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PYROLYSIS GAS CHROMATOGRAPHY OF INSULATING POLYMERS USED IN ELECTRICITY GENERATORS

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SUMMARY

Pyrolysis gas chromatography was applied to the study of generator insulating materials in a nitrogen atmosphere at 500–750°C. The materials were modified polyester and epoxy resins. The samples were pyrolysed in a directly heated furnace coupled on line with a gas chromatograph. Light hydrocarbons, carbon oxides and higher-molecular-weight degradation products were identified. The polymer compositions could also be determined.

INTRODUCTION

Besides their mechanical characteristics, the operational safety of high power electricity generators mostly depends on the properties of insulating materials. During the past 20 years, research has been conducted with the aim of understanding the thermal degradation of insulating polymers.

Pyrolysis gas chromatography (PGC) is a very powerful method for the investigation of the structures and properties of polymers[1,2]. The basic materials of insulating polymers are mainly different phenoplasts, modified polyesters and epoxy resins. The pyrolysis of phenoplasts has been investigated by Guiochon and co-workers[3-5]. They demonstrated that the methyl groups on the alkylated phenols formed during pyrolysis are in the *o*-, *o'*- and *p*-positions, which are active sites and originate from the methylene and ether bridges ($-CH_2-O-CH_2-$) connecting the phenol units.

There are few publications concerning the PGC of polyester resins, mainly because the chemical reactions of these resins with suitable reagents present a more ready analytical method of elucidating their structures. Nevertheless it is useful to study the unsaturated polyester and alkyl resins by PGC because for use as insulators they are often modified with phenoplasts or epoxy resins to improve their heat resistance and insulating properties. Because of their wide range of applications, the epoxy resins have frequently been investigated by pyrolysis. There are many types of epoxy resins, but most of the world production is based on the reaction of 2,2-bis-

(*p*-hydroxyphenyl)propane (Dian or Bisphenol A) with epichlorhydrin. The pioneering work of Lee[6,7] resulted in the identification of most of the degradation products, especially the phenol homologues. Among the phenol homologues he found *p*-vinylphenol and *p*-isopropenylphenol which are both typical products of Dian decomposition. The work of Bishop and Smith[8] meant a real step forward in the evaluation of the degradation mechanism of epoxy resins.

Several types of generator insulating materials have been studied by Freedman[9] using gas chromatography–mass spectrometry (GC–MS). He proposed the establishment of a fault diagnosis system, based on the determination of the characteristic degradation products in the cooling gases of generators.

EXPERIMENTAL

The pyrolysis experiments were performed in a nitrogen atmosphere. Some measurements were carried out in the hydrogen atmosphere used as cooling gas, but no important differences in the composition of the degradation products were detected.

The following insulating materials were studied: epoxy resin-bonded mica (Samicatherm); polyester resin-bonded glass fibre (Asta); polyester base coating lac (Titeron 51) and epoxy base casting resin (Araldite B). Thermal degradation of these materials at temperatures in the range 500–750°C was investigated by PGC using an Hewlett-Packard Type 5720 A gas chromatograph with flame ionization detection (FID) and a 7123 A chart recorder. The data were evaluated by a Spectra-Physics System I computing integrator. Fig. 1 shows the pyrolyzer coupled on line to the gas
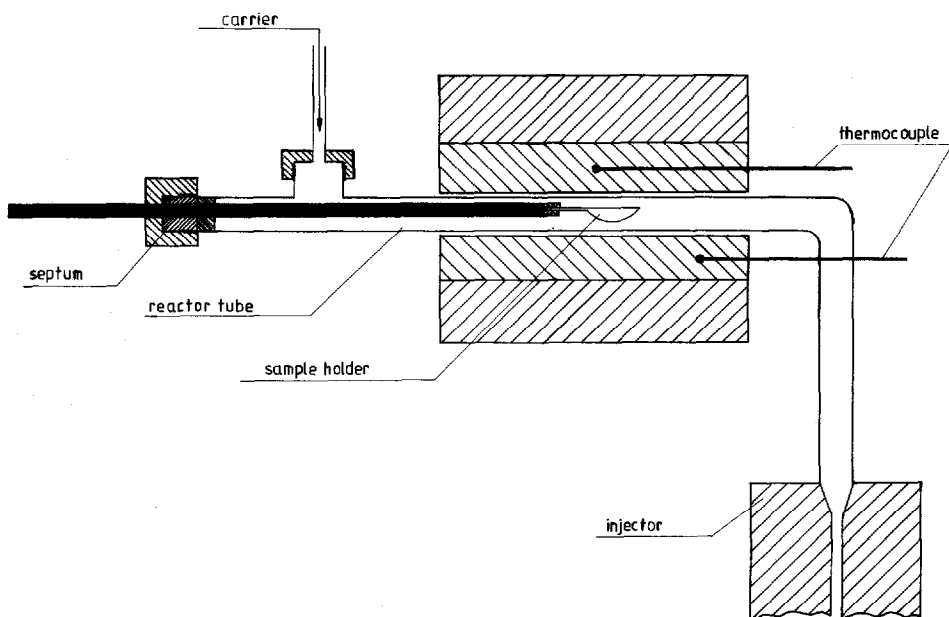

