

INFLUENCE OF CARBON BLACK ON THERMAL PROPERTIES AND FLAMMABILITY OF CROSS-LINKED ELASTOMERS

Grażyna Janowska* and P. Rybiński

Faculty of Chemistry, Institute of Polymer and Dye Technology, Technical University of Łódź, Łódź, Poland

The paper presents the results of testing thermal properties and combustibility of butadiene-acrylonitrile rubber vulcanizates with different contents of bounded acrylonitrile: Perbunan NT 1845 and Perbunan NT 3945 from Bayer. The rubbers were cross-linked by means of dicumyl peroxide. Four types of carbon black with different specific surfaces were used as fillers. The test results were obtained with the use of the derivatograph, DSC-204 of Netzsch, measurements of flammability by the method of oxygen index and in air.

The results of measurements have shown that the thermal stability and flammability of the vulcanizates under investigation are affected by the activity of solid phase and the degree of surface development as well as the flexibility of polymeric chain and the degree of its unsaturation. A clear relationship has been found between the thermal properties and flammability of the cross-linked butadiene-acrylonitrile rubbers.

Keywords: carbon black, elastomers, fillers, flammability, nitrile rubbers, oxygen index, thermal analysis, thermal stability, thermal transitions

Introduction

Carbon black is one of the most important filler used in the rubber industry. The properties of elastomeric mixes and end products depend on the polymeric matrices and kind of carbon black [1, 2]. Carbon black consists of 90–94% of C, 0.1–8% of O and 0.2–1% of H and has a crystallographic structure of graphite. The surface of carbon black consists of graphite layers with characteristic edges similar to the structures of organic systems. It is assumed that the chains of elastomers are absorbed on the edges of graphite layers [3, 4]. The surface of carbon black can be compared to degraded polycyclic aromatic hydrocarbons with various degrees of oxidation, which results in its great reactivity. The groups occurring on the surface of carbon black can be of an acceptor character, e.g. carboxyl, anhydride, lactone, hydroxyl or carbonyl group, as well as of a donor character, e.g. a γ structure of pyrone. On the surface of an energetically heterogeneous carbon black, carboxyl groups predominate, but the value of pH of carbon black used in the industry is higher than 7 due to the adsorption of various substances.

The mechanism of interaction between carbon black and macromolecules is complex. The addition of carbon black to elastomers exerts a considerable effect on both their thermal stability and flammability [5–8]. Carbon black brings about immobilization of macromolecules in the absorptive layer to decreasing

the amplitude of thermal vibration and consequently the probability of degradation. The higher thermal stability of elastomer filled with carbon black is also due to the fact that carbon black is capable of scavenging macro-radicals resulting from degradation. On the surface of most carbon black types one can observe a high concentration of paramagnetic centers showing a character of stable radicals.

The present paper discusses the effect of the specific surface of carbon black on the thermal stability and flammability of butadiene-acrylonitrile rubbers with various content of bounded acrylonitrile, commonly used in the rubber industry.

Experimental

The subject of our studies included peroxide vulcanizates (18N and 39N) of butadiene-acrylonitrile rubbers: Perbunan 1845 (NBR18) and Perbunan 3945 (NBR18) from Bayer [9, 10]. The rubbers were cross-linked by means of dicumyl peroxide. Four types of carbon black with different specific surfaces were used as fillers (Table 1).

Elastomer mixtures containing 20 phr of carbon black/100 phr of polymer prepared by means of laboratory rolling mill were vulcanised in the electric press at temperature 160°C. The optimal time of vulcanisation was found by means of WG-02 vulcameter according to PN-ISO-3417:1994.

