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Influence of cryogenic modification of silica on thermal properties and flammability of cross-linked nitrile rubber

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Abstract The article presents the results of testing thermal properties and combustibility of butadieneacrylonitrilerubber with 18% contents of bounded acrylonitrile, NBR 18. Two types of silica, Zeosil 175C and Ultrasil VN-3, with different specific surfaces were used as filler.Zeosil 175C and Ultrasil VN-3 were modified via cryogenic dezaggregation method. The activity ofunmodified and cryogenic modified silica toward butadiene-acrylonitrile rubber were investigated.The sulphur and peroxide vulcanizates contained 20, 30, 40, and 50 phr. of the filler were studied.The article discusses also the test results of thermal stability and flammability of NBR 18 containingsilica prepared "in situ" from alkoxysilane precursor.The test results were obtained with the use of derivatograph, measurements of flammability by themethod of oxygen index, and in air.The effect of the silica modification on the SEM and AFM was also examined.The method of cryogenic modification enables to achieve increase of mineral fillers activity towardselastomer and reduction in the flammability of NBR 18 vulcanizates.It has been found that the modification of the vulcanizates of NBR 18 with tetraethoxysilane thatmakes it possible to form silica "in situ" reduces the flammability of cross-linked rubbers.

Keywords Nanofillers · Flammability · Silica · Oxygen index · Thermal analysis

Except carbon black, silica is one of the most important filler used in the rubber industry. 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. Active silica is commonly used to prepare rubber mixes and finally rubber goods.

The properties of elastomeric mixes and end products depends on the polymeric matrices, content of a filler, size and a shape of its primary particles, aggregates and agglomerates, their distribution in a matrix, a content of loosely and tightly bounded rubber and structure formed from interacting fillers particles [1].

It is assumed, that big agglomerates (above 20 μm), composed of loosely packed aggregates exert particularly detrimental effect on properties of vulcanizates. Under external stresses they break, initiating formation of microcracks, whose propagation in matrix leads finally to a rubber rupture.

Problem agglomerates of silica has been minimized by specific additives, mixing procedures, or by means of a new cryogenic dezaggregation method modification of mineral fillers and by using silane-coupling agents [2, 3].

The present article presents the results of studies concerning the thermal stability and flammability of cross-linked butadiene–acrylonitrile rubber containing untreated silica, and silica modified by cryogenic method.

This article shows also a fragment of research concerning the flammability and thermal stability of vulcanizates containing silica formed in situ from silica precursors.

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Our investigation was focused on cross-linked butadiene–acrylonitrile rubber, Perbunan 1845 (NBR 18) containing 18% acrylonitrile units. The rubber was cross-linked by means of dicumyl peroxide from Merck-Schuhardt, and sulphur with accelerating of curing (MBT). Two types of silica with different specific surfaces were used as fillers: Ultrasil VN-3 (234 $m^2 g^{-1}$) and Zeosil 175 C (175 $m^2 g^{-1}$).

The cryogenic modification of silica (Ultrasil VN-3 and Zeosil 175C) consisted in its out-gassing and saturation with aqueous solution of dispersing agent and next freezing all system by the use of liquid nitrogen. Then, the modified fillers were dried to a constant mass.

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

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.

SEM examinations of the modified fillers, and dispersion of the filler synthesized in the medium of elastomers 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 Metrology Series 2000 camera from Molecular Imaging (USA) in 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 into acetone and dried with stream of air to degrease and remove impurities. AMF photographs were analysed with the use of the WSxM program from Nanoyec Electronica S.L. (Spain).

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^{-1}.

The flammability of vulcanizates was determined by the method of oxygen index according to PN-EN-ISO 4589-2:2006. 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 dimensional 100 × 10 × 4 mm, 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.

Experimental

The presence of silica does not change the character of thermal transformations of nitrile rubber cross-linked with dicumyl peroxide (Figs. 1, 2). The first two exothermic processes recorded in the DTA curves at about 200 and 335 °C are connected with the thermal cross-linking of elastomers.

