Investigations on the Mechanism of Flame Retardancy in HET Acid Containing Unsaturated Polyester Resins

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Synopsis

Unsaturated polyesters containing varying amounts of HET acid (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid) were synthesized and cured with styrene to give flame-retarding unsaturated polyester resins. The thermal properties were investigated by DTA (differential thermal analysis), TVA (thermal volatilization analysis), SATVA (subambient thermal volatilization analysis), and weight loss measurements. The studies revealed that the reverse Diels–Alder reaction of the HET acid units present in the polyester backbone proceeds in the temperature range 300–350°C and yields hexachlorocyclopentadiene. The influence of the HET acid content on the mass distribution of the products of pyrolysis (450°C) was analyzed b means of a gas chromatograph coupled with a mass spectrometer. With increasing HET acid content, the total amount of aromatics evolved from the cured resins is decreased. Concurrently, the relative amount of styrene produced is decreased while the relative amounts of toluene and ethyl benzene are increased. This finding strongly suggests that the hexachlorocyclopentadiene interferes as a chain transfer agent with the unzipping reaction of the polystyrene chains. Further support for this interpretation is derived from the enhanced char formation with increasing HET acid content, as observed by the weight loss measurements.

INTRODUCTION

Standard unsaturated polyester resins essentially cannot resist the action of flame and are classified as fairly flammable materials.[1] The increasing utilization of unsaturated polyester resin laminates for the manufacture of vehicles and building materials demands the development of flame-retardant systems to reduce fire hazards. One of the methods to achieve fire retardancy in the unsaturated polyester resin systems is to incorporate flame-retarding monomers in the unsaturated polyester backbone. One of the most important of such flame-retarding monomers is the Diels–Alder adduct of hexachlorocyclopentadiene and maleic acid, commonly designated as HET acid (*h*exachloroendomethylene *t*etrahydrophthalic acid).[2]

Hexachlorocyclopentadiene   Maleic acid   HET acid
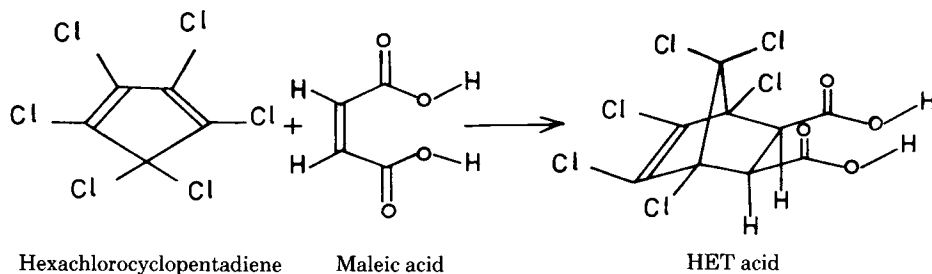
It is well known that the double bond of HET acid does not participate in the

crosslinking reaction under normal conditions.[1]   The fact that HET acid can be esterified at rates similar to fumaric acid makes it superior to other chloro derivatives like tetrachlorophthalic anhydride.   Though considerable interest has been shown in unsaturated polyester resins based on tetrachlorophthalic anhydride and tetrabromophthalic anhydride,[3,4] laboratory studies to evaluate the parameters which govern the flammability characteristics of HET-acid-based unsaturated polyester resin systems are scarce.

To attain a better understanding on the mechanism of the flame-retarding action of HET acid, a family of new model unsaturated polyesters containing varying amounts of HET acid was synthesized and subsequently cured with styrene.   The materials were characterized using DTA, TVA, SATVA, and weight loss measurements in the temperature range of up to 450°C.   Isothermal pyrolysis studies were performed at 450°C.   This low pyrolysis temperature was chosen to study the influence of the flame retardant on the primary degradation reactions.   The products of pyrolysis were identified and quantified using GC/MS technique.   Interpretation of these data was attempted with respect to the mechanism of the flame-retardant action of HET acid in the styrene-cured unsaturated polyester resins.

