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EFFECT OF THE TOP LAYER MODIFICATION OF POLYMERS ON THEIR THERMOSTABILITY AND FLAMMABILITY

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Thermal properties, ageing resistance and flammability of peroxide vulcanizates of butadiene-acrylonitrile rubber Perbunan NT 1845 (NBR) of Bayer, modified in bulk and on a surface with synthesized hybrid functional poly(methylsiloxanes) were investigated. The derivatographic, DSC, oxygen index and FTIR methods were applied. It was stated that addition of poly(methylsiloxanes) caused distinct increase of ageing resistance and of NBR vulcanizates and decrease of their thermal decomposition rate and flammability, providing self-extinguishing samples. The mechanism of addition reactions of Si–H bond to multiple bonds of NBR has been proposed.

Keywords: *elastomers, flammability, functional poly(methylsiloxanes), hybrid inorganic–organic modifiers, modification of elastomers, polymers, sol–gel method, thermostability*

Introduction

Polymers are usually modified, physically or chemically in whole volume, what is not rational in many cases, from the point of view of material properties and costs of process as well. It should be taken into consideration that many physical phenomena and chemical reactions, influencing usability of polymer materials are initiated in their top layers. It concerns, e. g. migration and surface segregation of low molecular mass (or oligomeric) substances, oxidative ageing, thermal destruction and ignition. Recently a gradient structure of many commonly used polymers has been detected [1–6]. For instance, a degree of cross-linking or a content and structure of crystalline phase could be quite different in the inner part of a sample and at its surface. Such gradient structure highly affects properties of the material. Owing to the application of sol–gel method new perspectives have been opened for modification of polymer materials at their surface.

Modification could be performed in a few ways. A modifier could be synthesized:

- at surface of a sample (in situ)
- or separately, and applied as a liquid or in a form of solution or emulsion

If an appropriate modifier would be introduced directly to polymer during processing its surface segregation should be expected [7].

In the present paper we report results of our studies concerning modification of polar elastomer systems, namely, peroxide vulcanizates of butadiene-acrylonitrile rubber with poly(methylsiloxanes) [8]. It was reported that poly(siloxanes) exhibit excellent hydrophobic and thermal properties and are applied as coating materials [9].

Experimental

The peroxide vulcanizates of butadiene-acrylonitrile rubber, Perbunan NT 1845 of Bayer (NBR), containing 18 mass% of acrylonitrile were used [10]. They were modified with the use of hybrid inorganic-organic agents. We have synthesized the following types of reactive hybrid poly(methylsiloxane) modifiers, containing different functional groups: Si–H and $Si–CH=CH_2$:

- poly(dimethyl-*co*-methylhydro)siloxanes:

$$Me_3SiO(Me_2SiO)_x(MeHSiO)_yOSiMe_3 \quad (A, B)$$

- α,ω-divinyl(polydimethylsiloxane):

$$CH_2=CH–Me_2SiO(Me_2SiO)_xSiMe_2–CH=CH_2 \ (C)$$

where $Me=CH_3$, (A) $x=66$, $y=10$; ($M_n=4260$, $M_w=12200$); (B) $x=22$, $y=10$; ($M_n=2750$, $M_w=9100$); (C) $x=45$ ($M_n=3280$, $M_w=9640$).

Reactive substituents were inserted to the molecules in order to facilitate their grafting on surface of polymers. Poly(dimethyl-*co*-methylhydro)siloxane (A) was prepared by hydrolytic polycondensation of the mixture of chlorotrimethylsilane Me_3SiCl (7.6 cm^3, 0.06 mole), dichlorodimethylsilane Me_2SiCl_2 (236.9 cm^3, 1.98 mole), and chlorodimethylsilane $MeHSiCl_2$ (31.2 cm^3, 0.30 mole). To vigorously stirred solution of chlorosilanes in 170 cm^3 of petroleum

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ether, 384 cm^3 of distilled water was added dropwise at –10 to 0°C, within 3.5 h. Stirring was continued for 30 min and then acid layer was separated. Organic layer was washed four times with 100 cm^3 portions of distilled water until neutral and dried with anhydrous magnesium sulfate. The mixture was filtered through sintered funnel and solvent was distilled off from the filtrate. The volatile linear and cyclic cyclosiloxanes were removed by vacuum distillation at 150°C/3 mm Hg. Yield: 95.8 g (56.4%); viscosity (η): 48.0 cP.

