

EFFECT OF CARBON BLACK ON THE THERMAL PROPERTIES AND FLAMMABILITY OF *cis*-1,4-POLYISOPRENE VULCANIZATES

G. Janowska and L. Ślusarski

INSTITUTE OF POLYMERS, TECHNICAL UNIVERSITY, ŁÓDŹ, POLAND.

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The effect of carbon black with various particle sizes and specific surfaces on the thermal properties of the sulphur vulcanizates of *cis*-1,4-polyisoprene was studied by means of thermal analysis. It was found that the addition of carbon black does not change the nature of the thermal processes in isoprene rubber vulcanizates essentially, but it distinctly affects the positions of the peaks recorded in the DTA curves. The specific surface of carbon black affects the temperature of the first exothermic process and the temperature and rate of destruction of cross-linked polyisoprene. The presence of carbon black brings about a reduction in the flammability of *cis*-1,4-polyisoprene vulcanizates. The specific surface of carbon black influences the value of the oxygen index OI.

The mechanical properties of elastomers are strongly affected by carbon black. Its effect is a symptom of interfacial interactions of a physical and chemical nature as well as of the formation of a three-dimensional structure of carbon black particles in the elastomeric system [1-4]. The activity of carbon black as a filler depends on its specific surface, on its ability to form the mentioned structure, and also on functional groups and unpaired electrons present on the surface of the particles. Carbon black consists mainly of carbon and additionally contains small amounts of oxygen, hydrogen, sulphur and mineral compounds. For example, the chemical composition of carbon black Sterling 106 APF is as follows: H 0.39%, C 98.39%, S 0.62%, O₂ 0.35%, ash 0.30% [1]. It may be expected that carbon black exerts a considerable influence on the thermal properties of elastomers, but a relatively low number of reports have been published on this subject [2-9]. The present study was aimed at this problem, particular attention being paid to the question of whether the specific surface of carbon black is of importance in this case.

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Experimental

Materials

The objects of our studies were vulcanizates of synthetic *cis*-1,4-polyisoprene, Cariflex IR-307 of Shell Chem. Co., containing carbon blacks of different particle sizes with different specific surfaces. The viscosity average molecular weight of the rubber was $M_v = 589\ 000$. A non-filled polyisoprene vulcanizate was also included in the investigations. The properties of the various carbon blacks are given in Table 1 and the compositions of the rubber compounds in Table 2. *cis*-1,4-polyisoprene was chosen for the studies since the thermal properties of its vulcanizates have been quite well established [10-12]. The composition of mixtures was almost typical, paraffin oil being used instead of the softeners generally applied, such as petroleum or coal tar products. This approach had the aim of facilitating interpretation of the results.

Table 1 Specific surfaces of investigated carbon blacks

Trade name of carbon black	Type of carbon black according to ASTM D2516-76	Specific surface, m ² /g	
		Literature data [13]	Result of own investigation
Sterling S01	N-539	40	37
Statex 93	N-601	42	42
Vulcan 3	N-330	83	81
Vulcan M	N-339	90	95
Vulcan 9	N-110	143	139

Methods

The rubber compounds were vulcanized in an electrical press for 30 min at a temperature of 150°.

The thermoanalytical investigations were carried out with a Paulik-Paulik-Erdey derivatograph, under the following conditions: environment - air, standard substance - Al₂O₃, temperature range 25-800°, sample size - 90 mg, heating rate 7.9 deg/min, sensitivity: DTA 1/5, DTG 1/20, TG 100. The thermoanalytical measurements were performed with samples previously disintegrated. The specific surface of the carbon black was measured by the method of nitrogen adsorption, using a Strohlein areameter according to Standard BN-81/6048-02.12.

Table 2 Compositions of rubber mixtures

Component	Parts by weight per 100 parts by weight of elastomer
<i>cis</i> -1,4-polyisoprene	100
Stearic acid	1
Zinc oxide	5
Paraffin oil	6
Carbon black	50
Sulphur	3
N-cyclohexylobenzothiazyl sulphenamide	1.2
Phenyl- β -naphthylamine	1
Together	167.2

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of non-filled *cis*-1,4-polyisoprene vulcanizate. The first symptoms of degradation and thermooxidative destruction of *cis*-1,4-polyisoprene cross-linked with sulphur appear already at 200°. This change, with maximum at 255°, becomes endothermic at 300° due to the oxygen deficiency in the pyrolysis zone. The small exothermic peak recorded at 540° is a sign of combustion of the solid substance remaining to an extent of about 3.3% after decomposition of the sample.

