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Synthesis of Silica in Elastomer's Matrix

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Summary: We tried to synthesise silica's fillers in polar and nonpolar elastomers. Di-, tri- and tetraalkoxysilanes were used as a precursor of silica. Such functionality allowed us to obtain a filler with different ratio of crosslinking. We could expect some interactions between elastomer and silanes, which contained additional functional groups. We investigated vulcanizates by using the following methods: crosslink density in toluene and 10 % solution of ethylenediamine in toluene, mechanical properties, IR microscopy, DMA. It appeared that alkoxysilanes influenced advantageously on elastomers and properties.

Introduction

Carbon black, silica or mineral fillers are usually used as a filler. Silica is more commonly used due to its specific properties of filled elastomers. Usually silica-reinforced rubber is prepared by mechanical mixing. However, there are some problems with good dispersion of silica because of the small size of particles and their large specific area. As a result silica tends to create aggregates [1]. It is possible to overcome these difficulties by synthesis of silica in elastomer medium by sol-gel reaction [2,3]. This reaction allows to obtain silica with particles of nanometer size. The idea of this reaction is based on hydrolysis and condensation of organometalic compounds. The typical precursor of silica is tetraethoxysilane (TEOS). It is possible to use trifunctional silanes $R'Si(OR)_3$, where R' is unreactive during hydrolysis reaction [4]. As for the polymers which are often used as polymer medium in sol-gel reaction we should mention polydimethylsiloxane [5], polybutadiene [6], styrene-butadiene rubber [7] and acrylonitrile-butadiene rubber [8].

The aim of our work was the synthesis of silica's filler in polar and nonpolar elastomer and the determination of the properties of the vulcanizates.

Materials

The objects of our studies were: acrylonitrile-butadiene rubber (NBR, Chemigum N-300), carboxylated acrylonitrile-butadiene rubber (XNBR, Krynac X 7.5) and ethylene-propylene copolymer (EPM Dutral Co 054).

We used the following silanes as precursors of silica's networks: tetraethoxysilane TEOS, N-

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2-aminoethylo-3-aminopropylotrimethoxysilane DAMS, octylotriethoxysilane OES, octadecylotrimethoxysilane ODMS, N-2-aminoethylo-3-aminopropylo-methylodimethoxysilane DMMS. The silanes, in liquid form, were added during the preparation of rubber mixes.

EPM was crosslinked by dicumyl peroxide (DCP), (EPM - 100 phr, DCP – 2 phr), NBR by sulphur with 2,2-dithiobisbenzothiazole (MBTS) and tetramethylthiuram disulphide (TMTD), (NBR – 100 phr, ZnO – 5 phr, Stearic acid – 1 phr, S – 2 phr, MBTS – 1,5 phr, TMTD – 0,2 phr). In the case of XNBR DAMS or DCP were used as crosslinking agents, (XNBR – 100 phr, DAMS – 0:20 phr, DCP - 0:1 phr).

Methods of Investigations

Rubber mixes were prepared by using a laboratory two-roll mill at a temperature of approximately 35 ^{0}C. The samples were vulcanizated at 160 ^{0}C. Then vulcanizates EPM were placed in hydrochloric acid atmosphere at room temperature for 7 days, while vulcanizates XNBR and NBR were placed in moisture atmosphere and after that dried in a vacuum dryer for a few days at 50 ^{0}C.

Crosslink density of the vulcanizates was calculated from the measurement of equilibrum swellinig in toluene, toluene under ammonia treatment or 10 % solution of ethylene diamine in toluene. The mechanical properties of the vulcanizates were determined according to PN ISO 37:1998 using dumbbell Zwick type 1435. Dynamical Thermal Analysis DMTA was carried out using apparatus DMA 2980 TA Instuments. IR spectra of films of vulcanizates were recorded on a BIO RAD FTS 175C spectrometer.

Discussion

We were able to obtain a filler with different crosslinking degree due to different functionality of silanes (Table 1). Using difunctional silanes in the mixtures of silanes with higher functionality could lead to silica which contained some linear fragments. In the case of using DAMS we obtained NBR vulcanizates with relatively high tensile strength TS = 10,44 MPa in comparison with vulcanizate without any silane as well as to vulcanizate containing TEOS. We observed an increase in the value of tensile strength after using both together DAMS and TEOS, TS = 17,28 MPa.

