Thermal Degradation Studies of Different Polar Polyethylene Copolymers

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ABSTRACT: The thermal degradation of different polar polyethylene copolymers, ethylene/methylacrylate (EMA), ethylene/ethylacrylate (EEA), ethylene/butylacrylate (EBA), ethylene/methylmethacrylate (EMMA), and ethylene/hydroxyethylmethacrylate (EHEMA), was studied by using thermogravimetric analysis (TGA), infrared analysis (FTIR), and size exclusion chromatography (SEC). Weight loss measurements of the different copolymers were performed at 333°C by using a nitrogen atmosphere in a TGA instrument. The samples thus aged were then characterized with the help of FTIR and SEC. Degradation reactions, such as ester pyrolysis, chain scission, and gelation, were investigated. EBA, EEA, and EHEMA undergo ester pyrolysis, which is affected by the structure of the ester moiety. EHEMA reacts additionally by transesterification and thus forms crosslinks. EMA and EMMA do not react by ester pyrolysis. It is concluded that the reaction products formed during ester pyrolysis support chain scission, and therefore, these reactions are observed more for EBA and EEA than for EMA and EMMA. Finally, the rate of chain scission is higher for EMMA than for EMA. This is explained as being due to an initiation of chain scission at the α—C—C bond, in which formed radicals are stabilized by the additional methyl group in EMMA. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1465–1473, 2002; DOI 10.1002/app.10510

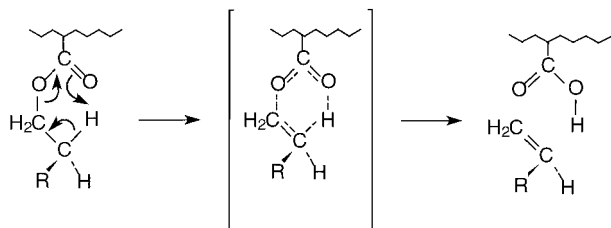**Key words:** thermal degradation; polyethylene

INTRODUCTION

The first ethylene copolymers, including ethylene vinyl acetate (EVA), were synthesized and patented in the 1930s by ICI in Great Britain in the same laboratories where low-density polyethylene (LDPE) was discovered.[1] Today, the term EVA copolymer covers a diverse family of materials containing from 2 to 50% by weight (wt %) of vinyl acetate. The copolymer is used in a wide range of applications where it can be subjected to very high temperatures during the manufacture. The limited thermal stability of EVA, resulting in acetic acid formation and gelation at temperatures as low as 200°C,[2–4] makes it essential to find alternatives. An understanding of the thermal stability and degradation of different copolymers is therefore crucial. The solution was the introduction of different acrylate-based copolymers. These provide better thermal stability but otherwise possess similar properties to EVA. Such copolymers consist of comonomers such as methyl acrylate, ethyl acrylate, butyl acrylate, acrylic acid, and methacrylic acid and are indus-

Reaction 1   Ester pyrolysis.
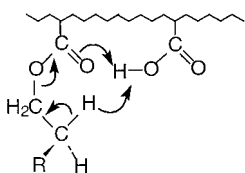

Reaction 3   Anhydride formation.

trially copolymerized with ethylene in high pressure reactors.

In this article, the thermal stability of some of these more novel acrylate-based copolymers are compared.
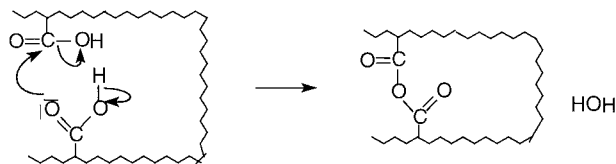
Previous Work

The earliest work of importance that investigated the thermal degradation of ethylene/acrylate copolymers was published by Clampitt.[5] He studied the thermal degradation of an ethylene/isopropyl acrylate copolymer during extrusion. It was found that the ester was thermally cracked during processing, giving propene as the major volatile product and carboxylic and anhydride groups as residues. This degradation was accompanied by an extensive main-chain cleavage.

