to less oxygen permeability and reduction in stabilizer migration from the polymer matrix. Results show that in comparison between two polyfunctional monomers M1 has better thermal stability than the other one because of cyclization and cyclopolymerization during irradiation [15]. In contrast, M2, which is a trifunctional methacrylate monomer has lower thermal stability at high doses.

ACKNOWLEDGEMENT

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