* Author for correspondence: janowska@p.lodz.pl

Table 1 The results of thermal analysis of carbon black

Carbon black	Specific surface/m ² g ⁻¹	T_5 /°C	T_{50} /°C	ΔT_s /°C	Q_s /kJ kg ⁻¹
Sapex 20	25	480	615	540–640	48.200
Carbex 539	45	470	590	590–690	43.700
Carbex 330U	85	460	610	560–680	40.400
Sakap 6	150	455	570	580–690	36.300

T_5 – temperature of 5% mass loss

T_{50} – temperature of 50% mass loss

ΔT_s – temperature range of carbon black burning

Q_s – heat of combustion of carbon black determined on the base of DTA curves

Thermal analysis was performed in air by means of Paulik, Paulik, Erdey derivatograph at temperature ranging from 20 to 800°C using weighted portions 90 mg and a heating rate of 7.9°C min⁻¹. The thermal analysis was also carried out under nitrogen by the method of scanning dynamic calorimetry by means of DSC-204 of Netzsch at temperature ranging from 20 to –100 and –100 to 500°C using weighted portions 5–7 mg. The heating rate was 10°C min⁻¹.

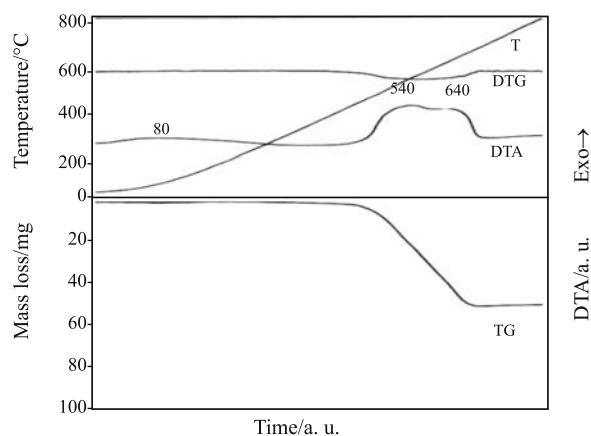
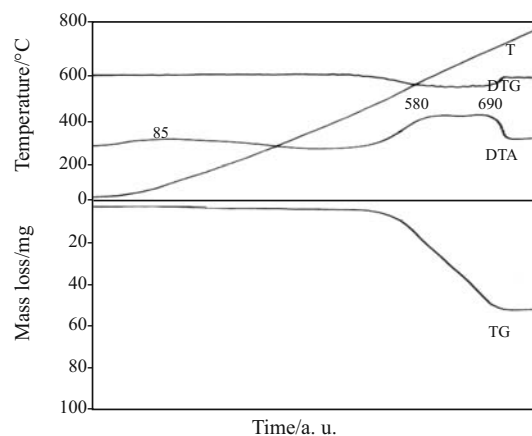
The flammability of vulcanizates was determined by the method of oxygen index according to PN-ISO 4589-2 and in air. In both cases, the same samples were used in the vertical position. They were ignited for 15 s with the use of burner supplied with propane–butane mixture. In measurements in air, the time of the sample combustion or time, after which samples were self-extinguished, was measurement.

