A comparative study of thermal 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 carbon black (CB) on the thermal ageing characteristics of poly(ethylene-co-vinyl acetate) (EVA) was investigated. EVA, containing 13% vinyl acetate (VA), and poly(ethylene-co-vinyl acetate)/carbon black mixture (EVA/CB) containing 13% VA and 1% CB were aged at 85°C in air up to 30 weeks. Sol-gel analysis experiments were made to determine the percentage gelation of both virgin and aged samples. FT-IR measurements were performed to follow the chemical changes which took place in the samples during ageing. Dynamic and isothermal thermogravimetric studies were performed for determination of the thermal stabilities of virgin and aged samples.

Sol-gel analysis results showed that EVA itself has a tendency to form a gel under thermal treatment, whereas EVA/CB never becomes a gel when being thermally aged under the same conditions. As a result of FT-IR measurements, some oxidation products such as ketone, lactone and vinyl species were observed through thermal ageing of EVA. It is also clear that these kind of oxidation products did not appear to a considerable extent in EVA/CB. Thermal analysis experiments exhibit that thermal stability of EVA decreased through thermal ageing; whereas that of EVA/CB remained almost unchanged. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: poly(ethylene-co-vinyl acetate); carbon black; thermal properties; degradation; ageing

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), ethylene-butyl acrylate (EBA) and ethylene-ethyl acrylate have wide range of utilization in different industries. Among the numerous ethylene copolymers, due to its wide range of properties depending on its vinyl acetate content, 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 used as soles, and in many other industries as an hot melt adhesive, a coating, etc. Several works have looked at EVA itself and also its degradation characteristics.

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

Detailed studies on the thermal degradation of EVA, compared with EBA was performed by Sultan and Sörvik. They investigated the volatile decomposition products, changes in unsaturation and side group structure, molecular weight 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. undertook a sequence of studies on thermal oxidation of EVA and exhibited the main degradation routes for EVA during the thermal oxidation process. The species formed during thermal oxidation were proposed. Some spectroscopic analyses were performed considering thermal oxidation of EVA as well as in the presence of some stabilizers. Discoloration of thermally aged EVA were also evaluated in these studies.

Ageing characteristics of EVA and poly(ethylene-co-vinyl acetate)/carbon black (EVA/CB) is very important because of its usage in the fields where the products are exposed to sunlight and/or heat. In some countries, like in Turkey, climate has a great effect on the ageing of EVA. EVA/CB which contains 13% VA and 1% CB is a widely used polymer in particular by Turkish State Railways (TCDD) due to its elastic structure and insulation property. In this comparative study; accelerated thermal ageing characteristics of EVA (13% VA) and EVA/CB (13% VA and 1% CB) were investigated.

EXPERIMENTAL

Materials

EVA, containing 13% VA and of density 0.9288 kg/l, was supplied by Elf-Atochem Co. in the form of granules. EVA/CB
plates including 13% VA and 1% CB was 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 low-density polyethylene (LDPE). Xylene, used as solvent for EVA and EVA/CB, for determination of gelation, was obtained from Merck.

Ageing of materials
EVA granules, and EVA/CB specimens of dimensions 3.4 mm x 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.

Analyses

Determination of percentage gelations
For investigation of the influence of thermal ageing on the gelations of EVA and EVA/CB, sol-gel analyses were performed. Xylene was used as solvent in soxhlet extractor and was fluxed through each sample for 14 h. Gel percentages were calculated gravimetrically according to the following equation:

\[
\% \text{ Gel} = \frac{m}{m_0} \times 100
\]

where \( m_0 \) and \( m \) are the masses of samples before and after extraction, respectively.

FT-IR studies
FT-IR studies were carried out by means of Nicolet 520 model spectrometer. Samples were pressed in a hotplate at about 100 °C for 10 sec in order to obtain film forms. Samples, crosslinked to a high extent, were scraped to get tiny particles and then were mixed with KBr.

Thermogravimetric analyses (TGA)
Thermogravimetric analyses were performed by utilizing Du Pont Instruments-Thermal Analyzer, Model 951. Dynamic thermogravimetric studies were carried out under nitrogen atmosphere, and 10 °C/min heating rate was used. Dynamic thermogravimetric study results indicated the thermal stabilities of virgin and aged EVA and EVA/CB. Two types of iso-thermal thermogravimetric studies were performed. One was under nitrogen atmosphere at 350 °C, and was used to determine the percentages of volatile degradation products of virgin and aged samples. The other was under oxygen atmosphere at 195 °C, and was used to determine the thermo-oxidative stabilities of virgin and aged EVA and EVA/CB.

