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COMPARISON OF VARIOUS PYROLYZERS IN THE STUDY OF POLYMER COMPOSITIONS

K. V. ALEXEEVA AND L. P. KHRAMOVA
Research Institute of the Tyre Industry, Burakova 27, Moskow E-275 (U.S.S.R.)

SUMMARY

Three types of pyrolysis device (an electrically heated filament unit, a quartz-tube furnace unit and a Curie-point pyrolyzer) were used in the decomposition of polymers. The pyrolysis temperature was varied in the range 420–980°.

INTRODUCTION

Pyrolysis gas chromatography is at present widely used for the analysis of polymers[1,2]. The pyrolysis decomposition reaction is influenced by a number of variables that are sometimes difficult to control, the main factors being the temperature and the method of heating the sample, which depend on the type and construction of the pyrolytic device.

At present, the most commonly used pyrolysis units are based on electrically heated filaments (Nichrome, tungsten, platinum, etc.)[3,4], on the tube-furnace technique[5] and on the technique involving high-frequency induction heating of a ferromagnetic conductor to its Curie temperature[6].

The studies carried out in our laboratory were aimed at comparing pyrolyzers of such types for use in the tyre industry.

EXPERIMENTAL

The thermal decomposition of the samples was carried out in pyrolyzers of the three above types.

The filament unit used was constructed in our laboratory[7], and consisted of a coiled filament that was wound from 110 × 0.6 mm Nichrome wire and had a resistance of 0.6 ohm in the circuit. The Nichrome filament was heated from the ambient temperature to a maximum of approximately 500–900° for 5 sec. The precise measurement of the temperature was not carried out during pyrolysis, and the approximate value was estimated from the previously obtained calibration. Temperature control was achieved by using a voltage supply control.

We used a Shimadzu, Type PYR-IA, commercial unit as a furnace-type pyrolyzer. The pyrolysis chamber consisted of a quartz tube (170 mm × 6 mm I.D.) and a metal joint. The furnace was operated at a temperature of 420–900° and the samples were introduced into the hot zone in a platinum boat.

Pyrolysis in the Pye-Unicam Curie-point pyrolyzer was also carried out. Ferromagnetic wires with Curie temperatures of 480° (Ni–Fe, 60:40), 510° (Ni–Fe, 45:55), 610° (Co–Ni, 60:40), 770° (Fe) and 980° (Fe–Co–V) were used.

All samples were pyrolysed in argon, which was used simultaneously as the carrier gas. The outlet flow-rate of the argon was 40 ml/min.

The polymers pyrolysed were polyisoprenes and polybutadienes with different microstructures*, styrene–butadiene rubbers (SBR) and blends of homopolymers. The polymers and their blends were sampled as 2% solutions in benzene.

Tsvett-3 and Tsvett-4 gas chromatographs (U.S.S.R.) with flame ionization detectors and with temperature programming from 25° to 200° at a rate of 7°/min or 10°/min were used.

The pyrolytic degradation products were resolved on a 2.5-m stainless-steel column packed with thermally-treated (1150–1200°) INS-600 (U.S.S.R.) with a specific surface area of 2.5–3.0 m^2/g and charged with 25% of potassium carbonate and 5% of potassium hydroxide, or on a 3.0-m column packed with 20% of polyphenyl ether (5 rings) on 30–40-mesh Chromosorb A.