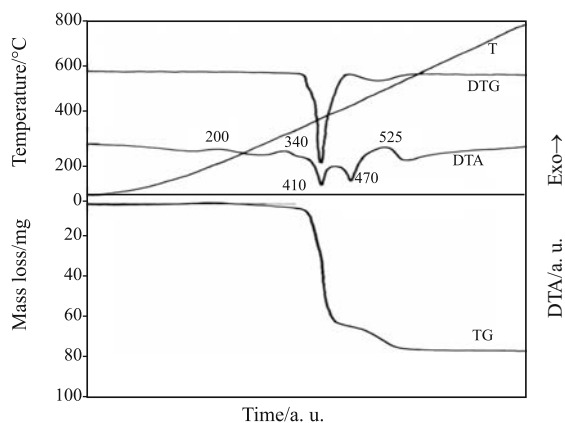
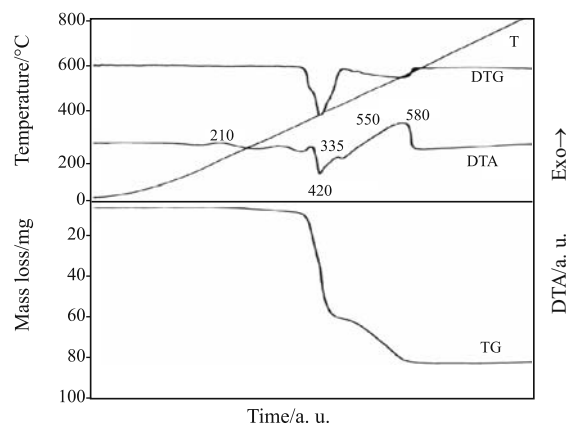
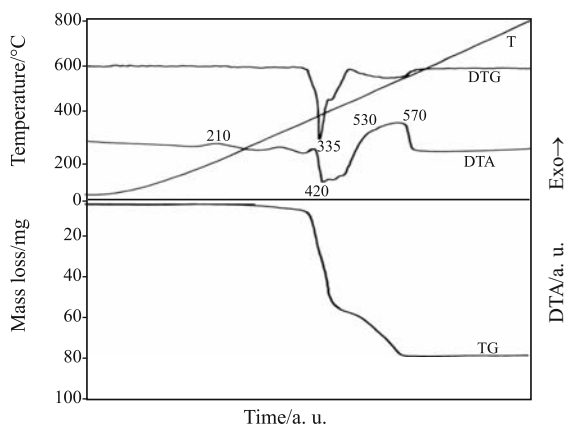
Results and discussion

Carbon black is not decomposed in the atmosphere of a neutral gas, but it burns completely in air as demonstrated by high exothermic peaks on DTA curves (Figs 1 and 2). The thermal decomposition of carbon black caused by its combustion begins above 540°C, thus beyond the region of thermal decomposition of most elastomers [7, 8]. The exothermic broadened

peaks recorded at a temperature of about 80°C in derivatograms are connected with thermo-oxidative processes and desorption of low-molecular-mass products from the surface of carbon black. The larger the specific surface of carbon black, the greater is the mass loss associated with these processes. A low quantity of oxygen in the form of absorptive layers on the surface of carbon black decreases its thermal stability (Table 1), which can cause a carbon black with a large specific surface to show a smaller protective effect in the elastomeric composition.

The addition of carbon black to an elastomeric mix does not change the character of thermal changes in cross-linked nitrile rubbers (Figs 3–5), but it clearly increases their thermal stability determined by indicators T_5 and T_{50} (Table 2). This may be due to the capability of carbon black to catalyze cyclization and cross-linking of elastomers, which facilitates the increase in their thermal stability [8, 11, 12]. From the data obtained by derivatography it follows that the presence of carbon black increases the temperature of initial, intensive thermal decomposition of vulcanizates, T_R . It has been found that the influence of filler on the thermal destruction rate of vulcanizates in the case of oxygen deficiency within the reaction zone depends on the content of AN units in the rubber. Carbon black causes a significant reduction in the thermal decomposition rate of NBR18

**Fig. 1** TG, DTG, DTA curves of Sapex 20**Fig. 2** TG, DTG, DTA curves of Sakap 6


Fig. 3 TG, DTG, DTA curves of NBR18 vulcanizate

Fig. 5 TG, DTG, DTA curves of NBR18 vulcanizate containing 20 phr of Sakap 6

Fig. 4 TG, DTG, DTA curves of NBR18 vulcanizate containing 20 phr of Sapex 20

vulcanizates, while it does not change dm/dt of NBR39 vulcanizates. The complex mechanism of the polymer-filler interaction has not been sufficiently explained as yet. We believe that the decrease in the thermal destruction rate of NBR18 vulcanizates filled with carbon black may be due to the considerably higher degree of limitation of segmental chain mobil-

ity of this elastomer around filler particles as compare with that of NBR39. The decrease in the segmental mobility reduces the amplitude of thermal vibration and consequently limits also the degradation and destruction processes.

