Adsorption of Curatives and Activity of Silica toward Elastomers

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Summary: To characterize an activity of silica toward elastomers usually the parameters of the filler structure and a possibility of its interactions with macromolecules of a matrix are taken into consideration [1,2,3]. As a rule, low molecular weight substances of different polarity are dissolved in a rubber mix (e.g. accelerators, activators, crosslinking substances, etc). They undergo adsorption on the surface of active fillers what exerts an effect on a structure of a network formed and influences mechanical properties of vulcanizates at the same time.

Introduction

From our research it follows that fillers activity in elastomers depends on the kind of applied crosslinking system. Crosslinking substances adsorption on the filler surface leads to the change of its surface properties and its dispersion in an elastomer matrix. The character of filler-elastomer interactions changes as well.

We investigated surface properties of silica modified with crosslinking substances and we determined parameters that influence a strengthening effect of the filler, mainly its ability to create its own network, so called "structure", in the elastomer matrix.

The crosslinking system adsorption on the filler surface results in a heterogeneous crosslinks distribution. Probably an area around the filler particles is vulcanised in a higher degree then. Heterogeneity of the elastomer networks has the influence on vulcanizates mechanical properties – tensile strength and elongation at break [4].

Experimental

Our studies concerned elastomers of different character: the polar one – butadiene-acrylonitrile rubber NBR Nipol N 41 (containing 21 % of acrylonitrile, Nippon Zeon Co.) and of aliphatic character – ethylene-propylene rubbers EPM Dutral Co 054 and EPDM Keltan 712.

The object of our studies was precipitated silica of specific surface 175 m^2/g Zeosil 175 MP, produced by Rhône Poulenc.

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The NBR and EPDM elastomers were crosslinked by sulphur in the presence of accelerator - diphenylguanidine (DPG) or dibenzothiazyl disulfide (MBTS). EPM was crosslinked with the following peroxides: dicumyl (DCP), dibenzoyl (DBP), di-tert-butyl (DTBP) and di-2,4-chlorobenzoyl (DCBP) peroxides. Elastomers mixes were filled with 30 phr of silica.

Methods of Investigation

We deposited zinc oxide (ZnO) on the silica surface from a solution of $Zn(NO_3)_2$ at 450 – 480 °C during 4,5 – 8 hours. Crosslinking substances were adsorbed on the surface of silica from their solution in toluene or carbon tetrachloride. For this purpose the proper amount of curative solution was poured over the weighed portion of silica, which had been dried at 110 °C for 24 h. Then the dispersion was mixed for fifteen minutes and the solvent was evaporated. Modified silica was dried in 110 °C in a vacuum oven during 48 hours. The quantity of curatives adsorbed on the silica was determined by elementary analysis method.

To obtain a deeper insight into a mechanism of phenomena occuring in the mixes we studied surface properties of silica by inverse gas chromatography (IGC). The chromatographic measurements at infinite dilution were carried out with a Perkin-Elmer apparatus fitted with a flame ionization detector of high sensitivity.

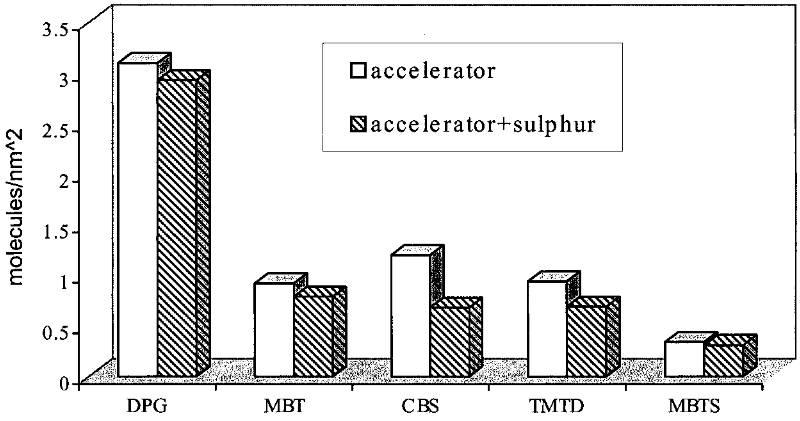
We investigated also rheological properties of silica suspensions in paraffin oil – analogue of ethylene-propylene rubber.

The mechanical properties and hysteresis of the vulcanizates were determined using Zwick apparatus, model 1435.