Table 1. Mechanical properties of NBR vulcanizate.

Silane	σ_{100} [MPa]	σ_{300} [MPa]	TS [MPa]	ε_B [%]
-	1,52	2,62	4,30	438
20 DAMS	1,41	2,42	10,44	974
20 TEOS	1,44	2,64	3,37	369
10 DAMS 10 TEOS	1,47	2,24	17,28	610
10DMMS 10 TEOS	1,28	1,52	12,70	804
7DMMS 7 DAMS 7 TEOS	1,26	1,59	13,00	685

$\sigma_{100,\ 300}$- stress at elongation 100 %, 300 %, TS – tensile strength, ε_B – elongation at break.

As we can see (Figure 1) the vulcanizates obtained by using the mixture of DAMS and TEOS had the highest value of crosslink density, whereas in the case of DMMS and TEOS or DMMS, DAMS and TEOS we did not notice any significant differences.

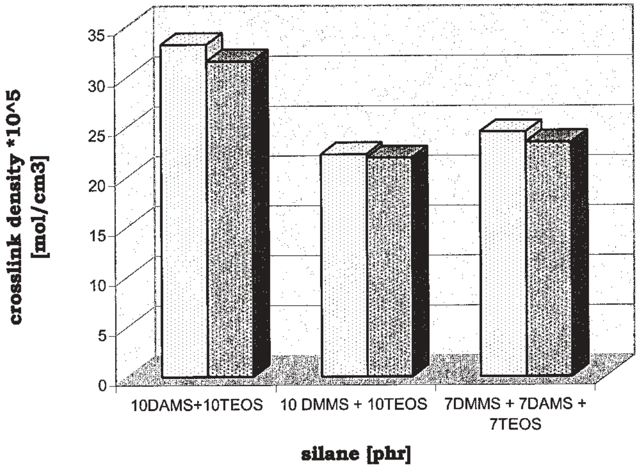

Figure 1. Dependence of crosslink density of NBR vulcanizates on silanes functionality.

⬚ Crosslink density calculated from equlibrum swelling in toluene

▩ Crosslink density calculated from equlibrum swelling in toluene with amonia

Table 2 shows the values of crosslinking degree, decrease in crosslinking degree under ethylenediamine treatment, crosslinking efficiency and mechanical properties of XNBR vulcanizates.

Table 2. Crosslink density and mechanical properties of XNBR vulcanizates containing DAMS.

Crosslinking agent	$\nu*10^{-5}$ [mol/ cm^3]	$\Delta\nu*10^{-5}$ [mol/ cm^3]	$W*10^{-2}$	σ_{100} [MPa]	σ_{300} [MPa]	TS [MPa]	ε_B [%]
DCP	11,76	1,50	454,0	0,91	1,42	2,21	468
5 DAMS	8,10	0,94	40,5	1,05	1,58	5,54	657
10 DAMS	11,56	3,01	25,7	1,31	2,46	8,87	563
20 DAMS	14,88	4,19	16,5	2,11	8,07	12,04	374
*5 TEOS	13,85	3,15	30,8	1,43	3,07	8,40	509
*10 TEOS	13,75	3,70	30,5	1,45	2,97	11,15	591
*20 TEOS	16,74	5,89	37,2	2,51	8,28	8,28	374

ν- crosslink density of the vulcanizates, $\Delta\nu$– decrease of crosslink density under the influence of ethylenediamine, W- crosslinking efficiency, *DAMS content: 10 phr. The rest of abbreviations are the same as in table 1.

The following results showed that DAMS acted as a crosslinking agent in the case of carboxylated acrylonitrile-butadiene rubber. The greater content of DAMS, the bigger crosslink density and lower the crosslinking efficiency. We could explain such behaviour through the lack of solubility of silicone compounds with functional groups of elastomer. The reaction of crosslinking went on the surface of silicone domains with functional groups of elastomer. As the amount of DAMS increased, enhanced the decrease in crosslink density under the influence of ethylenediamine. We supposed it was connected with the ionic bounds. Their presence was confirmed by IR analysis. The bands, typical of carboxyl anion COO^- (1650-1550 cm $^{-1}$) and amine cation (1625 cm $^{-1}$) present in spectra of XNBR vulcanizates, containing DAMS, could confirm such an idea. Probably, due to that we observed an additional phase transition on tan delta = f (temperature) in the temperature range 30-40^{0}C, in the case of vulcanizate containing 20 phr DAMS (figure 2).

