

CHROMSYMP. 828

## ANALYSIS OF COMPOSITE MATERIALS BY USE OF PYROLYSIS GAS CHROMATOGRAPHY

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### SUMMARY

A method of stepwise heating of the specimen in the pyrolysis cell of a chromatograph followed by gas chromatographic separation of the evolved compounds is proposed for the analysis of polymer-containing materials. The experiments were conducted on a Biochrom-26 chromatograph with a filament-type pyrolysis cell. The technique enables the determination of polymers in any proportions, high-boiling organic ingredients (stabilizers, plasticizers, etc.) and also volatile organic compounds present in the specimen.

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### INTRODUCTION

Polymer-based materials used in technology have complex compositions, containing individual homopolymers, copolymers or mixtures of polymers of different types as well as various chemicals imparting valuable properties to the material after its processing. Depending on the proposed usage, low-molecular-weight organic chemicals (plasticizers, stabilizers, etc.) differing in their structures and properties, volatile compounds resulting from chemical transformations, special polymer and non-polymer additives and also mineral components and fillers can be present. Most polymer materials, *e.g.*, filled vulcanizates, are partly or fully insoluble in the usual organic solvents. The traditional methods of analysis of composite polymer materials<sup>1-3</sup> do not enable the identification of the components with sufficient reliability because of their lack of specificity and low sensitivity. The most efficient method of analysis of organic constituents of composite polymer-containing materials is pyrolysis gas chromatography (GC) with stepwise heating of the specimen in the pyrolysis cell of the chromatograph.

The correctness of the results of analysis of such materials depends to a great extent on proper sampling and preliminary treatment of the material. The sampling of viscous-flow polymer-containing materials and solutions is simple because in these instances the specimen can be homogenized. In the case of solids or elastic solids the specimens may be non-homogeneous and the analysis can be deemed to be correct if the amount of any individual constituent is at least one order of magnitude less than the weight of the specimen taken for analysis.

The technique of stepwise heating of the specimen in the pyrolysis cell of a

chromatograph does not call for a special pretreatment of the specimen, such as the isolation of the polymer, the removal of the solvent, the isolation of the ingredients, inorganic fillers, etc. Thus this technique makes it possible to determine, in a single experiment without specimen pretreatment, volatile compounds, high-boiling organic ingredients, contaminating impurities, special polymer and non-polymer additives.

One of the main tasks is the identification of the individual constituents of the specimen; the quantitative measurement of certain constituents is also possible. When individual non-polymer constituents are to be identified, the pyrolysis conditions can be predicted on the basis of their physicochemical properties, such as boiling point. The quantitation of the components requires a more rigorous approach to the selection of the conditions of pyrolysis and chromatographic separation.

Several analytical schemes can be used in the stepwise heating of the specimen in the pyrolysis cell. The temperature can be raised: (1) in a linear programming mode; (2) in a stepwise heating mode; (3) by applying a train of energy pulses to the thermoelement which warms up in the same manner after each pulse; (4) by applying increasing energy pulses to the thermoelement so that each step results in the heating of the specimen to a higher temperature than that achieved in the previous step.

The chromatographic analysis of the evolved components is possible in a single step; in this case (on stepwise heating of the specimen) the chromatographic column operates as an accumulator. In more complex cases, the chromatographic separation of the liberated products should be carried out after each specimen heating step in the pyrolysis cell.

The stepwise heating of the specimen in the pyrolysis cell enables the separation of the specimen into fractions: volatile impurities, high-boiling non-polymer additives, the base polymers, special polymer additives or contaminating polymer impurities, mineral constituents. The pyrogram thus obtained can serve as a basis for identification of the volatile substances evolved by various generally accepted methods as well as by vapour-phase pyrolysis<sup>4-6</sup>. There is often no need for a thorough identification of each component of the composite material; sufficient information can be obtained by comparing the pyrograms of the specimen and a reference analyzed under identical conditions.