EXPERIMENTAL

Materials

HET acid, fumaric acid and 1,4-butanediol were supplied by Vianova (Austria) as gift samples.   Phthalic anhydride was supplied by Loba Chemie (Austria). These chemicals (technical grade) were used without further purification. Styrene (Merck for synthesis) was purified by distillation *in vacuo* before use.

Preparation of the Unsaturated Polyesters

The unsaturated polyesters were prepared by azeotropic condensation.[5]   The reactants were placed in a three-necked round flask equipped with a water separator.   Toluene was used to remove the water.   The condensation was carried out in nitrogen atmosphere at approximately 180°C to prevent crosslinking. During the reaction, the extent of polyesterification was followed by acid-number determination.   Approximately 0.5 g of reaction mixture was pipetted out of the flask.   After removing the toluene *in vacuo*, the sample was dissolved in a mixture of acetone and toluene and titrated with methanolic KOH, using phenolphthalein as indicator.   When the acid number of about 50 mg KOH/g unsaturated polyester was reached, the condensation was stopped by rapid cooling.   The residual toluene was removed by rotary evaporization *in vacuo* to constant weight.   Six different samples were prepared.   The components constituting the polyesters are listed in Table I.   The polyesters were stored in the refrigerator before further use.

Curing of the Unsaturated Polyesters

0.7 parts by weight of the unsaturated polyester was melted and mixed with 0.3 parts by weight of styrene.   The mixture was cured by adding 1% by weight of benzoyl peroxide and was kept at 90°C for 1 h.   Subsequently, a post-curing at 120°C for 3 h was allowed.   These unsaturated polyester resins were charac-

TABLE I
Composition of Unsaturated Polyesters

Sample code	Feed composition [mol] of various components[a]				Acid number of polyesters (mg KOH/g)
	(1)	(2)	(3)	(4)	
UPA	1	0.0	1.0	2.2	42.77
UPB	1	0.2	0.8	2.2	47.69
UPC	1	0.4	0.6	2.2	52.62
UPD	1	0.6	0.4	2.2	48.54
UPE	1	0.8	0.2	2.2	51.36
UPF	1	1.0	0.0	2.2	55.21

[a] Components: (1) fumaric acid; (2) phthalic anhydride; (3) HET acid (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid); (4) 1,4-butanediol.

terized as described below. To distinguish the cured polyester resins clearly from the uncured polyesters the letter S (styrene) is added to the code for the respective uncured polyester samples (cf. Tables I and II).

Methods

DTA Studies

A Mettler system TA 2000 was used to record the DTA curves. Typically 5 mg of the sample was encapsulated in aluminium sample pans and empty pans were used as references. The lids of the pans were perforated with a needle so that the measurements were carried out in air atmosphere. Dynamic studies were performed by heating the material from 30°C to 490°C at a heating rate of 10°C/min. The thermograms were corrected for their base lines.

Besides the dynamic measurements, isothermal decomposition studies of the cured resins were performed. The oven was kept at 350°C. The pan with the sample was positioned in the hot cell. The samples reached the oven temperature within 2 min. The DTA traces were recorded for 40 min; subsequently, the weight loss was measured. The same type of isothermal studies were done at 370°C, 390°C, and 410°C, respectively.

TABLE II
Peak Maxima of DTA Traces of Cured Unsaturated Polyester Resins

Sample code	Sample weight (mg)	Temperature region of decomposition, peak maximum	
		350–380°C First peak	380–480°C Second peak
UPFS	3.89	366	433
UPES	5.21	362	423
UPDS	4.45	364	426
UPCS	4.79	365	415
UPBS	6.43	365	415
UPAS	4.01	360	410

TVA and SATVA Studies of the Decomposition of the Unsaturated
Polyester Resins

Additional information about the decomposition of the resins was obtained by TVA and SATVA.[6–8] The schematic diagram of the all glass apparatus used in these studies is shown in Figure 1. Samples (typically 100 mg) were kept at approximately 0.5 Pa for 5 min at 40°C, and then were heated at a rate of 10°C/min to 440°C. The temperature was maintained at 440°C for 5 min. During these stages, the change of pressure was recorded yielding the TVA trace. The volatile products were trapped in the SATVA trap (no. 2, Fig. 1), cooled with liquid nitrogen. Subsequently, the coolant was removed and the changes of pressure caused by the evolution of volatile products were recorded as SATVA pattern. The less volatile products generally condense at the colder part of the pyrolysis tube, which is termed the "cold ring fraction."