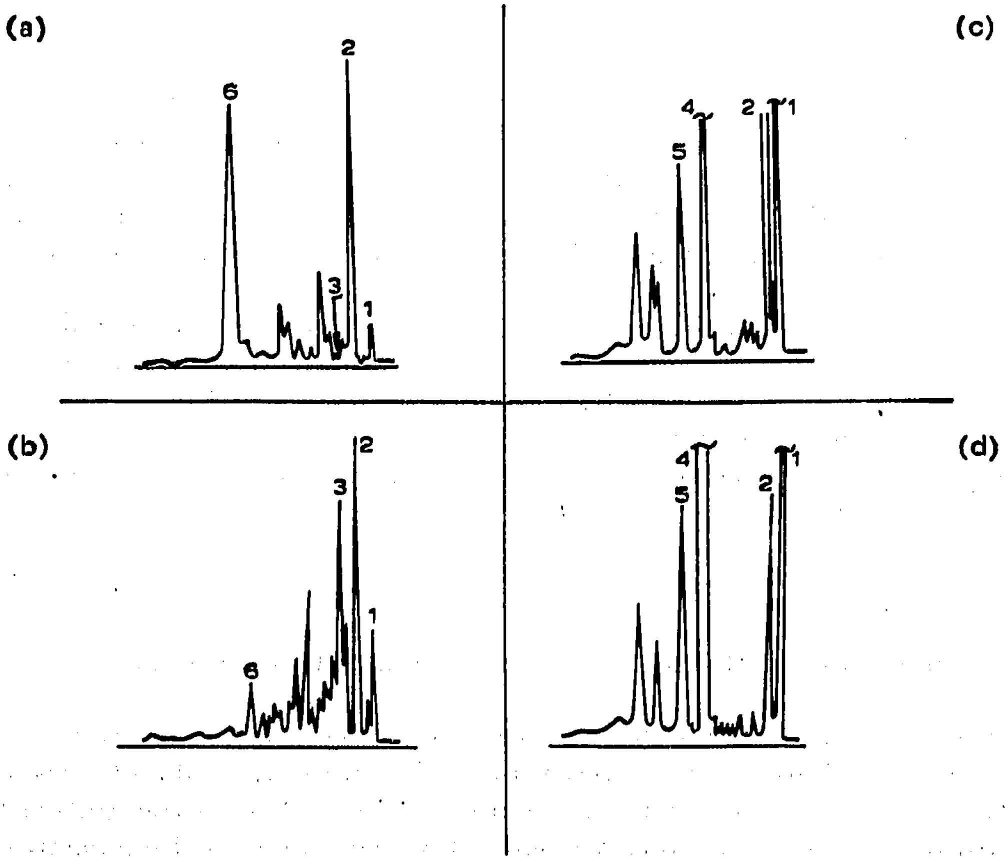

Fig. 1. Pyrograms of 1,2-polybutadiene (b and d) and 1,4-*cis*-polybutadiene (a and c) obtained by pyrolysis in the furnace (c and d) and in the Curie-point pyrolyzer (a and b). Pyrolysis temperature 770°. Peaks: 1 = light gases; 2 = butadiene; 3 = unidentified characteristic peak for 1,2-additions; 4 = benzene; 5 = toluene; 6 = vinylcyclohexene.

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* The term "microstructure" is a generally accepted term. It implies addition-types of monomer units (for example, 1,2- and 1,4-additions in polybutadiene and 1,2-, 3,4- and 1,4-additions in polyisoprene), *cis* and *trans* forms and the distribution sequence of different monomer units in the copolymer (random or block).

RESULTS AND DISCUSSION

The qualitative composition of the pyrolysis products depends to a large extent on the temperature and especially on the method of heating the sample to a certain pyrolysis temperature. Fig. 1 shows the pyrograms of two polybutadienes that differ in their microstructures: sample 1 (Figs. 1a and c) contains 97.5% of 1,4-*cis*, 1.0% of 1,4-*trans* and 1.5% of 1,2-addition forms; sample 2 (Figs. 1b and d) contains 10% of 1,4-*trans* and 90% of 1,2-addition forms. The sample was pyrolysed at 770° in a Curie-point pyrolyzer that was used in conjunction with the Tsvett-3 gas chromatograph (Figs. 1a and 1b), and in the quartz-tube furnace of the Shimadzu, Type PYR-IA, pyrolyzer that was used in conjunction with the Tsvett-4 gas chromatograph (Figs. 1c and d). It can be seen from the pyrograms that the qualitative composition of the pyrolysis products formed by the thermal decomposition of the polymer differ significantly when the different pyrolyzers are used, other conditions being the

