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INFLUENCE OF GAMMA IRRADIATION ON THE AGEING CHARACTERISTICS OF POLY(ETHYLENE-co-VINYL ACETATE) AND POLY(ETHYLENE-co-VINYL ACETATE)/CARBON BLACK MIXTURE

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In this comparative study, the effect of gamma rays on the ageing characteristics of poly(ethylene-co-vinyl acetate) (EVA) and poly(ethylene-co-vinyl acetate)/carbon black mixture (EVA/CB) was investigated in terms of thermal stability. EVA, containing 13% vinyl acetate (VA), and EVA/CB, containing 13% VA and 1% carbon black (CB), were aged at 85°C in air up to 30 weeks for thermal ageing. Same substances were aged by means of UV light with a wavelength in the vicinity of 259 nm, in air, up to 400 h for UV ageing. Same substances were also irradiated with gamma rays at ambient conditions up to 400 kGy. Following these experiments, samples which had been irradiated with gamma rays, were subjected to thermal and UV ageing under the same conditions as for unirradiated samples.

Dynamic thermogravimetry studies were performed for determination of the thermal stabilities of the samples. 10 and 50% mass losses were calculated for the samples from their respective curves. As a result of thermal analysis experiments, it was found that CB dramatically loses its protective property against thermal ageing of EVA after gamma irradiation. On the other hand, gamma irradiation does not have any significant effect on the UV ageing characteristics of EVA and EVA/CB in terms of thermal stability.

Keywords: *carbon black, gamma irradiation, poly(ethylene-co-vinyl acetate)*

Introduction

Restricted properties and limited use of homopolymers alone, has given rise to exploration of composites, copolymers, blends, etc. Copolymers such as poly(ethylene-co-vinyl acetate) (EVA), poly(ethylene-co-butyl acrylate) (EBA), poly(ethylene-co-ethyl acrylate) (EEA) have wide range of uses in different industries. Especially EVA has become one of the most useful copolymers in the transportation industry as an insulator, in the electric industry as a cable insulator, in the shoe industry as soles, and in many other industries as a hot melt adhesive, a coating, etc. Therefore, investigation of the degradation and stabilisation of EVA and EVA based mixtures is of considerable importance.

One of the earliest studies about thermal degradation of EVA was performed by Razuvaev *et al.* [1]. They investigated the influence of thermal degradation products and some additives on the copolymer deacetylation.

In a study, carried out by Geuskens *et al.* [2], the influences of gamma rays and UV light on poly(vinyl acetate) (PVA) were investigated and compared. They estimated the products of radiolysis and photolysis of PVA. They also proposed some mechanisms for chemical changes undergoing during radiolysis and photolysis of PVA.

Black and Charlesby [3] performed one of the earliest studies on gamma irradiation of polymers. They showed the changes in chemical structure and physical properties of polyethylene upon irradiation with gamma or X-rays. Formation of crosslinks, main chain fracture, and unsaturation were among these changes. These experiments were done also in the presence of oxygen.

A study on thermal degradation of electron beam cured EVA was performed by Dutta *et al.* [4] They explained the decomposition mechanisms and showed the effect of electron beam on the thermal stability of EVA.

A series of studies on the thermal degradation of EVA, comparing with EBA were performed by Sultan and Sörvik [5–7]. They investigated the volatile decomposition products, changes in unsaturation and side group structure, molecular mass changes after thermal degradation of these polymers. Degradation mechanisms of thermal ageing of EVA and EBA were explained in these studies.

Recently, Allen *et al.* [8, 9] undertook some studies on the ageing and thermal oxidation of EVA and exhibited the main degradation routes for EVA during thermal oxidation process. The species formed during thermal oxidation were proposed. Some spectroscopic analyses were performed considering ther-

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mal oxidation of EVA as well as in the presence of some stabilisers. Discolouration of thermally aged EVA were also evaluated in these studies.

Some other works were also performed on the preparation [10, 11] of EVA based polymer blends and composites, and investigation of their thermal stability and ageing behaviour [12, 13].