As mentioned above, carbon black is a scavenger of free radicals. Thus, its presence inhibits free radical reactions and, at the same time, increases the probability of recombination of primary macro-radicals by prolonging their dwell time in the cage. If however the influence of carbon black as free radical scavenger may be one of the reasons to reducing thermal decomposition rate of the filled NBR18 vulcanizates, this does not manifest itself in the filled NBR39.

The results of thermal analysis show that carbon black burns easier in the presence of rubber. The process of carbon black burning begins at a considerably higher temperature and takes place within a considerably wider temperature range than the burning of residue resulting from the thermal decomposition of elastomer and carbon black contained in the vulcanizate (Figs 1–3, Tables 1 and 2).

Table 2 Effect of carbon black on thermal properties of NBR18 and NBR39 vulcanizates in air

Vulcanizate	$T_5/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_R/^\circ\text{C}$	$dm/dt/\text{mm}$	$P_W/\%$	$P_\ell/\%$	$\Delta T_s/^\circ\text{C}$	$P_{800}/\%$
18N	380	415	380	101	22.2	20.1	490–570 ^{x)}	6.7
18N Sapex 20	385	425	385	78	27.7	22.1	530–570	7.8
18N Carbox 539	385	430	390	75	26.6	21.3	520–590	10.5
18N Carbox 330U	395	435	395	62	26.7	21.0	540–595	10.0
18N Sakap 6	395	440	395	75	27.8	22.2	550–580	8.3
39N	340	410	360	45	28.9	27.5	520–595 ^{x)}	6.6
39N Sapex 20	355	425	360	46	38.9	31.3	520–570	6.1
39N Carbox 539	360	430	365	48	41.1	33.0	525–590	6.1
39N Carbox 330U	365	435	370	46	40.5	32.6	525–575	6.7
39N Sakap 6	370	440	370	45	40.0	32.1	520–590	5.0

ΔT_s – temperature range of burning of residue after thermal destruction of filled vulcanizate,
^{x)} and unfilled vulcanizate