The polymers making up the composite material are identified from the pyrograms through the use of different methods of interpretation depending on the complexity of the specimen<sup>7</sup>. Special volatile additives are determined on the basis of the retention parameters of corresponding peaks. The mineral constituents are mechanically removed from the pyrolysis unit after the analysis of the organic portion and can be analyzed by independent methods.

## EXPERIMENTAL

### *Instruments and materials*

The experiments were conducted on a Biochrom-26 chromatograph with a filament-type pyrolysis unit and a flame ionization detector, a 1-mV recorder and an amplifier with scale sensitivity of  $2 \cdot (100 \cdot 5 \cdot 10^{-12})$  A for detecting impurities and between 20 and  $1000 \cdot (100 \cdot 5 \cdot 10^{-12})$  A in other cases. Packed  $2 \text{ m} \times 3 \text{ mm}$  columns were employed; methylsiloxane stationary phases (SE-30, OV-1), 5% on Chromatone

N-AW-DMCS (0.316–0.4 mm), were used as sorbent in most cases. In some experiments, Reoplex 400 (15%) and poly(phenyl ether) 4E 5F (five rings), 7–10%, were used. The carrier gas (argon) flow-rate was 20–40 ml/min.

### *Specimens*

Commercial samples of polymers of different types or of polymers of the same type but prepared by different manufacturers were analyzed. Reference specimens of composite materials (unfilled vulcanizates) were prepared in the laboratory by mixing the components on a micromill according to a chosen recipe and curing the mixes.

### *Technique*

The 50–100  $\mu\text{g}$  specimens (the weight was increased by one order of magnitude when determining volatile impurities) were cut from a sample with a razor-blade and placed with a needle in the coil-shaped filament of the pyrolysis cell. Viscous-flow specimens or solutions were introduced by syringe and the solvent was removed outside the chromatograph by use of a fan.

Depending on the purpose of the analysis, in some cases the filament with the specimen was not heated in the first step and the volatile substances were desorbed from the specimen by means of the evaporator of the chromatograph. Energy was supplied to the filament according to a programme chosen to suit the purpose of the analysis and the properties of the components to be detected. The non-volatile portion of the specimen was pyrolyzed at filament temperatures as high as 700–770°C, the duration of the power supply being 5–10 s.

The chromatographic separation of the compounds produced by desorption or pyrolysis was carried out in one or several steps after the isolation of all organic constituents or individual components of the specimen.

## RESULTS AND DISCUSSION

The application of pyrolysis GC to the study and analysis of polymers is not new; however, as the experimental technique undergoes improvement and knowledge of the subject becomes more profound, new applications become possible. Until recently, the most extensive use of pyrolysis GC has been in the identification and quantitative analysis of individual polymers or simple polymer mixtures in polymer-containing specimens with a limited number of components<sup>7–10</sup>. The pyrograms of composite materials are much more complex since they result from the superposition of the pyrograms of individual high-molecular-weight compounds, the peaks of the liberated thermally stable volatile additives (stabilizers, plasticizers, modifying agents, etc.), the peaks of the compounds arising from chemical interactions in the processing of the constituents or in the synthesis of composite materials from raw mixes.

The heating of the specimen in the pyrolysis cell of a chromatograph is accompanied by desorption and evaporation of volatile compounds at temperatures close to the boiling point. Further heating of the specimen to the pyrolysis temperature leads to the disintegration of the non-volatile organic portion so that the mineral constituents remain in the pyrolysis unit. Some compounds formed on pyrolysis can undergo partial vapour-phase pyrolysis and give rise to small amounts of compounds having other structures. Pyrolysis of individual polymers is known to result in a