In our previous studies, we investigated the accelerated thermal [14] and UV [15] ageing characteristics of EVA and poly(ethylene-co-vinyl acetate)/carbon black mixture (EVA/CB), since EVA/CB, with 13% VA and 1% CB, is a widely used material in particular by Turkish State Railways (TCDD) due to its elastic structure and insulation property. After these studies, we concluded that EVA is a material that is susceptible to both heat and UV light; whereas EVA, containing 1% CB, is a durable material against heat, but vulnerable to UV light. In addition, we examined the effect of gamma rays on these materials, and found that the gamma irradiation does not improve these substances' thermal stabilities [16].

In this comparative study, the effect of gamma rays on the ageing characteristics of EVA (13% VA) and EVA/CB (13% VA and 1% CB) was investigated in terms of thermal stability. It is thought to be important, since any possible change in these materials' chemical and physical properties could affect their industrial consideration.

Experimental

Materials

EVA, containing 13% VA and of density 0.9288 kg L^{-1}, was supplied by Elf-Atochem Co. in the form of granules. EVA/CB plates with contents of 13% VA and 1% CB were obtained from Panel Co., Inc., Turkey. EVA, used in the preparation of this EVA/CB mixture, obtained from Elf-Atochem Co.; whereas masterbatch (PE Black 99209) from Viba Co., Italy, in the form of 50% dispersion of CB, type SRF, in LDPE.

Methods

Ageing of materials

EVA granules, and EVA/CB specimens of dimensions 3.4×3.9 mm with 1.9 mm thickness were placed in a laboratory oven which was set to 85°C, in air, and were aged at different intervals of time up to 30 weeks for thermal ageing. Samples with the same physical properties were irradiated with UV light with an intensity of 12 000 lm at a distance of 15 cm, in air, at ambient temperature; and were aged at different intervals of time up to 400 h for UV ageing. Besides, gamma irradiated samples were also aged under the same conditions as for unirradiated samples.

Irradiation of materials

Samples were irradiated with gamma rays at ambient conditions up to 400 kGy by using a ^{60}Co gamma source.

Thermogravimetric analyses (TG)

Thermogravimetric analyses were performed by utilizing DuPont Instruments-Thermal Analyzer, Model 951. Dynamic thermogravimetric studies were carried out under nitrogen atmosphere; and 10°C min^{-1} heating rate was used. Dynamic thermogravimetric study results indicated the thermal stabilities of samples.

Results and discussion

Figures 1a and b show the dynamic TG curves of virgin and thermally aged EVA and EVA/CB, respectively. Virgin EVA and EVA/CB show the typical step degradation profile with the initial stage involving acetic acid evolution and the second involving main chain degradation [9, 17]. Both first and second degradation steps are shifted to low temperatures in the thermally aged EVA, due to increase of oxidation and the chain scission reactions with ageing which were explained previously [14]. On the other hand, CB incorporated the first and second decomposition temperatures remaining almost the same as that of virgin EVA/CB mixture. Only a slight decrease was observed at the main chain degradation step of the sample, which was thermally aged for 30 weeks. These results clearly show that 1% CB is a very effective stabiliser against thermal degradation of EVA at 85°C. This conclusion is also supported by the numerical data obtained from their respective curves 10 and 50% mass losses both for EVA and EVA/CB, which are given in Table 1.

Figures 1c and d show the dynamic TG curves of virgin and UV aged EVA and EVA/CB, respectively. First and second degradation steps are shifted to lower temperatures both in the UV aged EVA and EVA/CB. As a consequence, CB failed to prevent EVA from UV degradation contrary to that in the case of thermal degradation (Table 1).

Under high-energy radiation, radicals are formed at high concentrations in close proximity to one another so that second-order crosslinking reactions are favored compared with first-order chain scissions [18]. This explanation seems to be true in the case of EVA and EVA/CB, because typical thermal degradation route does not change significantly upon irradiation with gamma rays for both EVA and EVA/CB (Figs 2a and b). It can be said that both chain scission and crosslinking take place simultaneously during irradiation of EVA and EVA/CB with gamma rays [16] (Table 1).

