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# New Type of Inorganic Filler with a Core-Shell Structure

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**Summary**: We tried to use a new kind of filler with "core-shell" structure as a crosslinking agent for carboxylated butadiene-acrylonitrile rubber. We thought that the substance would be better dispersed in the polymer matrix than zinc oxide. Silica ($ZnO/SiO_2$) whose surface was modified with amorphous zinc oxide from zinc nitrate was used. Its properties were investigated using gas chromatography.

Finally we obtained unconventional networks containing ionic and complex bonds (as a result of reaction of elastomers' functional groups i.e. carboxyl groups with the appropriate neutralizing agent as metal oxide). Ionic clusters were formed in vulcanizates which influenced the mechanical properties and crosslinking efficiency. We confirmed the presence of these unconventional bonds by IR spectroscopy and DMTA analyses.

## Introduction

Zinc oxide is one of the most important compound of elastomers blends. It plays a role of an activator of sulphur curing accelerators [1,2]. Stearic acid with ZnO caused changes of the amount of bounded sulphur and crosslinking efficiency increased [3,4].

Zinc oxide is a filler characterized by good heat conduction and high density.

Zinc oxide can be a crosslinking substance of elastomers which contains reactive functional groups such as polychloroprene or chlorosulphonated polyetylene. It should be mentioned that the reaction of carboxylic groups presented at carboxylated acrylonitrile-butadiene rubber (XNBR) and metal oxides leads to salt formation [5].

ZnO can be used for neutralization of carboxyl groups which were introduced into ethylene-propylene rubber as a result of monoallyl maleate modification [6]. Then ionic crosslinks which are responsible for enhancement of mechanical properties and stress disipation of vulcanizates are formed [7,8].

Looking at all ZnO properties we took into consideration a possibility of creation and investigation of a new kind of light strengthening filler which had a core-shell structure.

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## Materials

The investigated material was carboxylated acrylonitrile-butadiene rubber (XNBR) containing 27 wt % of acrylonitrile and 6,71 wt % of methacrylic acid (Krynac X7,5; Bayer). We used precipitated silica Zeosil 175MP (Rhone Poulenc de Decines). Another filler was zinc oxide (ZnO). Rubbers were crosslinked by organic peroxide DCP (dicumyl peroxide) or by silica whose surface was modified with zinc oxide in a wet process of precipitation ($ZnO/SiO_2$) [9].

## Methods of Investigation

Rubber mixes were prepared using a laboratory two-roll mill at temperature about $35^0$C. Each sample was vulcanized at $160^0$C. Crosslink density of the vulcanizates was calculated from measurements of equillibrium swelling in toluene, toluene with ethylenediamine, chloroform and chloroform with acetic acid. The mechanical properties of vulcanizates were determined according to ISO37 using dumbbell Zwick type 1435. We investigated mechanical relaxation of polymers using that apparatus. IGC measurements were performed with commercial equipment (Perkin-Elmer) provided with a flame ionization detector of high sensitivity. Surface properties of fillers were carried out at infinite dilution conditions. Dynamical-mechanical thermal analysis (DMTA) was done using apparatus DMA 2980TA Instrument. IR spectra (attenuated total reflection (ATR) or photoacoustic spectroscopy (PAS)) of the rubber and vulcanizates were recordered on Bio Rad FTS 175C.

## Results and Discussion

Surface properties of silicas are given in table 1. Zinc oxide modification of silicas' surface caused a decrease in specific surface and dispersive component of the surface energy in comparison to non-modified filler. The surface of silica was rougher if the amount of ZnO was higher. Higher values of morphology index of $ZnO/SiO_2$ fillers were the evidence for that.