Fig. 1. The directly heated pyrolyzer coupled to the gas chromatograph.

chromatograph. The furnace was directly heated by a temperature programmer. The samples, $3 \cdot 10^{-4}$–$5 \cdot 10^{-4}$ g, were kept in the furnace for 10 s.

The C_1–C_4 hydrocarbons, carbon oxides and the organic degradation products of higher molecular weight were determined by means of packed columns. A 2.5 m × 1/8 in. SS Porapak N (80–100 mesh) column was used for the hydrocarbons and carbon oxides. Carbon monoxide and carbon dioxide were measured by methanization over a nickel catalyst (FID)[10]. The catalyzer tube (8 cm × 1/4 in. SS Ni on Chromosorb P, 60–80 mesh) was placed between the column and detector. The carrier gas (hydrogen) flow-rate was 30 cm^3/min, and the temperature was 90°C (isothermal). The C_1–C_4 hydrocarbons were measured without the catalyzer tube, at a carrier gas (nitrogen) flow-rate of 30 cm^3/min and at temperatures from 65 to 120°C increased at a rate of 8°C/min. The higher-molecular-weight degradation products were identified, on the basis of known mixtures and of pyrolysis of polymers of known structures, by use of two columns: 2 m × 2 mm I.D. glass, 10% SP 1000 on Chromasorb W HP (100–120 mesh); 2 m × 2 mm I.D. glass, 0.1% SP 1000 on Carbopack C (100–120 mesh) (Supelco). Temperatures: 65 (2 min) to 255°C at 8°C/min (see Fig. 2). Carrier gas: nitrogen, 20 cm^3/min.

RESULTS

We determined the quantity of C_1–C_4 hydrocarbons formed over the quoted temperature range. The total, amount of hydrocarbons did not increase over 650°C in the cases of Titeron and Samicatherm, which means that the decomposition is complete, while in the cases of Araldite and Asta a further increase was observed. This is in accord with the thermal stabilities of the polymers, which according to our investigations lie in the following order: Titeron, Samicatherm < Asta, Araldite B. We can conclude that, in general, by 650°C a noticeable amount of light hydrocarbons has been formed (see Table II).

The amount of carbon monoxide and carbon dioxide formed from the studied polymers at 650°C was determined. The CO/CO$_2$ ratio is shown in Table I. The pyrolysis of the Dian monomer and its polymer Araldite 6097 (Ciba-Geigy) gave predominantly carbon monoxide, which shows the presence of ether bonds, while the cross-linked Araldite B also gave an important amount of carbon dioxide because the ester bonds formed during the polymerization decompose. The CO/CO$_2$ ratio for Asta and Titeron confirmed the polyester structure proposed previously[11]. It can be stated that the amounts of carbon monoxide and carbon dioxide formed during pyrolysis provide useful information on the ratio of ether and ester bonds and hence the degree of cross-linking and the type of polymer.

The measurement and identification of the higher-molecular-weight degradation products provides the possibility of elucidating the otherwise unknown structures of the polymers. By 500°C all the decomposition products were present, and only their ratio changed with temperature. Considering the measurements at different temperatures, we can state that the relative amounts of phenol and benzene homologues decrease above 600°C, indicating decomposition of the aromatic rings. At the same time, the relative amounts of light hydrocarbons increase. In the case of the phenolic resins, the ratio of benzene to phenol increases above 700°C, indicating cleavage of the phenolic hydroxy groups.

