

Thermal Degradation of EVA and EBA—A Comparison.

II. Changes in Unsaturation and Side Group Structure

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SYNOPSIS

This is the second in a series of papers in which the thermal degradation of ethylene–vinyl acetate (EVA) and ethylene–butyl acrylate (EBA) copolymers are compared. The EBA samples contain 0.8, 1.6, and 5.4 mol % butyl acrylate (BA), respectively, and the EVA samples 1.2 and 6.7 mol % vinyl acetate (VA). The samples were heated in nitrogen in a tubular oven at 285, 333, 350, 370 and 390°C for 6–120 min. The samples were analyzed with IR, NMR, gravimetry, and titration of carboxylic groups. The EVA samples were rapidly degraded by deacetylation, which was complete after about 30 min at 333°C. A linear relation between the loss of acetate groups and the formation of *trans* double bonds was found. A small amount of keto groups and traces of lactones were also observed. The data confirm the previously proposed mechanisms for deacetylation and the formation of acetaldehyde. A mechanism for lactone formation is suggested. The deacetylation rate is increasing with the VA content, presumably because of an increased amount of block sequences and an enhanced acid catalytic effect. The acrylate sidegroups are much more stable than the acetate groups, and are similar in stability to the main hydrocarbon chain. The BA decomposition results in carboxylic and anhydride groups. Decarboxylation also occur and increases with the thermal treatment. In LDPE and EBA the increase in unsaturation is small and mainly due to vinyl end groups formed via β -cleavage or disproportionation. In EVA the formation of vinyl end groups is suppressed.

INTRODUCTION

Earlier investigations in this series¹ concern volatile degradation products, formed during pyrolysis in the temperature range 150–280°C of ethylene–vinyl acetate (EVA) and ethylene–butyl acrylate (EBA) copolymers. The main decomposition product from EVA is acetic acid (HAc), which is formed already at the lowest temperature investigated, 150°C. Minor amounts of acetaldehyde were also observed.

EBA is much more stable than EVA. Butene is the main volatile product. Minor amounts of hydrocarbons, acrylate-containing fragments, and, possibly, carbon dioxide were also observed.

In this work, data from the analysis of the residual products are reported.

EXPERIMENTAL

A series of commercial LDPE, EBA, and EVA polymers, free from all kinds of additives, were obtained as granules (see Table I).

Thermal Degradation

The pyrolysis was performed in a tubular oven, 1.20 × 0.065 m. It was originally constructed for the thermal degradation of polyethylene and is described elsewhere.² It is designed for adequate control of temperature and atmosphere and contains a low temperature section for conditioning and cooling of the samples. The present design is given in Figure 1.

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Table I Samples Investigated

Sample	Commercial Name	Supplier	MI ₂ (g/10 min)	Density (kg/m ³)	Comonomer		Unsaturation ^a						M _w ^c LS ^c × 10 ⁻³	LCB ^d 1000 C
					(wt %)	(mol %)	Trans A ₉₆₅ A ₂₀₁₀	Vinyl A ₉₁₀ A ₂₀₁₀	Vinylidene A ₈₈₅ A ₂₀₁₀	M _n ^b × 10 ⁻³	M _w ^b × 10 ⁻³			
LDPE	DFDS-6600	NESTE	0.31	921	—	—	< 0.1	0.3	0.7	20	167	299	1.0	
EBA-0.8	DEX-915	NESTE	3.5	922	3.7	0.83	< 0.1	0.2	0.6	15	124	147	1.6	
EBA-1.6	EBA-907	NESTE	1.1	923	6.9	1.6	< 0.1	0.3	0.7	16	136	145	1.1	
EBA-5.4	DXM-410	NESTE	4.0	925	20.6	5.4	< 0.1	0.5	0.8	21	123	187	1.0	
EVA-1.2	DQD-1824	UCC	0.9	928	3.5	1.2	Disturbance	< 0.1	0.2	22	103	97	1.5	
EVA-2.2	Baylon V18T	BAYER	0.5	928	6.4	2.2	Disturbance	< 0.1	0.7	29	375	—	1.1	
EVA-11.4	Evathene-2805	ICI	5.0	950	28.0	11.4	Disturbance	—	—	—	—	—	—	

^a Relative number of unsaturations calculated from IR absorbance for respective unsaturation peak at 965, 910, and 885 cm⁻¹ divided by the absorbance for the reference peak at 2010 cm⁻¹.

^b Determined by size exclusion chromatography. Using refractive index detector.

^c Determined by light scattering coupled on line to the size exclusion chromatograph.

^d LCB/1000 C = number of long chain branches per 1000 carbons.

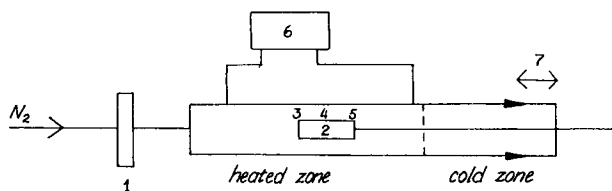


Figure 1 Heating device: (1) rotameter; (2) sample holder; (3–5) thermocouples; (6) temp regulator; (7) loading zone.

The temperature variations were less than $\pm 3^\circ\text{C}$ and were slightly dependent on the absolute temperature level.

The granules were pressed for 90 s at 130°C between thoroughly cleaned Teflon films to a thickness of 0.27 ± 0.005 mm. The films were placed on microscope glass slides, which previously had been cleaned overnight in fuming nitric acid, washed in distilled water, and stored in ethanol. The sample films were conditioned for 2 h in ultrapure nitrogen in an exciccator at room temperature and then for 20 min in the cooled zone of the oven. After pyrolysis, the samples were allowed to cool down for 10 min in this zone. The degradation and conditioning temperatures were 285, 333, 350, 370, and 390°C , respectively 75, 86, 90, 92, and 95°C . The experiments were performed in ultrapure nitrogen (AGA SR 99.999% N_2).