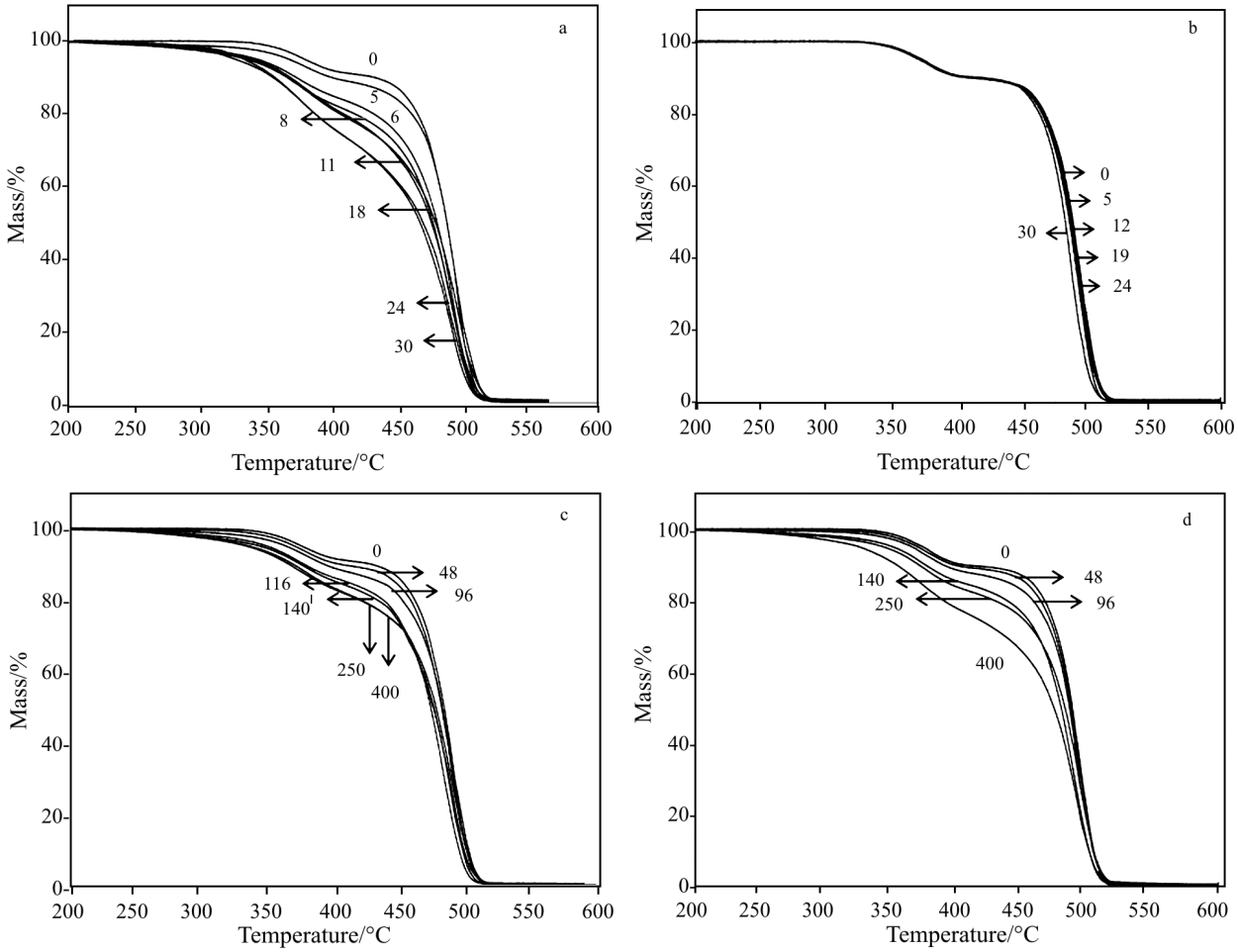

Fig. 1 a and b – dynamic curves of thermally aged EVA and EVA/CB, respectively. Numbers on the curves indicate the thermal ageing time in weeks. c and d – dynamic curves of UV aged EVA and EVA/CB, respectively. Numbers on the curves indicate the UV ageing time in h

Table 1 Degradation temperatures of some of the samples calculated from their respective curves. All values are given in °C