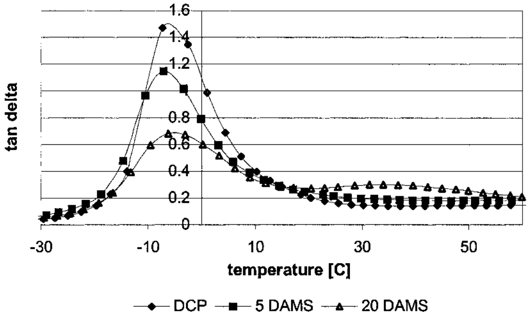

Figure 2. Tangent loss of XNBR vulcanizates obtained by using DAMS or DCP versus temperature.

As we used aminosilane as a crosslinking agent we observed the increase in crosslink density and higher concentration of ionic crosslinks. In such a case we were able to obtain vulcanizates with good mechanical properties in comparison with peroxide vulcanizate. Stress at elongation 100 % and 300 %, as well as tensile strength increased as the amount of DAMS was bigger. As for the vulcanizates containing DAMS and TEOS the stress at elongation 100% and 300% changed in the same way, the tensile strength increased in the beginning.

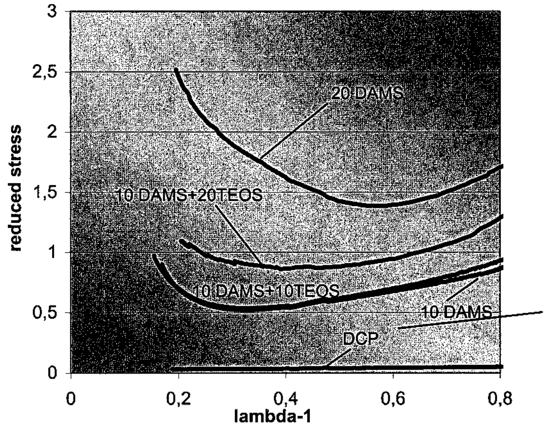

Figure 3. Reduced stress ($\sigma/\lambda-\lambda^{-2}$) as a function of the inverse extension ratio (λ^{-1}) of XNBR vulcanizates, (deformation rate 2 mm/min).

Figure 3 compares stress – strain isotherms for vulcanizates crosslinked by using DAMS or DCP. The vulcanizates containing 20 DAMS and 10 DAMS + 20 TEOS are seen to have significantly higher modulus than the rest of vulcanizates. The difference suggests that the filler synthesised in this medium had a greater reinforcing efficacy.

To synthesise filler in EPM medium we used silanes containing long aliphatic chains, which guaranteed their good dispersion in elastomer. We supposed that the dispersion of ODMS was better than that of OES. Trifunctional silanes influenced crosslink density but this effect was greater in the case of ODMS (table 3). We did not observe significant changes in the value of crosslink density after adding equal amounts of OES and TEOS in comparison with vulcanizate which contained only trifunctional silane. The tensile strength increased significantly when ODMS and TEOS were used.

Table 3. Crosslink density and mechanical properties of EPM.

Silane	$\nu*10^{-5}$ [mol/cm^3]	δ_{100} [MPa]	δ_{300} [MPa]	TS [MPa]	ε [%]
-	1,99	1,15	1,37	3,28	875
10 OES	4,01	0,94	1,24	2,50	830
20 OES	3,77	0,93	1,19	3,83	934
10 OES 10 TEOS	3,40	1,10	1,59	3,85	699
10 ODMS	6,30	1,08	1,38	2,62	628
20 ODMS	7,83	1,25	1,66	3,08	591
10 ODMS 10 TEOS	4,70	1,29	1,84	6,48	798

Abbreviations are the same as in table 2.

Conclusion

N-2-aminoethyl-3-aminopropyltrimethosilane was a crosslinking agent for carboxylated acrylonitrile-butadiene rubber. Crosslink efficiency decreased as the amount of silane increased. Some crosslinks had ionic nature.

Organosilicon compounds had a good influence on mechanical properties of the samples of acrylonitrile-butadiene rubber with or without carboxyl groups and ethylene-propylene copolymer. It was possible to obtain vulcanizates with relatively high tensile strength in comparison with vulcanizate without silane.

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