TABLE I

THE CO/CO₂ RATIO IN THE DEGRADATION PRODUCTS AT 650°C

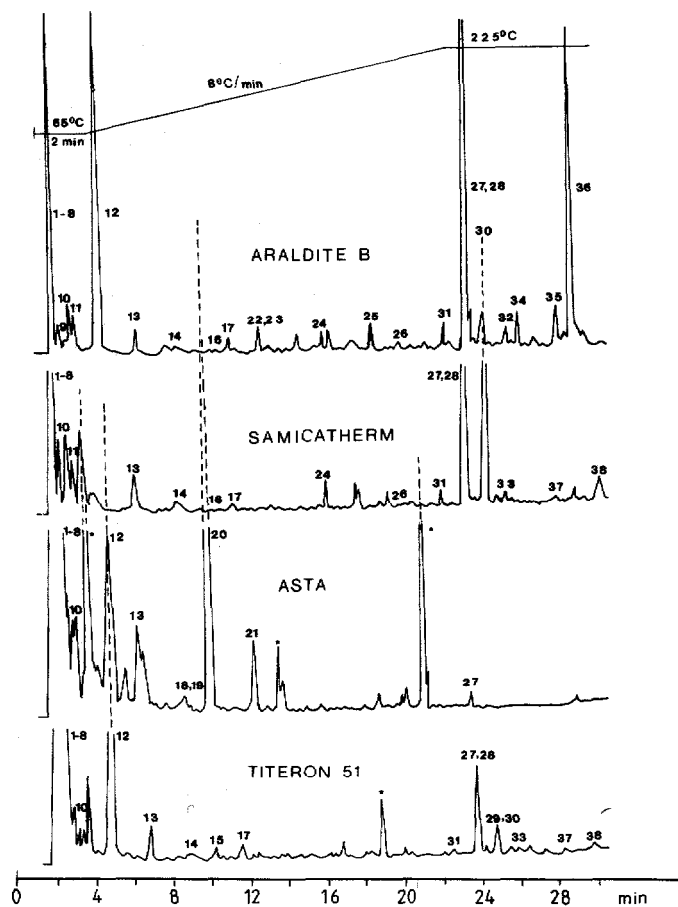| Polymer	CO/CO_2 ratio
Samicatherm	9.3
Araldite B	5.4
Araldite 6097	26.2
Dian	19.0
Titeron	0.86
Asta	2.44

Fig. 2. Pyrolysis chromatograms of the studied polymers at 650°C. Column: 2 m × 2 mm I.D. glass, 10% SP 1000 on Chromosorb W HP (100–120 mesh). Carrier gas: nitrogen, 30 cm³/min. FID: attenuation, 1000 × 1. Oven: increased from 65 (2 min) to 225°C (hold) at a rate of 8°C/min. Chart speed: 0.75 cm/min. Unidentified peaks are indicated by asterisks.

TABLE II

THE IDENTIFIED DEGRADATION PRODUCTS AT 650°C (IN AREA %)

No.	Compound	Titeron	Asta	Araldite	Samicatherm
1	Methane	10.5	5.3	12.3	8.5
2	Ethylene	11.0	6.2	4.2	7.2
3	Ethane	8.3	1.5	1.2	1.4
4	Acetylene	—	—	1.5	—
5, 6	Propane + propylene	9.5	5.2	6.3	8.1
7	Propyne	—	1.5	2.1	—
8	Isobutane	8.6	4.8	3.9	5.3
9	2,3-Epoxybutane	—	—	0.4	1.0
10	Acetone	1.2	3.7	1.4	2.3
11	2,3-Epoxypropanol	—	—	1.1	2.5
12	Benzene	27.8	12.4	16.1	2.2
13	Toluene	2.4	4.8	1.6	3.4
14	Ethylbenzene	0.7	—	0.8	1.7
15	Isopropylbenzene	0.5	—	—	—
16	n-Propylbenzene	—	—	0.2	0.2
17	sec.-Butylbenzene	1.5	—	1.4	0.7
18, 19	m- + p-Xylene	—	3.0	—	—
20	o-Xylene	—	37.5	—	—
21	o-Diethylbenzene	0.2	8.0	—	—
22, 23	m- + p-Diethylbenzene	—	—	0.8	—
24	Vinylbenzene (styrene)	—	—	1.0	1.6
25	Di-n-propoxymethane	—	—	0.8	—
26	Dihydropyran	—	—	0.6	0.2
27, 28	Phenol + o-cresol	4.2	0.7	17.0	31.2
29, 30	m- + p-Cresol	1.7	—	2.5	11.2
31	2,6-Dimethylphenol	0.4	—	0.8	0.8
32	p-Ethylphenol	—	—	1.4	—
33	2,4,6-Trimethylphenol	0.8	—	—	1.0
34	p-Isopropylphenol	—	—	1.2	—
35	p-Vinylphenol	—	—	4.5	—
36	p-Isopropenylphenol	—	—	8.3	—
37	Tetramethylphenol	0.6	—	—	1.9
38	Pentamethylphenol	0.53	—	—	1.6

