J Therm Anal Calorim (2010) 100:1037–1044
DOI 10.1007/s10973-009-0553-y

Influence of surface modification on thermal stability and flammability of cross-linked rubbers

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Received: 23 April 2009 / Accepted: 8 October 2009 / Published online: 18 November 2009

Abstract The paper discusses the test results of thermal stability and flammability of cross-linked diene rubbers containing silica prepared "in situ" from alkoxysilane precursors. The effect of the surface modification of unfilled vulcanizates by means of aqueous solutions of halogens, boron and organo-phosphoric compounds on their flammability was also assessed. The thermal analysis has been performed in air with the use of derivatography. The flammability of vulcanizates has been determined by the method of oxygen index and in air. It has been found that the modification of the vulcanizates with tetraethoxysilane that makes it possible to form silica "in situ" considerably reduces the flammability of cross-linked rubbers. The surface modification of the vulcanizates with halide and organo-phosphoric compounds allows one to radically decrease their flammability. The boric flame-retardant agents are the most effective modifiers. The most beneficial results were obtained with the use of boric acid.

Keywords Elastomers · Flammability · Surface modification · Thermal properties

Introduction

Polymeric materials are characterized by heterogeneity in respect of composition and structure. The performance parameters of goods made of polymeric materials depend on their top layer that differs from the inside of material in physical and often chemical terms. This is due to the fact that many physical phenomena and chemical reactions occur on the surface of polymeric materials, including processes such as oxidation, segregation and migration of low molecular or oligomeric components, known in the technology of polymers as a blooming process. Thus, the processes responsible for ageing, diffusion, thermal stability and flammability begin in the top layer of polymers [1].

Recently more and more attention is paid to the modification of polymeric materials in order to impart desirable properties to them. It can be done by various methods. A modifier can be formed either in situ on the material surface or mechanically applied to it. Modifiers can also be incorporated into the polymer matrix in the form of liquid, solution or emulsion. Their migration to the polymer surface usually results from superficial segregation [2].

A considerable progress has been recently accomplished in the production of polymeric materials that meet specified requirements concerning their thermal stability and flammability. Only in exceptional case such materials are prepared with the use of expensive flame-retardant special or specialized polymers. In most cases, one can use general purpose polymers, an appropriate selection of polymeric composition and various modifications of raw materials as well as surfaces of ready-made products [3, 4].

This study presents the test results of thermal stability and flammability of cross-linked diene rubbers containing silica prepared "in situ" from appropriate alkoxysilane

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precursors. The effect of the surface modification of unfilled vulcanizates by means of aqueous solutions of halogens, boron and organo-phosphoric compounds on their flammability was also assessed.

Experimental

Materials

Our investigation was focused on cross-linked butadiene–acrylonitrile rubbers, Perbunan 1845 (NBR 18) and Perbunan 3945 (NBR 39) from Bayer containing 18 and 39% of acrylonitrile units, respectively, as well on butadiene rubbers: SKD II and Br 1220 differ from one another contents *cis–trans* monomeric units, and butadiene–styrene rubber containing 25% of styrene units from Synthos Dwory.

The rubbers were cross-linked by means of dicumyl peroxide from Merck-Schuhardt, disulphide tetramethylothiuram (TMTD), and sulphur with accelerating agent of curing process (MBT).

The silica filler was synthesized from tetraethoxysilane (TEOS, from Aldrich) in the medium of NBR 18 rubber cross-linked with dicumyl peroxide.

The surface modification was carried out by the use of aqueous solutions of halogens, that is chlorine water (900 mL of distilled water was saturated by the gas chlorine by the period 4 h) [5], Lugol's solution (1 phr iodine, 2 phr potassium iodide, 97 phr water) [6] and bromine water (3 phr bromine, 97 phr water) [7], as well as saturated aqueous solution of di-sodium tetraborate decahydrate ($Na_2B_4O_7 \times 10\ H_2O$, from POCH S.A Gliwice), saturated alcohol solution of boric acid ($H_3BO_{3,}$ from POCH S.A Gliwice) and liquid organo-phosphoric compounds from Bayer, known under the trade name Disflamolle such as:

- Diphenyl-(2-ethylhexyl)-phosphate; DPO
- Diphenylcresylphosphate; DPK
- Tricresyl phosphates; TKP
- Tris(2-ethylhexyl) phosphate; TOF.