P_{800} – residue at temperature 800°C

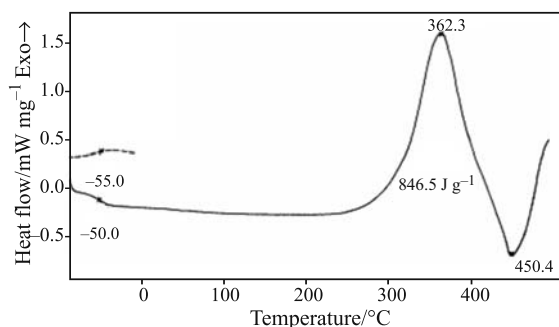


Fig. 6 DSC curves of NBR18 vulcanizate

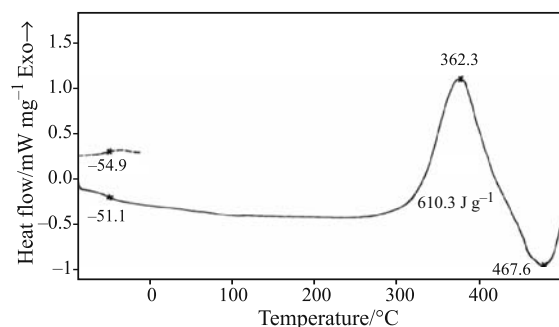


Fig. 8 DSC curves of NBR18 vulcanizate containing 20 phr of Sakap 6

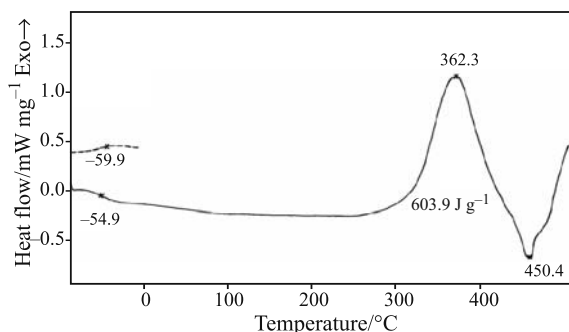


Fig. 7 DSC curves of NBR18 vulcanizate containing 20 phr of Sapex 20

As expected, carbon black increases the residue after the thermal decomposition of vulcanizates, P_w , and the residue after the thermal decomposition of elastomer contained in the vulcanizate, P_e . The increase in both P_w and P_e clearly depends on the content of acrylonitrile in the rubber and is considerably higher than in the case of NBR39 vulcanizates.

This allows one to believe that the flammability of vulcanizates of this rubber will be considerably reduced under the influence of incorporated carbon black. The increase in P_w and P_e means that a lower quantity of volatile decomposition products, including flammable substances, will pass to flame.

The thermal analysis of the vulcanizates under investigation was also carried out under the atmosphere of neutral gas (Figs 6–8, Table 3). The DSC curves, within the range of minus temperature, show changes connected with the processes of glass transition temperature of the cross-linked polymers (Figs 6–8). The increase in the content of AN in rubber increases the polarity of macromolecules and their interaction. Therefore, NBR39, both before and after its cross-linking, shows a considerably higher glass transition temperature than that of NBR18 (Table 3). The results of measurements show that under the influence of added carbon black, Sapex20, T_g of rubbers is considerably depressed (Figs 6, 7, Table 1). This is due to the slight interaction between polymer macromolecules and carbon black particles with a small specific surface (Table 1), whose presence causes the polymer chains to draw aside resulting in a small increase of their segmental mobility. The presence of carbon black with a large specific surface, Sakap6, does not change T_g of rubber (Figs 6, 8, Table 3). The separation of polymer macromolecules under the influence of this carbon black is compensated in this case by the polymer-filler interactions. The DSC curves of both unfilled and filled with carbon black vulcanizates show a high exothermic peak

Table 3 Effect of carbon black on thermal properties of NBR18 and NBR39 vulcanizates in nitrogen

Vulcanizate	Cooling		Heating			
	$T_g/^\circ\text{C}$	$\Delta T_g/^\circ\text{C}$	$T_g/^\circ\text{C}$	$\Delta T_g/^\circ\text{C}$	$T_c/^\circ\text{C}$	$Tdt/^\circ\text{C}$
NBR 18	-58.3	-64.3–-51.7	-51.5	-54.6–-45.4	361.3	447.0
18N	-55.0	-61.4–-48.7	-50.0	-57.0–-43.1	362.3	449.0
18NSapex20	-59.9	-70.3–-49.5	-54.9	-63.9–-46.0	362.1	448.1
18NSakap6	-54.9	-61.4–-48.3	-51.1	-62.1–-40.2	362.0	467.4
NBR 39	-27.8	-34.1–-21.4	-20.8	-22.8–-18.8	360.4	449.1
39N	-25.1	-28.9–-21.3	-19.0	-21.5–-16.6	363.3	442.1
39NSapex20	-30.2	-23.7–-36.6	-18.6	-21.0–-16.2	363.2	438.0
39NSakap6	-24.8	-19.5–-30.2	-19.0	-21.0–-17.0	363.3	432.0

ΔT_g – temperature range of glass processes
 T_c – temperature of cross-linking
 Tdt – temperature of destruction

above 270°C connected with the thermal cross-linking of rubbers (Figs 6–8). The presence of carbon black does not exert any significant influence on the temperature of the maximum rate of this process. The processes of thermal destruction of the examined vulcanizates begin above 430°C (Table 3).