The thermal degradation of ethylene/butylacrylate copolymer (EBA) at 285 and 333°C was extensively investigated by Sultan and Sörvik.[2–4] Corresponding with the results of Clampitt, the main degradation products of EBA are butene and carboxylic acid and the anhydride groups remaining on the polymer chain. Sultan and Sörvik suggested the autocatalyzed ester pyrolysis presented in reactions 1–3, which is similar to corresponding reactions of polyacrylates.[6] The carboxylic acid can alternatively undergo a decarboxylation.[7] All these ester reactions are accompanied by chain cleavage such as β-scission and disproportionation of primary radicals. A similar degra-

dation pattern to that discussed for EBA was reported by McNeill and Mohammed,[8] who compared thermal degradation (nonisothermal 10 K/min end point 600°C) of EEA with polyethylacrylate (PEA) and LDPE.

EXPERIMENTAL

Materials

The thermal stability of the following different copolymers of ethylene and acrylate or methacrylate were investigated:

Ethylene/butylacrylate (EBA, 4.3)
Ethylene/ethylacrylate (EEA, 4.8)
Ethylene/hydroxyethylmethacrylate (EHEMA, 1.8)
Ethylene/methylacrylate (EMA, 5.7)
Ethylene/methylmethacrylate (EMMA, 4.9)

The number following the abbreviation indicates the comonomer content as mol %. The copolymers are more extensively described in Table I.

Experiments and Evaluations

The polymers were degraded isothermally at 333°C in a thermogravimetric analysis (TGA) instrument (Mettler TGA850) by using a nitrogen atmosphere (containing < 10 ppm oxygen). For ordinary TGA measurements, sample weights of 6–8 mg are recommended. Further investigations, however, required an amount of approximately 23–26 mg. Consequently, the aging was performed with a sample weight of 23–26 mg cut into aluminum cups and for comparison of the weight loss behavior with only 6–8 mg cut into alumina crucibles. In both cases, the temperature program consisted of two sequences, first heating from 30 to 333°C at 100 K/min and second the isothermal sequence for various intervals at

Reaction 2   Ester pyrolysis catalyzed by formed carboxylic acid.

Table I Ethylene/acrylate copolymers investigated in this work

Type	Comonomer (wt %)	Comonomer (mol %)	$MFR_2^{190°C}$ (g/10 min)	T_M (°C)	T_{cr} (°C)	Cryst. (%)	M_n	M_w	MWD
EBA	BA 17	4.3	6	96.7	79.6	25.6	17.400	202.000	11.6
EEA	EA 15	4.8	ca.8	94.5	76.2	18.6	—	—	—
EHEMA	HEMA 8	1.8	1.5	107	—	29	20.400	154.000	7.5
EMA	MA 15.6	5.7	15 ± 5	86.6	66.8	23.1	15.300	177.000	11.7
EMMA	MMA 14.1	4.9	8	99.4	79	27.6	17.200	74.500	4.3

333°C. The nitrogen flow was kept constant at 50 mL/min.

After this treatment, the samples were cut out of the pans, pressed to a thickness of 0.1–0.6 mm, and investigated by using a Perkin–Elmer 1760X-FTIR instrument. The relative amount of hydroxyl and anhydride groups were calculated as the peak area at 3500 and 1815 cm^{-1}, relative to the peak area of the carbon–carbon band at 2020 cm^{-1}, which can be considered as a reference peak remaining unchanged during aging. The characteristic band for carboxylic acid at 1710 cm^{-1} was evaluated as the peak height relative to the reference peak. Finally, the amount of vinyl and vinylidene groups were determined as the number per 1000 CH$_2$ groups according to ASTM D 3124-72 using the bands at 910 and 888 cm^{-1}, respectively. Details of the FTIR evaluations are given in Table II.