Poly(methylhydrosiloxane) (B) was similarly prepared by hydrolytic polycondensation of Me_2SiCl_2 (132.8 cm^3, 1.10 mole), $MeHSiCl_2$ (52.1 cm^3, 0.50 mole), and Me_3SiCl (12.7 cm^3, 0.10 mole), in hexane (85 cm^3), with 274 cm^3 of water. Yield: 56.0 g (65.4%); η=30.9 cP.

α,ω-Divinyl(polydimethylsiloxane) (C) was synthesized by heterocondensation of poly(dimethylsiloxane-α,ω-diol) $HO(Me_2SiO)_{45}H$ (105.0 g, 0.031 mole; WS-62, Wacker Chemie) with 8.8 cm^3 (0.064 mole of chlorodimethylvinylsilane $Me_2(CH_2{=}\,CH)SiCl$, in petroleum ether (50 cm^3), in the presence of 9.0 cm^3 (0.065 mole) of triethylamine. Reaction mixture was refluxed for 4 h, cooled down to room temperature and left overnight. Then 50 cm^3 of distilled water was added to reaction flask and mixture was stirred for 2 h. Water layer was separated and removed. The organic layer was dried by azeotropic distillation with 50 cm^3 of benzene. An excess of 1,3-divinyltetramethydisiloxane was distilled off at 139°C under atmospheric pressure. Yield: 103.1 g (94%); η=8336 cP.

All products were thoroughly characterized by spectroscopic methods: IR as well as ^{1}H- and ^{29}Si-NMR [11], and also by other analytical techniques: size exclusion chromatography (SEC), etc. Dynamic viscosities were measured with a cone-plate Brookfield viscometer HBDV IIcP+.

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. Modification in bulk was performed through addition of hybrid overmentioned inorganic-organic agents during preparation of rubber mixes.

Surface modification was achieved by swelling of vulcanizates in liquid hybrid substances at 25°C for 24 and 72 h.

FTIR spectra of vulcanizates in the form of thin membranes were recorded using spectrometer Bio-Rad 175 C.

Cross-link densities of the rubbers were determined on the basis of equilibrium swelling measurements, Q_w, using the Flory–Rehner equation [12].

Thermal analyses of vulcanizates were carried out both in air and nitrogen by means of Paulik, Paulik, Erdey system derivatograph and DSC-204 of Netzsch [13, 14].

Flammabilty of vulcanizates was determined by the oxygen index method, according to the standard PN-ISO 4589-2.

Mechanical properties were determined using Zwick apparatus, mode 1435, according to the standard PN-ISO 37:1998.

Results and discussion

Taking into consideration interactions between hybrid modifiers and polymer matrix, we expected different modification effects, depending on polarity of a matrix. Migration of hybrid modifiers to the surface is accompanied with surface segregation. In the case of unpolar elastomer matrix – polar segments should be present outside of the surface, as it is shown in the upper part of the picture (Fig. 1). Using polar elastomer matrix we expect reverse orientation of modifier molecules (Fig. 1).

Surface properties of modified rubbers depend on:

- molecular mass of modifiers (Fig. 2)
- orientation of hybrid molecules (Fig. 3)
- and possibility of grafting (Fig. 4)

Orientation of molecules of hybrid modifiers depends on their chemical structure. The effect of surface modification is significantly stronger if modifiers could be chemically bonded to the surface of vulcanizates. Grafting of modifiers onto a surface is very effective when reactions of functional groups take place.

We have observed the effect of synthesized poly(methylsiloxanes) modifiers on cross-linking density of NBR vulcanizates which was determined from the results of equilibrium swelling measurements (Table 1). It results from better solubility of dicumyl peroxide as a cross-linking agent in modifiers than in elastomer matrix what causes greater cross-linking of polysiloxanes and probably phase separation took place.