Figure 2 shows the thermal curves of carbon black Vulcan M. As for various other carbon blacks, one can recognize here signs of several thermal transformations. At about 180° a 2% weight loss takes place, which is associated with the desorption of water and possibly other low-molecular substances from the surface of the carbon black. The thermal effect of this process is negative but low; only the DTA curve slope is changed within this region. Within the range 200–470°, an extensive endothermic process with rather low thermal effect is observed, accompanied by a further weight loss amounting to 4%. In our opinion, this is a sign of the thermal dissociation of functional groups present on the surface of the particles. A strongly exothermic process of carbon black combustion starts above 470° and is completed at 780°. In the DTA curve within this range, one can observe two broadened maxima, but these are not reflected in the TG curve slope. Oxidation of the outer layers of carbon black particles probably occurs with a somewhat higher thermal effect than that of the inner layers.

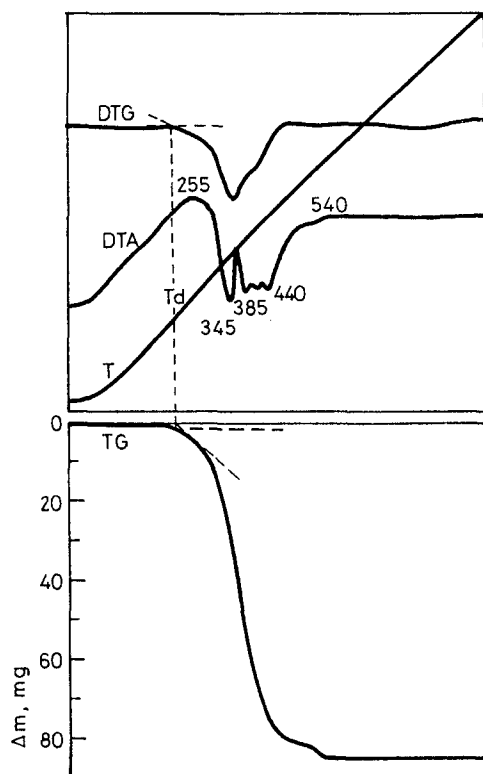


Fig. 1 Thermoanalytical curves of *cis*-1,4-polyisoprene sulphur vulcanizate, Td—temperature of the onset destruction

In fact, the main thermal changes in the elastomer and carbon black do not coincide. However, the addition of carbon black to the elastomer clearly affects its thermal stability. This is illustrated by the thermoanalytical curves of *cis*-1,4-polyisoprene vulcanizate filled with Vulcan M (Fig. 3).

At temperatures up to about 240° a 2% weight loss takes place, as in the case of carbon black. The maximum of the degradation and thermooxidative destruction of *cis*-1,4-polyisoprene filled with carbon black is shifted upwards by about 35 deg as compared with the sample containing no carbon black. Similarly, the thermal destruction (with an oxygen deficiency) in the presence of carbon black takes place at a temperature higher by 20 deg and to a lower extent. However, the combustion of the mentioned solid residue and the carbon black contained in the sample proceeds more easily than the combustion of carbon black itself; it is already complete at about 650°.