The thermal decomposition of vulcanizates begin at $T > 390$ °C for 18N as shown by the endothermic peaks at $T = 420$ and 465 °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 $T = 535$ °C (Fig. 1) and $T = 525$ °C (Fig. 2) is connected with the combustion of residue after the decomposition of cross-linked rubber (Tables 1, 2).

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} (Fig. 2; Table 2). It has been found that the maximal

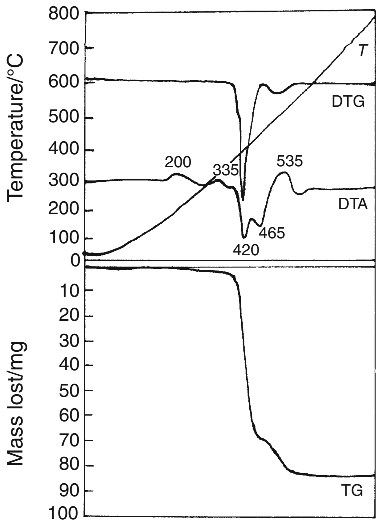

Fig. 1 Thermal curves of peroxide vulcanizate of NBR 18, 18N

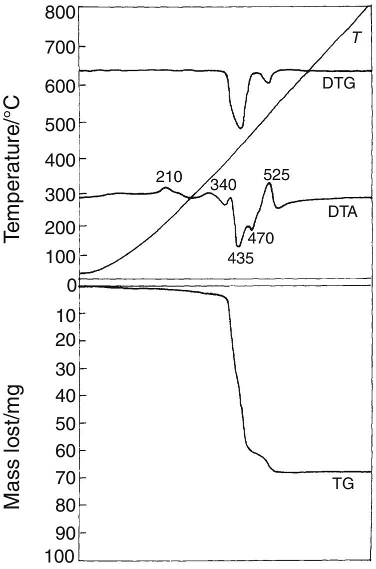

Fig. 2 Thermal curves of peroxide vulcanizate of NBR 18 containing 30 phr of Ultrasil VN3 30

Table 1 Content of components in elastomer matrix in phr

Sample	NBR 18	DCP	ZnO	KS	Ultrasil VN-3
18N	100	0.2	5	1	–
18NU20	100	0.2	5	1	20
18NU30	100	0.2	5	1	30
18NU40	100	0.2	5	1	40
18NU50	100	0.2	5	1	50

Table 2 The results of thermal analysis of vulcanizates containing silica

Sample	T_5/ °C	T_{50}/ °C	T_R/ °C	T_{Rmax}/ °C	d*m*/d*t*/ 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

Pw—residue after the thermal decomposition of vulcanizate

Pe—residue after the thermal decomposition of cross-linked rubber

P_{800}—residue in $T = 800$ °C

T_{Rmax}—temperature of the maximal rate of thermal decomposition elastomer

T_5—temperature of elastomer 5% mass loss

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

decomposition rate of the cross-linked elastomer, d*m*/d*t*, 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 [4].

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 d*m*/d*t*, 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 2). 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 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.

During combustion of the vulcanizates filled with silica, non-flammable gaseous products can be formed, first of all, in the form of water vapour. 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 $\equiv$Si(OH) and twin =Si(OH)$_2$ silane groups and siloxane bridges =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 vapour dilutes the flammable gaseous product passing to flame.

From the point of view of the reduction in vulcanizate flammability, a very important role is played also by the structure of the boundary layer being formed during combustion of the filler-containing vulcanizate [5, 6]. Under the influence of silica, it becomes more thermally stable and impedes the flow of mass and energy between flame and sample.

In the case of NBR vulcanizates, the boundary layer is thermally stable because is formed from partially carbonized elastomer. Inert and insulating char locks up the fuel for further combustion and also provides insulation to inner layers from further heating [7].

The boundary layer is particularly efficiency in reduction of vulcanizate flammability if it's formed by the use of nano-particles of filler (Table 3).

