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THERMOANALYTICAL TESTING OF RUBBER-GRADE CARBON BLACKS*

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The thermoanalytical behaviours of 9 carbon black types alone and in mixtures with rubber were studied. It was shown that the thermoanalytical tests carried out with rubber-grade carbon blacks help to predict their reinforcing effects. In measurements in the temperature range around 250° the weight losses indicate the activities of carbon blacks in rubber compounds. This test method may well supplement other test methods applied earlier to characterize carbon blacks.

The rubber compounds serving as the bases for rubber articles contain 30—40% of various fillers. The purpose of dosing fillers is partly to improve the processability and technical properties of the compounds and partly to cheapen the products. Among the fillers, an outstanding place is taken by the rubber-grade carbon black types manufactured by the furnace, channel and thermal processes.

Table 1

Characteristic properties of the tested carbon blacks

Trade names of carbon blacks	Type	ASTM designation	Colour index	Iodine number, mg I_2/g	Oil number, ml/g	C	H	O
						contents, %		
Sevecarb MT	MT	N-980	0.95	11.6	0.4	98.45	1.11	0.34
Noir Thermal T 68	MT	N-980	1.02	16.2	0.4	96.21	1.23	2.56
PGM-25	Lamp	—	1.19	18.4	0.5	98.55	1.22	0.23
PGM-33	SRF	N-761	1.07	26.6	0.8	98.59	0.46	0.95
PM-50	FEF	N-550	1.22	42.3	1.0	92.29	1.04	6.67
PM-75	HAF	N-330	1.34	75.7	1.1	96.98	1.09	1.93
PM-100	ISAF	N-220	1.53	126.0	1.1	96.20	0.83	2.97
Corax 6	ISAF	N-220	1.57	119.5	1.0	97.03	0.85	2.12
Vulcan 6H	ISAF-HS	N-242	1.56	117.8	1.0	94.09	0.75	5.16
DG-100	MPC	S-301	1.95	94.1	1.0	92.40	1.26	6.33

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For the determination of the characters and properties of rubber-grade carbon blacks, several processes are known: determination of the specific surface area, the particle size, the oil number, the blackness-grade, the volatile matter content, etc. From the property values obtained, conclusions can be drawn as to the activities, or the "reinforcing effects" of the carbon blacks in the compounds.

Apart from determination of the volatile matter, thermal methods have not been applied to characterize carbon blacks.

Our tests extended to 9 carbon black types; the most important characteristics of these are listed in Table 1, in order of decreasing carbon black activity.

Experimental

The tests were carried out in two temperature ranges: up to 250° with a heating rate of 1.25°/min and up to 1000° with a heating rate of 5°/min. The TG, DTG and DTA curves were taken in both air and nitrogen streams. In the latter case a flow velocity of 3–4 l/min was applied. The test apparatus used was a derivatograph, supplied by Magyar Optikai Művek (Hungarian Optical Works).

Results

Carbon blacks

The temperature range up to 250° was selected as that attained in high-temperature curings. Despite the facts that the two cases are not identical, and that their

Table 2

Percentage weight-changes of carbon blacks in air and nitrogen streams up to 250°

Carbon black	In air, %		Appearance	In nitrogen stream, %		Appearance
	150°	250°		150°	250°	
MT (1)	0.64	0.85	=	0.77	1.09	=
MT (2)	1.16	1.51	=	1.32	1.44	+
Lamp	1.65	1.65	+	0.78	0.97	/
SRF	–	–	+	0.75	1.20	+
FEF	1.55	2.33	+	1.75	2.34	+
HAF	2.4	2.6	+	2.17	2.76	+
ISAF (1)	1.92	2.31	=	1.96	2.55	=
ISAF (2)	1.81	2.21	=	1.99	2.80	=
ISAF-HS	2.90	3.48	=	2.72	3.11	=
MPC	3.98	4.6	=	4.22	4.64	=

= – DTA curve of baseline character,
+ – DTA curve of slight exothermic character, without peak,
/ – DTA curve of slight endothermic character, without peak

effects upon the blacks are different too, conclusions can be drawn from the measurements as to the behaviours of blacks.

From the results in Table 2 it can be seen that up to 250° the volatile matter is generally 1–3%; only with channel blacks containing oxidative groups does it reach 4.6%.

In 70% of the cases the loss of weight measured in a nitrogen stream is higher than or identical to the value measured in air. The reason for this is that in air desorption is accompanied by oxidation and the loss of weight decreases. This is also indicated by the DTA curve being of baseline form or slightly exothermic. The surface groups after oxydation were identified by UV spectroscopy on solvent-extracts of the blacks. Carboxyl, carbonyl, lactone, and phenolic hydroxyl groups were found.