The molecular weight distribution (MWD) of the samples previously studied by FTIR was determined by size exclusion chromatography (SEC). The evaluation of the peak area to calculate how much of the sample was dissolved additionally enabled the determination of the gel content. The chromatograph, a Waters 150C, was equipped with a refractive index detector (RI) and an on-line viscometer. The analyses were carried out at 135°C by using 1,2,4-
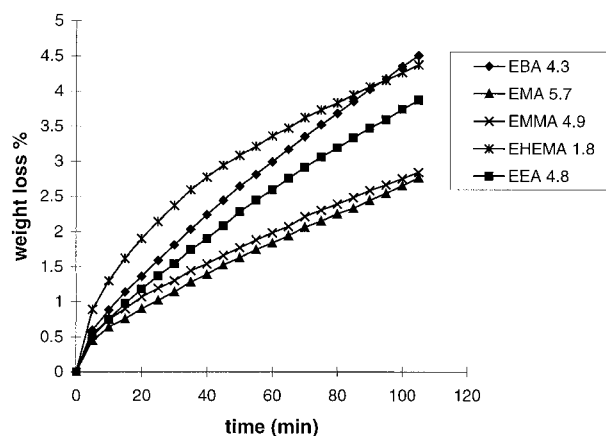
Table II FTIR Analysis

Structure	Peak Position (cm^{-1})	Baseline (cm^{-1})
Carboxylic acid	1710	Total peak height
Anhydride	1815	1838–1789
Hydroxyl	3500	3730–3156
Vinyl	910	930–860
Vinylidene	888	930–860
Hydrocarbon chain	2020	2110–1990

trichlorobenzene (TCB) as eluant. The column set used consisted of three TSK-Gel columns ($2\times$ mixed bed + 10^7 Å). Sample concentration was about 2.5 mg of polymer in 3.5 mL of TCB and 5–6 h dissolution time at 135°C (gentle stirring used). Samples were filtered only by the on-line filter after the injector. The system was calibrated with narrow MWD polystyrene standards and broad MWD linear polyethylenes. Corrections for long-chain branching were performed according to the principles developed by Drott and Mendelson.[9]

RESULTS

The weight losses of the different copolymers, 6–8 mg sample weight, are presented in Figure 1. The results for EBA are similar to the ones reported by Sultan and Sörvik.[2–4] The comparison of the acrylate and methacrylate copolymers (Fig. 1) shows that EMA and EMMA degrade similarly and both are more stable than EBA, EEA, and

Figure 1 Weight loss measured with TGA 333°C isothermal (6–8 mg).
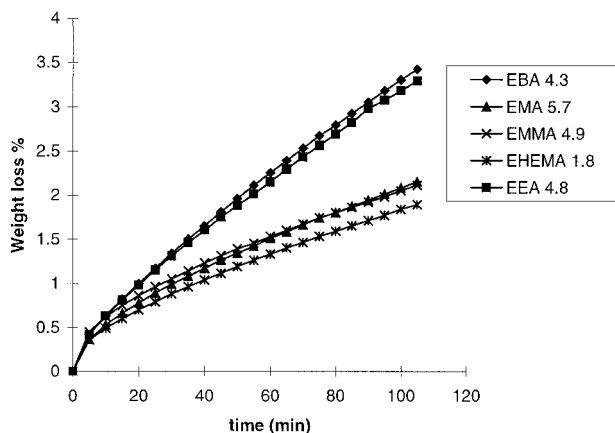
Figure 2 Weight loss measured with TGA 333°C isothermal (20–25 mg).

Figure 3 Solubility of EHEMA 1.8 after different aging time intervals at 333°C.

EHEMA. EHEMA loses its weight most rapidly. Measurements with a larger sample amount (23 mg) lead surprisingly to the opposite results (Fig. 2). For the other polymers, no significant differences are observed.

SEC chromatograms show that the molecular weight decreases during aging, indicating chain cleavage. EHEMA was not possible to fully dissolve after degradation (Fig. 3). For the other polymers, no gelation was observed. In Figure 4, the relative changes in the number of molecules, expressed as