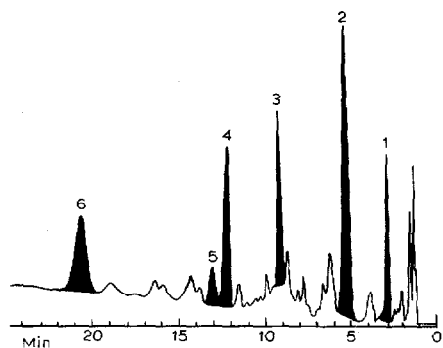


Fig. 1. Pyrogram obtained for a polymer material. Peaks: 1 = butadiene; 2 = isoprene; 3 = chloroprene; 4 = acrylonitrile; 5 = vinylcyclohexene; 6 = dipentene.

specific spectrum (pyrogram) enabling the identification of the polymer. The situation obviously becomes more complicated if the material contains several polymers, particularly when their concentrations are different. In these cases the polymers are identified on the basis of individual characteristic products of pyrolysis. Thus, Fig. 1 shows an example of a pyrogram of a composite material used in a gasket of an apparatus operating under specific conditions. The characteristic peaks, indicate that the material contained three types of polymers: natural or synthetic isoprene rubber characterized by isoprene and dipentene peaks (2 and 6); polychloroprene (chloroprene, peak 3); butadiene-acrylonitrile rubber characterized by butadiene (1), acrylonitrile (4) and vinylcyclohexene (butadiene dimer) (5) peaks. The relative sizes of the peaks of acrylonitrile and vinylcyclohexene enable us to conclude that the butadiene-acrylonitrile rubber corresponds to the SKN-40 grade of nitrile rubber<sup>11</sup>. The pyrolysis products were separated on a 3 m × 3 mm column packed with Chezasorb and 15% of Reoplex 400 (0.316–0.4 mm); the temperature of the column was raised from 45 to 180°C at 8°C/min. The flow-rate of argon was 20 ml/min.

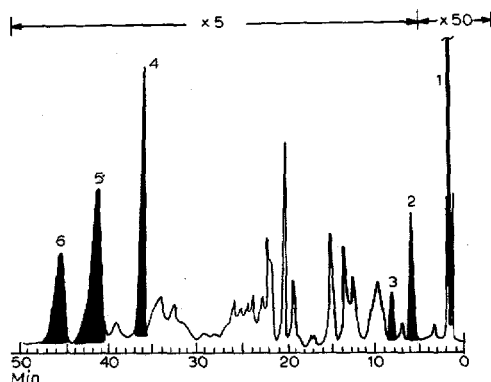


Fig. 2. Chromatogram of a composite material; the specimen was heated to the pyrolysis temperature and the evolved products were separated on a column with SE-30, the temperature being increased from 50 to 300°C, at 6°C/min. Peaks: 1 = butadiene; 2 = acrylonitrile; 3 = vinylcyclohexene; 4 = dibutyl phthalate; 5 = Neozone D; 6 = dioctyl phthalate.

The heating of the evaporator and of the filament of the pyrolysis cell to a temperature close to the boiling point of the components forming part of the composite material under analysis leads to the desorption of thermally stable compounds which arrive at the chromatographic column having the initial programmed temperature and are accumulated in the column. Thermally stable components can also be isolated from the specimen at the pyrolysis temperature of the polymers present in the specimen. In a number of cases, the overall chromatogram obtained on separation under optimum conditions makes possible the simultaneous identification of the polymer composition, components and other polymer and non-polymer impurities. Thus, Fig. 2 demonstrates the possibility of a simultaneous determination of the type of the polymer (butadiene-acrylonitrile rubber), stabilizer (Neozone D) and phthalate plasticizers (dibutyl phthalate and dioctyl phthalate). Fig. 3b also indicates the possibility of simultaneous identification of the polymer and the phenol-type stabilizer (Ionol). However, the reliability of a simultaneous identification is insufficient because as a rule polymers and mineral fillers in composite materials are contained in large amounts and the concentration of other components is not high, usually 0.5–10%. For this reason the pyrolysis gives rise to peaks from ingredients and additives which are small in comparison with the characteristic peaks of polymers and can be missed in single-step heating of the specimen in the pyrolysis cell (Fig. 3a). An increase in the recording sensitivity (Fig. 3b) is not helpful since the peaks of other