Isothermal Pyrolysis of the Unsaturated Polyester Resins and Analysis of
the Products of Pyrolysis by GC/MS Techniques

The isothermal pyrolysis experiments were carried out in the TVA apparatus at 450°C *in vacuo* for 35 min. The volatile products were trapped in the sample collecting trap (no. 3, Fig. 1), which contained 0.5 mL of acetone kept at liquid nitrogen temperature. The acetone together with the products of pyrolysis was transferred to a glass finger (no. 4, Fig. 1).[9] The products were separated in a gas chromatograph and identified using a mass spectrometer. A Hewlett Packard Gas Chromatograph Model 5830 with an OV-17 column (5 min 60°C, 10°C/min to 160°C, 30 mL helium/min) was used. The gas chromatograph was coupled to a Balzers QMG 511 mass spectrometer by a jet separator.

RESULTS AND DISCUSSION

DTA Studies

The DTA curves of the unsaturated polyester series are shown in Figure 2. The exothermal decomposition begins at approximately 180°C for all the polymers. The rate of this reaction increases and a maximum is reached at 260°C.
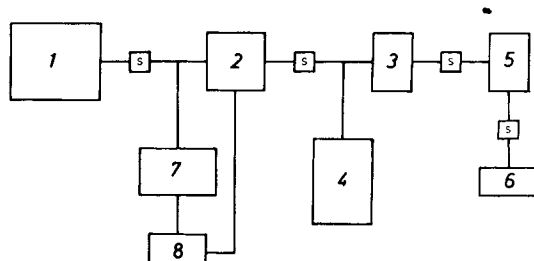

Fig. 1. Schematic layout of the thermal volatilization and subambient thermal volatilization apparatus: (1) oven containing the pyrolysis tube (glass) with the sample; (2) SATVA trap; (3) sample collecting trap; (4) glass finger suitable to transfer the products to the gas chromatograph; (5) main trap; (6) pump; (7) Pirani gauge; (8) recorder; (S) stopcocks.
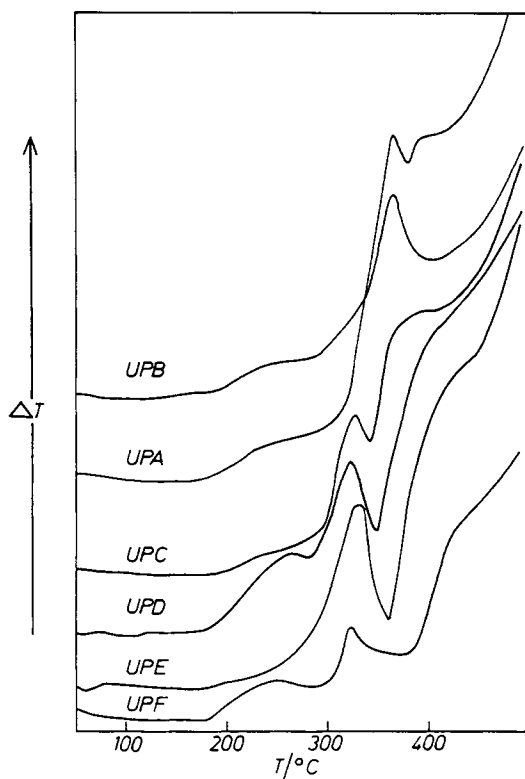
Fig. 2. DTA thermograms of the unsaturated polyesters. For composition of the various samples (UPA—UPF), cf. Table I. Heating rate: 10°C/min.

This first stage of decomposition is overlapped by a severe exothermal decomposition shifting its maximum decomposition rate gradually from 320°C to 340°C for the polyesters UPF to UPA. This shows that this stage of decomposition is shifted only slightly to higher temperatures with increasing HET acid content in the unsaturated polyester. The extent of the completion of this second stage decomposition depends upon the HET acid content and is much more pronounced in the UPF sample. Inspection of the curves in the higher temperature region shows that the rate of exothermal decomposition increases continuously, and no further maximum can be observed in the temperature region studied.