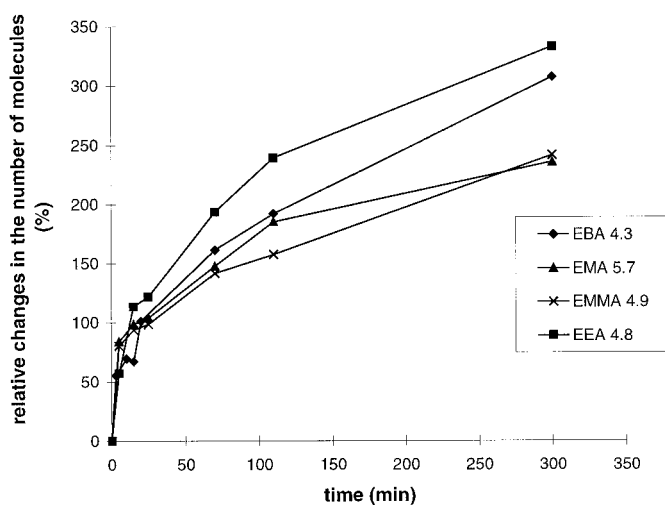$$\frac{M_n^{-1} - M_{n0}^{-1}}{M_{n0}^{-1}} \times 100$$

are presented. Chain cleavages are dominant for all polymers that were possible to fully dissolve. Both EMA and EMMA have a higher concentration of comonomer than EEA and EBA. Still, they show a higher stability with respect to chain scissions. EEA shows somewhat more chain scission than EBA. EEA contains somewhat more comonomer, which at least partly explains this difference.

The change in number of vinyl and vinylidene groups during aging is presented in Table III. Initially, the number of vinyl groups increases in all copolymers. However, although this tendency continues in EMA and EMMA during the investigated aging time, a reduction of these groups in EBA, EEA, and EHEMA can be observed after

Figure 4 Changes in relative number of molecules versus time of heat exposure.

Table III   Unsaturations; Number of Groups per 1000 CH$_2$ Groups

	Aging time (min)	Vinyl	Vinylidene
EBA	0	0.2	0.2
	3	0.2	0.2
	10	0.3	0.3
	15	0.3	0.1
	20	0.2	0.2
	70	0.4	0.1
	110	0.3	0
	300	0.2	0
EEA	0	0.1	0.2
	5	0.3	0.2
	15	0.3	0.2
	25	0.3	0.2
	70	0.3	0.1
	110	0.5	0.1
	300	0.1	0
EHEMA	0	1.0	1.0
	5	1.3	1.0
	15	1.2	0.9
	25	1.4	1.0
	70	1.3	0.9
	110	1.4	0.9
	300	0.9	0.5
EMA	0	0.1	0.2
	5	0.3	0.2
	15	0.4	0.3
	25	0.4	0.3
	70	0.5	0.3
	110	0.5	0.3
	300	0.6	0.4
EMMA	0	0.2	0.2
	5	0.5	0.3
	15	0.6	0.3
	25	0.5	0.3
	70	0.7	0.3
	110	0.8	0.4
	300	0.9	0.4

reaching a maximum. A similar trend may be true for vinylidene groups. However, the initial increase in the latter copolymers is less pronounced. Comparing EMA and EMMA, a more rapid increase of vinyl groups can be stated for EMMA.

The evaluations of the FTIR spectra made after various aging intervals are presented in Table IV. Figure 5 shows that the number of carboxylic acid and anhydride groups increases in EBA. Additionally, the growth of a peak at approximately 1760 cm^{-1} can be observed. This was explained by Sultan and Sörvik[3] as the formation of intramo-

lecular anhydride with a ring structure consisting of more than six units. EEA behaves similarly. The anhydride is formed to a much lower extent in EHEMA. Despite the inability of EMA to form an olefinic compound from the ester moiety, the presence of carboxylic acid can also be observed. This can be explained by traces of acrylic acid (0.01%) in the monomer. In contrast to EBA and EEA, the content of carboxylic acid and ester carbonyl groups remained constant in EMA and EMMA during the investigated time interval. EHEMA shows a significant decrease in OH groups (Fig. 6).

DISCUSSION

Ester Pyrolysis, Anhydride Formation, and Transesterification

Ester pyrolysis and anhydride formation, which are outlined in reactions 1–3, can be observed in EBA and EEA. These reactions do not occur in EMA and EMMA. This is reasonable because these copolymers are not able to form the respective olefin.