Methods

Rubber mixes were prepared with the use of a laboratory two roll mill at room temperature and were vulcanized in an electrical press at 160 °C for a time $\tau_{0.9}$, which was determined by means of WG2 vulcameter according to PN-ISO-3417:1994.

The modification with teraethoxysilane was carried out by swelling the peroxide vulcanizates of NBR 18 in TEOS for 48 h at a temperature of 30 °C. To perform the sol–gel process, the swollen shaped samples were immersed in a 10% aqueous solution of ethanoldiamine at $T = 30$ °C. After 24 h the vulcanizates were thoroughly rinsed with water and dried to a constant weight at $T = 60$ °C [8].

The dispersion of the filler synthesized in the medium of elastomer was assessed by the method of scanning microscopy, using vulcanizate fractures in liquid nitrogen with a gold layer deposited on their surface a "JEOL" type 35C apparatus.

The modification with aqueous solutions of halogens, boron and organo-phosphoric compounds was carried out by swelling prepared for flammability test specimens with dimensional 100 × 10 and thickness 4 mm, in the aqueous solutions of halogens by the period 2, 12 and 24 h, in the case boron and organo-phosphoric compounds for 24 h.

Thermal analysis was performed in air by means Paulik, Paulik, Erdey derivatograph at the temperature ranging from 20 to 800 °C using weighted portions 90 mg and a heating rate of 7.9 °C/min.

The flammability of vulcanizates was determined by the method of oxygen index according to PN-EN-ISO 4589-2:2006 [9]. The flammability in air was also tested, using the same specimens as in the case of oxygen index. In both cases, the same samples, with dimension 100 × 10 × 4, were used in a vertical position. They were ignited for 15 s with the use 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 [10–12].

Results and discussion

In practice, elastomers are used in the form of mixtures with fillers mostly such as carbon black, silica, chalk and zinc oxide.

In the technology of elastomers, silica is mechanically dispersed in the polymeric matrix during the mixture preparation. However, due to its significant polarity and large specific surface, it is difficult to disperse a conventional silica in the polymer matrix as there are formed aggregates with considerable dimensions [13].

The results obtained by means of SEM show that the difficulties connected with silica dispersion in the elastomer medium can be eliminated by its "in situ" synthesis in the polymer matrix (Fig. 1).

From the literature review, it follows that the content of silica obtained "in situ" in a vulcanizate depends on both the density of elastomer cross-linking and the rubber solubility in tetraethoxysilane. In the case of non-polar rubbers such as butadiene or butadiene–styrene rubber or natural rubber, the values of their swelling in TEOS amount even to 300%, while in the case of rubbers with high polarity, it does not exceed 50% [8]. Therefore, to

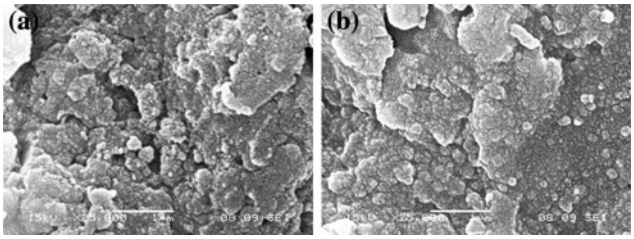

Fig. 1 SEM images of vulcanizates containing silica formed "in situ" **a** peroxide vulcanizate, **b** sulphur vulcanizate

