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EFFECT OF THE MODIFICATION OF SILICA ON THERMAL PROPERTIES AND FLAMMABILITY OF CROSS-LINKED BUTADIENE-ACRYLONITRILE RUBBERS

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The paper presents the results of testing the thermal stability and flammability of butadiene-acrylonitrile rubber vulcanizates with different contents of combined acrylonitrile: Perbunan NT 1845 and Perbunan NT 3945 from Bayer, containing unmodified and bromine- or iodine-modified silica. The test results were obtained with the use of a derivatograph, measurements of flammability by the method of oxygen index, in air and also with the use of a cone calorimeter. The effect of the modification on the zeta potential was also examined.

A considerable reduction in the flammability of nitrile rubber vulcanizates filled with silica can be obtained by the modification of filler with bromine or iodine. All the vulcanizates containing modified silica are self-extinguishing. An appropriate filling of NBR 39 vulcanizates with bromine-modified silica makes it possible to obtain non-flammable polymeric materials. They neither ignite nor glow under the action of a flame source for 30 s.

The findings can be a rational basis for the synthesis of modified silica that can act as active filler and effective flame-retardant agent at the same time.

Keywords: *cone calorimeter analysis, fillers, flammability, nitrile rubber, oxygen index, silica, thermal analysis, thermal stability, thermal transitions*

Introduction

Elastomers containing no fillers are of insignificant practical importance. In practice, elastomers are commonly used in the form of mixtures with fillers, whose content amounts usually to 30–50%. Fillers impart appropriate processing capabilities to elastomers and defined usability to end products. They exert a significant influence on the thermal stability and flammability of elastomers [1–8]. Much attention has been paid to mineral fillers, especially silica. Active silica is commonly used to prepare rubber mixes designed for technical goods, using, first of all, rubbers resistant to oils and greases such as chloroprene and nitrile rubbers. Rubber elements made from these mixes, designed for oil wells and refineries, show considerably better resistance to the action of natural gas and crude oil than similar mixes containing carbon black.

Both thermal properties and combustibility of elastomers depend on their chemical structure and network structure. In the assessment of polymer flammability an important part is played by the results obtained by the methods of thermal analysis [9, 10]. Butadiene-acrylonitrile rubbers at elevated temperature (170–315°C) undergo mainly thermal cross-linking processes, what is a result of butadiene monomeric units polymerization [11]. Acrylonitrile mers' content in copolymer significantly influences the thermal cross-linking efficiency, thermal cyclization, rate and activation energy of thermal decomposition. Mentioned parameters affect on nitrile rubbers flammability [10].

The present paper presents the results of studies, unavailable in the literature as yet, concerning the thermal stability and flammability of cross-linked butadiene-acrylonitrile rubbers containing untreated silica and silica modified with aqueous solutions of bromine and iodine.

Experimental

The subject of our studies included peroxide vulcanizates (18N and 39N) of butadiene-acrylonitrile rubbers: Perbunan 1845 (NBR 18) and Perbunan 3945 (NBR 39) from Bayer. The rubbers were cross-linked by means of dicumyl peroxide. Two types of silica with different specific surfaces were used as fillers: Ultrasil VN3 (234 $m^2\ g^{-1}$) and Zeosil (175 $m^2\ g^{-1}$).

Elastomer mixes prepared by means of a laboratory rolling mill were vulcanized in an electric

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press at a temperature of 160°C. The optimal time of vulcanization was found by means of a WG-02 vulcameter according to PN-ISO 3417:1994.

The modification of silica consisted in its saturation with bromine water or Luggol's solution at room temperature for 24 h. Then, the modified fillers were dried to a constant mass. The quantity of absorbed iodine or bromine was assessed by elementary analysis.

In order to assess the donor-acceptor properties of the bromine- or iodine-modified silica, its zeta potential was determined in an aqueous medium as a function of pH. Measurements were carried out by means of ZETASIZER 2000 apparatus. The concentration of samples for the analysis was 0.05 g L^{-1}. The values of pH of the tested dispersions were changed with a 0.1 n solution of HCl or NaOH. Based on the prepared diagrams of the dependence of zeta potential of silica on pH of dispersion, the isoelectric point or the pH value, at which the electrokinetic potential is zero, was determined.

SEM examinations of the modified fillers were carried out by means of Jeol scanning microscope. The sample surfaces were dusted with gold.