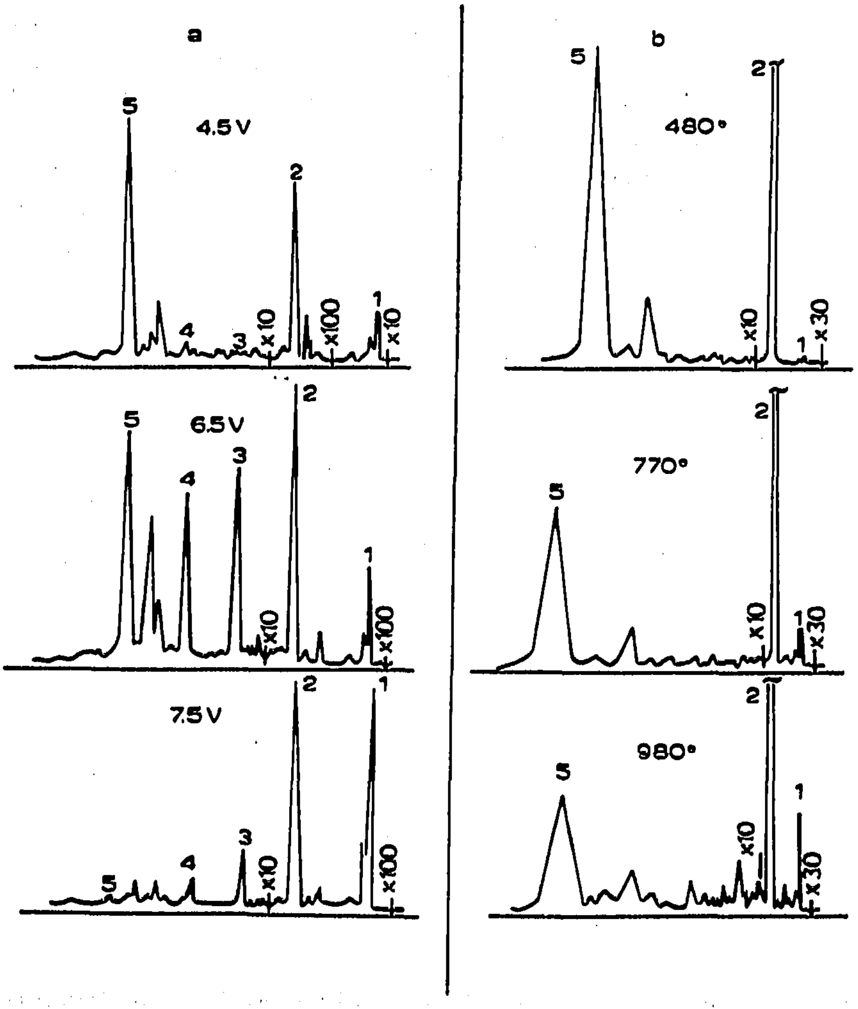

Fig. 2. Pyrograms of 1,4-*cis*-polyisoprene obtained by pyrolysis in the Curie-point pyrolyzer at different temperatures and in the filament pyrolyzer. Conditions: (a) column 2.5 m × 4.0 mm I.D., packing 25% K_2CO_3 and 5% KOH on INS-600 (0.25–0.5 mm), argon flow-rate 40 ml/min, column temperature-programmed from 25° to 200° at 7°/min; (b) column 2.5 m × 4.0 mm I.D., packing 20% polyphenyl ether on 30–40 mesh Chromosorb A, argon flow-rate 40 ml/min, column temperature-programmed from 25° to 200° at 10°/min. Peaks: 1 = light gases; 2 = isoprene; 3 = benzene; 4 = toluene; 5 = dipentene.

same. The patterns of the polybutadiene pyrolysis products obtained at 770° using the furnace are not specific. The qualitative compositions of the pyrolysis products of the samples that differ in their microstructures are identical with each other. The presence of benzene, toluene and light gases* in large amounts in the pyrolysis products of other polymers, such as polyisoprenes, shows that these components were formed as a result of secondary reactions. The patterns of the pyrolysis products of a large number of hydrocarbon polymers obtained by the pyrolysis of samples in a tube-furnace pyrolyzer differ only in the presence of the characteristic monomer. Therefore, polymers that differ in their microstructures cannot be identified from their pyrograms obtained by pyrolysis in the furnace.

In the thermal decomposition in the Curie-point pyrolyzer, mainly the corresponding monomers, dimers and other characteristic components for each type of polymer are formed. The yield of light gases and other non-specific components is low. The pyrograms obtained are specific for each polymer that differs in composition and microstructure (Figs. 1a and b).

When the Curie-point pyrolyzer is used at different pyrolysis temperatures in the range 480–980°, the qualitative composition of the pyrolyzate does not change (Fig. 2). At higher temperatures (980°) there occurs only a small increase in the yield of secondary products of reaction, including light gases.

In the case of the furnace-type pyrolyzer, the qualitative composition of the pyrolysis products changes sharply with increase in the temperature, as can be seen from the pyrograms in Fig. 3. The most characteristic pattern foı 1,4-*cis*-polyisoprene

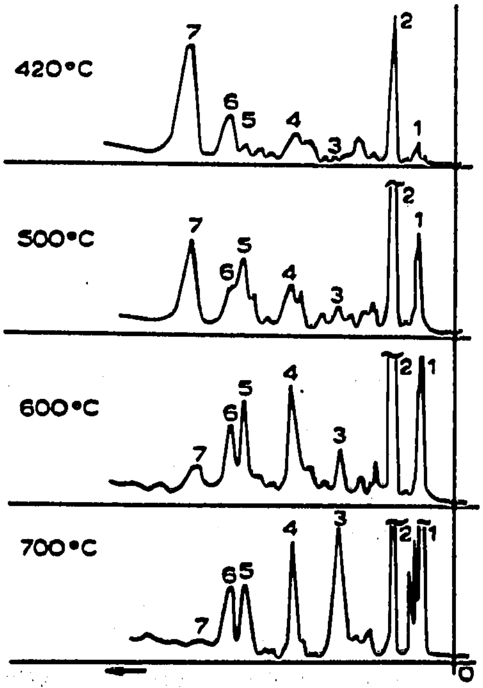

Fig. 3. Pyrograms of 1,4-*cis* polyisoprene obtained in the furnace-type pyrolyzer at different temperatures. Conditions: column 3 m × 3 mm I.D., packing 20% polyphenyl ether on 30–40-mesh Chromosorb A, argon flow rate 40 ml/min, column temperature-programmed from 50° to 150° at 10°/min. Peaks: 1 = light gases; 2 = isoprene; 3 = benzene; 4 = toluene; 5 and 6 = unidentified components; 7 = dipentene.