Results

Polar compounding ingredients adsorb on the silica surface. From our investigation it follows that the amount of the adsorbed accelerators depends on their structure and the presence of sulphur. The surface of silica has an acidic character so substances with the basic character should be adsorbed preferably. It was found that diphenylguanidine (DPG) was easily adsorbed on silica from solution in toluene. An accelerator with more acidic character than DPG, e.g. dibenzothiazyl disulfide (MBTS), was adsorbed on the silica surface in quantity that is about ten times lower (Fig. 1).

I



DPG – diphenylguanidine

MBT – 2-mercaptobenzothiazole

CBS – cyclohexylbenzothiazole sulfenamide

TMTD – tetramethylthiuram disulfide

MBTS – dibenzthiazyldisulfide

II

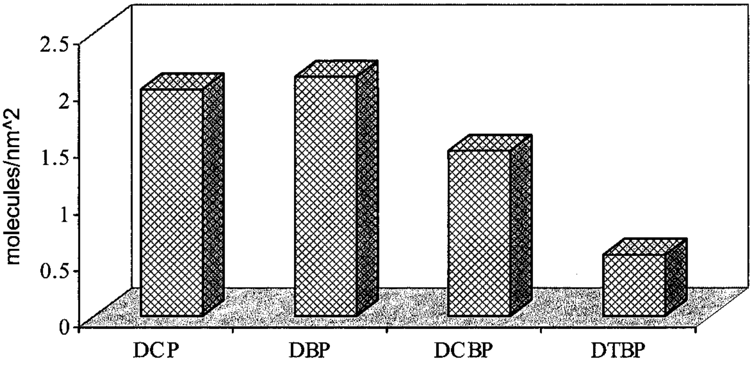


Fig. 1. Adsorption (molecules/nm^2) of accelerators (I) and crosslinking substances (II) on silica surface.

Symbols of curatives applied are explained in EXPERIMENTAL

We investigated an effect of accelerators adsorption on silica strengthening behaviour toward elastomers. From the results obtained it follows that the activity of silica toward EPDM depended on the type of crosslinking system applied. Examination of data given in Table 1 leads to the conclusion that silica displays greater activity in rubber crosslinked with sulphur and MBTS in comparison with the vulcanizates crosslinked with S_8 /DPG.

Diphenylguanidine, which was adsorbed on the silica surface easily and in great amount, hindered contact between active sities of the silica and elastomer and then the formation of hydrogen bonds between Si-OH groups of the filler. Thus, the filler ability to create its own network in the elastomer matrix has been much reduced, what is of great importance from the point of strengthening effect.

From Fig. 1 (II) it followed that DCP and DBP were adsorbed on the silica surface in the greatest degree among the peroxides applied. Silica revealed the most strengthening behaviour in the vulcanizates that were crosslinked with these peroxides. However, silica treated with DCP from its solution in toluene caused the decrease of tensile strength of the vulcanizates in comparison with the vulcanizates containing non-modified filler.

Table 1. The influence of crosslinking system applied on the properties of ethylene-propylene vulcanizates containing silica.

Rubber	**Curative**	s^F/s^0	$\sigma^F_{100}/\sigma^0_{100}$	σ_{100} **[MPa]**	**TS [MPa]**	ε_B **[%]**
EPDM	S_8+MBTS	1,70	2,95	3,45	11,2	540
EPDM	S_8+DPG	3,41	2,12	2,69	8,8	740
EPM	DCP	1,40	1,73	1,73	9,7	778
EPM	DCP(SiO_2)*	1,80	1,00	1,30	8,8	1032
EPM	DBP	1,45	1,67	1,50	10,9	894
EPM	DCBP	1,25	1,30	1,40	5,2	941
EPM	DTBP	1,04	1,27	1,40	7,4	862

DCP(SiO_2)* - dicumyl peroxide adsorbed on the silica surface from the solution in toluene;s^F / s^0 - ratio of sol content of filled vulcanizates to unfilled

σ_{100} - stress at 100 % elongation, TS - tensile strength, ε_B - elongation at break

It can be concluded that crosslinking system ingredients, adsorbed on the silica surface, undergo desorption in a small degree during vulcanisation and the reactions leading to the crosslinking of the rubber have taken place mainly in the vicinity of the filler particles. As a consequence a distribution of crosslinks in the elastomer matrix is non-uniform. Increased sol content in the vulcanizates, containing the accelerator (DPG) or peroxide (DCP, DBP) adsorbed in a considerable amount on the filler surface, testify in favour of this hypothesis.

