

# Pyropolycarboranes: The Base for Self-Lubricating Materials with Gas Lubricant

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## Synopsis

This paper reports the results of an investigation of pyropolycarboranes, nondeformable thermally stable cross-linked polymeric materials obtained by pyrolysis of carborane-containing polymers. Carborane-containing polyamides and polyesters were heated in air under pressure and analyzed by thermomechanical and thermogravimetric methods. Moreover, the friction properties of the filled materials have been investigated. The effect of hydrogen liberation on the friction of filled pyropolycarboranes at elevated temperatures was used in developing self-lubricating materials with friction coefficients at 300–400°C.

## INTRODUCTION

Progress in the chemistry of high-molecular weight compounds and in physico-chemistry of filled polymers led to the development of a new class of thermally stable polymers known as the polycarboranes.

Different classes of carborane-containing polymers are synthesized from polyamides, polyesters, polybenzimidazoles, polyimides, and polybenzoxazoles.<sup>1–3</sup> The distinctive characteristic of the carborane-containing polymers is their tendency to form secondary products (“coke residues”) in high yield at elevated temperatures.

In the processing of these polymers under controlled pyrolysis conditions, nondeformable thermally stable cross-linked polymeric products called “pyropolycarboranes” were obtained.

We previously examined the behavior of carborane-containing polyamides and polyesters during heating in air under pressure and analyzed their behavior by thermomechanical and thermogravimetric methods, IR spectroscopy, and elemental and x-ray analysis. It was found that the chemical and physical structure of the pyropolycarboranes and their properties are determined by the carborane nucleus isomerism, and carborane group position in the macromolecule unit, and the synthesis conditions of the initial polymer.

## EXPERIMENTAL

*Thermomechanical studies* were performed on a “plate-plate” plastometer<sup>4</sup> constructed on the basis of a Heppler consistometer. Flow curves for polymeric materials at a load of 100–200 kg/cm<sup>2</sup> and a plate-parallel compression of the specimen were obtained when heated at a constant rate of 5°C/min. The resulting flow curves characterize the deformation properties of the products at increased temperatures and loads.

*Thermogravimetric studies* were carried out on a F. Paulik–I. Paulik–L. Erdey derivatograph (MOM, Hungary) at a heating rate of  $4.5^{\circ}\text{C}/\text{min}$ . The gaseous products of carborane polymers analyzed on a Tsvet-4 chromatograph (USSR) while heating the specimens in a pyrolysis cell in the temperature range  $250\text{--}500^{\circ}\text{C}$  in vacuo ( $10^{-1}$  Torr).

Chromatographic analysis of the gaseous decomposition products of a *m*-carborane-containing polyamide liberates only hydrogen up to  $500^{\circ}\text{C}$ . CO and  $\text{CO}_2$  are absent.

*Friction properties:* Dry friction tests were conducted on a butt-end-friction apparatus U-47.<sup>5</sup> In the U-47 apparatus scheme (Fig. 1), the steel bush is fixed; the sample rotates. Loading and measuring the temperature is accomplished through the fixed steel bush. The sample is a bush identical to the steel bush. Friction occurs at the butt-end ring-surface,  $2.69\text{ cm}^2$  in area. Heating of the friction assembly is accomplished by an outer electric heater. The tests were carried out in air at a constant rate of  $\sim 2\text{ m}/\text{sec}$  and a constant unit load of  $\sim 2\text{ kg}/\text{cm}^2$  in the temperature range  $25\text{--}400^{\circ}\text{C}$ . The resulting dependence of the friction coefficient on temperature under the above described conditions is called "thermofriction curve."

Friction coefficient of the carborane-containing materials was compared with that of the polymeric composite materials (without polytetrafluorethylene) on the basis of solid lubricants of the  $\text{MoS}_2$  and graphite type. The lowest friction coefficient ( $0.02\text{--}0.04$ ) was observed during 6–10 hr tests.

## RESULTS AND DISCUSSION

Two polyamides and three polyesters were used as carborane-containing bonding agents for the filled self-lubricating materials. The structures of the polymers are numbered (1–5) (Table I) along with some of their properties. The curves (Fig. 2) illustrate the flow characteristics of these five materials at elevated temperatures under loads of  $200\text{ kg}/\text{cm}^2$ .

The five polymers fall into three groups (I–III in Fig. 2) according to their behavior. The type-I material is a *m*-carborane-containing polyamide (the upper curve, specimen 1 of Table I) does not appreciably deform; this property is characteristic of both the starting polymer and its processing products.