Sample	Virgin	Thermal (24 weeks)	UV (400 h)	Gamma (100 kGy)	Gamma (100 kGy)+ thermal (24 weeks)	Gamma (100 kGy)+ UV(400 h)
EVA (10% mass loss)	422	353	367	432	345	369
EVA (50% mass loss)	486	468	477	485	410	480
EVA/CB (10% mass loss)	411	415	354	419	361	370
EVA/CB (50% mass loss)	489	486	475	490	462	481

100 kGy was chosen to illustrate the effect of gamma irradiation on the ageing characteristics of EVA and EVA/CB. Then, samples were thermally or UV aged under the same conditions as for unirradiated samples. As can be seen from Figs 3a and b, thermal stabilities of both EVA and EVA/CB decrease with thermal ageing time. Gamma irradiation has no improving effect on EVA. In addition, degradation profile of EVA shows that EVA becomes far less durable against heat treatment (numerical comparison are given in Table 1). Moreover, acting as a protective agent *vs*. thermal degradation when not exposed to gamma rays, CB loses its protecting property when it is irradiated with gamma rays. Concurrent occurrences of chain scission, cross-linking and oxidation on the macromolecular backbone structure during gamma irradiation [16], plus further possible chain scission and oxidation reactions during thermal ageing apparently prevent CB from stabilising the EVA *vs*. heat (Table 1).

Figures 3c and d show the TG curves of EVA and EVA/CB, respectively, which were UV aged af-

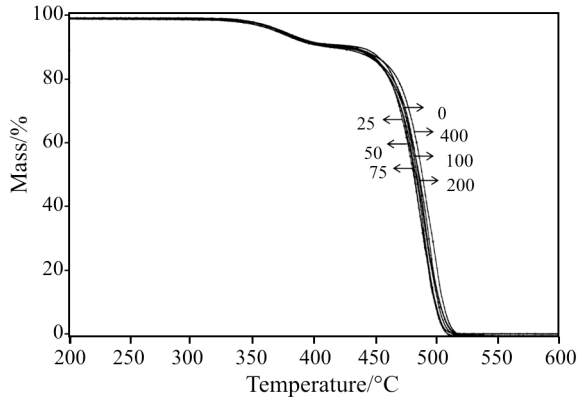

Fig. 2a Dynamic curves of gamma irradiated EVA; Numbers on the curves indicate the irradiation dose in kGy

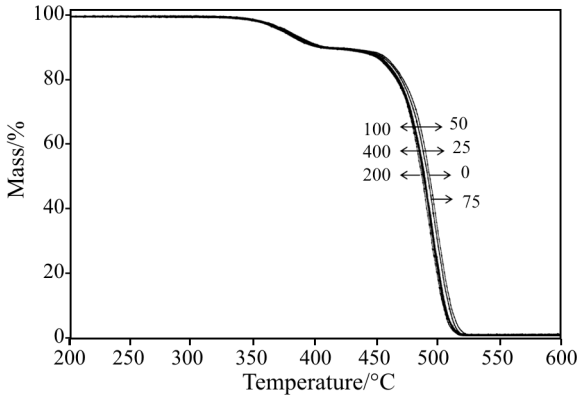

Fig. 2b Dynamic curves of gamma irradiated EVA/CB. Numbers on the curves indicate the irradiation dose in kGy