In our laboratory a cryogenic method of hydrophilic mineral fillers dezaggregation has been elaborated. It is based on the following assumptions. During aggregation of primary particles of fillers empty voids, pores, inside aggregates are formed. Typically pores have size in the order of a few nanometers. They are accessible to water

Table 3 The results of flammability measurements of vulcanizates containing unmodified and cryogenic modified 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[a]
18NU50	0.298	40[a]
18NU50Z	0.305	30[a]
18NZ50	0.285	360
18NZ50Z	0.310	117[a]

18NU50Z—vulcanizate containing 50 phr of Ultrasil VN-3 modified by cryogenic method

18NZ50—vulcanizate containing 50 phr of Zeosil 175 C silica

18NZ50Z—vulcanizate containing 50 phr of Zeosil 175 C modified by cryogenic method

[a] Self-extinguishing samples in air

vapour particles. The water introduction into the nanopores of silica and freezing of the system bring about shattering of aggregates structure as a results of an increase of water volume during freezing. However, from our studies it follows that reaggregation of filler primary particles during evaporation of adsorbed water at elevated temperature take place. To avoid reaggregation we have applied an appropriate intercalating agent [8].

Our method of a filler modification and application of adequately chosen dispersing agent enables decrease in size of its particles which greater part is contained in nano range (Fig. 3).

The expected reduced flammability of vulcanizates containing silica, has been confirmed by the measurements of flammability by the method of oxygen index and in air. With the increase in silica content, the value of OI increases and the duration of samples combustion grows longer, but the time, after which samples extinguish in air is shortened (Table 3).

The vulcanizates containing modified silica show the smallest OI value and the time after which samples extinguish in air is smaller for vulcanizates containing modified silica in comparison with samples containing untreated filler (Table 3).

The results obtained by means of AFM show that the modified silica is considerably better dispergated in polymer matrix than unmodified filler (Fig. 4).

The conventional untreated silica, e.g. Ultrasil VN-3 or Zeosil 175 C due to its significant polarity, large specific surface and present silanol groups on its surface, is highly aggregated in the rubbery matrix.

This problem has been minimized by specific additives or mixing procedures [1], and by using silane-coupling agents [2].

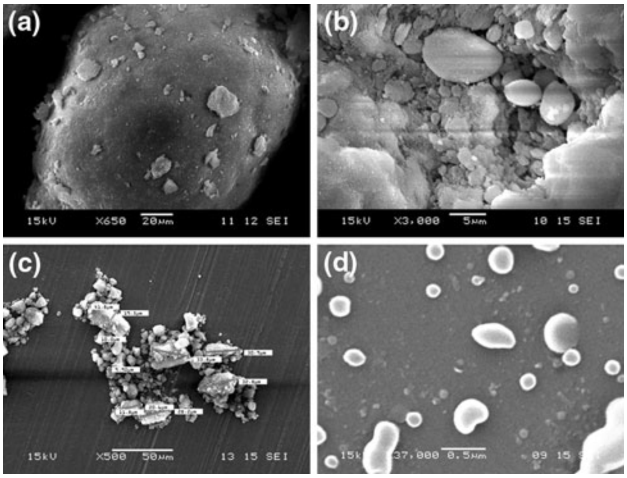

Fig. 3 SEM photo **a** unmodified Zeosil 175 C, **b** modified Zeosil 175 C, **c** unmodified Ultrasil VN-3, **d** modified Ultrasil VN-3

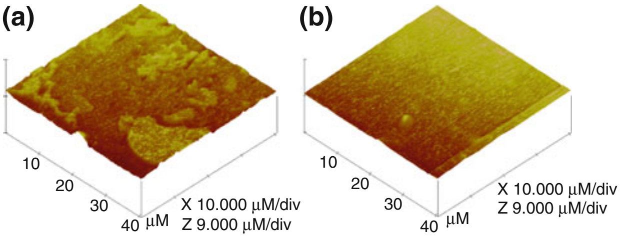

Fig. 4 AFM photographs of vulcanizate containing Ultrasil VN-3: **a** silica unmodified, **b** silica modified by cryogenic method

A alternative method of silica incorporation into rubbers is the "in situ" sol–gel process. Two reactions are generally used to describe the hydrolysis and condensation of silica precursors.