The surface of vulcanizates containing silica was assessed from photographs taken by means of a Metrology Series 2000 camera from Molecular Imaging (USA) in a contact mode at a scanning frequency of 1–4 Hz. Samples for measurements were vulcanized in a steel mould. A glass plate was inserted into the mould cavity to obtain vulcanizate surfaces with a low roughness. Prior to insertion, the surface of glass plate was washed with acetone and dried with a stream of air to degrease and remove impurities. AMF photographs were analyzed with the use of the WSxM program from Nanoyec Electronica S. L. (Spain).

Thermal analysis was performed in air by means of Paulik–Paulik–Erdey derivatograph at temperatures ranging from 20 to 800°C and a heating rate of 7.9°C min^{-1} [9–11].

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 a 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 sample combustion or time, after which samples were self-extinguished, was measured.

In flammability tests, a cone calorimeter from Atlas Electric Devices Company was also used. Samples with dimensions 100×100±1 mm and thickness 20±0.5 mm, conditioned to a constant mass at a temperature of 20±2°C and RH 50±5% were tested in a horizontal position according to ISO 5660 at a density of heat stream of 35 kW m^{-2}.

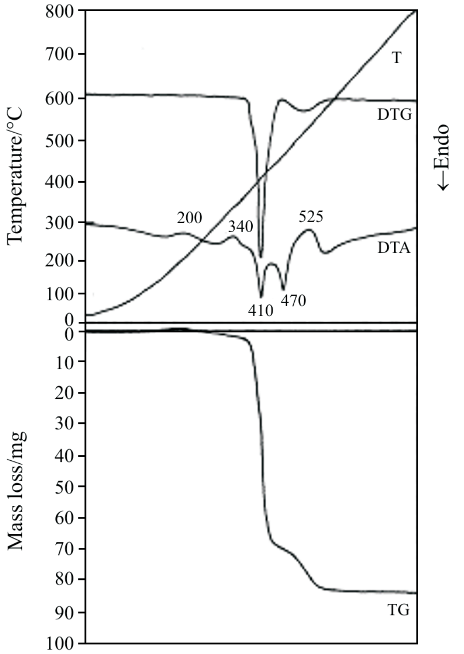

Fig. 1 Thermal curves of NBR 18 vulcanizate

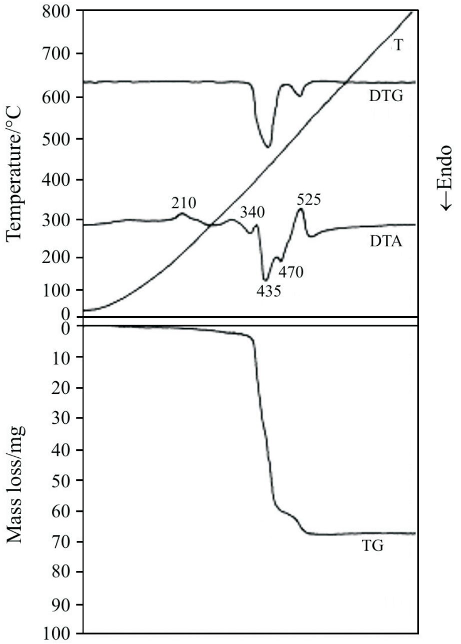

Fig. 2 Thermal curves of NBR 18 vulcanizate containing 30 phr of Ultrasil VN3 silica

Results and discussion

The presence of silica does not change the character of thermal transformations of nitrile rubber cross-linked with dicumyl peroxide (Figs 1 and 2). The first two exothermic processes recorded in the DTA curves at about 200 and 340°C are connected with the thermal

Table 1 The results of thermal analysis of vulcanizates containing silica

Sample	T_5/°C	T_{50}/°C	T_R/°C	T_{Rmax}/°C	d*m*/dt/mm	*Pw*/%	*Pe*/%	P_{800}/%
18N	380	420	380	415	90	22.2	22.0	6.7
18NU20	385	435	390	420	65	32.2	25.9	19.4
18NU30	390	445	395	440	42	32.2	24.0	23.9
18NU40	340	435	390	425	36	33.3	22.0	24.4
18NU50	395	450	405	435	39	43.3	31.2	33.9
39N	340	410	350	410	46	28.9	27.0	6.6
39NU30	325	435	365	425	32	38.3	35.5	22.2
39NU40	315	440	370	425	33	43.3	30.1	27.8
39NU50	310	455	375	430	29	47.7	31.1	33.3