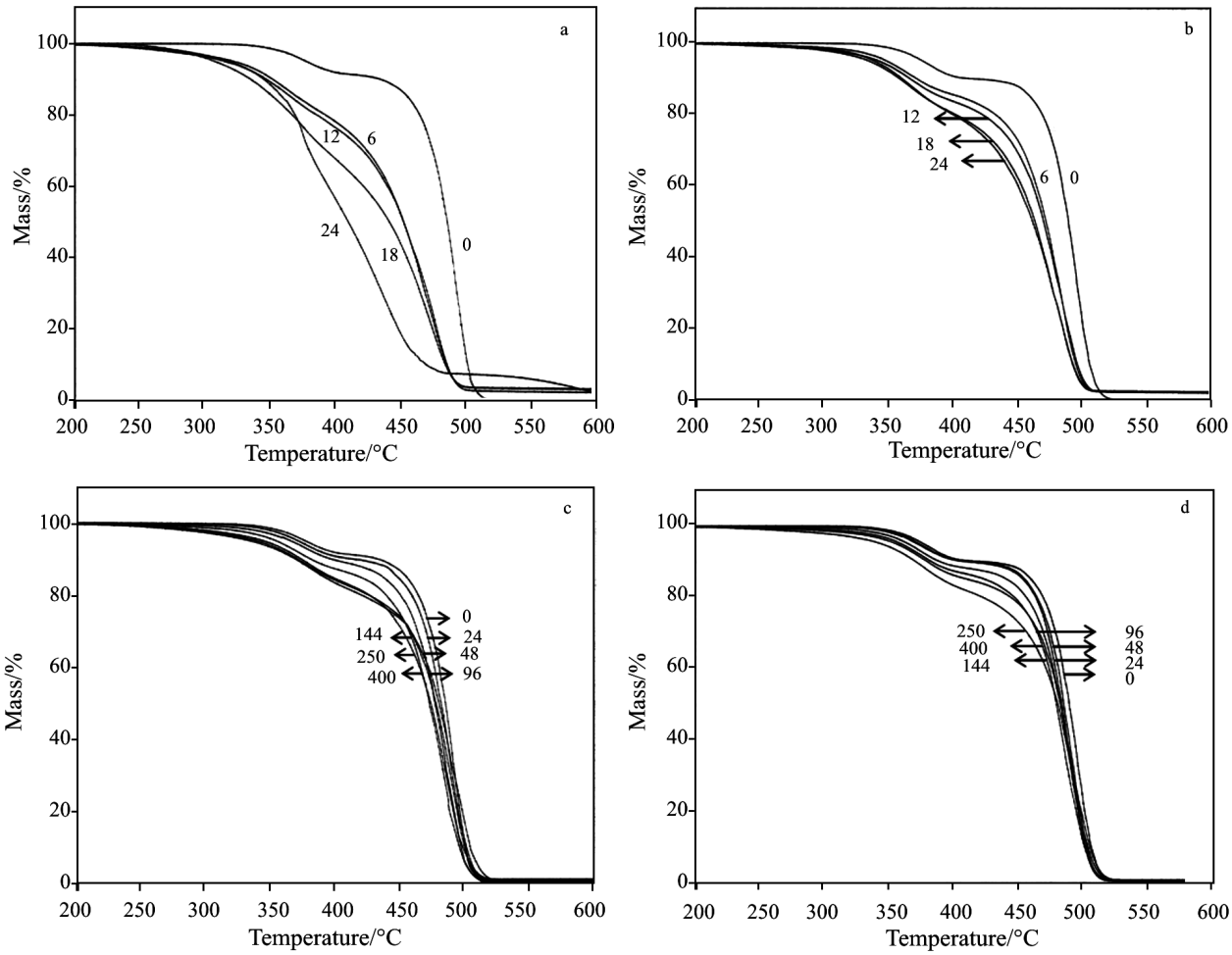

Fig. 3 a and b – dynamic curves of thermally aged EVA and EVA/CB, respectively, after irradiated with gamma rays at a dose of 100 kGy. Numbers on the curves indicate the thermal ageing time in weeks. c and d – dynamic curves of UV aged EVA and EVA/CB, respectively, after irradiated with gamma rays at a dose of 100 kGy. Numbers on the curves indicate the UV ageing time in h

ter irradiated with gamma rays at a dose of 100 kGy. Like the unirradiated ones, gamma irradiated ones are susceptible to UV light too. This means that the thermal stabilities of EVA and EVA/CB when they are exposed to UV light are almost the same as those of gamma irradiated and then exposed to UV light.

Conclusions

In order to investigate the effect of gamma rays on EVA and EVA/CB, samples were first subjected to either thermal or UV ageing, or gamma irradiation. Second, gamma irradiated samples (100 kGy) were subjected to either thermal or UV ageing again under the same conditions as for unirradiated ones. Dynamic curves indicated that CB dramatically loses its protective property *vs*. thermal ageing of EVA after gamma irradiation. However, gamma irradiation does not have any significant effect on the UV ageing characteristics of EVA and EVA/CB in terms of thermal stability.

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