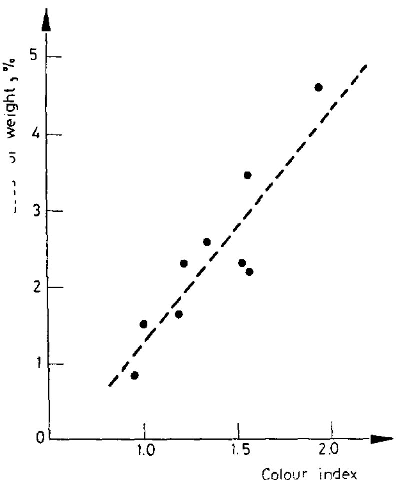

Fig. 1. Loss of weight at 250° in an air stream vs. colour index

The loss of weight increases with increase in the specific surface area of the blacks. This relationship is illustrated in Fig. 1, the loss of weight being plotted against the colour index.

The temperature range up to 1000° cannot be taken into consideration from the point of view of application in the rubber industry, but it may produce data on the structures of blacks and the materials absorbed on the surface; it also gives information on the oxidative degradation. The test results are reported in Tables 3 and 4.

The Tables list the beginning of oxidative degradation (T_0), the temperature measured at 15% weight loss (T_{15}), the temperature measured at the exothermic peak of the DTA curves (T_{max}) the corresponding weight loss and the total weight loss at the end of the test (at 1000°).

Table 3

Characteristic values measured during the test up to 1000°
(in air)

Carbon black	T_0,°C	T_{15},°C	Exothermic peak		Loss of weight at 1000°, %
			T_{max}, °C	loss of weight, %	
MT (1)	520	740	620	3.6	37.4
			820	22.6	
MT (2)	385	570	450	3.7	51.2
			605	17.1	
Lamp	490	630	530	2.8	87.7
			630	13.0	
SRF	450	670	555	4.7	44.4
			790	25.8	
FEF	430	610	505	3.7	62.0
			665	25.6	
HAF	460	630	500	1.6	60.0
			670	21.6	
			705	25.6	
ISAF (1)	455	625	490	2.7	58.3
			670	20.6	
			740	33.5	
ISAF (2)	485	630	595	1.0	64.4
			695	25.8	
ISAF-HS	410	605	575	11.5	62.3
			690	27.7	
MPC	470	600	570	10.4	71.7
			690	31.8	

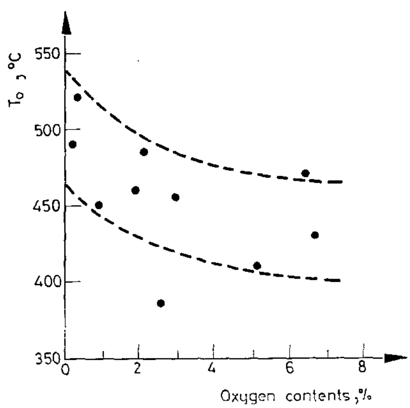

Fig. 2. Relationship between the initial temperatures of oxidative degradation of carbon blacks and their oxygen contents (test in an air stream)

Table 4

Characteristic values measured during the test at 1000°
(in nitrogen)

Carbon black	T_0,°C	T^{06}_{15},°C	Exothermic peak		Loss of weight at 1000°, %
			T_{max}, °C	loss of weight, %	
MT (1)	510	755	610	3.7	33.3
			770	16.8	
MT (2)	395	620	460	3.8	45.5
			700	21.6	
Lamp	500	640	595	8.2	90.0
SRF	460	670	550	4.6	45.5
			770	24.2	
FEF	445	620	495	3.8	51.4
			785	31.3	
HAF	480	640	505	3.0	60.0
			685	22.0	
			750	31.0	
ISAF (1)	460	630	495	2.8	53.6
			665	19.7	
			760	30.1	
ISAF (2)	465	610	570	8.7	87.1
ISAF-HS	470	625	595	11.2	61.8
			675	23.4	
MPC	505	680	580	6.3	32.3

Oxidative degradation started between 400 and 500°. The beginning was influenced by the atmosphere in which the test was carried out. In the majority of cases the degradation process in nitrogen started about 10–20° later. At the same time the start of the degradation is influenced by the specific surface area of the carbon black sample and the oxygen-containing groups on the surface. Both promote the start of the oxidative process. In Fig. 2 the relationship between the starting temperatures of oxidative degradation of the blacks and the oxygen contents is illustrated.