The most detailed degradation studies have been made at 285 and 333°C , in accordance with previous degradation studies of polyethylene.²⁻⁵

Gravimetry

Microscope glass slides and samples were placed for not less than 24 h in an exciccator before weighing. The weighing was performed before and after degradation.

Content of Carboxylic Groups

The polymer samples were dissolved in toluene, at 80°C , under nitrogen atmosphere and titrated with a solution of KOH in isopropanol. The titrations were performed at 80°C with *p*-naphtolbensein as indicator.

The accuracy of the method was tested by titration of etylene-acrylic acid copolymers and found to be adequate. IR measurements confirmed that the anhydride (1810 cm^{-1}) and carboxylic acid (1705 cm^{-1}) groups were totally transformed to carboxylates (1585 cm^{-1}) (see Fig. 9).

NMR Measurements

The content of vinyl acetate (VA) and butyl acrylate (BA) in the copolymers were determined by proton NMR (Varian XL 200) on 3% solutions of EVA and EBA in a mixture of trichloro benzene and deuterated benzene (3 : 1) at 90°C . The spectras were obtained at 200 MHz. The area of the peaks originating from CH_3 protons in respective functional groups were determined and compared with the area of the CH_2 peak. The following instrumental parameters were used:

Spectral window (Hz)	4000
Collection time (s)	1
Pulse angle (deg)	90
Pulse interval (s)	3

IR Measurements

Film samples were analysed in a Perkin-Elmer 399 IR spectrophotometer:

Structures	Film Thickness (mm)	Peak Position (cm^{-1})	Baseline (cm^{-1})
BA	0.5	840	860–810
VA	0.2	610	670–570
Hydrocarbon chain	0.5 or 0.2	2010	2100–1975
Vinylidene	0.5	885	930–860
Vinyl	0.5	910	930–860
Trans vinylene	0.5	965	980–930

The measurements were normalized by comparison with the $-\text{CH}_2-$ absorption peak at 2010 cm^{-1} , and expressed as an absorption index, e.g., A840/A2010.

The IR absorption index for BA and VA groups were calibrated by comparison with proton NMR measurements and elemental analysis of several additive-free commercially available copolymers (Figs. 2 and 3).

RESULTS AND DISCUSSION

Thermal Stability of BA and VA Groups

In Figures 4 and 5 the relation is given between remaining amounts of BA, resp. VA groups, and the degradation time at 285 and 333°C .

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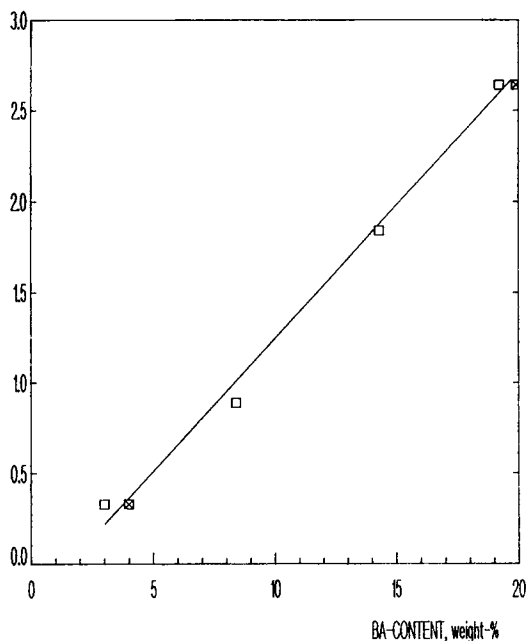
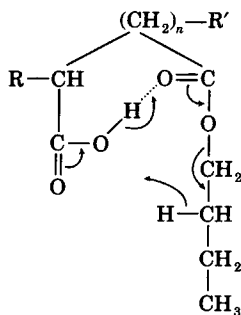


Figure 2 Calibration curve for determination of BA content in EBA by IR: (□) quantification by ¹H-NMR; (⊗) quantification by elemental analysis.

In accordance with our previously reported results concerning volatile degradation products, only a minor degree of degradation is noticed for the EBA copolymers at 285°C. At 333°C the degradation is clearly seen. The degradation rate decreases with time. The data in Figure 6 show that the reaction is not a simple first-order process as the curves cross over each other. Carboxylic acid groups formed during the pyrolysis might catalyze further degradation by development of hydrogen bonds:



The high thermal stability of the BA-group is illustrated in Figure 6. After 24 min degradation at 390°C a substantial part of the acrylate groups still remains in the polymer. This severe treatment results in a

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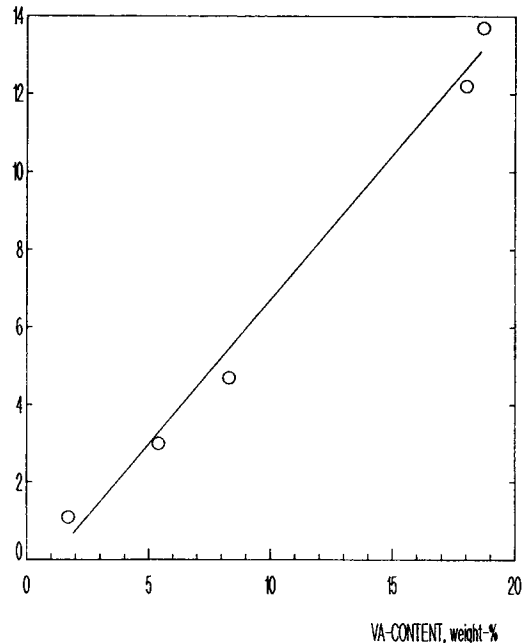


Figure 3 Calibration curve for determination of VA content in EVA by IR. Quantification by ¹H-NMR.