The group II polymers (specimens 2, 3, and 4 of Table I) include two of the three *o*-carborane-containing polyesters and the *p*-carborane-containing polyamide (the lower curves of Table I) and are characterized by high flow in the initial state typical of conventional thermoplastics. Flow decreases with increasing processing temperature due to crosslinking which leads to the formation of a cross-linked nondeformable product, pyropolycarborane (the upper  $450^{\circ}\text{C}$  curve).

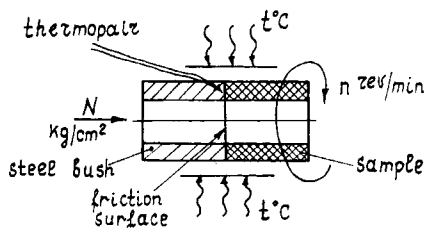


Fig. 1. Friction scheme for apparatus U-47.

TABLE I  
Structure and Some Properties of the Polymers

No.	Structural formula of the unit	dl/g	T soft °C	Initial temperature of weight change °C	Coke residue, % of initial weight in air, 900°C
1		1.18	no soft	250	85
2		1.26	240	400	75
3		0.31	240	400	60
4		0.3	200	400	85
5		0.65	300-320	400	85

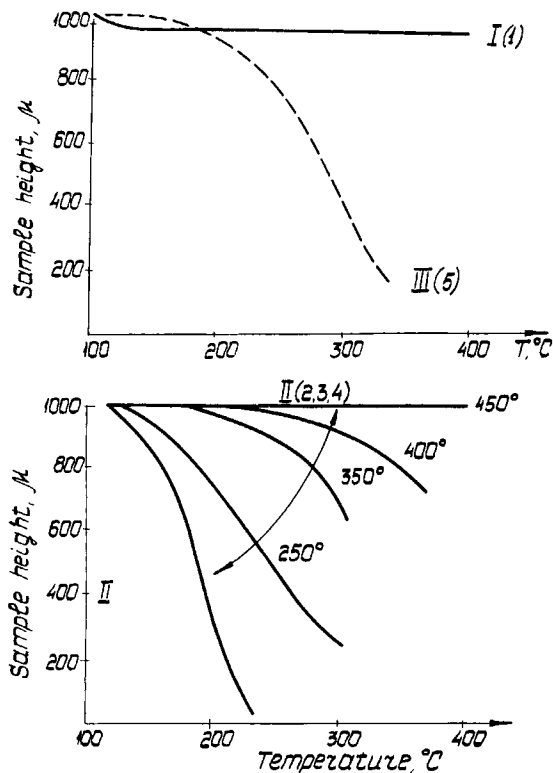


Fig. 2. Flow curves for carborane-containing polymers and pyropolycarboranes.

The third type of polymer includes the *o*-carborane-containing polyarylate (specimen 5 of Table I) which is a highly flowing product both in the initial state and after processing.

Investigation of the friction properties of the filled systems based on structurally different polyesters and graphite showed that the polymers of types II and III (Fig. 2) may serve as bonding agents for antifrictional self-lubricating materials in carborane-containing polyesters.

The use of type-III carborane-containing polyester as the bonding agent leads to thermoplastic antifrictional products of the conventional type. In this case, the processing does not change the chemical structure of the bonding agent, but shapes the material into a definite form on softening and melting. The material based on this carborane-containing bonding agent (type III, number 5) is notable for its enhanced thermal stability in the high-temperature range.

On the other hand, the use of type-II carborane-containing polymers leads to nondeformable antifrictional materials. In this case, the polymer undergoes the desired chemical transformations leading to the formation of cross-linked products, pyropolycarboranes.

The friction properties of the *o*-carborane-containing polyesters numbers 3, 4, and 5 are illustrated in Figure 3. A characteristic of these self-lubricating materials is their low friction coefficient in the temperature range from 200 to 400°C.

In the case of carborane-containing polyamides (i.e., number 1, Type I and

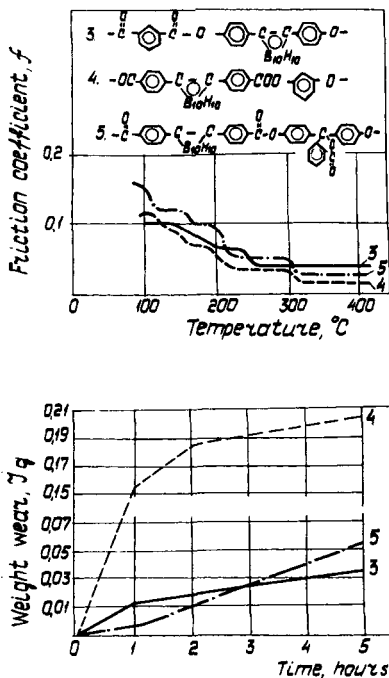


Fig. 3. Friction properties of carborane-containing polyesters.

number 2, Type II), graphite-filled materials were obtained that had the same thermally induced secondary cross linking; they became polycarboranes upon heating. The thermofriction properties of these graphite-filled *m*- and *p*-carborane-containing polyamides are given in Figure 4.