18N – unfilled NBR 18 vulcanizate; 18NU20, 18NU30, 18NU40, 18NU50 – NBR 18 vulcanizates containing 20, 30, 40 and 50 phr of Ultrasil VN3 silica, respectively; 39N – unfilled NBR 39 vulcanizate; 39NU30, 39NU40, 39NU50 – NBR 39 vulcanizates containing 30, 40 and 50 phr of Ultrasil VN3 silica

cross-linking of elastomers. The thermal decomposition of vulcanizates begin at T>390°C for 18N as shown by the endothermic peaks at T=410 and 470°C (Fig. 1) and at T=435 and 470°C (Fig. 2). These processes proceed without the contribution of oxygen since the rate of formation of volatile destruction products is higher than that of oxygen diffusion to the reaction zone. The exothermic peak recorded at T=525°C is connected with the combustion of residue after the decomposition of cross-linked rubber.

The results of derivatographic analysis show that the addition of silica clearly increases the thermal stability of silica-containing vulcanizates determined with T_{50} as well as with the temperature of initial decomposition, T_R, and temperature of the maximal rate of this process, T_{Rmax} (Table 1). It has been found that the maximal decomposition rate of the cross-linked elastomer, dm/dt, is also decreased under the influence of silica. In our opinion, this results from the polymer-filler interactions, whose mechanism is very complex and has not been sufficiently explained as yet. The immobilization of elastomer macromolecules adsorbed on the surface of solid phase decreases the amplitude of their thermal vibration and consequently also the probability of degradation and destruction.

From the point of view of the reduction in vulcanizate flammability, a very important role is played not only by the mentioned decrease in the value of dm/dt, but also by the increase in the residue, *Pw*, after the thermal decomposition of vulcanizate, especially in the residue resulting from the destruction of cross-linked elastomer, thus *Pe* (Table 1). If the increase in the value of *Pw* under the influence of silica results from the decreased content of elastomer in the sample under analysis, the increase in *Pe* is due to the polymer-filler interaction.

The expected reduced flammability of vulcanizates containing silica, resulting from the thermal analysis, has been confirmed by the measurements of flammability by the method of oxygen index and in air (Table 2). With the increase in silica content, the value of OI increases and the duration of sample combustion grows longer, but the time, after which samples extinguish in air is shortened. This is particularly important in the case of cross-linked rubber NBR 18, whose flammability is considerably greater than that of NBR 39 [10]. Under the influence of filler, whose content amounts to 40 phr (parts by mass per 100 prts by mass of elastomer), NBR 18 vulcanizates extinguish in air.

The decrease in the flammability of cross-linked vulcanizate in the presence of silica is brought about by the considerable reduction in the thermal decomposition rate of polymer. Thus, smaller quantities of volatile and flammable products of destruction pass to flame, the more so as part of them is adsorbed on the filler surface. A very important role is played also by the structure of the boundary layer being formed during combustion of the filler-containing vulcanizate. Under the influence of silica, it becomes more thermally stable and impedes the flow of mass and energy between flame and sample. During combustion of the vulcanizates filled with silica, non-flammable gaseous products can be formed, first of all, in the form of water vapor. From the thermal analysis it follows that the examined silica samples contained 5.6% of water. Water is adsorbed on the functional groups on the silica surface. These groups include single ≡Si(OH) and twin =Si(OH) silane groups and siloxane bridges

Table 2 The results of flammability measurements of vucanizates containing silica

Sample	OI	Time of burning in air/s
18N	0.270	360
18NU20	0.273	369
18NU30	0.286	405
18NU40	0.292	41*
18NU50	0.298	40*
39N	0.295	71*
39NU30	0.310	37*
39NU40	0.322	28*
39NU50	0.333	23*

*self-extinguishing samples in air

=Si(OH)–O–Si(OH)=. During combustion, a gradual desorption of water takes place, the evaporation of water decreases the energetic balance of the system and water vapor dilutes the flammable gaseous product passing to flame.