The increase in the thermal stability of nitrile rubbers under the influence of carbon black facilitates the reduction in their flammability determined by both the value of OI and the combustion time in air (Tables 2, 4). Independently of the content of AN in rubber, this effect is the higher, the larger is the specific surface of carbon black (Tables 1, 4). The reduction in the flammability of NBR18 vulcanizates is due to the limitation of the thermal destruction rate of the cross-linked elastomer in the presence of carbon black, which results in a decreased quantity of gaseous flammable products passing to flame. On the other hand, the reduction in the flammability of NBR39 vulcanizates under the influence of carbon black is brought about mainly by the increase in the residue. P_e , after the thermal decomposition of cross-linked polymer in the presence of filler. It should be however clearly stressed that it is the structure of the boundary layer between flame and the sample that has a considerable contribution to the reduction in the flammability of vulcanizates filled with carbon black. The boundary layer is formed by the strongly cross-linked elastomer, and in the case of NBR39 also cyclized elastomer. Thus, it is thermally resistant and makes the mass and energy flow between the solid and gaseous phases difficult. The carbon particles in the boundary layer play the role of sorbents of volatile decomposition products of elastomers. The larger the specific surface of carbon black, the higher is its sorption capability.

Table 4 The results of flammability measurements of vulcanizates

Vulcanizate	OI	Time of burning in air/s
18N	0.270	360
18N Sapex 20	0.280	369
18N Carbox 539	0.285	362
18N Carbox 330U	0.290	390
18N Sakap 6	0.317	68 ^x
39N	0.295	71 ^x
39N Sapex 20	0.310	61 ^x
39N Carbox 539	0.347	54 ^x
39N Carbox 330U	0.355	49 ^x
39N Sakap 6	0.372	45 ^x

^x – self-extinguishing sample in air

Conclusions

The effect of carbon black on the thermal properties of elastomers differs according to their types. Beside the activity of solid phase and the degree of its surface development, a significant part is played, among other things, by the flexibility of elastomer chain and the degree of its unsaturation.

Under the influence of carbon black in the examined vulcanizates the thermal decomposition rate of the cross-linked NBR18 is decreased, and in the case of NBR39, the solid residues, P_w and P_e , are increased.

NBR39 vulcanizates are characterized by a considerably lower flammability than that of NBR18. Among NBR18 vulcanizate, only that filled with carbon black with the largest specific surface is self-extinguishing.

Acknowledgements

The authors would like to express their thanks to the Bayer company for providing free of charge samples of Perbunan NT 1845 and Perbunan NT 3945 which were used in this study.

References

- 1 D. J. Burlett, *J. Therm. Anal. Cal.*, 75 (2004) 531.
- 2 M. Sen and M. Copuroğlu, *J. Therm. Anal. Cal.*, 86 (2006) 223.
- 3 J. B. Donnet and E. Custodero, *C.R. Ac. Sci.*, 314 (1992) 579.
- 4 J. B. Donnet and E. Custodero, *Carbon*, 30 (1992) 813.
- 5 A. K. Sircar, *Rubber Chem. Technol.*, 46 (1977) 640.
- 6 T. Kleps, D. Jaroszyńska and M. Piasiewicz, *J. Thermal Anal.*, 36 (1990) 1213.
- 7 G. Janowska and L. Ślusarski, *J. Thermal Anal.*, 37 (1991) 713.
- 8 G. Janowska, *Scientific Bulletin of Technical University of Łódź*, Nr. 801, Łódź 1998.
- 9 J. Chruściel, G. Janowska, P. Rybiński and L. Ślusarski, *J. Therm. Anal. Cal.*, 84 (2006) 339.
- 10 G. Janowska and P. Rybiński, *J. Therm. Anal. Cal.*, 87 (2007) 511.
- 11 D. W. Brazier and G. H. Nickiel, *Rubber Chem. Technol.*, 48 (1975) 661.
- 12 D. W. Brazier and N. V. Schwartz, *J. Appl. Polym. Sci.*, 22 (1978) 113.

Received: July 11, 2007

Accepted: July 12, 2007

DOI: 10.1007/s10973-007-8621-7