A different degradation pattern is observed in EHEMA, which obviously releases hydroxyl groups rapidly. However, the anhydride peak grows only relatively slowly and the amount of carboxylic acid decreases. Further on, a crosslinking reaction occurs. These facts lead to the conclusion that the transesterification outlined in reaction 4 may take place, which has been previously observed in poly-2-hydroxyethyl acrylate (PHEA).[10]

It is difficult to compare the rate of ester pyrolysis of EHEMA with EBA and EEA. Perhaps the hydroxyl group in the ester moiety destabilizes the intermediate cyclic structure in reaction 1 and thus slows down the reaction. However, the consumption of formed carboxylic acid by a mechanism analogous to reaction 4 is also possible and explains the decrease of carboxylic acid in EHEMA during aging. The occurrence of this mechanism would clearly forbid conclusions concerning ester pyrolysis drawn from measuring the content of carboxylic acid.

The reactions discussed above are typically equilibrium reactions. Hence, the weight loss, which requires the volatile reaction products to diffuse to the surface and to evaporate, is thus strongly in competition with the reverse reac-

Table IV   FTIR Analysis of Functional Groups

Time (min)	EBA	EEA	EHEMA	EMA	EMMA
Carboxylic acid: Absorption index of the 1710 cm^{-1} band relative to the reference band					
0	0.13	0.15	0.49	0.21	no distinct change observed
3	0.32	-	-	-	
5	-	0.25	0.31	-	
10	0.33	-	-	-	
15	0.38	0.26	0.32	0.23	
20	0.37	-	-	-	
25	-	0.34	-	-	
70	0.68	-	-	-	
110	0.77	-	0.21	-	
300	1.45	-	0.16	0.24	
Anhydride: Absorption index of the 1815 cm^{-1} band relative to the reference band					
0	0	0	0	not detectable	not detectable
3	0.01	-	-		
5	-	0.02	0.05		
10	0.02	-	-		
15	0.01	0.08	0.05		
20	0.01	-	-		
25	-	0.16	0.05		
70	0.50	0.50	0.05		
110	1.34	0.94	0.08		
300	3.88	3.11	0.11		
Hydroxy: Absorption index of the 3500 cm^{-1} band relative to the reference band					
0			50.7		
5			41.9		
15			47.8		
25			41.2		
70			33.4		
110			26.5		
300			9.6		

tions. This competition probably contributes to the large influence, especially for EHEMA, of the sample weight in TGA measurements.

Chain Scission and Gelation

The gelation process in EHEMA is remarkable because it appears intermolecularly, whereas the anhydride reaction in EBA and EEA apparently occurs only intramolecularly. Two possible explanations can be proposed. First, the mobility of the CH$_2$CH$_2$OH— arm in EHEMA can be expected to be higher than that of the carboxylic hydroxyl group in EBA or EEA. The latter is thus not able to reach an adjacent chain and reacts preferably intramolecularly. Second, the amount of crosslinks in EBA or EEA is simply too low to be detected as gelation.