As previously mentioned, the characteristic decomposition products of the Dian base epoxy resins are p-vinylphenol and p-isopropenylphenol, identified in the case of Araldite B. The ratio of p-vinylphenol to p-isopropenylphenol greatly increases above 700°C as a consequence of loss of methane from the p-isopropenylphenol.

The optimum pyrolysis temperature of the insulating materials tested is 650°C as at higher temperatures the ratio of simple molecules increases and so the pyrolysis chromatograms are no longer characteristic of the chemical structures of the polymers. As an example, the results of the pyrolysis of the four materials at 650°C are shown in Fig. 2. Table II lists the identified degradation products. The percentage areas provide only an estimate of the relative amounts of the degradation products because it is not possible to use an internal standard with this kind of technique.

Taking into account that the generator insulating materials used industrially are generally polymers modified with different additives, the determination of their structures is not an easy job, but it can be carried out. According to our data, the structures of the studied insulators can be summarized as follows: Titeron 51, phthalic acid and glycerol base polyester modified by *m*-cresol resin; Samicatherm, novolac base epoxy resin, the novolac being prepared from *m*-cresol and 3,5-dimethylphenol; Araldite B, Dian [2,2-bis(*p*-hydroxyphenyl)propane] base epoxy resin cross-linked by phthalic acid; Asta, probably *o*-dicarboxymethylbenzene and glycerol or ethylene glycol base polyester.

In the case of polyester resins, the PGC method does not often give enough information for the determination of the structure. In the case of Asta, the polyester-like character was also confirmed, besides other facts, by the large amount of carbon dioxide formed. The presence of *o*-dicarboxymethylbenzene monomer is suggested by the large amount of *o*-xylene formed. As is seen from Fig. 2, we have not yet been able to identify some of the important degradation products of Asta.

CONCLUSIONS

The degradation products unambiguously characterize the chemical structure of the polymers studied. The data obtained from the PGC measurements of the insulating materials used in electricity generators can be applied in the following areas: the quality control of polymers; the control of the technological processes involved in the generator production; the classification of the chemical structures of insulating materials.

The C_1–C_2 hydrocarbons, being permanent gases, make it possible to detect immediately any failure occurring in the cooling gases of working generators.

REFERENCES

1 M. P. Stevens, *Characterisation and Analysis of Polymers by GC*, Marcel Dekker, New York, London, 1969.
2 R. W. May, E. F. Pearson and D. Scotchern, *Pyrolysis Gas Chromatography*, The Chemical Society, London, 1977.
3 J. Zulaica and G. Guiochon, *J. Polym. Sci., Part B*, 4 (1966) 567.
4 C. Landault and G. Guiochon, *Anal. Chem.*, 39 (1967) 713.
5 J. Martinez and G. Guiochon, *J. Chromatogr.*, 5 (1967) 146.
6 L. H. Lee, *J. Polym. Sci., Part A*, 3 (1965) 859.
7 L. H. Lee, *J. Appl. Polym. Sci.*, 9 (1965) 1981.
8 D. P. Bishop and D. A. Smith, *J. Appl. Polym. Sci.*, 14 (1970) 205.
9 A. N. Freedman, *J. Chromatogr.*, 157 (1978) 85.
10 K. Torkos, J. Borossay and Á. Székely, *J. Chromatogr.*, 286 (1984) 314.
11 C. Merritt and C. Di Pietro, *Anal. Chem.*, 44 (1972) 57.