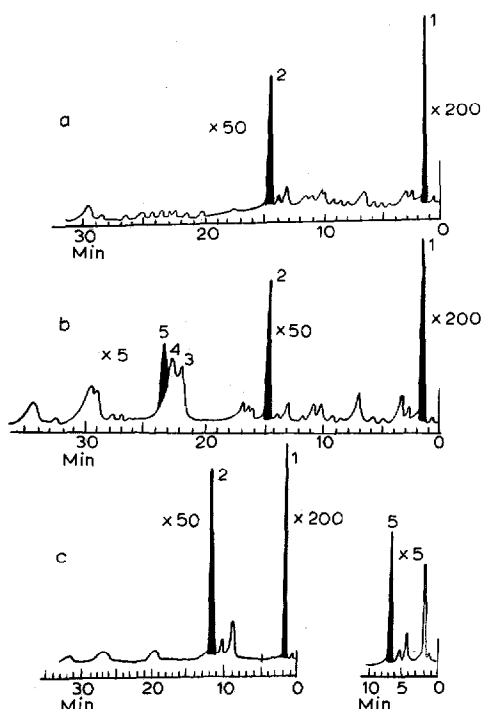


Fig. 3. Pyrograms of synthetic isoprene rubber (a, b) and chromatograms obtained on two-step specimen heating (c). Peaks: 1 = isoprene; 2 = dipentene; 3 and 4 = unidentified pyrolysis products; 5 = Ionol (stabilizer). The attenuation is indicated in the figure ( $\times 200$ ,  $\times 50$  or  $\times 5$ ).

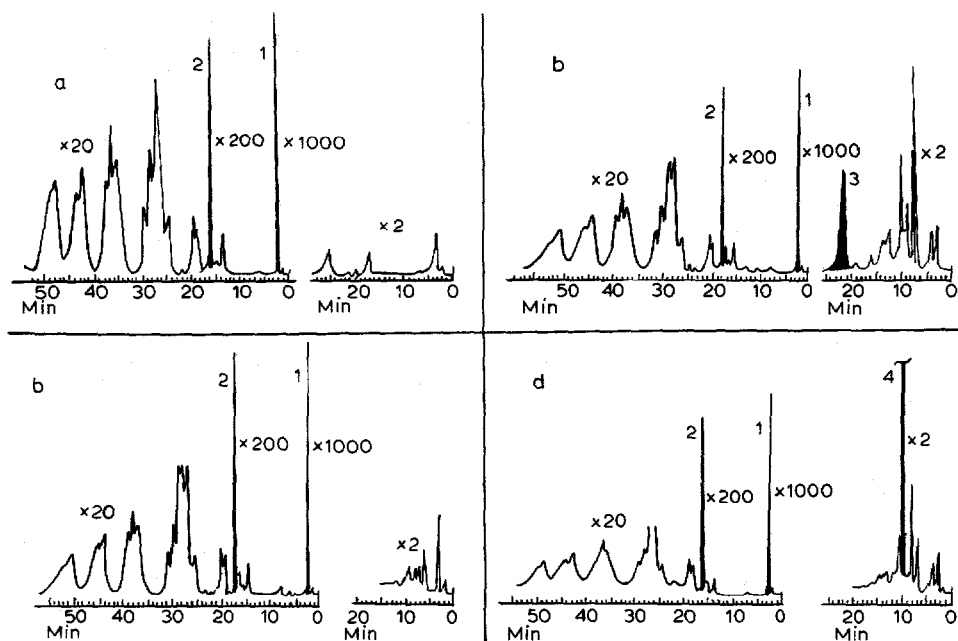


Fig. 4. Chromatograms of isoprene rubbers from different producers. (a) Natural rubber; (b)–(d) synthetic isoprene rubber, samples 1–3. Peaks: 1 = isoprene, 2 = dipentene, 3 = Neozone D, and 4 = Ionol.

pyrolysis products also grow and some peaks can overlap with the peak of the compound to be detected (Fig. 3b). In such cases, stepwise heating of the specimen in the pyrolysis cell should be employed in order successively to isolate the constituents directly in the chromatograph and to separate the liberated compounds chromatographically after each heating step, as shown in Fig. 3c. This technique makes it possible to separate the constituents of the composite material into groups in the chromatograph and is exemplified by Fig. 4c: in this case a group of volatile impurities (the oligomer portion of synthetic isoprene rubber) and the stabilizer (Neozone D) were isolated and characteristic peaks (1 and 2) were obtained in a single chromatographic experiment enabling the determination of the polymer type.