Based on the results of zeta potential measurements, it has been found that the modification of the silica sample examined with bromine water changes the character of their surfaces from acidic to basic: a different value is shown by its electrokinetic point (PI), i.e. the pH value, at which the electrokinetic potential is zero. In the case of unmodified silica, PI is about 2. The adsorption of iodine on the silica surface makes no radical change in the PI value, while the modification with bromine shifts it towards higher values of pH, about 10 (Figs 3 and 4). Considering the fact that the difference in electronegativity between bromine and iodine is rather slight, we believe that iodine, first of all, is adsorbed physically on the silica surface, while bromine is also chemically combined with the filler surface, as confirmed by the results of elemental analysis. The content of iodine and bromine combined with Ultrasil VN-3 silica is 18.45 and 20.3%, respectively, while after its extraction with water for 72 h, the iodine content decreases to 1.47% and that of bromine to 5.81%. The higher quantity of bromine combined with the silica surface in relation to that of iodine may also result from more aggressive action of bromine on the silica surface. The SEM photographs show the disintegration of silica grains under the influence of bromine water (Fig. 5).

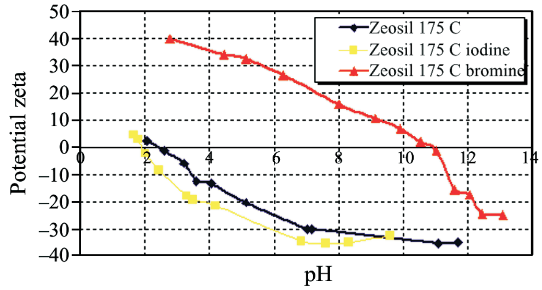

Fig. 3 Electrokinetic zeta potential (ζ) of Zeosil 175C silica before and after its modification with iodine or bromine *vs*. of pH of water medium

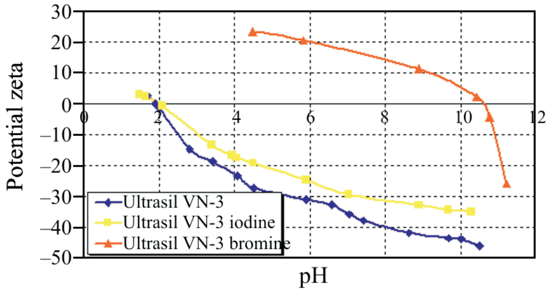

Fig. 4 Electrokinetic zeta potential (ζ) of Ultrasil VN3 silica before and after its modification with iodine or bromine *vs*. of pH of water medium

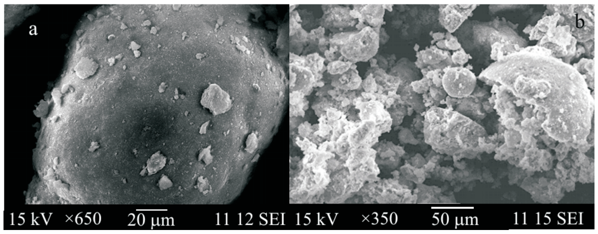

Fig. 5 SEM photographs of Zeosil 175C silica: a – before modification, b – after modification with bromine water

The modification of silica with iodine or bromine does not impede its incorporation into the polymer matrix. Nevertheless, it has been found that in the case of Ultasil VN-3 modified with iodine, its dispersing in rubber is considerably better than that of this silica modified with bromine (Fig. 6).

From the derivatographic analysis it follows that the modification of filler does not affect the character of thermal transformations of cross-linked NBR 18 and NBR 39 and makes no significant changes in the temperature of initial thermal decomposition (Figs 7 and 8, Table 3). It has been found that the polarity of rubbers affects the processes of thermal decomposition of their vulcanizates filled with modified silica. The modification of silica considerably decreases the thermal decomposition rate of NBR 39 vulcanizate, but does not exert such an influence on NBR 18 vulcanizates (Table 3). On the other hand, irrespective of the polarity of rubber, the modification of filler increases both the residue after the thermal decomposition of filled vulcanizate, *Pw*, and the residue after the decomposition of cross-linked elastomer, *Pe*. The increase in *Pw* and *Pe*, resulting from the susceptibility to carbonization under the influence of elevated temperature, becomes more pronounced in the case of NBR 39 vulcanizates. From the comparison of the residues after the thermal decomposition of samples heated to T=800°C, P_{800}, it follows that the content of mineral substances at this

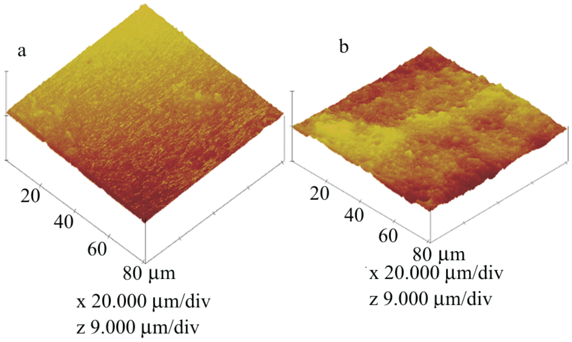

Fig. 6 AFM photographs of vulcanizate containing Ultrasil VN3 silica: a – silica modified with iodine, b – silica modified with bromine