The DTA studies of the cured polyester resins are presented in Figure 3. In comparison with the uncured polyesters, the onset of the first exothermal reaction is shifted to higher temperatures (250°C) in the case of the cured polyester resins. A two-stage decomposition with maximum decomposition rates in the ranges of 350–380°C and 380–480°C, respectively (Table II), can be observed in all the cases.

The rate of decomposition of the sample UPFS is remarkably high in the second stage of decomposition compared to the first stage. Going to the unsaturated polyester resins with HET acid (UPAS–UPES), it can be seen that the peak height of the second stage of decomposition decreases with increasing HET acid content. Since the weight of the samples of UPFS and UPAS is approximately the same, it can be seen qualitatively from the traces of these samples
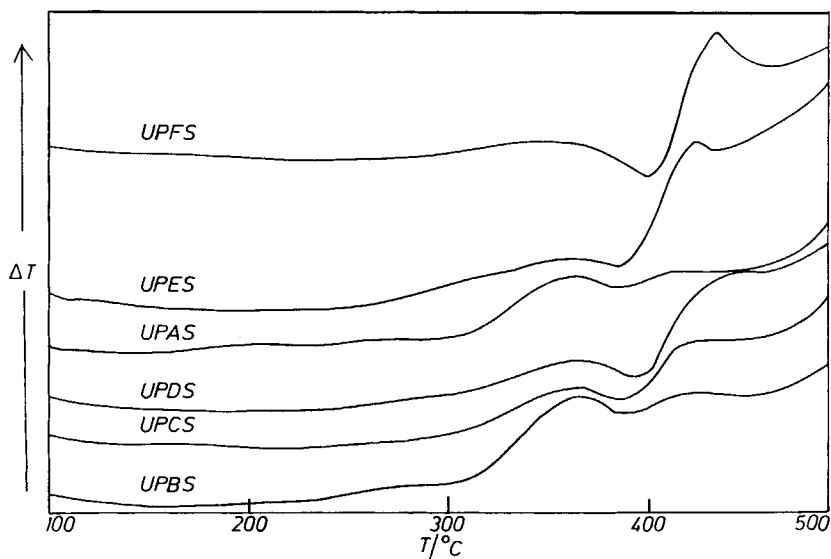
Fig. 3. DTA thermograms for the cured unsaturated polyester resins. Samples UPAS—UPFS are products obtained by curing UPA—UPF with styrene; cf. Table I.

that the heat evolved during the decomposition process is much lower in UPAS compared to UPFS.

Isothermal DTA studies were performed to relate the weight loss to the heat evolved during decomposition. Since appreciable quantities of heat of decomposition seemed to have been evolved during the heating up period already, it was not possible to correlate the areas of the DTA curves (i.e., the heat evolved during the isothermal decomposition experiment) with the weight loss data. The weight loss data are listed in Table III. In general the weight loss increases with decreasing content of HET acid. In any case the weight loss goes through a minimum with increasing temperature of pyrolysis. This minimum is in the region between the two stages of decomposition (cf. Fig. 3) of the dynamic DTA experiments discussed above. At lower temperatures it seems there is some reaction, which results in higher weight loss. Obviously, by the rapid heating (300°C/min), this reaction cannot develop fully when the sample passes the temperature range in question. On the other hand, this reaction seems to be hindered at higher temperatures, so that the weight loss is not so extensive, at higher temperatures of pyrolysis.

TABLE III
Weight Loss % for Cured Unsaturated Polyester Resins. Samples Kept at Different Temperatures for 40 min in DTA

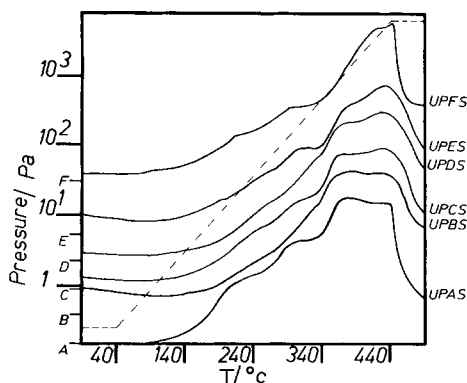| Sample | Weight loss (%) at measuring temperature | | | |
	350°C	370°C	390°C	410°C
UPAS	70.57	55.37	62.73	65.23
UPCS	77.68	63.05	69.34	71.83
UPFS	88.34	84.02	71.90	77.73
UPFS	—	85.08	—	—