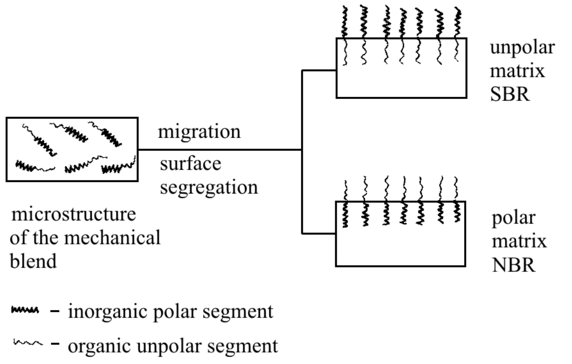


Fig. 1 Expected distribution of the modifiers in the elastomer matrix:modification in bulk

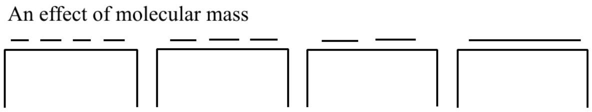


Fig. 2 Effect of modifiers molecular mass on surface properties of modified rubber

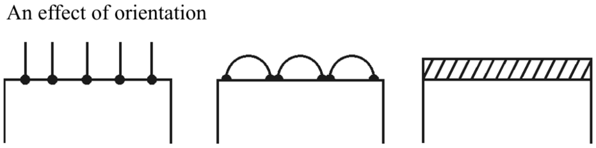


Fig. 3 Effect of hybrid molecules orientation on surface properties of modified rubber

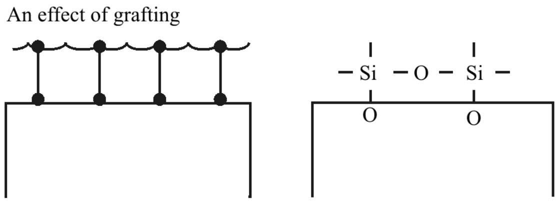


Fig. 4 Effect of modifiers grafting possibility on surface properties of modified rubber

The introduction of modifiers into elastomer does not change the character of thermal transitions of peroxides vulcanizates although increase of index T_{50} values especially in the case of poly(siloxane) (A) has been observed (Figs 5 and 6, Table 1). The presence of polysiloxanes clearly decreases the rate of thermal decomposition of vulcanizates. The biggest influence on destruction rate was stated in the case of application of polysiloxane C, terminated with vinyl functional groups. On the other hand the residues both after decomposition of vulcanizates and cross-linked elastomer were higher for samples modified with poly(siloxane) (A) of the formula $Me_3SiO(Me_2SiO)_{66}(MeHSiO)_{10}SiOMe_3$. The decrease in destruction rate results probably from free radicals scavenging by products of thermal decomposition of the modifiers.

Introduction of polysiloxanes into rubber mix caused decrease of glass transition temperature, T_g, of cross-linked elastomer, what is especially evident from DSC data obtained during cooling process. Thermal cross-linking and destruction processes take place at slightly higher temperatures for modified samples (Table 2).