RESULTS AND DISCUSSION

Sol-gel analyses
Before investigation of chemical changes in the structure of EVA and EVA/CB, the effect of thermal ageing on the gelations of EVA and EVA/CB was investigated. The effect of thermal ageing on the percentage gelations of EVA and EVA/CB, aged at 85 °C in air up to 30 weeks, are given in Fig. 1. As shown from Fig. 1, percentage gelation increased up to 50% for EVA with thermal ageing time, whereas in EVA/CB no gelation was observed until around 24 weeks. After 24 weeks, gelation began to appear; and only 1.6% gelation was observed at the end of 30 weeks.

Gelation in polymers is generally referred to as crosslinking of macromolecules by means of covalent bonds. Razuvaev et al. suggested that copolymer crosslinking proceeds by intermolecular cyclization of the polyene sequences of macromolecules. According to Sultan and Sorvik, crosslinks via randomly distributed double bonds could possibly occur after abstraction of hydrogen in the allyl position. The resonance stabilized radical is likely to combine with other macroradicals. A less frequent alternative is addition to double bonds. In the case of thermally aged EVA, these explanations are supposed to be true even though percentage gelation is not complete (100%). Sultan and Sorvik showed that crosslinking tendency increased with temperature, and is linearly related to the formation of internal double bonds in EVA. EVA/CB exhibits no significant gelation behavior. This is most probably due to radical scavenging property of CB resulting in prevention of crosslinking formation.

In order to determine the crosslink and chain scission reaction yields occurring during thermal ageing of both EVA and EVA/CB, the usual Charlsby–Pinner equation was modified. Charlsby–Pinner equation, \( s = s_0 + \frac{p_c}{q_0 + \frac{2}{2}} \), was used by many researchers so far for simultaneous determination of crosslinking and chain scission reaction yields of irradiated polymers by ionizing radiation. In this equation, \( s \) is the sol fraction, \( p_c \) is the chain scission yield, average number of main chain scissions per monomer unit and per unit dose, \( q_0 \) is crosslinking yield, proportion of monomer units crosslinked per unit dose, \( w_{20} \) is initial weight, average degree of polymerization, and \( D \) is irradiation dose. Although this equation was derived from by Charlsby–Pinner for determination of crosslinking and chain scission yields for irradiated polymers such as gamma or electron beam, it is assumed that this general equation can also be used for the simultaneously and thermally crosslinked and degraded polymers by the simple replacement of dose with ageing time. It is very interesting that no equation was defined in the literature until now for the determination of \( p_c \) and \( q_0 \) values of thermally modified polymers. Replacing the thermal ageing time instead of irradiation...
dose of ionizing radiation in Charlsby–Pinner equation, it becomes as follows:

\[ s + \sqrt{s} = p_o/q_o + 2/(q_o u_{2,0} t) \]

where \( t \) is ageing time.

In this equation, \( u_{2,0} \) was calculated as the ratio of weight average molecular weight (obtained from Elf-Atochem as 95,000 g mol\(^{-1}\)) to average weight of a monomer unit (calculated as 30.8), and was found as 3084. Plots of the reciprocal of ageing time, \( 1/t \times s + \sqrt{s} \); yield straight lines (with a regression coefficient, \( r = 0.970 \) for EVA and 0.990 for EVA/CB), and \( p_o/q_o \) and \( q_o \) were calculated from the intercept and the slope of the lines, respectively.

As a result of calculations, \( p_o \) and \( q_o \) (per day) were found as 0.554 and 2.86, respectively, for EVA; and 63.1 and 121, respectively, for EVA/CB. Even though the values for EVA/CB are much greater than EVA, when they are evaluated individually, one can conclude that EVA has a tendency to form crosslinks rather than chain scission, since \( p_o/q_o = 0.193 \) for EVA. However, with a value \( p_o/q_o = 1.93 \), EVA/CB seems to be a mixture which cannot crosslink readily.

**FT-IR studies and thermal degradation mechanisms of EVA and EVA/CB**

EVA and EVA/CB have almost the same spectra, because CB itself has no remarkable characteristic absorption bands and thus, does not influence the spectrum of EVA. The FT-IR spectra of virgin and thermally aged EVA and those of EVA/CB are given in Figs. 2 and 3, respectively, in the range of 1950–1550 cm\(^{-1}\). Main functional group changes were observed in this region. In order to calculate the absorbance value of a band which overlapped with another band or bands in FT-IR spectra, a band separation software program was used. Absorption at 723 cm\(^{-1} \) (\( A_{723} \)) is assigned to –CH\(_2–CH2–CH2–\) sequences. It was supposed that, during thermal degradation, the amount of these methylene sequences remain almost constant with respect to other bands at which significant changes occurred. Therefore, regarding the absorption at this wavenumber as constant, changes at any other band can be monitored.