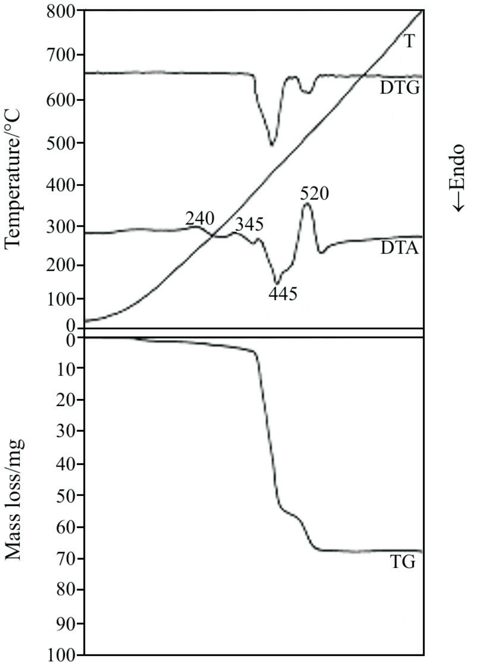

Fig. 7 Thermal curves of NBR 18 vulcanizate containing 30 phr of Ultrasil VN3 silica modified with iodide

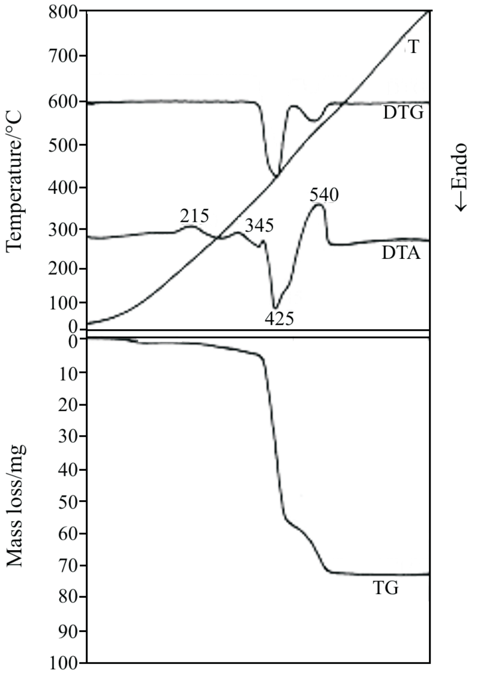

Fig. 8 Thermal curves of NBR 18 vulcanizate containing 30 phr of Ultrasil VN3 silica modified with bromine

temperature is decreased under the influence of silica modification. This is brought about by the thermal desorption of iodine or bromine in the modified fillers. In the residue of P_{800}, the content of these elements is about 0.3%.

The measurement results show that the silica modified with bromine or iodine considerably reduces the flammability of the filled vulcanizates of both rubbers. A particular distinct influence appeared in the case of NBR 18 vulcanizates, which extinguished in air owing to the presence of the modified silica. NBR 39 vulcanizates filled with the modified silica show higher values of OI and the time of their self-extinguishing is considerably shorter as compared to NBR 18 vulcanizates, which results from the chemical structure of elastomers [10] (Table 4).

With a higher degree of filling NBR 39 vulcanizate with Ultrasil VN-3 silica modified with bromine, amounting to 50 phr, it was possible to obtain non-flammable product. The action of a flame source on this vulcanizate for 30 s brought about neither ignition nor glow of it. This was probably due to the emission of considerable quantities of bromine compounds under the influence of elevated temperature, which made the ignition of the sample impossible.