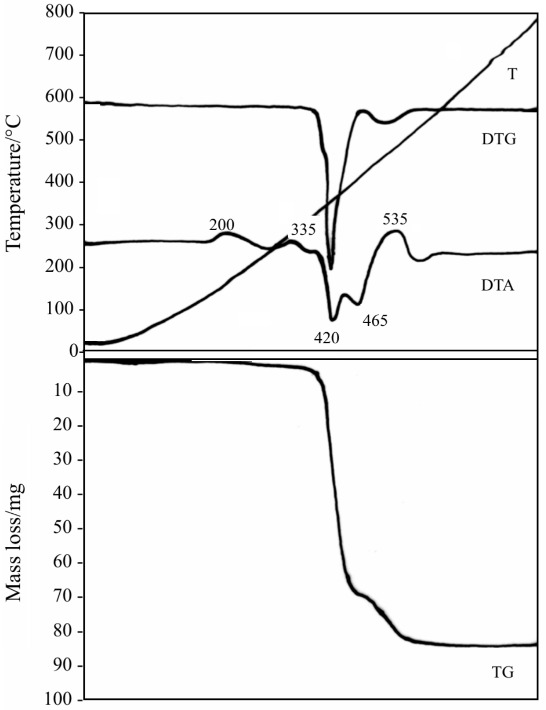


Fig. 5 DTA, TG and DTG curves of peroxide vulcanizate

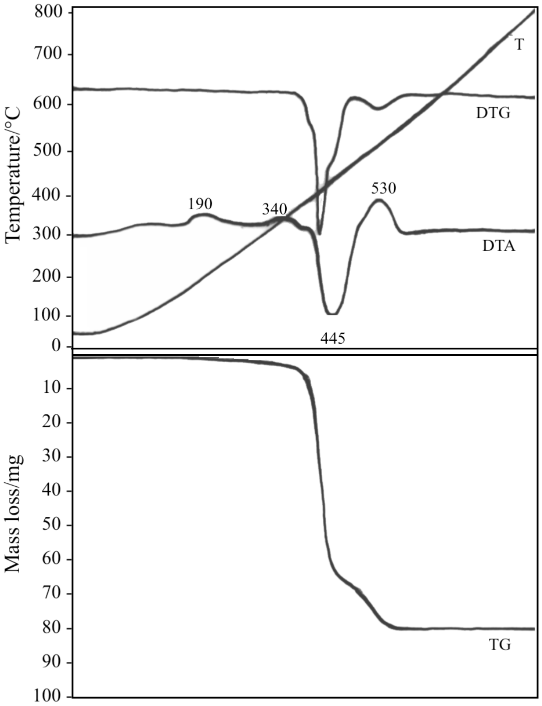


Fig. 6 DTA, TG and DTG curves of peroxide vulcanizate containing 10 phr of modifier (A)

We have determined flammability of two types of samples, i.e. containing dispersed modifier or impregnated with poly(siloxanes) (Table 3). It was stated good protection activity of modifiers used in flammability tests. The values of oxygen index, OI, increased proportionally to the content of poly(siloxane) modifier in vulcanizate. In some cases the samples were self-extinguishing in air. Decreased flammability of NBR peroxide vulcanizates is a result of formation of silica in situ in the top layer of the sample which increases its thermal stability and insulating ability, what as a consequence makes difficult the mass and energy flow between solid and gaseous phase during burning. Modification of

Table 1 Results of thermal analysis of modifiers and vulcanizates in air

Sample		T_5/°C	T_{50}/°C	T_R/°C	d*m*/d*t*/mm	P_p/%	P_e/%	P_{800}/%
Symbol	$\nu \cdot 10^{-4}$ mol cm^{-3}							
A	–	245	510	400	27	38.8	–	36.6
V	0.5639	380	415	385	94	22.2	21.1	6.6
V3A	0.4127	385	430	390	92	24.4	22.5	10
V5A	0.4127	385	430	390	90	24.4	22.1	10
V10A	0.3365	380	430	395	83	25.5	22.1	10
B	–	155	305	200	14	45.5	–	34.4
V3B	0.3235	380	420	380	83	18.8	17.4	5.5
V5B	0.3841	380	425	385	84	21.1	19.1	7.7
V10B	0.4274	350	425	380	87	23.3	20.2	8.8
C	–	280	480	440	34	27.7	–	25.5
V3C	0.4655	380	420	380	77	20	18.4	7.7
V5C	0.4500	375	415	380	73	22.2	20.1	8.8
V10C	0.4349	370	420	380	70	22.2	19.2	7.7

A, B, C– synthesized poly(methylsiloxane) modifiers, V – vulcanizate, V3A, V5A, V10A – vulcanizate containing 3, 5 or 10 phr of modifier A (phr – parts by mass per hundred parts by mass of rubber), ν – cross-link density of elastomer, mol cm^{-3}, T_5 and T_{50} – temperature of 5 and 50% mass loss, respectively, T_R – temperature of intensive outset of a sample decomposition, d*m*/d*t* – rate of thermal decomposition, P_p – residue after thermal decomposition, P_e – residue after thermal decomposition, calculated on basis of elastomer content, P_{800} – residue of sample at 800°C