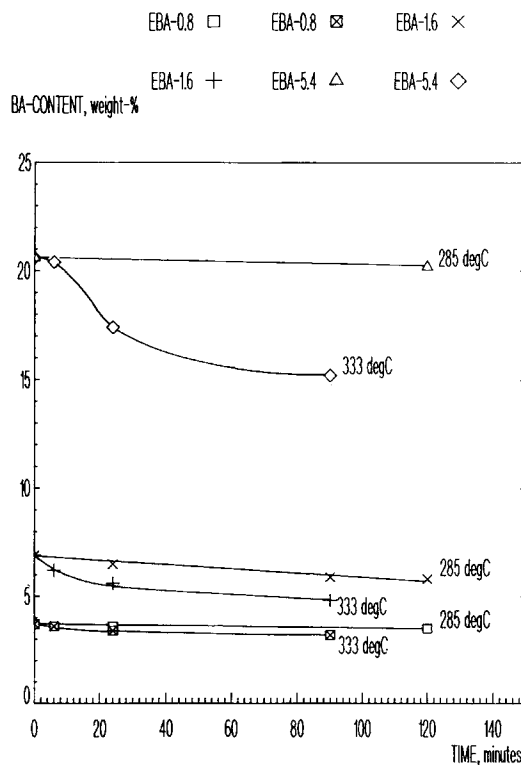


Figure 4 Remaining amount of BA groups after degradation at 285 and 333°C.

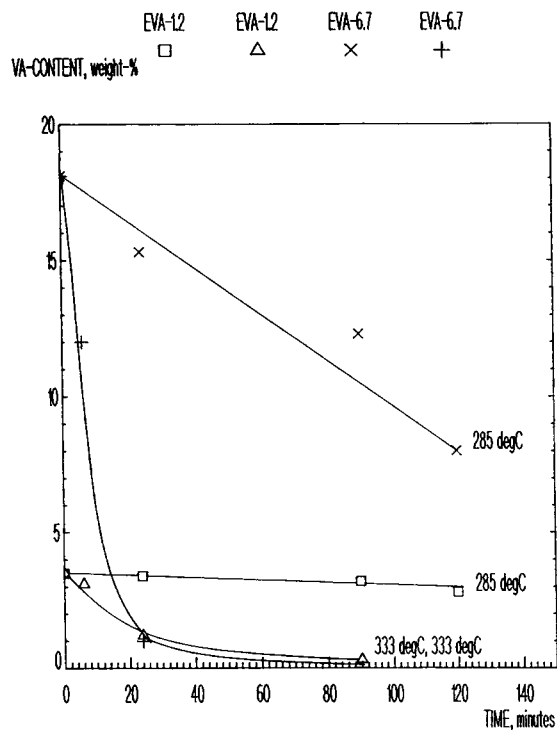


Figure 5 Remaining amount of VA groups after degradation at 285 and 333°C.

substantial degradation of the main chain structure,⁶ as is the case for the LDPE sample.

The EVA copolymers show a much higher degradation rate (Fig. 5). At 285°C, EVA-6.7 has lost more than half of the VA groups, while EVA-1.2 has lost 25% after 2 h treatment. At 333°C nearly all of the VA groups were lost in 24 min. This result is consistent with the fast evolution of acetic acid reported in Paper I of this investigation.¹

As shown by the degradation rate for EVA-6.7 and EVA-1.2, the deacetylation is increased considerably by the vinyl acetate content. As is the case with PVC, the acid fumes generated will catalyze the degradation. In block structures, an allyl activation effect is also present.

Nonvolatile Oxygen Containing Degradation Products

Polyethylene

IR measurements proved that the degradation was performed in an inert atmosphere. No increase in the carbonyl content was observed. A small peak at 1720 cm^{-1} in the untreated material is due to the chain transfer agent used.

EBA

Figure 7 shows the changes in the IR spectra in the carbonyl region 1600–1900 cm^{-1} during the degradation at 333°C. In Figure 8 the influence of temperature during a 24 min degradation is given. The changes follow the same pattern for all EBA copolymers investigated. Only the results for EBA-1.6 are therefore reported.

At 285°C, there are hardly any changes in the carbonyl region (Fig. 8), nor are there any changes in the C—O stretch region (Fig. 4). At higher temperatures the ester carbonyl peak at 1735 cm^{-1} is decreasing and new peaks are growing with temperature and time at 1645, 1705, and 1810 as well as a shoulder at 1760 cm^{-1} . The peak at 1645 cm^{-1} is due to unsaturated structures (see below). The peak at 1705 cm^{-1} is assigned to hydrogen bonded carboxylic groups.⁷

Non-hydrogen-bonded carboxylic groups absorb at 1735 cm^{-1} as well as the ester carbonyl.^{7,8} The observed changes therefore show that the ester pyrolysis result in hydrogen bonded carboxylic groups. This is further confirmed by the increase in a broad band in the region 3200–3300 cm^{-1} , ascribed to the stretching of hydrogen bonded OH groups.⁷ The stretching of non-hydrogen-bonded OH groups results in absorption at 3525 cm^{-1} .⁷ This peak is visible, but very small.

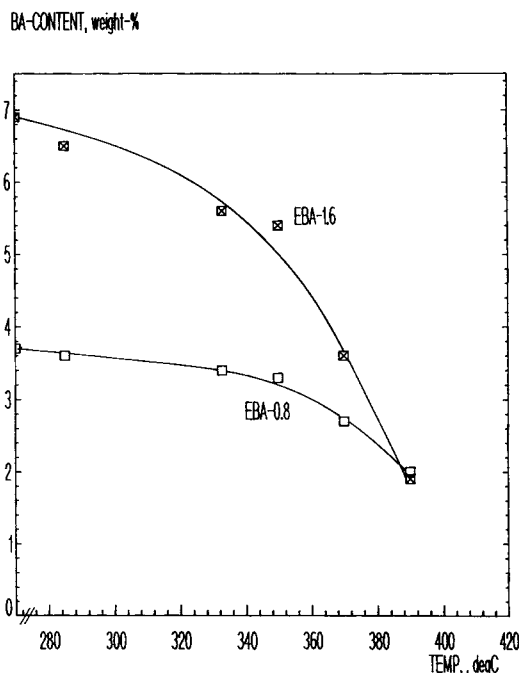


Figure 6 Remaining amount of BA groups after 24 min degradation.