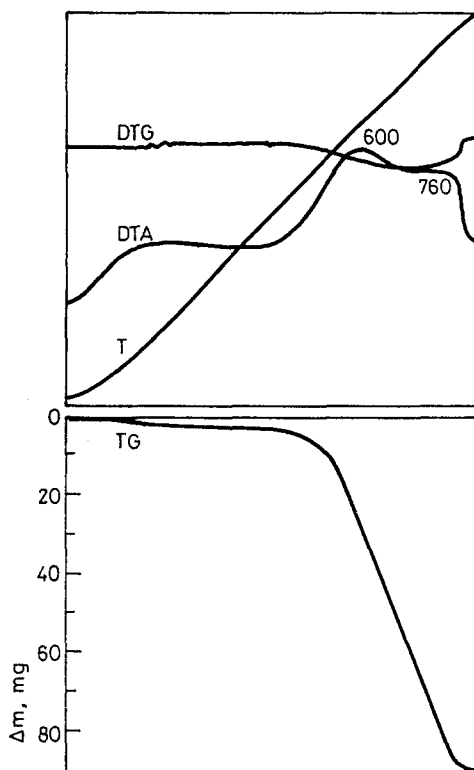


Fig. 2 Thermoanalytical curves of Vulcan M carbon black

We found a distinct effect of the specific surface of the carbon black on the temperature T_{\max} of the maximum rate of the first exothermic change of *cis*-1,4-polyisoprene vulcanizate (Fig. 4). When samples of carbon black with increasing specific surfaces are added to the elastomer, T_{\max} of the vulcanizate first increases and then, after exceeding the value $S = 100 \text{ m}^2/\text{g}$, slightly decreases.

The action of carbon black is presumed to consist mainly in retardation of the segmental mobility of the polyisoprene chains, which decreases the rate of oxygen diffusion into the reaction zone. Carbon black also acts as a scavenger and inhibitor of radical reactions, increasing the probability of primary recombination of macromolecules due to a prolongation of their dwelling time in the "cage". However, a certain amount of oxygen is introduced to the compound in the form of adsorption layers on the carbon black surface. This is probably the reason why carbon black with a considerable specific surface is not so effective in protective action (Fig. 4).

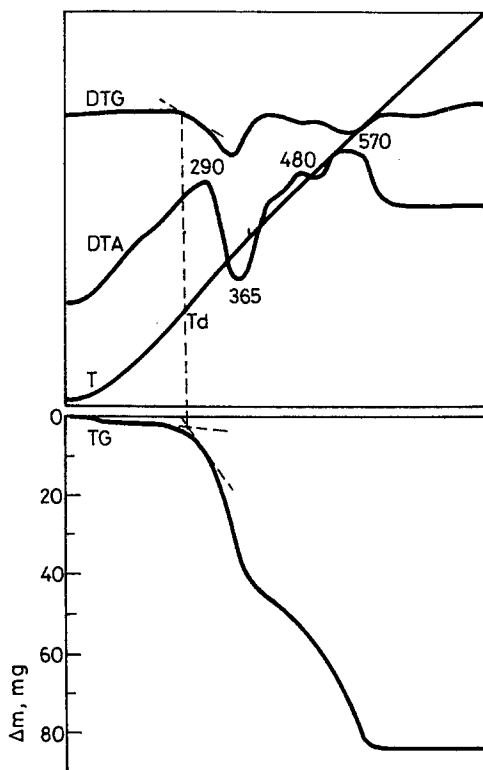


Fig. 3 Thermoanalytical curves of *cis*-1,4-polyisoprene sulphur vulcanizate, filled Vulcan M carbon black

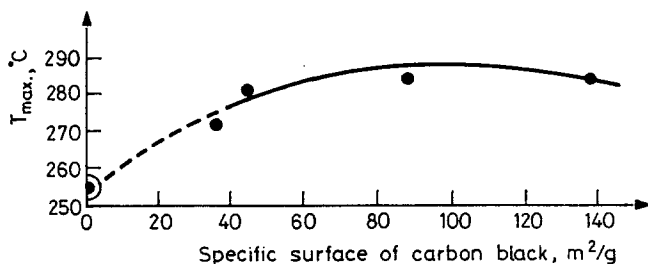


Fig. 4 Effect of carbon blacks on the maximum of the first exothermic *cis*-1,4-polyisoprene vulcanizates transition temperature, ●—unfilled vulcanizate

We also found a clear relationship between the specific surface of carbon black and its effects on the temperature and rate of destruction of cross-linked *cis*-1,4-polyisoprene (Figs 5 and 6). In this case, apart from the