Because of the gelation of EHEMA, SEC cannot be used for making any conclusions with respect to chain scissions. The other SEC results, however, allow differences to be detected. Sultan and Sörvik[3,4] previously found when comparing thermal degradation of EBA with LDPE that the presence of butylacrylate groups leads to a stronger tendency to chain cleavage. They explained this fact as being due to a higher content of tertiary positions and resonance stabilization of radicals formed at the acrylate groups. The good agreement of weight loss data reported by Sultan
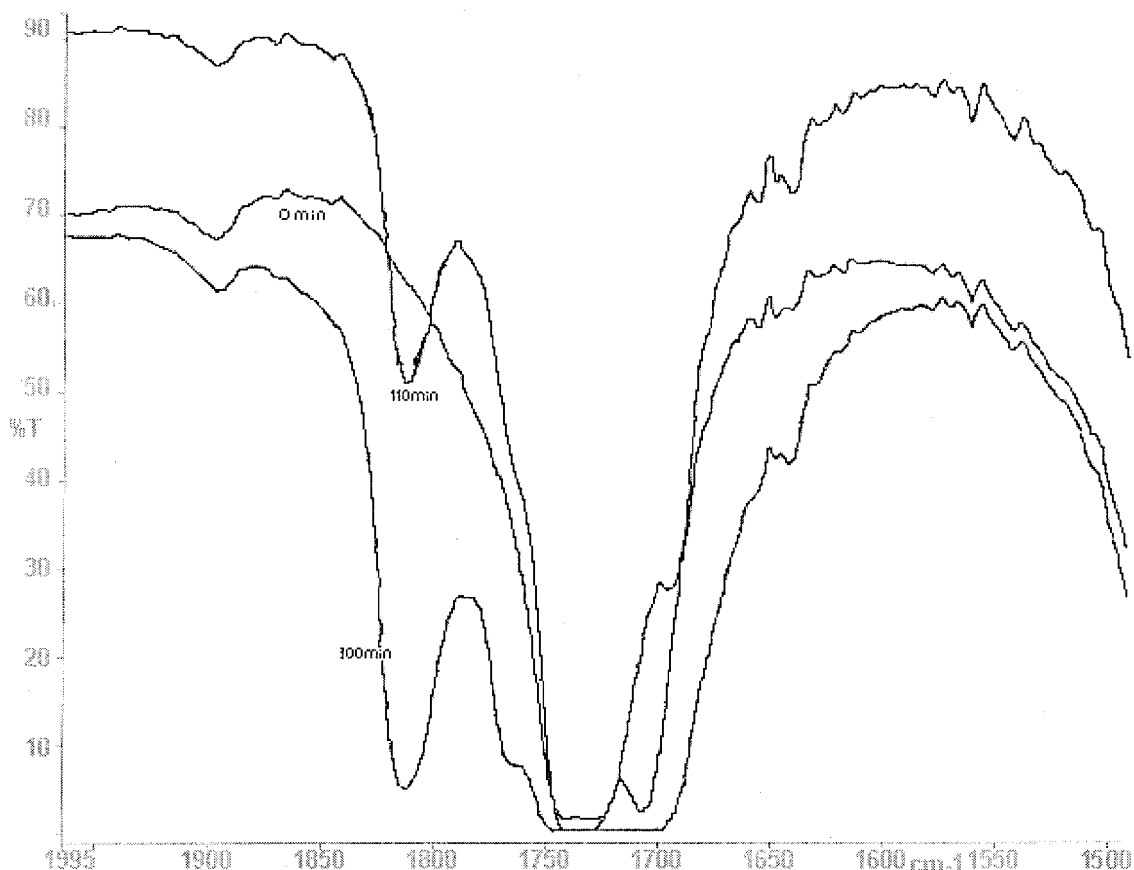
Figure 5 EBA degraded for different time intervals at 333°C. FTIR spectrum between 1965 and 1490 cm^{-1}.

and Sörvik concerning EBA with the present data also encourages the comparison of their LDPE data with present EMA and EMMA measurements. A weight loss of 0.7% in LDPE after 90-min aging at 333°C was reported. Because weight losses in EMA and EMMA are due to chain cleavage only, it can be confirmed that the introduction of acrylate groups supports chain cleavage (2.4% weight loss in EMA at similar conditions). The present SEC results additionally show that these copolymers, which undergo an ester pyrolysis (EBA and EEA), are more prone to chain cleavage than those which do not (EMA and EMMA). Consequently, it may not only be the presence of acrylate groups that accelerates this kind of reaction, but also its degradation products.

The FTIR analysis of vinyl and vinylidene groups appears to be in contradiction with the SEC data. An increase in vinyl and vinylidene groups is due to β-scission at secondary and tertiary radicals or due to disproportionation of primary radicals. Therefore, vinyl and vinylidene groups are typical reaction products of chain cleavage. Because EMA and EMMA show a more rapid increase than EBA and EEA, the conclusion may be drawn that these data indicate less cleavage in the latter copolymers. However, this may be misleading because the later decrease of these groups in EBA and EEA only can be explained by consecutive reactions or evaporation of low molecular weight chain fragments. Therefore, these numbers may not reflect the actual progress of chain cleavage. This particular behavior of vinyl and vinylidene groups in comparison with their behavior in EMA and EMMA is interesting, but cannot be explained within this study.