So it was obvious that zinc oxide formed concentrations on silica's surface. SEM images showed that the bigger content of ZnO on filler's surface the lower sillica's ability to disperse in elastomer's matrix and higher ability to create aggregates of molecules. Crosslink density and its decrease under ethylenediamine and chloroform treatment are shown in table 2. The results indicated that these solutions did not cause a decrease in crosslink density of peroxide vulcanizates. Introduction of silica into rubber mixes led to an increase in crosslink density of vulcanizates. We observed similar effect in filled vulcanizates containing zinc oxide as well.

Table 1. Surface properties of silicas at 100°C.

| filler | specific surface $[m^2/g]$ [10] | dispersive component of surface energy $[mJ/m^2]$ | Im | Im* |
|---|---|---|---|---|
| Zeosil 175 MP | 142,8 | 56,60 | 1,31 | 1,38 |
| 1% $ZnO/SiO_2$ | 105,5 | 33,98 | 1,50 | 1,60 |
| 8% $ZnO/SiO_2$ | 118,9 | 38,87 | 1,54 | 1,53 |
| 20% $ZnO/SiO_2$ | 69,3 | 38,20 | 1,36 | 1,40 |

Im- morfology index defined as the ratio of retention volume of linear alkane (octane) to branched one (trimethyl 2,3,4-pentane, * -dimethyl 2,5-hexane) [11,12].

It was cleared that modified silica cured rubber. The greater the content of ZnO onto silica's surface the higher crosslinking efficiency of elastomer (maximum value was observed for 4% $ZnO/SiO_2$). The calculations confirmed that it was possible to obtain a mono-layer of ZnO on Zeosil 175MP when the amount of metal oxide was small. An increase in the amount of ZnO (8, 12, 20%) caused its crystalization on filler's surface and plugging of pores what led to the decrease in specific surface (table 1) and crosslinking efficiency. Using zinc oxide as a crosslinking substance led to a formation of non-covalent bonds in elastomer's network which decreased in ethylenediamine solution or chloroform one (table 2). We noted that etylenediamine caused not only the destruction of ionic clusters but also the decrease in elastomer-filler interactions too. It is said that the decrease in crosslink density of vulcanizates filled with silica under amine treatment is an account of interactions between rubber and silica. Due to that the greater the amount of ZnO onto silica's surface the higher concentration of ionic bonds. We stated that the influence of chloroform-acetate acid solution on equilibrium probes swelling was worth mentioning. The vulcanizates solved themselves in it. Ionic clusters were mainly presented in vulcanizates containing zinc oxide or modified silica. The vulcanizates containing ionic bonds had better mechanical properties in comparison with peroxides-cure rubbers. We observed an increase in 100% modulus and a decrease in elongation at break if the amount of modifying substance onto silica's surface was greater. The vulcanizates to which we introduced zinc oxide as a curing agent had higher ability to relaxation than vulcanizates with only covalent bonds (table 2). It was clear that this process was dependent on ionic and aggregative nature bonds between metal oxide and rubber's carboxyl groups. We stated that vulcanizates filled with modified or non-modified silica were characterized by higher ability to stress scattering.

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

| filler and curing agent | $\nu_{tol}$ | $\Delta\nu_{am}$ $/\nu_{tol}$ | $\Delta\nu_{chlor}$ $/\nu_{tol}$ | crosslinking efficiency | $\sigma_{100}$ | $\varepsilon_r$ | $R_r$ | n |
|---|---|---|---|---|---|---|---|---|
| DCP | 7,703 | 0,043 | 0,065 | 296 | 0,99 | 647 | 3,48 | 0,0147 |
| DCP+$SiO_2$ | 13,067 | 0,195 | -0,003 | 503 | 2,55 | 573 | 16,75 | 0,0564 |
| ZnO | 3,914 | 0,104 | 0,236 | 5,29 | 2,33 | 559 | 27,56 | 0,0464 |
| ZnO+ $SiO_2$ | 5,108 | 0,247 | 0,068 | 6,90 | 5,51 | 529 | 30,72 | 0,0969 |
| 1% ZnO/$SiO_2$ | 3,547 | 0,299 | 0,099 | 9,57 | 1,24 | 1516 | 1,75 | 0,0792 |
| 4% ZnO/$SiO_2$ | 3,776 | 0,320 | 0,134 | 25,49 | 1,66 | 1577 | 4,17 | 0,0751 |
| 8% ZnO/$SiO_2$ | 4,080 | 0,380 | 0,308 | 13,77 | 1,66 | 1541 | 8,94 | 0,0745 |
| 12% ZnO/$SiO_2$ | 5,682 | 0,393 | 0,430 | 12,80 | 2,69 | 600 | 15,46 | 0,0758 |
| 20% ZnO/$SiO_2$ | 7,209 | 0,461 | 0,560 | 9,73 | 2,92 | 654 | 23,14 | 0,0545 |