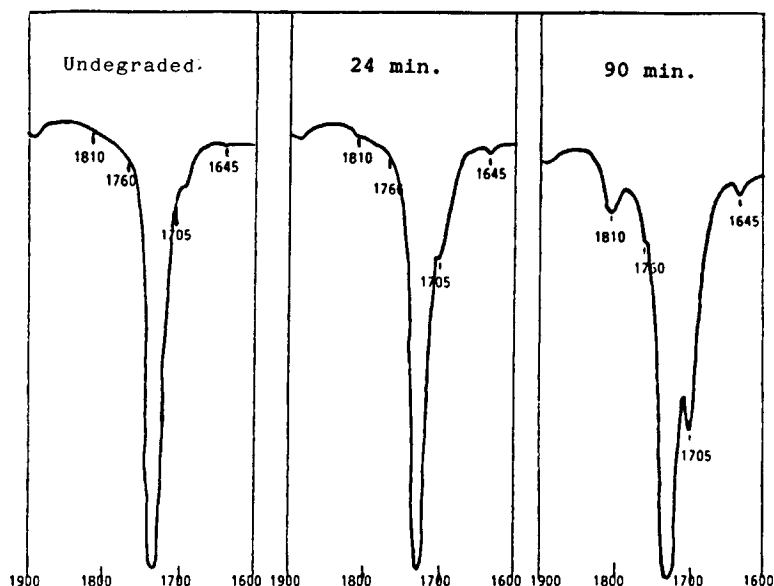


Figure 7 IR-spectra of EBA-1.6 degraded at 333°C for 24 and 90 min, carbonyl region.

At the degradation temperatures used, hydrogen-bonded carboxylic groups might transform to anhydride. According to Grant and Grassie⁷ the following IR-peak positions are assigned to three different types of anhydrides (Table II). Their results are in accordance with Randall et al.⁹ and Wasserman et al.¹⁰

The observed absorptions at 1810 and 1760 cm^{-1}

does not indicate any anhydride of type 1 (no absorption at 1850 cm^{-1}). A prerequisite for such a structure is head to head blocks in the copolymer. Obviously they are not present. Intermolecular anhydride formation should result in type 3 structures and molecular enlargements which could be broken with alkaline hydrolysis. Such enlargements were not observed to any great extent.⁶ We therefore con-

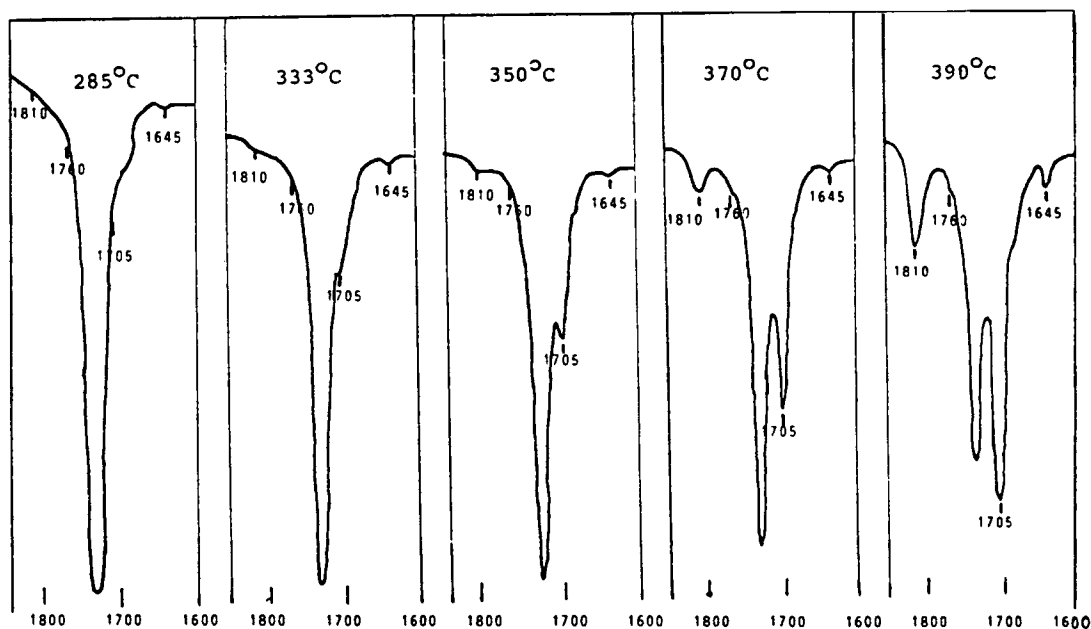
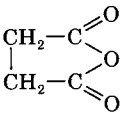
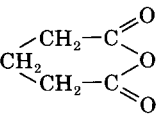
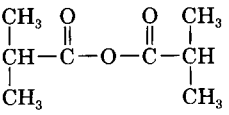


Figure 8 IR spectra of EBA-1.6 degraded 24 min between 285 and 390°C, carbonyl region.

Table II IR Absorption of Different Anhydrides⁷

Type	Name	Structure	IR Absorbance (cm ⁻¹)
1	Succinic anhydride		1855, 1776
2	Glutaric anhydride		1802, 1756
3	Isobutyric anhydride		1803, 1743

sider the anhydride formation to be mainly intramolecular.

As mentioned in our previous paper,¹ Grassie et al.¹¹ found a considerable decarboxylation, when degrading acrylate homopolymers thermally. In our investigation of volatile degradation products,¹ we could not prove whether carbon dioxide was formed or not.

In the present investigation we used titration with alcoholic KOH to determine the amount of carboxylic and anhydride groups. As is shown in Figure 9 these groups were totally transformed to potassium carboxylate, absorbing at 1585 cm⁻¹.^{9,12} Table III shows that the amount of titrated acid groups are less than the decrease in acrylate groups measured by IR. The difference increases with degradation.