A comparison of the chromatograms given in Fig. 4 leads to the conclusion that the application of multistep heating of a specimen in the pyrolysis cell of a chromatograph followed by chromatographic analysis of the liberated fractions can give much more information about the specimen than that provided by single-step pyrolysis GC. Thus, a single experiment (Fig. 4) can detect volatile impurities in rubbers of the same type (natural rubber, Fig. 4a and synthetic isoprene rubbers prepared by different manufacturers), the type of polymer and non-polymer additives. Thus it is possible to distinguish materials of different natures and also materials of the same type but with different properties.

Optimum separation of the evolved compounds in experiments on polymer-containing composite materials was achieved on columns with methylsiloxane stationary phase SE-30, Reoplex 400 and poly(phenyl ether) 4E 5F (five rings). Since these stationary phases possess different polarities and selectivities, the retention

TABLE I

THE ORDER OF EMERGENCE OF THE PYROLYSIS PRODUCTS OF SOME SYNTHETIC POLYMERS, STABILIZERS AND PLASTICIZERS ON COLUMNS WITH DIFFERENT STATIONARY PHASES

Compound	$T_b$ ( $^{\circ}C$ )	Non-polar phase (SE-30)		Ester phase (Reoplex 400)		Poly(phenyl ethers)	
		Emergence order	$T_e$ ( $^{\circ}C$ )	Emergence order	$T_e$ ( $^{\circ}C$ )	Emergence order	$T_e$ ( $^{\circ}C$ )
Isobutylene	-6.0	1	50	1	50	1	50
Butadiene	-4.6	2	50	2	50	2	50
Isoprene	34.0	3	50	3	50	3	50
Chloroprene	59.4	4	50	4	50	4	50
Acrylonitrile	77.3	5	68	6	—	5	—
Vinylcyclohexene		6	84	7	106	8	136
Styrene	145.2	7	95	10	157	9	160
$\alpha$ -Methylstyrene	163.5	8	115	11	169	11	175
Dipentene	176.6	9	125	9	145	10	170
Peak 43 characteristic of butyl rubber	—	10	154	12	—	12	185
Peak 46 characteristic of butyl rubber	—	11	180	—	—	13	190
Ionol	256	12	198	—	—	—	—
Quinol ED	163*	13	230	—	—	—	—
Dibutyl phthalate	340	14	252	—	—	—	—
Product 4010 NA	366	15	268	—	—	—	—
Neozone D	399	16	282	—	—	—	—
Santoflex 13	—	17	292	—	—	—	—
Product NG-2246	—	18	298	—	—	—	—

\* At 13 mmHg.

times (volumes) and the elution orders of the compounds on columns with different phases are not coincident. Table I gives the elution order and the emergence temperatures of the characteristic products of pyrolysis of synthetic polymers, some stabilizers and plasticizers.

The method of stepwise heating of the specimen in the pyrolysis cell of the chromatograph is more rapid in comparison with other well known methods, furnishes more detailed information on polymer-containing specimens of complex composition, including those with mineral additives and fillers and provides a large body of new qualitative information in a single experiment. The data obtained give a better idea of the properties of the composite material under scrutiny. This method can be used commercially in order to evaluate the quality of a material, to monitor its compliance with specifications by comparing the material's pyrogram with that of a reference specimen. It will also be useful in arbitrage analysis on the purchase or delivery of the material to another enterprise.

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