The main thermal degradation product of EVA is acetic acid which forms due to ester pyrolysis.\(^{2,6,9}\) Mechanism of ester pyrolysis is shown in Scheme 1; so it is anticipated that the absorption at 1740 cm\(^{-1} \) (\( A_{1740} \)) should decrease with thermal ageing. The formation (Scheme 2) and the destruction of aldehydes to form carboxylic acids (Scheme 3), however, made it difficult to follow the changes at around 1740 cm\(^{-1} \). (Statistically every 21 –CH\(_2–CH2–\) sequence includes one acetate group in the structure of EVA with 13% VA; thus, aldehydes were frequently formed on the –CH\(_2–CH2–\) segments of macromolecules during thermal ageing.\(^{10}\) ) As a consequence, due to these competitive reactions total changes were not significant for EVA and EVA/CB (Fig. 4a).

The amount of aldehydes in the virgin EVA/CB is twice as that of EVA. This might be due to some oxygen containing groups which could be formed in EVA/CB during its manufacturing stages.

Figure 2. FT-IR spectra in the range 1950–1550 cm\(^{-1} \) of virgin and thermally aged EVA in air, at 85 °C. Numbers on the curves represent thermal ageing time (in weeks).

**Figure 3.** FT-IR spectra in the range 1950–1550 cm\(^{-1} \) of virgin and thermally aged EVA/CB in air, at 85 °C. Numbers on the curves represent thermal ageing time (in weeks).

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significant relative change at this region in thermally aged EVA/CB.

Mechanism in Scheme 4 was proposed for non-oxidative decomposition. In the presence of oxygen, however, hydroperoxides can form on the macromolecule chains during the thermal degradation of polymers, \(^6,11,12\) and these unstable structures decompose to yield ketone groups (Scheme 5). Variation of ketone groups was followed by the ratio of absorbance at 1715 cm\(^{-1}\) to absorbance at 723 cm\(^{-1}\). As can be seen from Fig. 4(b), ketone formation in EVA increased until the end of 18 weeks; after this week, it decreased to a small extent, probably due to decomposition of keto groups. Fig. 4(b) also indicates that, addition of CB into EVA prevents the substantial formation of keto groups during thermal ageing.

Another species formed as a consequence of thermal degradation is lactone.\(^3,5\) Increase at 1780 cm\(^{-1}\) in Fig. 2 was assigned to lactone formation. In EVA/CB (Fig. 3), no significant change was observed at 1780 cm\(^{-1}\). Mechanism in Scheme 6 was proposed for lactone formation associated with a back-biting process in the vinyl acetate moieties by the acetate groups forming methane.\(^2,6,12\) Lactone formation in thermally aged EVA and EVA/CB was followed by the ratio of absorbance at 1780 cm\(^{-1}\) to absorbance at 723 cm\(^{-1}\).

The change of \(A_{1780}/A_{723}\) with thermal ageing time is given in Fig. 4(c). Lactone formation also increased almost continuously during thermal ageing of EVA. However, the amount of formation of lactone is less than that of ketone in every step of ageing, since ketone formation is easier than lactone formation due to the conformational arrangements. Lactone formation was not observed in EVA/CB due to the steric hindrance of CB.

Samples, which were subjected to thermal ageing (except CB containing ones), exhibited yellowing behavior during this procedure. It is well known that yellowing (or even darker colors from brown to black) is a consequence of formation of unsaturated groups.\(^3,6,12\) These unsaturated groups are generally vinyl, vinylidene, and trans-vinylene groups which are responsible for coloring. Mechanisms of formation of trans-vinylene, vinyl, and vinylidene are shown in Schemes 1, 7 and 8, respectively.\(^3\) Vinyl type of unsaturation forms by
\( \beta \)-cleavage of tertiary radicals. Sultan and Sørvik\(^3\) showed that LDPE has considerably higher initial vinylidene content in its structure compared to EVA (1.2 mol% VA), because of multiple backbiting reactions in the LDPE. This might be due to milder polymerization conditions used in order to avoid acetate pyrolysis. The results of normalization for the band at 910 cm\(^{-1}\)/\( C_0 \) for which the vinyl groups formed in thermally aged EVA and EVA/CB, are shown in Fig. 4(d). Vinyl content in EVA increased continuously during thermal ageing, whereas in EVA/CB this formation was hindered by CB, due to its radical delocalizing property. The formation of vinylidene and \( \text{trans} \)-vinylene were not clearly observed due to high noise to signal ratio. This resulted from the difficulties in the preparation of thin films from crosslinked granules.