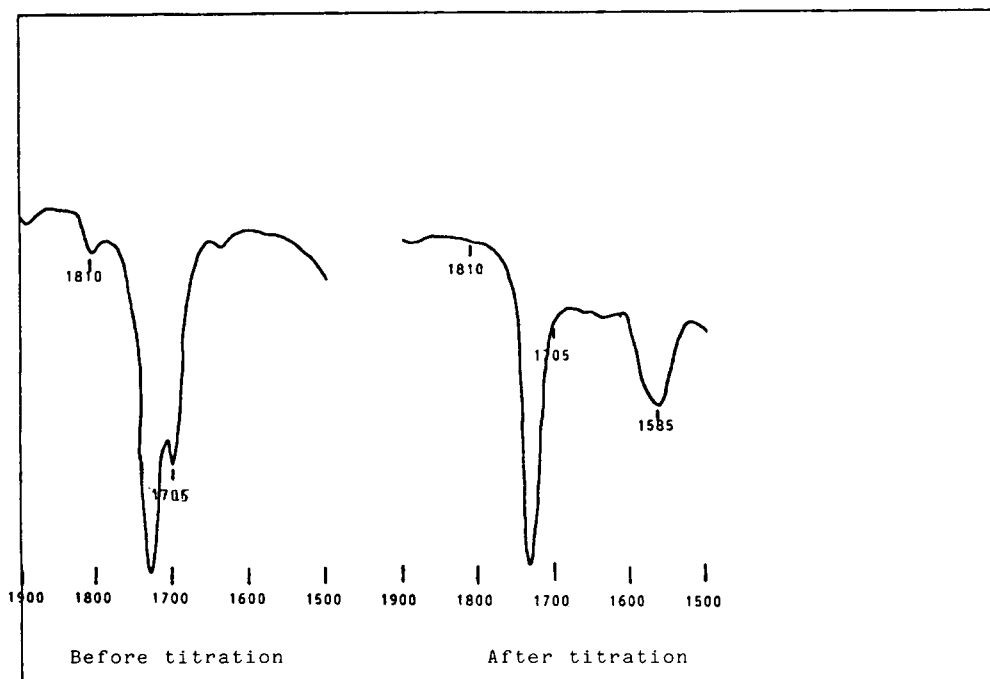
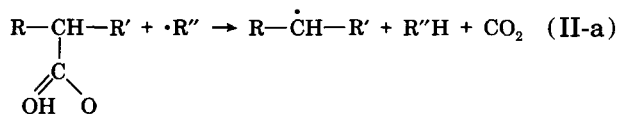


Figure 9 IR spectra for EBA-1.6 degraded for 90 min at 333°C, before and after titration with KOH, carbonyl region.

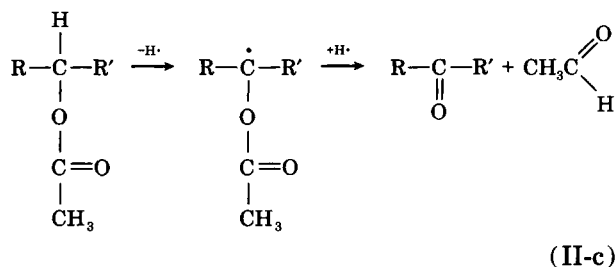
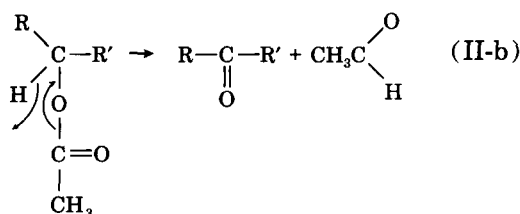
Presumably a slow decarboxylation reaction occurs. Grassie and Fortune suggest the following radical reaction¹³:



EVA

The changes in the carbonyl region during EVA pyrolysis are shown in Figure 10. Only peaks from the degraded EVA-1.2 are given as the changes in the other investigated sample follow the same pattern. Due to the formation of acetic acid, the ester peak at 1735 cm^{-1} is reduced. The same is observed for the C—O-stretch peak at 610 cm^{-1} (Fig. 5).

During the degradation a new peak appears at 1720 cm^{-1} . Compared to the original ester-peak it is small. It is due to keto groups,¹² and should be related to the formation of acetaldehyde described in Paper I.¹ In this paper the following mechanisms were suggested:



The small absorption at 1760 cm^{-1} could indicate the presence of lactones.¹² According to the suggested mechanisms below methane should be formed as well. As mentioned in Paper I,² several workers have observed the formation of methane when pyrolyzing poly vinyl acetate and EVA.¹⁴⁻¹⁹

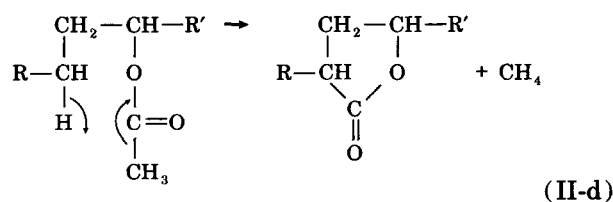
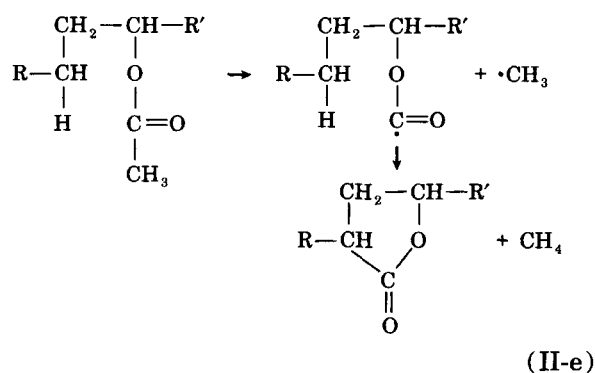


Table III Amount of Carboxylic Acid Groups in EBA-1.6, Determined by Titration

Pyrolyzing Conditions		Decrease ^a in BA content (mol/g $\times 10^6$)	Carboxylic Acid Groups (mol/g $\times 10^6$)
Temp (°C)	Time (min)		
—	—	—	< 1
333	6	5.5	4.6
333	24	10.1	9.4
333	90	16.4	12.9
390	24	39.0	29.8

^a Determined by IR.