$\nu_{tol}$ – crosslink density estimated from equilibrium swelling in toluene [$*10^{-5}$ mol/cm$^3$]; $\Delta\nu_{am}/\nu_{tol}$, $\Delta\nu_{chlor}$ $/\nu_{tol}$ –decrease of crosslink density under the influence of ammonia [%], crosslinking density- determined as the ratio of crosslink density to the amount of crosslinking substance $\sigma_{100}$ - 100% modulus [MPa], $\varepsilon_r$-elongation at break [%], $R_r$-tensile strength [MPa], n-relaxation rate.

Due to that greater relaxation rate was observed. The higher concentration of ZnO onto $SiO_2$ surface the lower relaxation rate of vulcanizates (because of higher crosslink density). It seemed that silica did not cause a significant changes of the glass temperature value of XNBR vulcanizates (figure 1). The same effect was observed in the case of peroxide and ZnO vulcanizates. Due to the presence of ionic clusters in elastomer's network we stated a second maximum of tangent delta in the range of temperatures $20 \div 75^0C$. This band did not appeare in peroxide vulcanizates.

We carried out IR analyses of two models: propionic acid + precipitated silica and propionic acid + modified filler (figure 2). They showed ionic interactions between filler and carboxyl groups of the rubber. We stated that lack of these interactions could be confirmed by the presence of peak 1370 cm$^{-1}$. It characterized deformation vibrations of C-O-H of carboxylic acids. The intensity of this signal decreased in the case of spectra of acid with modified silica.

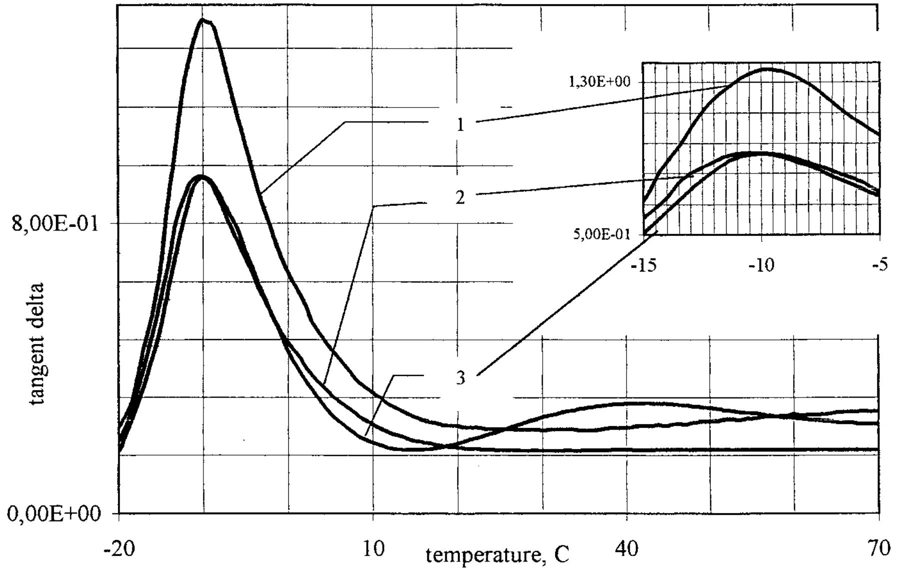

Figure 1. DMTA measurements (1-XNBR+DCP, 2-XNBR+DCP+$SiO_2$, 3-XNBR +ZnO/$SiO_2$).