Fig. 4. TVA thermograms of the cured unsaturated polyester resins. Except the curve for the sample UPAS, the curves of the samples UPBS, UPCS, UPDS, UPES, and UPFS are shifted on the ordinate by the distance $\overline{AB}$, $\overline{AC}$, $\overline{AD}$, $\overline{AE}$, and $\overline{AF}$, respectively. (- - -) Schematically represents the temperature profile.

TVA and SATVA Studies of the Cured Resins

Inspection of the TVA curves (Fig. 4) shows that the development of the volatile products can be observed around 100°C already. This is probably due to the residual styrene which is generally present ($\approx$1%) in the resins from incomplete curing.[10] The pressure drop at 440°C is not because the decomposition is completed, but rather because this is the end point of the analysis (the maximum oven temperature of the TVA oven is 440°C).

In the region of approximately 300°C a shoulder can be observed which is missing in the corresponding DTA curves. In the case of HET acid containing polyesters a maximum development of volatile products is detectable in the region of 370°C. Obviously this maximum corresponds to the first stage of decomposition discussed in connection with the DTA measurements. In the UPFS sample this maximum cannot be seen readily. This means that the first stage of decomposition can follow the same mechanism both *in vacuo* (TVA studies) and in atmospheric air (DTA studies). The second stage of decomposition discussed in the DTA studies cannot be compared with these TVA studies since the upper limit of the TVA oven is 440°C.

In Table IV the weight loss data obtained in the TVA studies discussed above are given. These data were calculated from the residual charred material (without the cold ring fraction) obtained after each TVA run. These data can be compared with the weight loss data obtained from the isothermal DTA studies. As observed in the DTA experiments, the weight loss increases with decreasing HET acid content. However, much more weight is lost in the TVA experiments compared to the DTA studies. This can be explained by the vacuum conditions

TABLE IV
Weight Loss during Temperature Programmed TVA Experiments Calculated from Residual Material (Omitting Cold Ring Fraction)

Sample	Weight loss (%)	Sample	Weight loss (%)
UPAS	81.26	UPDS	91.82
UPBS	84.20	UPES	95.59
UPCS	87.92	UPFS	98.60

in TVA. The weight loss differs by the amount of products which are not volatile under atmospheric pressure but readily volatile under high vacuum conditions. The SATVA curves obtained are shown in Figure 5. All the curves are similar, i.e., the main components obtained are not quite different. Because of the large number of products, the individual peaks are not resolved completely. Therefore, the SATVA traces may be regarded mainly as the finger print of the spectrum of the products of pyrolysis.

Isothermal Pyrolysis of the Cured Unsaturated Polyester Resins in High Vacuum and Analysis of the Products of Pyrolysis by GC/MS

The products of pyrolysis at 450°C were separated in a gas chromatograph, and the major components were identified by their mass spectra. A typical gas chromatogram is given in Figure 6. In Table V the gas chromatograph retention times, the fragment ions, their relative intensities, and the suggested structures are listed. Table VI shows the relative amounts of the major volatile components of pyrolysis as given by the peak areas of the FID response, corresponding to about 95% of the collected products. The relative amounts given by the FID response are not the true amounts due to unequal response for different compounds, especially for halogenated compounds, but these values can give a good picture of the trend which these products are following.