Changes in Unsaturation

In Table IV the absorption indices for vinyl, vinylidene, and *trans*-vinylene bonds are given. The acetate groups absorb in the same region 965 cm^{-1} , as the latter bonds. To calculate the content of these groups, a compensation for the absorption of the acetate groups must be carried out. Such calculations were carried out assuming the content of *trans*-vinylene bonds to be negligible in the undegraded polymer. This is the case with LDPE and EBA produced according to the same process (see table IV). In Figure 11 the changes in the IR spectra for EVA-1.2 are given. The changes for EVA-6.7 follow the same pattern, but do not allow for quantitative determination.

Trans Vinylene Bonds

In LDPE no visible changes in *trans*-vinylene bonds were observed. Earlier measurements show, however, a slight increase at higher degradation temperatures.³ EBA is following the same pattern. The following mechanisms for the formation of *trans* vinylene bonds have been proposed³:

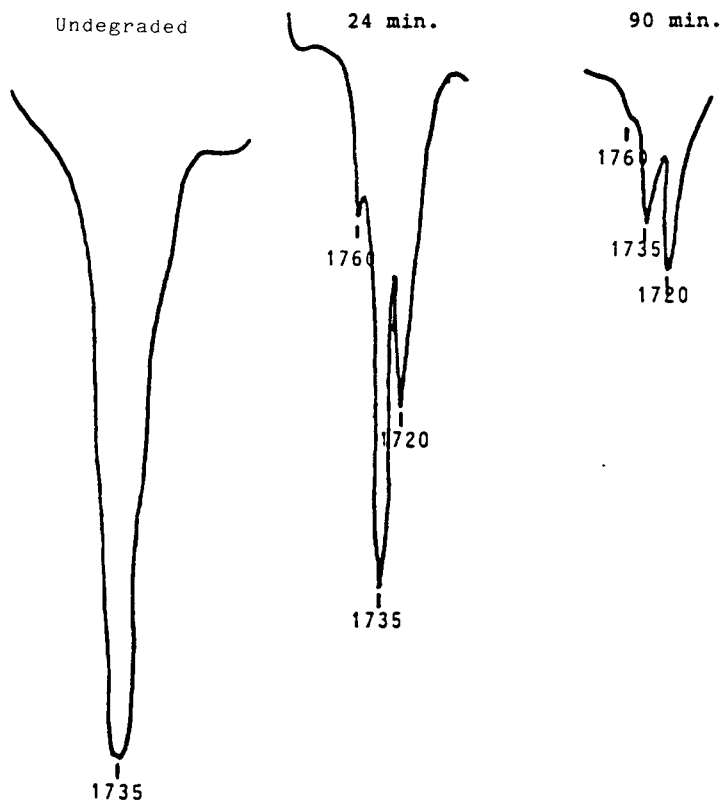
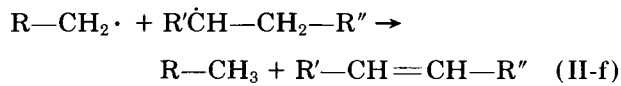


Figure 10 IR spectra of EVA-1.2 degraded at 333°C, carbonyl region.

—Disproportionation of secondary radicals:



—Isomerization of vinyl groups:

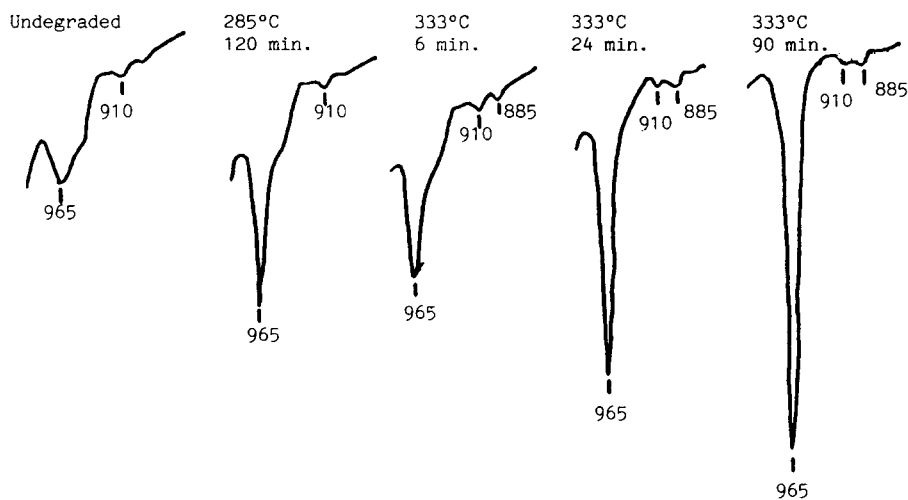
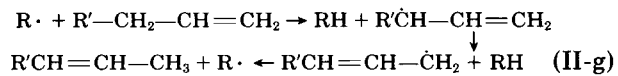
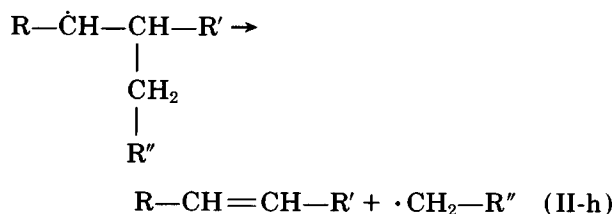


Figure 11 IR spectra of EVA-1.2 degraded at 285 and 333°C, unsaturated structures region.

— β -cleavage of secondary radical alpha to branch points:



EVA, on the other hand, shows a very pronounced increase already at mild degradation conditions. This is illustrated in Figure 11. In the undegraded sample the earlier mentioned acetate absorption at 965 cm^{-1} is observed. The original broad acetate peak at 965 cm^{-1} is gradually transformed into the sharper trans vinylene peak, while the unsaturation peaks at 910 and 885 cm^{-1} are practically unchanged.

Figure 12 clearly shows the connection between the increase in *trans*-vinylene and the reduction in vinyl acetate content. This is in accordance with the generally accepted mechanism for the deacetylation reaction.