According to our results the temperature measured at 15% weight loss is not appropriate for characterising the active surface areas of carbon blacks.

According to Maurer [1], the temperature measured at 15% weight loss is appropriate to describe the active surface areas of various carbon black types. This relationship, observed on butyl rubber-based vulcanizates, could only be demonstrated on carbon black samples (and not on polymer compounds), and even then with very great scattering: thus, our tests did not confirm the previous assumption or permit its extension.

For most of the samples the DTA curves contain two well-distinguishhable peaks. Although the change cannot be determined numerically in calories, as regards the proportions of the change it can be ascertained whether the oxidative degradation was accompanied by a minor or major heat development. The tendency was noticed that the greatest enthalpy change could be observed with blacks of the smallest specific surface area and secondary structure (PGM-25, Noir Thermal T 68, Sevacarb MT), while with blacks of greater specific surface area the extent of heat development was lower. Of course, the differences in the manufacturing processes (thermal process, furnace process) and the differences in the starting raw materials (gas, liquid or a blend of these) cannot be neglected.

According to the Kissinger method [2], oxidative degradation for rubber-grade black types is a primary reaction.

Carbon blacks in rubber compounds

The tests had to be carried out with a compound showing well the reinforcing effects of the ingredients, its composition being close to that normally used in the rubber industry, relatively simple and free from the influencing effects of other compound ingredients. Accordingly, the tests were made with the styrene-butadiene-based rubber compound shown in Table 5.

Table 5

Composition of test compound

	Parts per weight
SBR 1500	100.0
Zinc oxide	3.0
Stearic acid	1.0
Sulphur	1.75
Accelerator*	1.0
Carbon black	50.0
	156.75

* N,N-cyclohexyl-2-benzothiazyl-sulphenamide

The most important properties of the compounds and their vulcanizates are to be found in Table 6.

From the data of Tables 1 and 6, the relationship well known in the rubber industry can be demonstrated, that the reinforcing effect increases with the increase of the specific surface area of the black and with the increase of the values of the colour index and iodine number. This runs parallel with the increase of viscosity, tensile strength, modulus and hardness, and with the decrease of elasticity.

If the relationship between thermoanalytical characteristics and reinforcing effect is examined, the tests made up to 250° give well-assessable data. The loss of weight at 250° is proportional to the reinforcing effect, as can be seen in Figs 3,

Table 6

Some characteristic properties of carbon black-loaded SBR-based compound

Carbon black	Viscosity, ML 1+4/100°	Tensile strength, N/cm²	300% modulus, N/cm²	Hardness, Sh°	Elasticity, %	Young's modulus, MN/m²
MT (1)	54	1030	590	62	50.7	7.83
MT (2)	54	1100	530	63	49.5	7.65
Lamp	54	1770	750	61	48.5	8.27
SRF	62	2150	1000	64	47.0	9.39
FEF	70	2340	1765	73	42.1	15.05
HAF	74	2100	1795	71	38.4	17.08
ISAF (1)	77	2740	1925	73	36.3	21.07
ISAF (2)	82	2500	1880	74	35.9	24.71
ISAF-HS	82	2680	1790	74	33.5	27.21
MPC	77	3050	1680	78	31.3	31.40

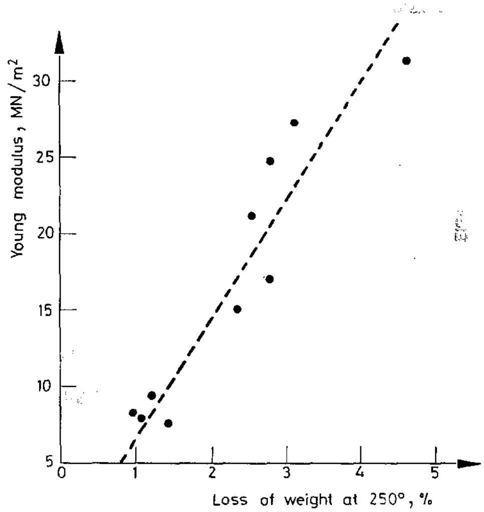

Fig. 3. Young's modulus vs. the loss of weight measured up to 250° in a nitrogen stream

4 and 5, where Young's modulus, the hardness and the elasticity are depicted as functions of the loss of weight.

In our view, the explanation of the relationship is that materials adsorbed and absorbed on the surface leave the carbon black surface, the extent of this being approximately proportional to the specific surface area. The reinforcing effect, however, changes linearly with the specific surface area between given limits, if the less dominant influencing role of the chemical nature of the surface is neglected.