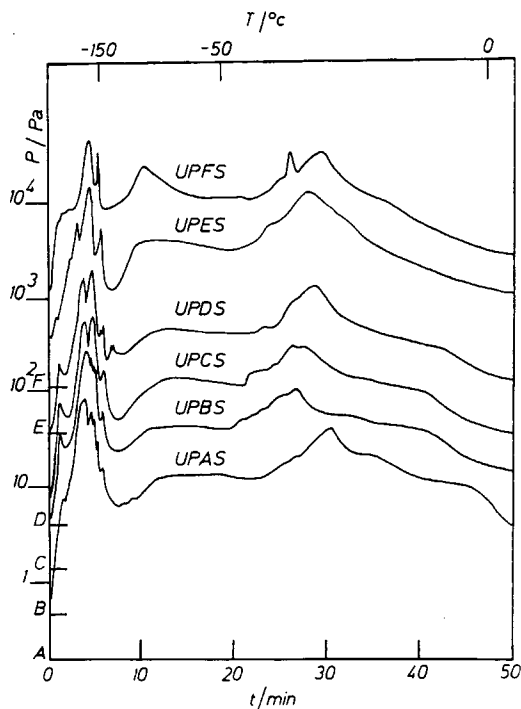The occurrence of butadiene and tetrahydrofuran can be readily explained,

Fig. 5. SATVA curves of the products of pyrolysis of the cured unsaturated polyester resins. Except the curve for the sample UPAS, the curves of the samples UPBS, UPCS, UPDS, UPES, and UPFS are shifted on the ordinate by the distance $\overline{AB}$, $\overline{AC}$, $\overline{AD}$, $\overline{AE}$, and $\overline{AF}$, respectively.
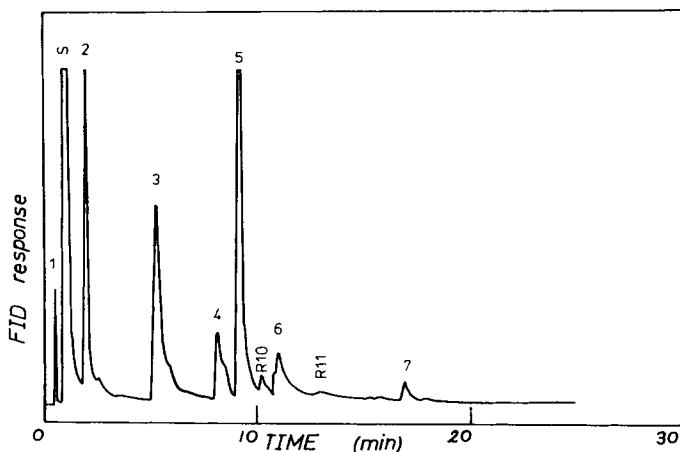
Fig. 6. Gas chromatogram of the products of pyrolysis of the sample UPAS (isothermal pyrolysis in high vacuum at 450°C for 35 min): (1) butadiene; (2) tetrahydrofuran; (3) toluene; (4) ethylbenzene; (5) styrene; (6) maleic anhydride; (7) hexachlorocyclopentadiene; (S) solvent (acetone); (R10) unidentified product with a retention time of 9.93 min; (R11) unidentified product with a retention time of 11.33 min.

assuming the degradation of the butanediol component present in the unsaturated polyester main chain. The ratio of butadiene to tetrahydrofuran formed during the isothermal pyrolysis of various cured unsaturated polyester resins is nearly the same (the ratio of butadiene to tetrahydrofuran is ≈ 1:10, cf.

TABLE V

GC/MS Analysis of Main Products of Isothermal Pyrolysis of Unsaturated Polyester Resins at 450°C in High Vacuum for 35 min

Retention time (min)	Mass/charge relative intensity										Suggested structure
0.45	39	27	41	54	53	26	49	50			Butadiene
	1000	930	837	814	721	698	674	651			
1.95	42	41	43	27	71	39	72	29	15	40	Tetrahydro-
	1000	600	331	315	284	246	238	192	161	123	furan[a]
5.23	91	92	39	65	51	63	50	27	89	62	Toluene[a]
	1000	523	185	177	108	108	69	58	54	54	
6.51	43	39	15	27	29	83	55	98			Methyl-
	1000	136	136	125	91	91	76	30			allylketone?
7.92	91	106	51	65	39	77	78	92	27	50	Ethyl-
	1000	290	174	167	145	130	109	101	101	87	benzene
9.12	104	78	103	52	77	50	39	52	63	102	27	Styrene[a]
	1000	733	527	393	327	207	153	133	120	107	107	
9.93	55	27	41	39	54	62	29	26	43	49	?
	1000	450	400	267	217	167	133	100	100	100	
10.71	26	54	25	53	98	13	27	24			Maleic
	1000	649	176	108	95	81	68	61			Anhydride
11.33	43	55	59	27	39	41	113	26	19	54	?
	1000	932	373	305	305	271	271	254	237	237	
16.87	237	239	235	95	60	130	119	141	127	143	Hexachloro-
	1000	597	558	529	303	282	244	227	227	222	cyclopentadiene