Vinyl Groups

The formation of vinyl groups is connected with main chain cleavage³:

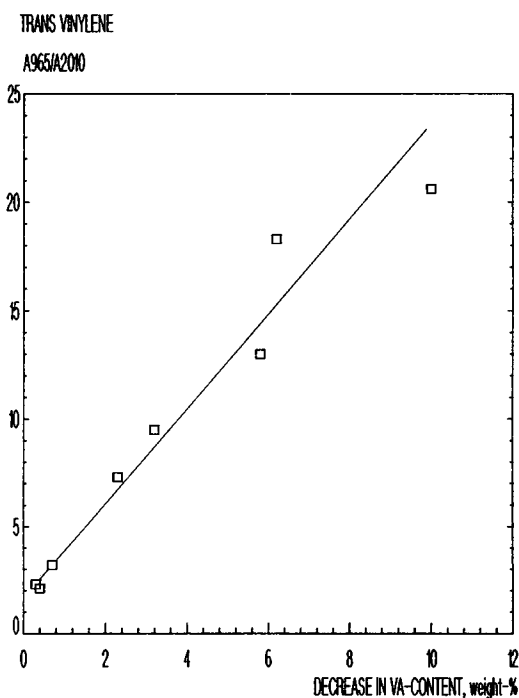
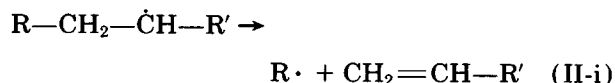


Figure 12 Decrease in VA content vs. relative increase in *trans*-vinylene groups in degraded EVA samples.

— β -scission at secondary radicals:



—Disproportionation of primary radicals:

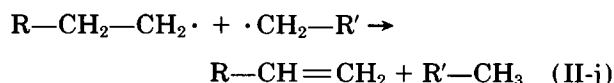
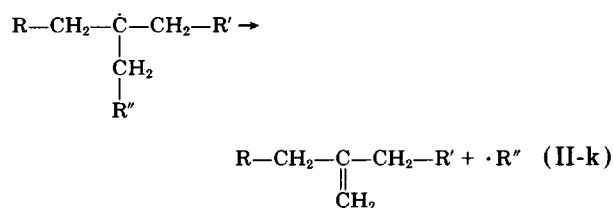


Table IV shows no appreciable changes in any of the samples at 285°C . At 333°C a clear increase is observed in LDPE and EBA. This is reasonable as random scission of CH_2 chains is increasing with temperature. Furthermore, disproportionation is increasing compared to combination when the temperature is increased.^{20,21}

The EVA samples show much slower increase in the vinyl content than LDPE. After 90 min at 333°C it is barely measurable. At this degradation level, hardly any of the original acetate groups remain and the gel formation is extensive.⁶ This behavior is possibly related to the high content of *trans*-vinylene unsaturations. A macroradical might then either add to the π -electron system or abstract hydrogen atoms in allyl position. This will lead to polymer enlargement rather than chain cleavages and the formation of vinyl groups.

Vinylidene Groups

This type of unsaturations is formed by β -cleavage of tertiary radicals³:



In virgin LDPE the content of vinylidene groups is relatively high compared to the other types of unsaturation. This is due to multiple backbiting reactions, leading to radicals at branch points.²² In our material, undegraded EBA shows the same vinylidene content as LDPE. This is reasonable as the polymers are produced in a similar way in the same reactor. On the other hand, EVA-1.2 show considerably lower initial vinylidene content. This might be due to milder polymerization conditions used in order to avoid acetate pyrolysis.

Table IV Relative Unsaturation Content

Sample	Pyrolyzing Conditions		Transvinylene	Vinyl	Vinylidene
	Temp (°C)	Time (min)	$\frac{A_{965}}{A_{2010}}$	$\frac{A_{910}}{A_{2010}}$	$\frac{A_{885}}{A_{2010}}$
LDPE	—	—	< 0.1	0.3	0.7
	285	24	< 0.1	0.2	0.7
	285	90	< 0.1	0.3	0.7
	285	120	< 0.1	0.3	0.7
	333	6	< 0.1	0.3	0.7
	333	24	< 0.1	0.4	0.8
	333	90	< 0.1	0.6	0.8
EBA-0.8	—	—	< 0.1	0.2	0.6
	285	24	< 0.1	0.2	0.5
	285	90	< 0.1	0.2	0.5
	285	120	< 0.1	0.2	0.5
	333	6	< 0.1	0.2	0.8
	333	24	< 0.1	0.4	0.8
	333	90	< 0.1	0.7	0.7
	350	24	< 0.1	0.8	0.7
	370	24	0.2	1.5	0.9
	390	24	0.6	3.0	1.0
EBA-1.6	—	—	< 0.1	0.3	0.7
	285	24	< 0.1	0.3	0.7
	285	90	< 0.1	0.3	0.6
	285	120	< 0.1	0.3	0.6
	333	6	< 0.1	0.4	0.7
	333	24	< 0.1	0.5	0.6
	333	90	0.2	0.8	0.6
	350	24	0.1	0.8	0.8
	370	24	0.4	1.5	0.7
	390	24	0.6	2.7	0.8
EBA-5.4	—	—	< 0.1	0.5	0.8
	285	24	< 0.1	0.5	0.8
	285	90	—	—	—
	285	120	< 0.1	0.5	0.8
	333	6	< 0.1	0.6	0.8
	333	24	< 0.1	0.6	0.7
	333	90	< 0.1	1.2	0.7
EVA-1.2	—	—	—	< 0.1	0.2
	285	24	0.5	< 0.1	0.2
	285	90	2.4	< 0.1	0.2
	285	120	3.1	< 0.1	0.2
	333	6	2.1	< 0.1	0.3
	333	24	7.3	< 0.1	0.3
	333	90	9.5	0.2	0.2

The increase in vinylidene content during the degradation is small and similar for all investigated polymers. This is reasonable as the branch point content is small 10–30/1000 carbons, in relation to the methylene group content in the hydrocarbon chains of the investigated polymers.