It is seen from the data (Figs. 3 and 4) that the type of thermofriction curve of each material depends largely upon the chemical nature of the polymeric bonding agent. A comparison of the results of gas liberation studies (Fig. 5) and the thermofriction curves of the polyamides (Fig. 4) shows that the temperature at the beginning of a decline in the friction coefficient coincides with that of the thermal transformations of the materials. For temperatures at which there is a maximum liberation of hydrogen, capable of being a gas lubricant, the material based on a *m*-carborane-containing polyamide (polymer number 1) has the lowest friction coefficient (at 250–400°C, the lower curve).

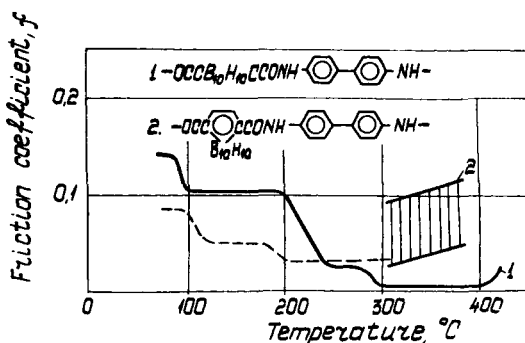
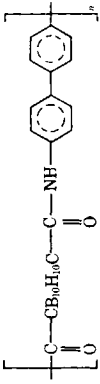
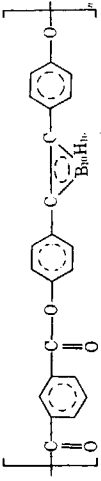
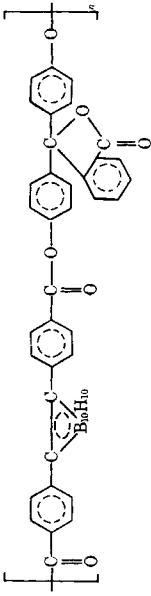


Fig. 4. Thermofriction curves for carborane-containing polyamides.

TABLE II  
Friction Properties of Materials Based on Carborane-Containing Polymers<sup>a</sup>

Polymer number on Table I	Structural formula of bonding agent	Friction coefficient		Weight wear, g/hr	
		room	350°C	room	350°C
1		0.12	0.02	0.001-0.008	0.004
3		0.1	at 400°C 0.04	0.002-0.004	at 400° 0.004-0.006
5		0.12-0.14	0.05	0.007	0.003

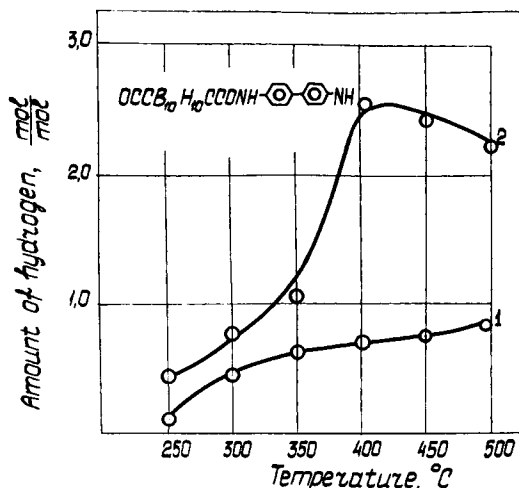


Fig. 5. Dependence of the amount of liberated hydrogen on temperature for *m*-carborane-containing polyamide pressed at 450°C (curve 1) and antifriction material (curve 2).

In contrast to the material based on polyamide number 1 (Fig. 4), the friction of a *p*-containing polyamide (number 2) is unsteady in the temperature range 300–400°C (see dotted line in Fig. 4), which is apparently associated with both the smaller amount of hydrogen liberated (Fig. 5) and the beginning of deformation in this temperature range.

It should be noted that the pyropolycarboranes based on *m*-carborane-containing polyamides (e.g., number 1) are characterized by the greatest liberation of hydrogen and that hydrogen is the only gaseous product accompanying their transformations at elevated temperatures.

This effect of hydrogen liberation in friction of the filled pyropoly-carboranes at high temperatures was used in the development of self-lubricating materials having the low friction coefficients at 300°C and above.

Table II shows the friction properties of several self-lubricating materials based on carborane-containing polymers. In addition to satisfactory wear resistance, these materials have low friction coefficients at elevated temperatures.

The results obtained above show that carborane-containing polymers and pyropolycarboranes can be effective regulators of friction and lubrication.

## References

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