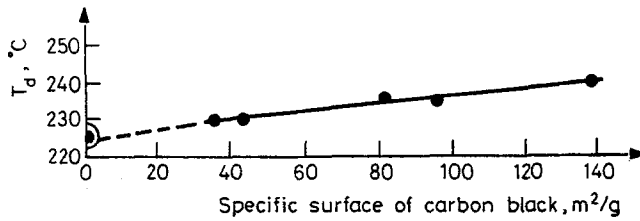


Fig. 5 Effect of carbon blacks on *cis*-1,4-polyisoprene vulcanizates destruction temperature, ●—unfilled vulcanizate

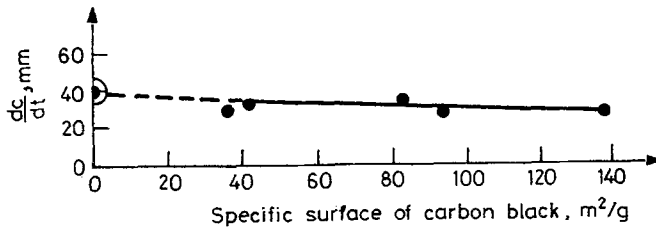


Fig. 6 Effect of carbon blacks on *cis*-1,4-polyisoprene vulcanizates decomposition rate, ●—unfilled vulcanizate

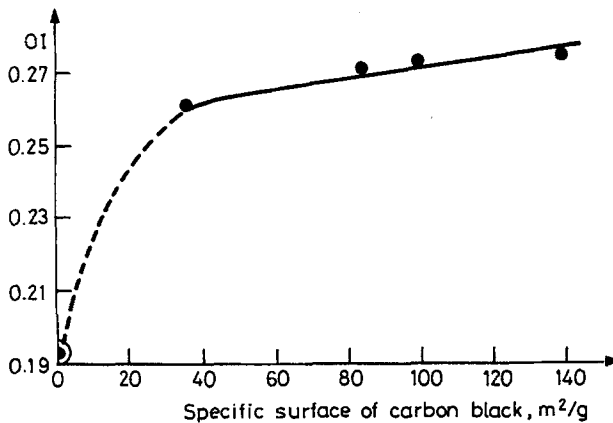


Fig. 7 Effect of carbon blacks on *cis*-1,4-polyisoprene vulcanizates oxygen index, (OI) ●—unfilled vulcanizate

reduced mobility of the polyisoprene chains and macroradicals, a role is also played by the adsorption of low-molecular destruction products of the vulcanizate on the carbon black surface. However, a higher oxygen index of filled vulcanizates results from a lower content of the flammable elastomer in the sample.

The specific surface of carbon black also influences the flammability of the filled polyisoprene vulcanizate (Fig. 7). This effect is connected with the inhibition of destruction, meaning that less volatile flammable substances are formed in the presence of carbon black, as shown by the results of the thermoanalytical measurements (Fig. 6). In our opinion, the added carbon black also changes the structure of the boundary layer between the sample and the flame. This layer plays a particular part in the combustion of the polymer since it is the path for the mass and energy transport. In the case of unfilled polyisoprene, the boundary layer is formed of strongly degraded macromolecules and liquid products of their decomposition [11]. Owing to the presence of the filler, the boundary layer possesses a higher thermal stability and is formed of considerably less degraded polymer and carbon black, which is an active sorbent of volatile products of destruction. The ability of carbon black to adsorb the volatile products increases with its specific surface.

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Zusammenfassung — Mittels Thermoanalyse wurde der Einfluß von Ruß mit unterschiedlicher Partikelgröße und unterschiedlicher spezifischer Oberfläche auf die thermischen Eigenschaften von Schwefelvulkanisaten von *cis*-1,4-Polyisopren untersucht. Es wurde festgestellt, daß die Zugabe von Ruß die thermischen Vorgänge in Isoprengum-mivulkanisaten nicht wesentlich verändert, daß jedoch die Lage der in den DTA-Kurven aufgezeichneten Peaks eindeutig beeinflußt wird. Die spezifische Oberfläche von Ruß beeinflußt die Temperatur des ersten exothermen Vorganges sowie Temperatur und Geschwindigkeit von Abbau des vernetzten Polyisoprenes. Die Gegenwart von Ruß führt eine Verminderung der Entflammbarkeit von *cis*-1,4-Polyisopren-Vulkanisaten herbei. Die spezifische Oberfläche von Ruß beeinflußt den Wert der Sauerstoffzahl.