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* "light gases" are a mixture of C_1 — C_3 hydrocarbons in which hydrogen may be present.

was obtained at 420°. At this temperature, however, only partial decomposition of the sample occurs, and some residue remains after the degradation of the sample. The yield of specific components is low. By increasing the pyrolysis temperature, the characteristic peak of dipentene (7) decreases and the peaks of non-specific components such as benzene (3), toluene (4) and light gases increase, as the secondary reactions participate actively at higher temperatures. Finally, at 740°, the characteristic peak of dipentene almost disappears into non-specific products.

When the filament unit is used, the thermal decomposition products change with increasing temperature up to about 900° (7.5 V). At high filament potentials, the pyrolysis of polymer is characterized mainly by the formation of monomers and light gases (Fig. 2a). The most representative pattern of the pyrolysis products was obtained at lower filament potentials (4.5–5.0 V).

To establish the effect of temperature on the character of the thermal decomposition of copolymer, the dependence of the ratios of the peak areas of characteristic components for SBR of different micro-structures (random and block copolymers) and blends of homopolymers (polystyrene and polybutadiene) on the pyrolysis temperature was determined.

The dependence of the ratios of the peak areas of styrene and butadiene on the potential applied to the filament that characterizes the pyrolysis temperature was established. From this relationship it can be seen that the maximum of the ratios occurred for blends of homopolymers and block copolymers, while in random copolymers no maximum was observed.

The temperature relationships obtained during the pyrolysis of polymer samples in the Curie-point pyrolyzer are similar in nature (Fig. 4). It was shown that the qualitative composition of the pyrolysis products does not change over the whole range of operating temperatures when the Curie-point pyrolyzer is used. Therefore, the possibility exists of using at the same time the dimer of butadiene (vinylcyclohexene) as a characteristic component related to the composition of the original polymer, as well as the monomer (butadiene). The curves shown in Fig. 4 were obtained on the basis of the ratios of the peak areas of vinylcyclohexene and styrene

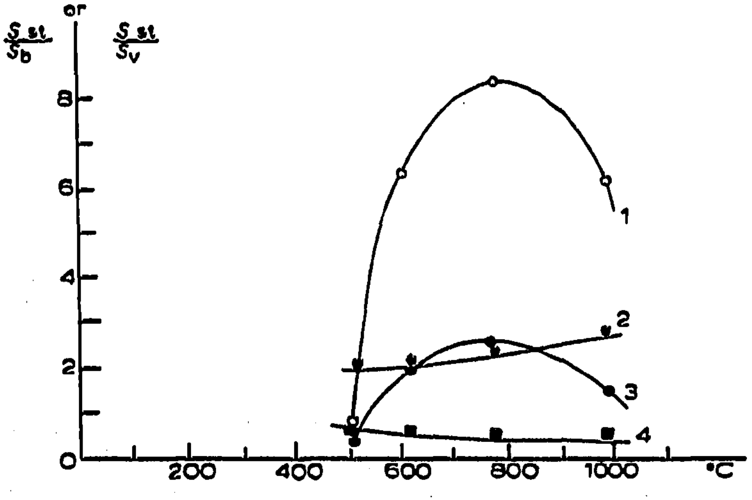

Fig. 4. Relationship between ratios of characteristic peak areas and pyrolysis temperatures with the Curie-point pyrolyzer. Curves: 1 and 3 = blends of homopolymers (polybutadiene and polystyrene); 2 and 4 = random SBR (Europrene 1500); 1 and 2 = ratios of peak areas of styrene and vinylcyclohexene; 3 and 4 = ratios of peak areas of styrene and butadiene.

(curves 1 and 2) and butadiene and styrene (curves 3 and 4) from the degradation of blends of homopolymers (curves 1 and 3) and the random copolymer Europrene 1500 (curves 2 and 4). It can be seen from Fig. 4 that the characteristic products for block copolymers and homopolymer blends pass through a maximum that occurs in the temperature range 700–800°. At this temperature the recovery of the monomer is at a maximum.

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