Influence of thermal ageing on the thermal stability of EVA and EVA/CB

Figures 5 and 6 show the dynamic TGA thermograms of virgin and thermally aged EVA and EVA/CB, in nitrogen atmosphere, respectively. As shown in Fig. 5, virgin EVA shows the typical step degradation profile with the initial stage involving acetic acid evolution and the second involving main chain degradation.\(^5\,\,8\,\,9\) Figure 5 indicates that, when thermal ageing time increases, degradation profile changes. Degradations at both stages become easier. Both first and second degradation steps are shifted to low temperatures in the thermally aged EVA, due to increase in oxidation and the chain scission reactions with ageing which were explained previously.

However, CB incorporated the first and second decomposition temperatures remaining almost the same as that of virgin EVA/CB mixture (Fig. 6). 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 allowed one to conclude that 1% CB is a very effective stabilizer against thermal degradation of EVA at 85°C.

Degradation activation energies of EVA and EVA/CB were calculated by using Freeman–Carroll equation and the data obtained from derivatives of dynamic thermograms of thermally aged EVA and EVA/CB were used in the calculations.\(^{13}\)

\[
\frac{\Delta \log(d/dT)}{\Delta \log(1 - c)} = n - \frac{E}{2.3R} \times \frac{\Delta(1/T)}{\Delta \log(1 - c)}
\]

where \( T \) is the temperature in Kelvin, \( n \) is the order of the reaction, \( R \) is the gas constant which has a value 8.314 J mol\(^{-1}\) K\(^{-1}\), \( E \) is the degradation activation energy, \( c \) is the conversion ratio and equals to \( (m_0 - m)/m_0 \), where \( m_0 \) is the initial mass and \( m \) is the mass at any time.

When \( \Delta(1/T)/\Delta \log(1 - c) \) vs. \( \Delta \log(d/dT)/\Delta \log(1 - c) \) is plotted, the slope of this plot gives the degradation activation energy and the intersection of ordinate indicates the order of reaction. The \( c \) and \( T \) values were obtained from derivatives of thermograms. The effect of thermal ageing time on the degradation activation energies of EVA and EVA/CB are shown in Fig. 7. Degradation activation energy of EVA continuously decreased with increasing thermal ageing time. Oxidation and chain scission are the main reasons for this decrease. Decreases in the thermal stability and the degradation activation energy of an oxidized polymer and the effect of molecular weight on these parameters have been well described in the literature by many researchers.\(^{14-17}\) However, degradation activation energy of EVA/CB neither increased nor decreased significantly due to stabilizing effect of CB.

As can be seen from Fig. 5, due to overlapping of first and second degradation steps, it is not easy to interpret and determine the amount of readily decomposing groups from dynamic TGA thermograms. For the detailed analysis of first
stage of degradation, the isothermal TGA analyses were performed in nitrogen atmosphere. Isothermal thermograms of virgin and thermally aged EVA samples in nitrogen atmosphere are given in Fig. 8. Isothermal-nitrogen thermograms of thermally aged EVA and EVA/CB were obtained at 350°C. This temperature is sufficient to break down all kinds of oxygen-containing groups. The plateaus in Fig. 8 clearly indicate that all the oxygen-containing volatile groups are eliminated from polymer at the end of 70 min. Figure 8 also indicates that oxidation or the amount of volatile products increases with the thermal ageing time. As can be seen from Fig. 9, EVA/CB has high resistance to thermo-oxidation since no significant change was observed in the isothermal thermograms. Even though the acetate groups are decreasing during thermal ageing, oxidation is rather higher than deacetylation. As a result of higher oxidation, oxygen-containing groups are continuously increased in thermally aged EVA. Due to stabilizing effect of CB, these changes are almost zero in thermal degradation of EVA/CB, compared to EVA. These results are consistent with the FT-IR results.