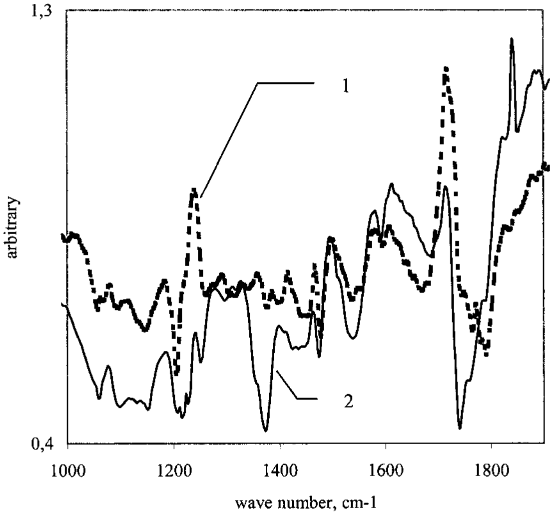

Figure 2. IR spectra of propionic acid incorporated onto silica's surface prepared using PAS method (1- ZnO/$SiO_2$, 2- $SiO_2$).

The transformation of dimers' singlet (1740 $cm^{-1}$) into two peaks (1764 and 1791 $cm^{-1}$) was observed due to ionic interactions. The asymetric stretching vibrations connected with carboxyl anions led to appearance of doublet in IR $SiO_2$/ZnO structure. It proves ionic interactions between ZnO and COOH groups of propionic acid.

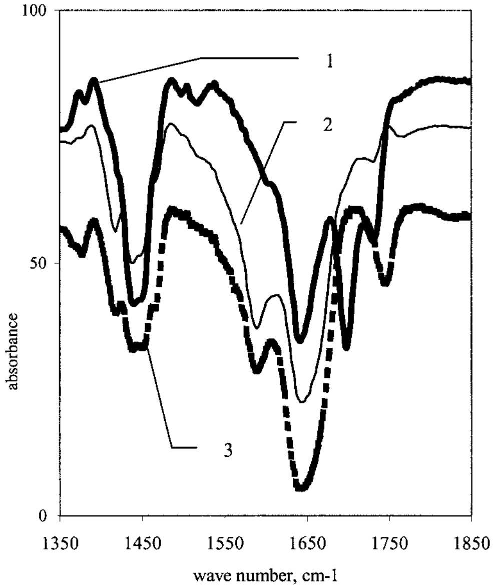

Figure 3. IR spectra of XNBR vulcanizates prepared using ATR method (1-XBR+DCP, 2-XBR+ZnO+$SiO_2$, 3-XNBR+ ZnO/$SiO_2$).

IR spectra of peroxide vulcanizate, ZnO one and elastomer which was cured using modyfied silica are shown (figure 3). It is obvious that using dicumyl peroxide as a curing substance does not lead to splitting of 1698 $cm^{-1}$ band. We noticed an additional peak (1589 $cm^{-1}$) in spectra of ZnO vulcanizate. It was caused by stretching vibrations of $COO^-$ anions. We did not have any peak (1417 $cm^{-1}$) attributed to deforming vibrations of COH groups. It proves ionic interactions in elastomers cured with zinc oxide or modified silica.

## Conclusion

Silica's surface properties changed as a result of modification with zinc oxide. The specific surface of silica was lower if the amount of precipitated ZnO was bigger. The same time values of the surface energy and morphology index decreased (apart from 20% ZnO/$SiO_2$ filler). It indicated that filler's surface expanded.

Modified silica was a curing substance which led to the creation of ionic crosslinks. Due to that mechanical properties of vulcanizates were better.

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