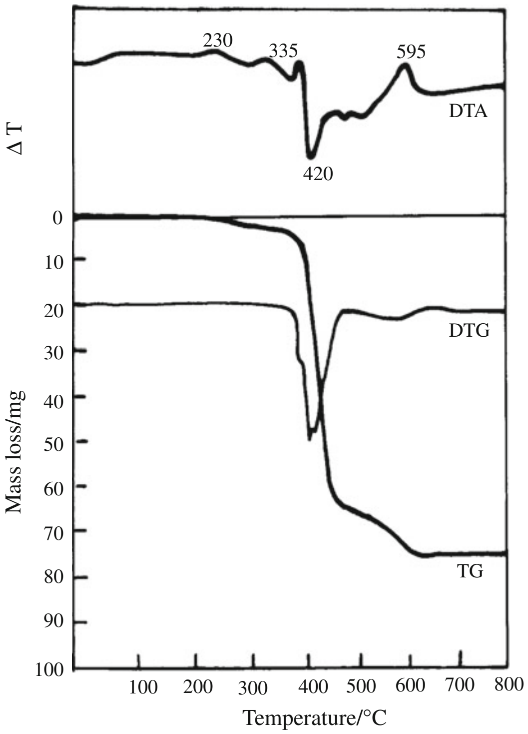

Fig. 2 DTA, TG and DTG curves of peroxide vulcanizate of NBR 18, 18N

examine the surface modification with alkoxy silanes, a rubber with a moderate polarity, i.e. NBR 18, was used.

From the analysis of SEM images of the NBR 18 composites it follows that the silica obtained in the sol–gel process possesses nano-metric dimensions.

Based on the thermal analysis, it has been found that the silica obtained neither alters the character of thermal changes in the cross-linked NBR 18 nor exerts any significant influence on the thermal stability of vulcanizates specified with parameters T_5, T_{50} and T_R. It seems to result from the small specific surface of silica formed "in situ", and consequently from slight polymer–filler interactions (Figs. 1, 2; Table 1).

It should be, however, clearly stressed that the presence of the filler formed "in situ" considerably decreases the rate of the thermal decomposition of cross-linked nitrile rubber, dm/dt, which indicates its positive influence on flame retardation in relation to unmodified samples, as a lower quantity of volatile destruction products, including flammable compounds, passes to the gas phase of combustion, i.e. to flame (Fig. 3)

Beneficial influence on combustion process is exerted also by increase of residue after heating of 18N–SiO_2 vulcanize up to 800 °C, P800 resulting from formed on a surface silica "in situ".

Vulcanizate 18NS contains five parts by weight of silicone oil/100 parts, added during the mix preparation in order to reduce the polarity of the polymeric matrix. Our test results show that this vulcanizate contains the highest quantity of silica formed "in situ" (Table 1).

The results of flammability tests show that vulcanizate 18NS–SiO_2 containing the highest quantity of silica among the sample tested is characterized by the highest value of oxygen index (OI).

The results of thermal analysis show that the silica formed "in situ" clearly decrease the maximal decomposition rate of the cross-linked elastomer, dm/dt, and what is very important from the point of view of the reduction flammability vulcanizate, increase the residue after the thermal decomposition of samples in $T = 800$ °C (Table 1).

The decrease in the flammability of cross-linked vulcanizate in the presence of silica formed "in situ" 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 the boundary layer. The isolating boundary layer formed by silica considerably limits the flow of mass and energy between the solid and gas phase of the burning sample.

It has been found that the network structure of nitrile rubber exerts a clear influence on the flammability of its vulcanizates containing silica formed "in situ". The presence of filler manifests itself especially clearly in the case of peroxide vulcanizates, whose samples are self-extinguishing in air. On the other hand, the combustion time in air of sulphur vulcanizates is clearly prolonged. The smaller influence of the "in situ" silica on the flammability of sulphur vulcanizates in comparison with peroxide vulcanizates results from the lower content of filler (Table 2).