Taking into account the fact that the flammability of NBR 18 is greater than that of NBR 39, and also the significant contribution of silica, especially modified with bromine, to reducing the flammability of filled

Table 3 The results of thermal analysis of vulcanizates containing modified silica

Sample	T_5/°C	T_{50}/°C	T_R/°C	T_{Rmax}/°C	dm/dt/mm	Pw/%	Pe/%	P_{800}/%
18NU30	390	445	395	440	42	32.2	24.0	25.0
18NU30I	375	445	385	435	44	38.9	27.9	23.9
18NU30Br	390	445	395	430	46	36.6	27.3	18.8
39NU30	325	435	365	425	33	38.3	35.5	24.4
39NU30I	345	460	355	415	32	49.4	36.9	22.2
39NU30Br	340	515	365	405	22	60.0	44.7	21.1
39NU50	310	455	375	430	29	47.7	31.1	33.3
39NU50Br	265	540	370	400	23	62.8	40.9	25.6
39NZ30	340	445	380	430	46	38.8	30.6	24.4
39NZ30I	325	442	375	420	34	46.6	38.4	21.7
39NZ30Br	320	495	385	415	21	57.6	46.2	20.8

18NU30I, 18NU30Br – NBR 18 vulcanizates containing 30 phr of Ultrasil VN3 silica modified with iodine or bromine, respectively; 39NU30I, 39NU30Br – NBR 39 vulcanizates containing 30 phr of Ultrasil VN3 silica modified with iodine or bromine, respectively; 39NU50Br – NBR 39 vulcanizate containing 50 phr of Ultrasil VN3 silica modified with bromine; 39NZ30I, 39Nz20Br – NBR 39 vulcanizates containing of Zeosil 175C silica modified with iodine or bromine, respectively

Table 4 The results of flammability measurements of vulcanizates containing modified silica

Sample	OI	Time of burning in air/s
18N2U30	0.286	405
18N2U30I	0.298	52*
18N2U30Br	0.293	25*
39N2U30	0.310	37*
39N2U30I	0.328	27*
39N2U30Br	0.324	27*
39N2U50	0.330	23*
39N2U50Br	0.335	**
39N2Z30	0.310	32*
39N2Z30I	0.333	38*
39N2Z30Br	0.335	36*

*self-extinguishing sample in air; **non-flammable sample

Table 5 The means values of parameters determining flammability of NBR 18 vulcanizates obtained by cone calorimeter

Parameter	18NU30	18NU30Br	18NU30I
Time to sustained ignitions/s	61.16	63.63	62.96
Average heat realize rate/kW m^{-2}	352.91	392.64	387.06
Maximum heat realize rate/kW m^{-2}	1711.62	1064.50	1944.07
Total heat release/MJ m^{-2}	67.71	48.35	59.26
Average effective heat of combustion/MJ kg^{-1}	37.70	28.24	38.65
Average mass loss rate/g s^{-1} m^{-2}	22.45	24.22	21.41
Maximum mass loss rate/g s^{-1} m^{-2}	47.26	31.60	48.97
Average specific extinction area/m^2 kg^{-1}	1056.64	1110.81	972.43
Average CO yield/kg kg^{-1}	0.0778	0.0937	0.0944
Average CO_2 yield/kg kg^{-1}	2.5815	2.6589	2.5209

NBR 18 vulcanizates, tests of flammability with these vulcanizates were also performed by the method of cone calorimetry (Table 5).

The incorporation of bromine- or iodine-treated silica into NBR 18 causes a considerable decrease in the amount of the total heat release, and in the case of brominated filler, also a clear decrease in the maximal rate of heat release (HRR) as well as in the maximal rate of mass loss. We believe that the decreased HRR of the vulcanizate filled with bromine-modified silica in relation to that filled with unmodified or iodine-modified silica may result from the particular capability of bromine to discontinue the combustion processes taking place in flame. It is not unlikely that iodine compounds, similarly as chlorine compounds, are emitted within a considerably wider range of temperature and are less active due to their lower concentration in the combustion zone.

The use of iodine- or bromine-modified silica makes it possible to obtain self-extinguishing NBR 18 vulcanizates with slightly changed parameters of fire hazard such as the average mass optical density of smoke or average emission of CO and CO_2.

Conclusions

The polymer-filler interactions increase the thermal stability of nitrile rubbers cross-linked in the presence of silica and reduce their flammability.

The modification of silica with bromine water changes the value of its isoelectric point, which does not impede its incorporation into the polymer matrix.

A considerable reduction in the flammability of nitrile rubber vulcanizates filled with silica can be obtained by the modification of filler with bromine or iodine. All the vulcanizates containing modified silica are self-extinguishing.

An appropriate filling of NBR 39 vulcanizates with bromine-modified silica makes it possible to obtain non-flammable polymeric materials. They neither ignite nor glow under the action of a flame source for 30 s.

The results of investigations can be a rational basis for the synthesis of modified silica that can act as active filler and effective flame-retardant agent at the same time.

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