To have deeper insight into the problem of curatives adsorption and its effect on the activity of silica, we studied also other ingredients of crosslinking system, e.g. zinc oxide. ZnO takes part in elastomers crosslinking increasing amount of bounded sulphur plus accelerators and crosslinking efficiency [5].

We determined surface properties of silica modified with ZnO and with crosslinking system (Table 2). As a consequence of the silica surface modification the dispersive component of the surface energy γ_s^D decreased, what may indicate a reduced ability of the filler particles to agglomerate in the elastomer matrix.

We calculated morphological index (I_m, I_m^*) being a measure of a roughness of the filler surface.

Table 2. Surface properties of silica in 90 °C.

Symbol	γ_s^D **[mJm^{-2}]**	I_m	I_m^*
SiO_2	66,21	1,32	1,38
ZnO / SiO_2	35,49	1,22	1,30
crosslinking system / SiO_2	28,75	1,43	1,46

γ_s^D – dispersive component of the surface energy

I_m, I_m^* – morphological index, defined as a ratio of retention volume of linear alkane (octane) to a branched one, respectively:

2,3,4 – trimethylpentane and 2,5 – dimethylhexane

SiO_2 – non-modified silica

ZnO / SiO_2 – silica modified with ZnO deposited on the filler surface from the solution of $Zn(NO_3)_2$

crosslinking system / SiO_2 – silica treated with S_8, DPG and ZnO

The treatment of silica surface with ZnO caused a decrease of the filler surface roughness. Whereas the crosslinking system adsorption on the surface of silica resulted in the increase of I_m and I_m^* value, what suggests that the surface of modified filler should be more heterogeneous compared with non-modified.

From our studies it followed that the crosslinking system ingredients adsorption on the silica surface resulted in a decrease of tensile strength of EPDM and NBR vulcanizates (Table 3). Treated silica caused an increase of stress at 100, 200 and 300 % elongation of EPDM vulcanizates.

Table 3. Mechanical properties of EPDM and NBR vulcanizates; symbols as in Table 1 and 2.

EPDM	σ_{100} **[MPa]**	σ_{200} **[MPa]**	σ_{300} **[MPa]**	**TS [MPa]**	ε_B **[%]**
-	1,00	1,41	1,99	2,26	329
SiO_2	1,77	2,60	3,78	16,32	657
ZnO / SiO_2	2,42	4,38	6,47	11,03	480
crosslinking system / SiO_2	2,21	3,64	5,09	10,87	536
NBR	σ_{100} **[MPa]**	σ_{200} **[MPa]**	σ_{300} **[MPa]**	**TS [MPa]**	ε_r **[%]**
-	1,12	1,76	2,61	3,06	393
SiO_2	1,89	2,89	4,29	16,12	609
ZnO / SiO_2	1,78	2,83	3,98	12,30	631
crosslinking system / SiO_2	1,78	2,76	3,96	11,01	588

Reduced strengthening effect of modified silica toward elastomers is supposed to be the result of a decrease ability of the filler to form its own network in the elastomer matrix. From our studies it followed that crosslinking system adsorption on the silica surface resulted in a decrease of the filler viscosity of suspensions in paraffin oil – an analogue of ethylene-propylene rubber (Table 4). We observed a decrease of ϕ value which suggested that the filler ability to form its own network in a liquid, modeling the elastomer matrix, is reduced due to adsorption of compounding ingredients on the silica surface. Compounds adsorbed on the filler surface caused deactivation of its active sites.

Table 4. Silica effect on the rheological properties of paraffin oil; symbols as in Table 2.

Symbol	**ϕ**	**ϕ / ϕ_0**	**k**	**n**
SiO_2	0,26	3,82	13,04	0,42
ZnO / SiO_2	0,20	2,94	1,47	0,73
crosslinking system / SiO_2	0,10	1,47	0,42	0,87

ϕ – percentage by volume of aggregates of silica,

ϕ_0 - percentage by volume of silica in paraffin oil (0,068),

k,n – rheological parameters of Ostwald and de Waele equation [6]

Conclusion

The strengthening effect of silica toward elastomers depends on a type of crosslinking system applied. Accelerators of donor character cause deactivation of the filler dispersed in EPDM matrix. Then, the filler ability to create its own network is decreased and interactions with the elastomer are reduced.

The modification of silica surface (carried out of the elastomer matrix) with crosslinking system or ZnO, that were adsorbed from the solution, caused a decrease of silica activity toward elastomers.

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