From the review of literature, it follows that the most effective flame-retardant compounds for polymers are chemicals containing halogen atoms in their molecules. They show quite a high effectiveness already at relatively low concentrations. However, to make a polymeric material non-flammable, it is often necessary to incorporate considerable quantities of these compounds into the elastomer matrix, which results in deteriorated processing of rubber as well as in worse performance properties of final products

Table 1 The results of thermal analysis of vulcanizates of NBR 18 containing silica obtained in the sol–gel process

Vulcanizate	Z/%	T_5/°C	T_{50}/°C	dm/dt/mm	T_R/°C	T_{800}/%	SiO_2/%	Conversion TEOS/%
18S1	–	390	450	85	420	10.00	–	–
18S1–SiO_2	47.5	390	430	60	420	14.45	4.45	16.3
18S2	–	390	420	76	410	10.02	–	–
18S2–SiO_2	44.1	390	430	55	415	13.91	3.89	20.6
18N	–	390	425	94	415	10.00	–	–
18N–SiO_2	46.4	390	420	77	415	15.56	5.56	25.0
18NS	–	390	430	72	420	13.34	–	–
18NS–SiO_2	49.2	390	435	65	415	20.00	6.66	23.3

18S1—sulphur vulcanizate. Content of components in elastomer matrix in phr (*phr* parts by wt. per hundred parts by wt. of rubber). NBR 100, MBT 0.5, S 0.5, KS 1, ZnO 5

18S1–SiO_2—sulphur vulcanizate 18S1 containing silica formed in situ

18S2—sulphur vulcanizate, NBR 100, MBT 0.5, S 1.0, KS 1, ZnO 5 (*KS* stearin acid)

18S2–SiO_2—sulphur vulcanizate 18S2 containing silica formed in situ

18N—peroxide vulcanizate NBR 18 100, DCP 0.2, KS 1, ZnO 5

18N-SiO_2- peroxide vulcanizate containing silica formed in situ

18NS—peroxide vulcanizate NBR 18 100, DCP 0.2, KS 1, ZnO 5, OS 5 (*OS* silicone oil)

18NS–SiO_2—peroxide vulcanizate 18NS containing silica formed in situ

dm/dt—maximum rate of elastomer thermal decomposition

P_{800}—residue after heating of elastomer up to $T = 800$ °C

T_R—initial temperature of elastomer thermal decomposition

T_5—temperature of elastomer 5% mass loss

T_{50}—temperature of elastomer 5% mass loss

Z—content of TEOS in vulcanizates

SiO_2—content of silica formed “in situ” in vulcanizates determined from TG curves

Conversion TEOS—Conversion TEOS determined from the Eq. [8]: Conversion TEOS $= \frac{W1}{W2} \times 100\,[\%]$ where $W1$ is real amount of silica determined from TG curves, $W2$ is theoretical amount of silica calculated on the basis equilibrium swelling in TEOS

and increased production costs [14]. These problems can be solved by the surface modification of final products.

Based on the data given in Table 3, it has been found that the surface modification of the vulcanizates under investigation with aqueous solutions of chlorine, iodine or bromine considerably reduces their flammability (Table 3).

The oxygen index of the peroxide vulcanizate modified with chlorine water for 2 h amounts to 0.334 (Table 3). The remaining samples are characterized by considerably higher values of OI, but due to the limited range of rotameter for the control of oxygen flow, it was impossible to precisely determine their values. The vulcanizates modified with chlorine water or Lugol’s solutions show self-extinguishing capability during their combustion in air. Their extinguishing time becomes shorter with increasing the modifying treatment duration.

The vulcanizates modified with chlorine water are characterized by a very slow combustion and it is only the sample interior that is burned out to a depth of about 1.5 cm, while the external sample shape remains unchanged.

The time of burner flame action on a sample was 15 s irrespective of the measuring method. The samples modified with bromine water failed to catch fire within 30 s of flame action. In the same way behaved the mentioned above vulcanizates modified with Lugol’s solutions for 24 h. Thus, one may consider them as non-flammable materials.

In the case of using bromine water, non-flammable vulcanizates can be obtained when the duration of their modification is 2 h.