According to our present tests, the starting temperatures of oxidative degradation of certain carbon blacks, the intensities of degradation, and the extent of the loss of weight give no information as to the activities and reinforcing effects of the carbon blacks. In order to illustrate this, the T and T_{15} values relating to the

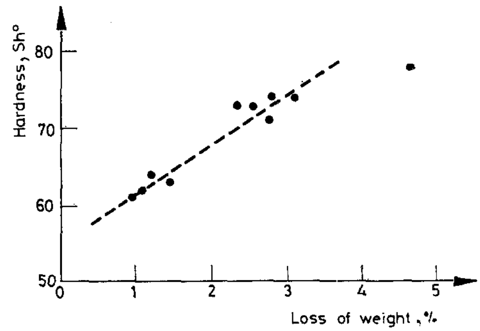

Fig. 4. Hardness of the vulcanizates *vs.* the loss of weight measured up to 250° in a nitrogen stream

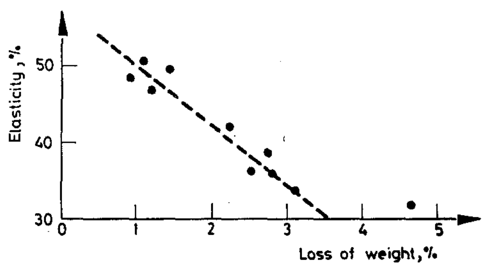

Fig. 5. Relationship between elasticity and loss of weight in a nitrogen stream

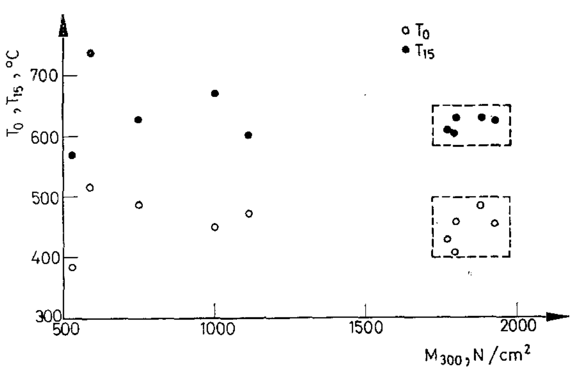

Fig. 6. T_0 and T_{15} *vs.* 300% modulus of the vulcanizate

300% moduli values are demonstrated in Fig. 6. The conclusion can be drawn from the Figure, however, that T_0 and T_{15} fall in the identical temperature range for carbon blacks of the same type and produced by the same process (HAF and ISAF).

In the case of the carbon blacks tested, these temperature ranges were around 450 and 625°.

References

1. J. J. MAURER, Rubber Age, 102 (1970) 47.
2. W. W. WENDLANDT, Thermal Methods of Analysis, New York, 1964.

RÉSUMÉ — On a étudié le comportement thermique de 9 types de noirs de fumée, seuls et en mélanges avec du caoutchouc. Les tests d'analyse thermique effectués sur des noirs de fumée destinés à l'industrie du caoutchouc permettent de prévoir l'effet renforçant de ceux-ci. Si les mesures sont effectuées vers 250°, la perte de poids indique l'activité des noirs de fumée dans le cautchouc. Cette méthode apporte des indications complémentaires des autres essais effectués précédemment pour caractériser les noirs de fumée.

ZUSAMMENFASSUNG — Das thermoanalytische Verhalten von 9 Typen von Ruß und in Gemischen mit Gummi wurde untersucht. Es wurde gezeigt, daß die an Ruß-Arten für die Gummi-Industrie durchgeführten thermoanalytischen Prüfungen sich für Voraussagen bezüglich der Verstärkungswirkung derselben eignen. Bei Messungen im Temperaturbereich um 250° zeigt der Gewichtsverlust die Aktivität des Rußes in den Gummiverbindungen an. Diese Testmethode kann die früher zur Charakterisierung von Ruß-Arten eingesetzten anderen Testmethoden gut ergänzen.

Резюме — Было изучено термоаналитическое поведение девяти типов газовой сажи и ее смесей с резиной. Показано, что термоаналитические тесты, выполненные с саженаполненными резинами, помогают установить их армирующее влияние. В случае измерений, выполненных в температурной области около 250°, потеря веса указывает на активность сажи в резиновой смеси. Этот тестовый метод может быть хорошим дополнением к другим тестовым методам, применяемым ранее для характеристики газовых саж.