Isothermal thermogravimetry studies which were carried out in oxygen atmosphere, were performed at 195°C. As seen from Fig. 10, virgin EVA has an oxygen uptake capacity which diminished through the third week until the sixth week. Weight increases in the initial stage of degradation indicates the oxygen penetration into the polymer structure.18,19 After the sixth week, oxygen uptake completely fell to zero. This can be explained by the rapid formation of decomposable oxygen-containing species such as aldehydes or ketones. When this formation reaches an equilibrium (around the sixth week), uptake of oxygen stops. Due to the prevention of oxidation by CB, oxygen uptake capacity never falls to zero until the end of 30 weeks in EVA/CB (Fig. 11). Moreover, time to reach the 10% mass loss decreased up to sixth week, and then increased continuously until the end of 30 weeks in EVA. This can be seen from Fig. 12. The continuous increase in the thermo-oxidative stability of EVA after the sixth week might be due to overcoming of crosslinking reactions on chain scission reactions, and the formation of relatively more sustainable oxygen-containing groups such as carboxylic acids. In EVA/CB, time period for 5% mass loss decreases up to twelfth week, then remains unchanged (Fig. 12). The total change is small when compared to EVA.
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To determine the thermal stability of EVA and EVA/CB, samples were subjected to thermal ageing at 85 °C and in air up to 30 weeks. Sol-gel analyses which were used to determine the crosslinking ratio showed that, EVA has a tendency to crosslink under thermal treatment; percentage gelation increased up to 50%, but percentage gelation of CB containing samples reached only up to 1.62% at the end of 30 weeks. This behavior was explained with the strong penetration of CB particles which hinders the EVA macromolecules from coming closer to form crosslinks. FT-IR spectra of virgin and thermally aged EVA and EVA/CB showed that, some chemical changes took place in EVA, during thermal ageing. Changes were significant around the carbonyl region. No significant changes were observed for EVA/CB. Ketone, lactone and vinyl formations at 1715, 1780 and 910 cm⁻¹, respectively, were observed in EVA, but not in EVA/CB. Dynamic thermograms which were carried out in nitrogen atmosphere indicated that, thermal stability of EVA decreased during thermal ageing. CB maintained the thermal stability of EVA. Degradation activation energies of EVA and EVA/CB, which were found by using derivative dynamic thermo-

gram data and Freeman–Carroll equation, showed that degradation activation energy of EVA decreased from 282 to 121 kJ mol⁻¹ during thermal ageing, whereas that of EVA/CB did not decrease to a significant extent. For detailed analyses of the first stage of degradations for EVA and EVA/CB, isothermal TGA analyses were performed at 350 °C in nitrogen atmosphere. Results indicated that the oxygen containing volatile products increased during thermal ageing in EVA, but not in EVA/CB. Isothermal thermogravimetry studies which were carried out at 195 °C, in oxygen atmosphere were employed in order to find the thermo-oxidative stabilities of EVA and EVA/CB. Oxygen uptake capacity decreased until the sixth week and reached to a value of zero. Time to reach the 10% mass loss in EVA decreased up to sixth week, followed by a continuous increase during 30 weeks, whereas time passed for 5% mass loss in EVA/CB decreased up to 12 weeks, then remained almost constant. As a conclusion, all these studies clearly showed that 1% CB is a very effective stabilizer against thermal degradation of EVA at moderate temperatures.

Considering the present length of the article to be rather long, we have decided to publish our experimental results, that compare the effects of different CBs, in addition to the CB which we have used, on the thermal ageing characteristics of EVA, in a separate article.

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REFERENCES


CONCLUSIONS

In order to investigate the ageing characteristics of EVA (13% VA) and EVA/CB (13% VA and 1% CB), samples were subjected to thermal ageing at 85 °C and in air up to 30 weeks. Sol-gel analyses which were used to determine the crosslinking ratio showed that, EVA has a tendency to crosslink under thermal treatment; percentage gelation increased up to 50%, but percentage gelation of CB containing samples reached only up to 1.62% at the end of 30 weeks. This behavior was explained with the strong penetration of CB particles which hinders the EVA macromolecules from coming closer to form crosslinks. FT-IR spectra of virgin and thermally aged EVA and EVA/CB showed that, some chemical changes took place in EVA, during thermal ageing. Changes were significant around the carbonyl region. No significant changes were observed for EVA/CB. Ketone, lactone and vinyl formations at 1715, 1780 and 910 cm⁻¹, respectively, were observed in EVA, but not in EVA/CB. Dynamic thermograms which were carried out in nitrogen atmosphere indicated that, thermal stability of EVA decreased during thermal ageing. CB maintained the thermal stability of EVA. Degradation activation energies of EVA and EVA/CB, which were found by using derivative dynamic thermo-

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