Table 2 Results of thermal analysis of vulcanizates in nitrogen

Sample	Cooling		Heating		T_c/°C	T_{dk}/°C
	T_g/°C	T_{range} of glass process	T_g/°C	T_{range} of glass process		
NBR 18	–58.3	–64.3/–51.7	–51.5	–54.6/–45.4	360.2	447.0
V	–58.1	–67.5/–48.7	–51.4	–57.6/–45.1	361.7	450.4
V3A	–58.9	–65.9/–52.0	–54.7	–56.3/–53.2	363.1	455.4
V10A	–59.2	–63.4/–55.1	–55.1	–62.5/–47.8	363.4	451.9
V10B	–60.5	–63.3/–57.7	–56.8	–63.5/–50.2	363.6	449.9
V10C	–61.2	–65.6/–56.8	–57.2	–62.5/–51.8	362.9	465.7

T_c – temperature of cross-linking; T_{dk} – temperature of destruction; T_{range} – temperature range

NBR vulcanizates eliminates also formation of liquid products of thermal decomposition which flowing along the sample transfer heat and increase contact of the elastomer with oxygen.

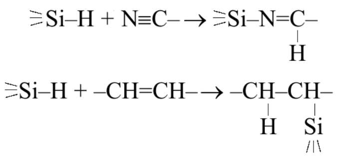
We have stated that modification of NBR vulcanizate with poly(siloxanes) clearly increases its ageing resistance (Table 4). It is caused by formation of protective film on the sample surface as a result of migration of modifier molecules during ageing process.

In order to check an effect of addition of poly(methylhydrosiloxanes) on cross-linking efficiency of NBR with dicumyl peroxide and on properties of its vulcanizates we have analyzed FTIR spectra and compared them with the spectra of poly(siloxanes). We have noticed substantial changes in the FTIR spectra of cross-linked butadiene-acrylonitrile rubber as a result of addition of modifiers A and B to NBR mixes (Fig. 7, Table 5).

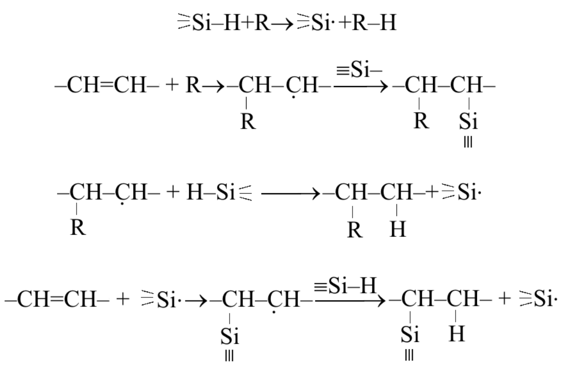
Introduction of modifiers into rubber mixes caused decrease of the intensities ratio of their transmission bands νSi–H/$\delta_{sym.}$CH$_3$–Si. On the other hand the intensities of νC≡N bands are lower in samples containing poly(siloxanes), than in unmodified vulcanizates (Fig. 7), so intensities ratio of transmission bands νSi–H/νC≡N increased with increasing content of modifier in vulcanizate.

Analysis of FTIR spectra showed on grafting of poly(methylhydrosiloxanes) to the elastomer chain. Hydrosilylation of multiple bonds with hydrosilanes is a very well-known reaction [15]. Taking into consideration significant decrease of intensities of transmission bands corresponding to double bonds C=C (911, 974, 721 and 1449 cm^{-1}) we propose that following addition reactions of the Si–H bond to multiple bonds C=C and C≡N take place (Scheme 1).

During vulcanization process could also proceed other radical reactions (Scheme 2).