[a] Pure substances were available and their retention times agreed with those given in the table.

TABLE VI
Relative Amounts of Isothermal Pyrolysis Products of Cured Unsaturated Polyester Resins in High Vacuum (at 450°C for 35 min)

Sample	Butadiene	Tetrahydrofuran	Benzene	Toluene	Ethylbenzene	Styrene	Methylallylketone?	R10[a]	Maleic anhydride	R11[b]	Hexachlorocyclopentadiene
						Products of pyrolysis/area (% of FID response)					
UPAS	1.39	14.66	2.83	20.75	7.39	27.88	2.23	2.81	8.65	3.44	1.96
UPBS	2.02	13.65	5.43	13.06	7.86	30.49	0.70	2.50	4.50	2.78	2.93
UPCS	1.73	16.06	1.95	16.90	7.73	35.71	0.00	2.40	8.59	2.12	0.99
UPDS	2.16	19.84	?	9.16	5.71	44.10	0.00	2.18	8.91	1.35	0.39
UPES	2.46	24.41	4.21	9.20	3.80	42.30	0.00	1.54	6.37	0.85	1.40
UPFS	1.71	15.23	6.75	6.51	0.97	63.15	0.00	0.70	3.26	0.52	0.00

[a] Unidentified product with a retention time of 9.93 min.
[b] Unidentified product with a retention time of 11.33 min.

Table VI). It can be concluded that the varying amount of HET acid in the samples has no influence on this particular type of degradation. Furthermore, the constancy in the ratio of butadiene to tetrahydrofuran suggests that the products are formed from a common intermediate by a route which is not influenced by a variation in the HET acid content.

Herlinger et al.[11] investigated the mechanism of degradation of poly(ethyleneterephthalate). The authors discussed a mechanism to explain the formation of the major product of pyrolysis, acetaldehyde,[12,13] from poly(ethyleneterephthalate). Applying this mechanism to butanediol-containing polyesters, the major product of pyrolysis should be methyl vinylketone. The absence of this product in the polyesters studied here clearly shows that polyesters made from butanediol exhibit a completely different degradation behavior. One of the components of degradation is maleic anhydride. In all the resins of the present investigation there is the same amount of fumaric acid units, but the amount of HET acid is varying (cf. Table I). As shown in Table VI, the maleic anhydride content in the pyrolysis products decreases with decreasing HET acid content in the cured unsaturated polyester resin. This finding suggests that maleic anhydride is formed from two different decomposition routes, one from the breaking of the fumaric acid units followed by isomerization during pyrolysis and the other from the reverse Diels–Alder reaction of the HET acid units and subsequent degradation.

The identification of hexachlorocyclopentadiene in the products of pyrolysis of the cured resins containing HET acid explicitly shows that the reverse Diels–Alder reaction takes place during pyrolysis. To obtain information about the temperature range at which this reaction takes place, the following experiment was performed: The pyrolysis tube (no. 1 in Fig. 1) was directly attached to the mass spectrometer, and the sample UPAS was heated in high vacuum in the same manner as described for the TVA runs. Evaluating the total ion current and the intensity of the peak for m/e of 272 (the most intense of the M^+ group of hexachlorocyclopentadiene, which is not given in the Table V due to its low relative intensity of 71), it was found that this peak appears in the region of 300°C and increases rapidly up to 350°C. Over 350°C, the intensity decreases slowly. Since none of the pyrolysis products show an m/e peak in this region (cf. Table V), the $m/e = 272$ peak may be assigned at least to hexachlorocyclopentadiene. This strongly suggests that the reverse Diels–Alder reaction of HET acid units present in the unsaturated polyester chain proceeds in the temperature range 300–350°C.