However, the comparison of the progress of vinyl groups in EMA and EMMA supports the SEC results, indicating more cleavage in EMMA than in EMA, which can be explained as being due to radical stabilization by the additional methyl group in EMMA.
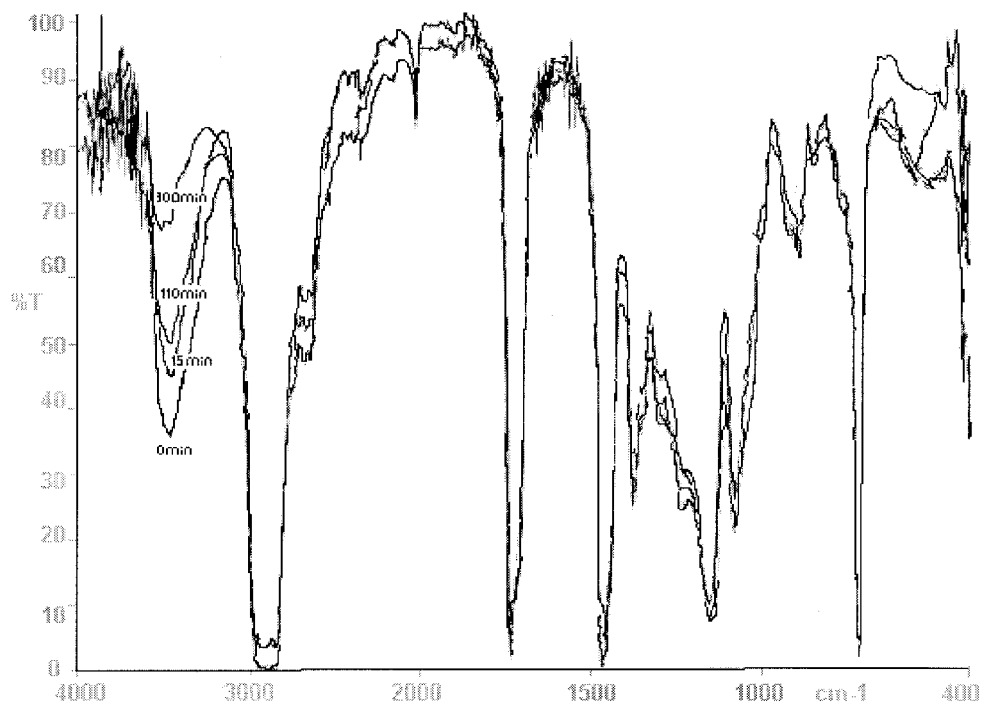
Figure 6   EHEMA degraded for different time intervals at 333°C. FTIR spectrum between 4000 and 400 cm^{-1}.

CONCLUSIONS

- EHEMA undergoes a transesterification and thus releases glycol. This reaction is accompanied by extensive gelation.
- EBA and EEA form carboxylic acid and anhydride by ester pyrolysis.
- The copolymers which undergo ester pyrolysis are more prone to chain cleavage than EMA and EMMA. Accordingly, it is not only the acrylate group that accelerates this kind of reaction, but also its degradation products.
- EMA and EMMA do not react by ester pyrolysis.

- More chain scission was observed in EMMA than in EMA. This indicates that the initiation of chain scission in ethylene acrylate copolymers is due to the breaking of the C—C bond next to the acrylate group. Hydrogen abstraction and β-breaks seem to be of less importance for explaining the higher tendency for chain scission in ethylene acrylate copolymers than polyethylene.
- Glycol, butylene, and ethylene formed during the degradation of EHEMA, EBA, and EEA, respectively, undergo reverse and consecutive reactions especially in thick samples.
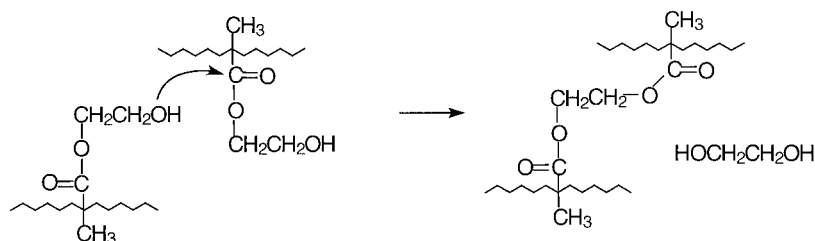
Reaction 4   Transesterification of EHEMA.

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