Scheme 1



Scheme 2 R · – organic radical, RO · – cumyloxy radical, RH – elastomer macromolecule

Table 3 The effect of modification with poly(siloxanes) on flammability of vulcanizates

Sample	Oxygen index, OI
V	0.285
V3A*	0.348
V5A*	0.350
V10A*	0.358
V3B*	0.322
V5B	0.344
V10B	0.365
V3C	0.310
V5C	0.322
V10C	0.328
V surface modified A* Modification time 24 h	0.333
V surface modified B Modification time 24 h	0.365
V surface modified B* Modification time 72 h	0.365

* self-extinguishing samples in air

Table 4 The effect of vulcanizates modification with poly(siloxanes) on change of their mechanical properties as a results of ageing process

Sample	Δ/%	
	ΔTS_b	ΔE_b
V	53.7	51.5
V5A	32.4	36.0
V5B	13.7	34.4
V5C	10.6	26.7

TS_b – tensile strength; TS_{b0}, TS_{b1} – tensile strength before and after ageing, E_b–elongation at break, E_{b0}, E_{b1} – elongation at break before and after ageing;

$$\Delta TS_b = \frac{TS_{b0} - TS_{b1}}{TS_{b0}} \cdot 100\%, \quad \Delta E_b = \frac{E_{b0} - E_{b1}}{E_{b0}} \cdot 100\%$$

Table 5 Intensities ratio of transmission bands νSi–H/$\delta_{sym.}$CH$_3$–Si (2169 and 1268 cm^{-1}, respectively) and νSi–H/νC–N (2169 and 2237 cm^{-1}, respectively) of modified vulcanizates of NBR

Sample	Intensities ratio of transmission bands	
	νSi–H/$d_{sym.}$CH$_3$–Si	νSi–H/νC≡N
V3A (V3B)	0.20 (0.34)	0.13 (0.16)
V5A (V5B)	0.23 (0.35)	0.20 (0.24)
V10A (V10B)	0.37 (0.47)	0.45 (0.53)
A (B)	1.05 (1.44)	–

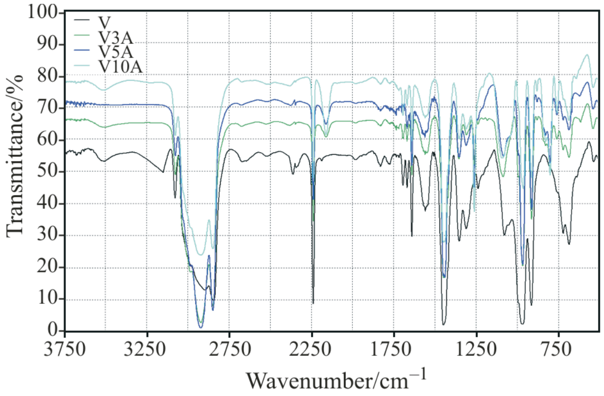


Fig. 7 FTIR spectra of NBR vulcanizates before and after modification with poly(siloxane) (A)

Conclusions

- Addition of poly(siloxanes) does not change character of thermal transitions of butadiene-nitrile rubber cross-linked with dicumyl peroxide, but decreases rate of its thermal decomposition and increases residue after this process, what is very important from combustibility point of view.
- Addition of poly(siloxanes) decreases flammability of NBR peroxide vulcanizates – it is a result of silica formation in situ in top layer, which increases its thermal stability and insulating ability, what makes difficult the mass and energy flow between solid and gaseous phase during burning.
- Reduction of flammability of vulcanizates containing poly(siloxanes) is also result of elimination of liquid products of thermal decomposition, formed during burning, which are flowing down along the sample and transfer heat and also increase contact with oxygen.

- Surface modification of vulcanizate causes considerable decrease in flammability; longer time of surface modification makes possible to obtain self-extinguishing samples.
- Addition of poly(siloxanes) considerably increases ageing resistance of NBR peroxide vulcanizates. It is caused by formation of protecting film on vulcanizate surface, as a result of poly(siloxane) molecules migration to the surface during ageing of samples.
- The surface modification of polymer materials by swelling with liquid modifiers is very simple and should find practical application.

Our studies are continued and other results will be published in a due course.

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