Weight Loss Measurements

The weight loss for the investigated samples are given in Table V and Figures 13 and 14. In order to obtain a rough estimate of the weight loss originating from main chain cleavage, corrections were made

Table V Weight Losses

Sample	Pyrolyzing Conditions		Weight Loss (wt %)	Decrease ^a in BA Alt. VA Content (wt %)	Calculated Weight Loss, Main Chain Cleavage (wt %)
	Temp (°C)	Time (min)			
LDPE	285	120	0.3	—	0.3
	333	90	0.7	—	0.7
EBA-0.8	285	120	0.3	0.2	0.2
	333	90	1.4	0.5	1.2
	350	24	0.9	0.4	0.7
	370	24	2.1	1.0	1.6
	390	24	6.1	1.7	6.0
EBA-1.6	285	120	—	—	—
	333	90	2.1	2.1	1.2
	350	24	1.2	1.5	0.5
	370	24	3.0	3.3	1.6
EBA-5.4	390	24	9.0	5.0	6.8
	285	120	1.3	0.7	0.9
	333	90	3.7	5.4	1.4
	285	120	1.3	0.7	0.9
EVA-1.2	333	90	3.4	3.2	1.2
	285	120	7.5	10.1	0.5
EVA-6.7	333	90	13.7	18.1	1.1

^a Determined by IR.

for volatile products (butene, resp. HAc) formed by side group degradation (see Table V).

The weight losses found for LDPE are low in accordance with earlier findings.⁴ For EBA with low comonomer content the total weight losses are fairly low at 285°C. They increase with temperature and BA content. Obviously the presence of BA groups increase the tendency to main chain cleavage. The rapid and complete acetate pyrolysis in EVA is clearly demonstrated. On the other hand, the main chain cleavage is low and is slightly decreasing with the VA content.

CONCLUSIONS

It has been confirmed that the decrease in VA content in EVA copolymers is fast already at 285°C. At 333°C the VA groups have been completely removed after about 30 min. The degradation rate increases with the VA content, which presumably is a result of the higher tendency for block formation and catalytic action of the acetic acid formed. A linear relationship between the increase in trans vinylene bonds and decrease in VA content exists, confirming the proposed ester pyrolysis mechanism.

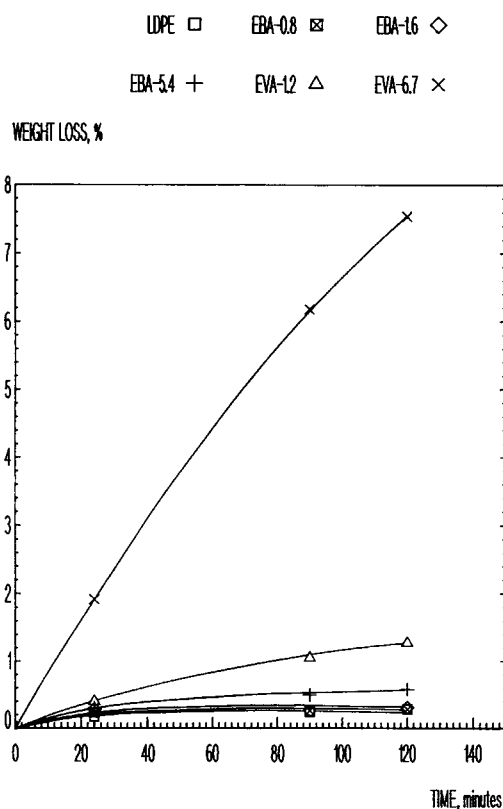


Figure 13 Weight losses at 285°C.

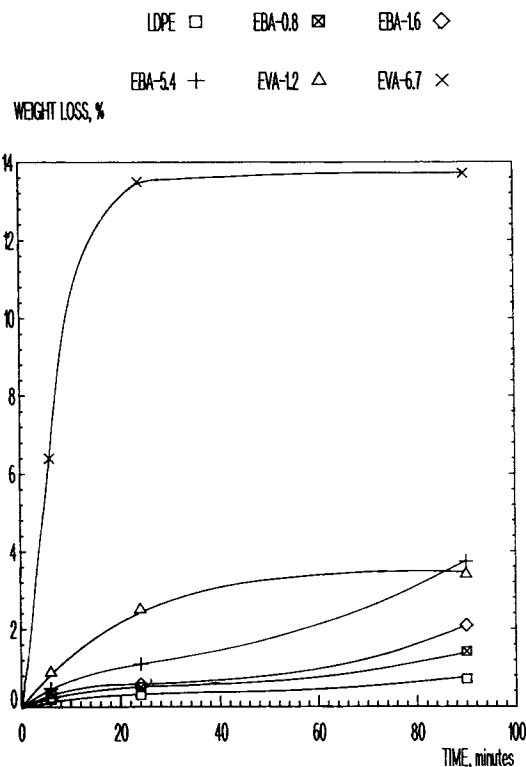


Figure 14 Weight losses at 333°C.

Small amounts of keto groups are also observed and support the earlier given mechanism for the acetaldehyde formation discussed in Paper I. There are also indications of lactone formation.

The decrease in BA content is considerably slower than the decrease in VA content. The acrylate side groups have similar stability as the main chain structure. The acrylate group decomposition results in carboxylic acid and anhydride groups along the hydrocarbon chain in accordance with mechanisms given earlier. A comparison between IR measurements and titration shows the presence of decarboxylation, increasing with thermal treatment.

Weight loss measurements show an increased tendency to main chain cleavage with increasing BA content. A tendency for the opposite behavior is observed for EVA.

Financial support from the Swedish board for technical development as well as Neste Polyeten AB, Sweden is gratefully acknowledged. The authors also thank Dr. Ludwig Binder and Mr. Frank Öhrn, Neste Polyeten AB, and Dr. Arne Holmström, Swedish National Testing In-

stitute, for constructive discussions as well as Dr. Thomas Hjertberg, who we also thank for the NMR analysis.

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Received September 20, 1990

Accepted January 28, 1991