Based on the data given in Table 3, we think that the radical decrease in the flammability of vulcanizates 18N modified with chlorine water, bromine water or Lugol’s solution is due to the intensive emission of chlorine, bromine or iodine compounds just before ignition or at the moment when flame appears. In the case of samples modified on their surface, the halogen compounds emitted pass to the gas phase considerably easier than in the case of vulcanizates containing incorporated flame-retardant compounds inside. This is because physical phenomena and chemical processes responsible for the flammability of polymeric materials are initiated just on their surfaces. Thus, to prevent ignition or considerably reduce the flammability of polymers, they should be subjected to surface modification (Table 3). The results obtained are interesting

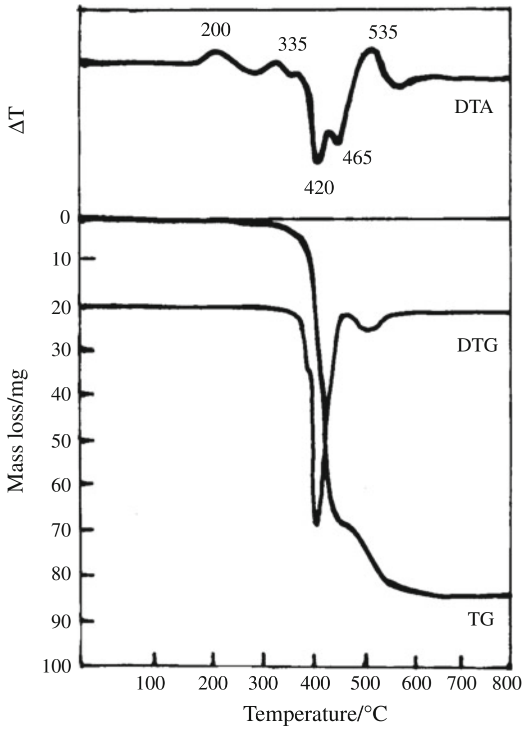

Fig. 3 DTA, TG and DTG curves of peroxide vulcanizate of NBR 18, 18N–SiO_2, containing silica formed in situ

Table 2 The results of flammability measurements of vulcanizates of NBR 18 containing silica obtained in the sol–gel process

Sample	OI	Time of burning in air/s
18S1	0.273	330
18S1–SiO_2	0.285	370
18S2	0.275	325
18S2–SiO_2	0.285	370
18N	0.265	300
18N–SiO_2	0.298	220[a]
18NS	0.285	100[a]
18NS–SiO_2	0.310	95[a]

[a] Self-extinguishing samples in air

Table 3 Flammability test results of surface modification vulcanizates 18N with aqueous solutions of halogens

Sample	OI	Time of burning in air/s
18N	0.265	300
18N–Cl2	0.334	60[a]
18N–Cl12	>0.370	55[a]
18N–Cl24	>0.370	37[a]
18N–I2	>0.370	75[a]
18N–I12	>0.370	77[a]
18N–I24	>0.370	–[b]
18N–Br2	>0.370	–[b]
18N–Br12	>0.370	–[b]
18N–Br24	>0.370	–[b]

18N—peroxide vulcanizates of NBR 18 rubber

18N–Cl—vulcanizate modified with chlorine water for 2, 12 and 24 h

18N–I—vulcanizate modified with Lugol's solution for 2, 12 and 24 h

18N–Br—vulcanizate modified with bromine water for 2, 12 and 24 h

[a] Self-extinguishing samples in air

[b] Non-flammable and non-glowing samples within 30 s of the flame action

and promising since the use of surface engineering methods for imparting special and useful properties to polymers is now in the initial phase of development [15, 16].

Taking into account the results given in the Table 3, we have decided to use also organo-phosphoric and boron compounds for the surface modification of vulcanizates.

Depending on chemical structure and application purpose, the effect of phosphorous compounds on the combustion processes manifests itself in both gas and condensed phase. According to Horold, phosphoric system acting in the solid phase should show a lower decomposition temperature than that of polymer. The thermally stable protective layer, formed in the initial stage of combustion, due to its low thermal conductivity, also in the temperature range of the polymers pyrolysis, inhibits the processes of its decomposition [17].