Hydrolysis:

$$\equiv \mathrm{Si{-}OR} + \mathrm{OH_2} \rightleftharpoons \equiv \mathrm{Si{-}OH} + \mathrm{ROH}$$

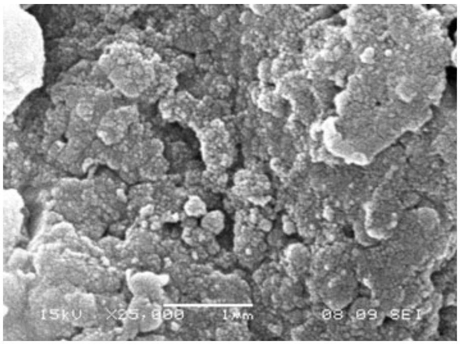

Fig. 5 SEM image of peroxide vulcanizates of NBR 18 containing silica formed "in situ"

Condensation:

$$\equiv \mathrm{Si{-}OH} + \equiv \mathrm{Si{-}OH} \rightleftharpoons\ \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{OH_2}$$

This simple process involves the swelling of a raw rubber [9] or rubber vulcanizates [2, 10] in a silica precursor, e.g. tetraethoxysilane or tetramethoxysilane.

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 (Fig. 5).

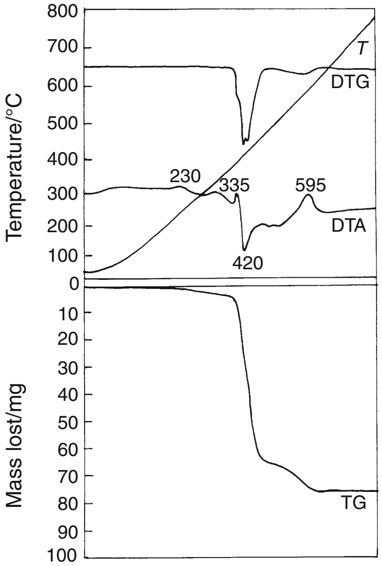

Fig. 6 Thermal curves of peroxide vulcanizate of NBR 18, 18N–SiO_2, containing silica formed in situ

Based on the derivatographic 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, 6).

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, d*m*/d*t*, 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.

Vulcanizate 18NS contains 5 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 4).

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). We think that the significant reduction in flammability determined by both the OI and combustion time in air of the vulcanizate tested, in which the content of silica formed in situ is relatively low, results from barrier effect (Table 5). 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.

Table 4 Influence of silica formed "in situ" on thermal properties of vulcanizates of NBR 18 rubber

Vulcanizate	Z/%	T_5/°C	T_{50}/°C	d*m*/d*t*/mm	T_R/°C	P_{800}/%	SiO_2/%	Conversion TEOS/%
18S	–	390	420	76	410	10.02	–	–
18S–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

18S—sulphur vulcanizate; (phr) NBR 100; MBT 0.5; S 1.0; KS 1; ZnO 5 (KS—stearin acid)

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

18N—peroxide vulcanizate (phr) NBR 18 100; DCP 0.2; KS 1; ZnO 5

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

18NS—peroxide vulcanizate (phr) 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

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 equation: Conversion TEOS $= \frac{W1}{W2} \times 100\,(\%)$, where W1 is the real amount of silica determined from TG curves and W2 is the theoretical amount of silica calculated on the basis equilibrium swelling in TEOS

Table 5 Influence of silica formed "in situ" on the flammability of vulcanizates

Sample	OI	Time of burning in air/s
18S	0.275	325
18S–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

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 5).

Conclusions

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

A considerable reduction in the flammability of nitrile rubber vulcanizates can be obtained by the use of modified silica.

All the vulcanizates containing cryogenic modified silica are self-extinguishing.

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.

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