The aromatic compounds benzene, styrene, toluene, and ethyl benzene constitute approximately 60–80% of the total pyrolysis products. Benzene is formed nearly in all the cases and its contribution to the total aromatics varies from 2% to 7%. Since the production of benzene from polystyrene units is possible only at very high pyrolysis temperatures (800°C and above),[14] it can be assumed that the benzene is produced only from the degradation of the phthalic acid units present in the polyester chain. The increase of benzene formation with increasing content of phthalic acid (cf. Table VI) strongly supports this argument.

Linear polystyrene decomposes in the temperature range 250–300°C while the crosslinked polystyrene degrades at 330–390°C.[15,16] From the pyrolysis studies of polystyrene,[14,17,18] it is evident that in the temperature region of

425–625°C, polystyrene yields approximately 65–75% of monomer and trace amounts of toluene and ethyl benzene. But an increase in the pyrolysis temperature, from 800°C to 1200°C, results in higher yields of toluene and ethyl benzene at the expense of monomer, due to the enhanced transfer reaction compared to the process of unzipping.

From the present investigation it is evident that even at 450°C the cured unsaturated polyester resins produce considerable amount of toluene and ethyl benzene. This supports the view that extensive chain transfer is taking place at this pyrolysis temperature. Hexachlorocyclopentadiene is regarded as a much stronger chain transfer agent[1] than HET acid. Since the reverse Diels–Adler reaction starts in the range of 300–350°C, the hexachlorocyclopentadiene formed, owing to its chain transfer action, interferes with the unzipping process of the polystyrene, resulting in the production of considerable amounts of toluene and ethyl benzene. The decreasing amounts of toluene and ethyl benzene and concomittent increase in the styrene content in the pyrolysis products with decreasing HET acid content strongly supports the foregoing reasoning. With increasing HET acid in the unsaturated polyester backbone, the total amount of aromatics formed during the pyrolysis decreases.

Highly chlorinated compounds added to the polymeric materials and/or incorporated in the system as a comonomer are generally known to increase the residual char during pyrolysis.[19] When the unsaturated polyester without any HET acid and the resin derived from it (UPF and UPFS) were subjected to pyrolysis at 450°C for 35 min, the percentage of the charred material was 5.8 wt % and 4.5 wt %, respectively. Similar studies on the HET-acid-based samples (UPA and UPAS) showed 13.7 wt % and 23.2 wt % of char residue, respectively.

Thus the unsaturated polyester having no HET acid and its styrene-cured resin give nearly the same percentage of char whereas HET-acid-based samples yield a higher percentage of char. This strongly supports the view that the hexachlorocyclopentadiene formed during the pyrolysis not only alters, as a transfer agent, the primary degradation of the polystyrene moiety, i.e., unzipping to yield the monomer styrene, but also simultaneously hampers the volatilization of the aromatic compounds.

CONCLUSIONS

The above investigations reveal that the flame-retarding action imparted by the HET acid in the styrene-cured unsaturated polyester resins in the temperature range up to 450°C can be attributed to the following mechanisms:

i. In the temperature range of 300–350°C, hexachlorocyclopentadiene is formed from the HET acid moiety by reverse Diels–Alder reaction. Due to the high transfer efficiency of hexachlorocyclopentadiene, the primary degradation reaction of the polystyrene moiety is altered. Owing to the suppression of the unzipping process of polystyrene, the char formation is increased.

ii. Since hexachlorocyclopentadiene is regarded as less flammable than the other volatile products evolved during pyrolysis and due to the heavy mass of this molecule, it will hinder the oxygen diffusion into the flame zone. In this way it acts as a flame cooling agent.

iii. Apart from the above primary influence, this halogen flame retardant will suppress the branching of the kinetic chain in the flame caused by some re-

actions of the H· radical.[20] This reactive radical is replaced by less reactive radicals (e.g., Cl·).

The above conclusions vividly show that the incorporation of HET acid in the backbone of the unsaturated polyester leads to flame retardancy in a multidirectional way.

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