We used organo-phosphoric compounds from Bayer, known under the trade name Disflamolle. They were also for bulk modification of the vulcanizates under investigation [18].

The flammability test results given in Table 4 show that the surface modifications of these vulcanizates have significantly reduced their flammability. This results, first of all, from the considerably lower quantity of liquid thermal decomposition products formed during vulcanizate combustion. From our observations it follows that these products are formed only in the surface layer of the sample under combustion. The increase in the OI value is accompanied by prolonged vulcanizate combustion in air, which is clearly visible in the case of nitrile rubber crosslinked with sulphur (Table 4). It should be stressed that in the case of surface modification of the samples tested, the effect of elastomer network structure is quite noticeable. The surface modification of sulphur vulcanizates made it possible to obtain samples that are self-extinguishing in air. It is worth mentioning that the surface modification with the use of Disflamolle DPK or TOF considerably impedes the ignition of sulphur vulcanization. They catch fire after a lapse of 25 s of the action of flame. This is due to the simultaneous action of sulphur and phosphorous compounds, which reduces the amount of destruction products

Table 4 Flammability test results of surface modification vulcanizates 18N with Disflamolle

Sample	OI	Time of burning in air/s
18N	0.265	300
18NDPK	0.290	345
18NDPO	0.278	328
18NTKP	0.296	364
18NTOF	0.284	338
18S	0.273	278
18SDPK	>0.370	547[a]
18SDPO	>0.370	386[b]
18STKP	>0.370	406
18STOF	>0.370	390[a,b]

18N—peroxide vulcanizates of NBR 18 rubber. Content of components in elastomer matrix in phr. (*phr* parts by wt. per hundred parts by wt. of rubber). NBR 100, DCP 0.2, KS 1, ZnO 5

18S—sulphuric vulcanizates of NBR 18 rubber. Content of components in elastomer matrix in phr. NBR 100, MBT 0.5, S 0.5, KS 1, ZnO 5

[a] The time of burner flame action on sample was 25 s

[b] Self-extinguishing samples in air

of the nitrile rubber cross-linked with sulphur, passing to the combustion zone.

It should be clearly stressed that in the case of surface modification of sulphur vulcanizates their time burning in air and time after which the tested samples has extinguished in air is similar. Vulcanizates modified with the use of Disflamolle DPK and TKP are completely burned in the air during 400–450 s (Table 4). On the other hand, samples modified with the use of Disflamoll DPO and TOF are characterized by a very slow combustion and in consequence are not burned completely (self-extinguishing samples).

The modification of polymeric materials with the use of halogen compounds, mostly bromine compounds, continues to be the subject of research in many scientific centers worldwide [19]. Unfortunately, during combustion of polymeric materials containing these compounds, toxic gases are emitted to the environment, which some time poses a greater hazard than fire itself [20]. Therefore, this kind of modification comes under strong criticism and frequently more and more papers and reports are published, persuading to restrict the production and use of bromine flame-retardants agents, and to benefit from replacing them by non-halogen compounds, among others, such as those described above phosphorus compounds or metal oxide and hydroxide compounds [21, 22].

Over recent years, one can observe increasing research reports on the use of boron compounds to impart non-flammability to constructional plastics [23, 24]. Therefore, it was encouraging to use boric acid and sodium tetraborate for the surface modification of elastomers (Table 5).

Table 5 Flammability test results of surface modification vulcanizates with boron compounds

Sample	OI	Time of burning in air/s
18N	0.265	300
39N	0.276	85[a]
KER1500	0.259	206
BR1220	0.265	174
SKDII	0.259	184
18NB	0.370	–[b]
39NB	0.370	68[a]
KER1500B	>0.370	–[b]
BR1220B	0.350	554[a]
SKDIIB	0.350	145[a]
18NTB	0.298	60[a]
39NTB	0.298	40[a]
KER1500TB	0.298	313
BR1220TB	0.304	262[a]
SKDIITB	0.304	252[a]

[a] Self-extinguishing samples in air

[b] Non-flammable samples

Content of components in elastomer matrix in phr (*phr* parts by wt. per hundred parts by wt. of rubber). Rubber 100, DCP 0.2, KS 1, ZnO 5

18N—peroxide vulcanizate of NBR 18 rubber

39N—peroxide vulcanizate of NBR 39 rubber

KER1500—peroxide vulcanizate of butadiene–styrene rubber KER 1500

BR1220—peroxide vulcanizate of butadiene rubber BR 1220

SKDII—peroxide vulcanizate of butadiene rubber SKDII

18NKBr—surface modification of peroxide vulcanizate 18N with boric acid

39NKBr—surface modification of peroxide vulcanizate 39N with boric acid

KER1500KBr—surface modification of peroxide vulcanizate KER1500 with boric acid

BR1220KBr—surface modification of peroxide vulcanizate BR1220 with boric acid

SKDIIKBr—surface modification of peroxide vulcanizate SKDII with boric acid

18NTB—surface modification of peroxide vulcanizate 18N with sodium tetraborate

39NTB—surface modification of peroxide vulcanizate 39N with sodium tetraborate

KER1500TB—surface modification of peroxide vulcanizate KER1500 with sodium tetraborate

BR1220TB—surface modification of peroxide vulcanizate BR1220 with sodium tetraborate

SKDIITB—surface modification of peroxide vulcanizate SKDIITB with sodium tetraborate

Based on the flammability test results given in the Table 5, one can conclude that the surface modification of polymeric materials with boron compounds is more effective method in comparison with the surface modification with organo-phosphoric compounds such as Disflamolle.

A radical reduction in the flammability of the vulcanizates under investigation can be obtained by their modification with boron compounds, especially boric acid. The oxygen index of the vulcanizate of nitrile rubbers 18NB and 39NB amounts to 0.370 (Table 5). It is particularly worth stressing that a non-flammable vulcanizate of butadiene–styrene rubber and self-extinguishing vulcanizates of butadiene rubbers can be obtained in view of the fact that these elastomers belong to the group of inflammable polymers.

The oxygen index value of the vulcanizates tested can be also increased by their modification with an aqueous solution of sodium tetraborate. The cross-linked nitrile and butadiene rubbers modified with the use of sodium tetraborate are self-extinguishing in air, while the modified vulcanizate of butadiene–styrene rubber burns in air considerably longer than the unmodified sample (Table 5).

Boron compounds as flame-retardant agents effectively act first of all in the condensed phase [25]. They take part in endothermic processes that result in the release of water and formation of a protective glassy layer.

$$2H_3BO_3 \xrightarrow{130-200\ ^\circ C} 2HBO_3 + 3H_2 \xrightarrow{260-270\ ^\circ C} B_2O_3 + 3OH_2$$

This glassy layer reduces the diffusion of volatile and flammable products of polymer thermal decomposition to the flame.

Among the boron compounds tested, boric acid is clearly a more effective flame-retardant agent.

Summary

The test results presented in this paper allow one to consider the surface modification to be a highly effective method for reducing the flammability of elastomeric materials.

The modification of the vulcanizates with tetraethoxysilane that makes it possible to form silica "in situ" considerably reduces the flammability of cross-linked rubbers as a result of the formation of a thermally stable, isolating boundary layer, which impedes the flow of matter and energy between the solid and gas phase of the sample under burning.

The surface modification of the vulcanizates with halide compounds allows one to radically decrease their flammability, making it possible to obtain non-flammable materials.

A considerable reduction in flammability resulting from the phosphorus–nitrogen synergism can be obtained by the surface modification of vulcanizates with the use of Disflamolle, but the process of their self-extinguishing is long and clearly dependent on the network structure. The boric flame-retardant agents are more effective modifiers than organophosphorus compounds. The most beneficial results were obtained with the use of boric acid. Its action consists in its dehydrating and forming a glassy protective layer that impedes the combustion of cross-linked elastomers.

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