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Activity of Fillers in Elastomer Networks of Different Structure

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Summary: The paper deals with interactions between low molecular weight substances and silica. Activity of SiO_2 towards ethylene-propylene-diene rubber (EPDM) also depends on the kind of crosslinking system used. Calcium carbonate, the filler exhibiting low interactions with elastomers does not show any changes in activity, due to application of different crosslinking systems. In our opinion, the observed increase of the fillers activity results from the modification of elastomer chains by crosslinking agents, influence of the latter on the formation of its own network (the so called "structure") in the elastomer matrix, and above all from nanoheterogeneous distribution of network crosslinks in vulcanizates. The non Gaussian probably bimodal distribution of crosslinks is likely to influence positively properties of elastomers. A similar effect is observed in peroxide vulcanizates of EPM produced with the use of the crosslinking coagents of polar nature. Behaviour of different kinds of carbon black in natural rubber (NR) crosslinked with dicumyl peroxide (DCP), sulphur donors or sulphur with accelerators is discussed. Reinforcing action of carbon black, particularly the active ones, showed to be more effective in sulphur than in peroxide vulcanizates.

Introduction

Filled elastomers are usually considered as two component systems. In fact an extent of interactions between an elastomer and filler is one of the important factors influencing rheological and mechanical properties of the system. For that reason a quantity of "Bound Rubber" or a degree of immobilization of macromolecules at interface are very often determined. However in such studies a type of the elastomer matrix and the presence of different auxiliary chemicals, dispersed or dissoluted in it, as a rule are neglected. In our previous paper it was demonstrated that both factors are of substantial importance [1,2]. In the lecture different new aspects of the problem are discussed. In cooperation between two laboratories, Institute of Polymers at Technical University of Lodz and Laboratoire de Chimie Physique at E'cole Nationale Superieure de Chimie de Mulhouse an effect of curatives adsorption by fillers has been thoroughly studied. From the data obtained it could be deduced that during preparation and storage of rubber mixes both types of commonly used crosslinking substances i.e. peroxides or sulphur as well as vulcanization accelerators are adsorbed by filler in extent depending on the fillers specific surface and its surface energy. During vulcanization, at elevated

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temperature the two processes occur simultaneously, desorption of curatives and crosslinking of a rubber matrix. Usually a rate of crosslinking reaction is faster as compared to a rate of in fact cooperative processes-desorption of low molecular weight substances and their diffusion in a polymer matrix. As a consequence a layer of an elastomer at a vicinity of filler particles is crosslinked stronger than its bulk. A distribution of crosslinks in the network formed is therefore not statistical but rather bimodal. The main thesis of the lecture was illustrated by the data concerning different types of carbon black and silica as well as precipitated calcium carbonate.

Experimental

MATERIALS

The fillers were dispersed in natural rubber (RSS I), ethylene-propylene (EPM) and ethylene-propylene-diene terpolymer (EPDM) (Dutral CO 054 and TER 054 produced by Montedison). The rubbers were crosslinked by DCP, tetramethylthiuram disulphide (TMTD), sulphur and 2-benzothiazolyl disulphide (S/MBTS) and diphenylguanidine (S/DPG). EPM was crosslinked with DCP in the presence of coagents i.e.monoallyl maleate(AM) and methylacrylamide (MA) or with di-tert-butyl peroxide (DTBP) and di-2,4-chlorobenzoic peroxide (DCBP). The surface properties of silica were determined 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. Retention volumes, corrected in the usual way, were take to calculate thermodynamic quantities, and Papirer et al. [3]. Wetting heat and heat of expulsion of heptane from the silica surface were determined by means of flow microcalorimeter, at the temperature 25°C. Adsorption of accelerators on the surface of silica, from their solution in dodecane was determined. For this purpose, 2% solution of an accelerator in dodecane was poured over a weighed potion of silica, which had been dried at 110°C for 24 h, then the whole was heated at 100°C for 24 h, and thereafter the silica was seperated by centrifugation. Then the content of accelerators remaining in the centrifuged dodecane and the quantity of accelerators adsorbed on the silica, were determined by elementary analysis method. Infrared spectra of the silica containing adsorbed accelerators were recorded using the Specord M. 80

spectrophotometer.

The rheological properties of suspensions of the silica in oil were investigated using the Haake Rotovisco coaxial-cylinder viscometer [4]. The dispersion medium used was squalene.

Crosslink density of vulcanizates was calculated from measurements of equilibrium swelling in toluene and in ammonia-saturated toluene. A swelling of the elastomer matrix was calculated according to method proposed by Blachy [5] and Parks [6]. The activity of fillers was evaluated on the basic of equilibrium swelling values. The empirical Parks-Lorenz [7] relationship has been used:

$$Q^F / Q^O = a \exp(-z) + b \qquad (1)$$

where Q^F and Q^O are the equilibrium swelling filled and unfilled vulcanizates respectively, z is weight of filler per unit weight of rubber matrix and a and b are constants. The coefficent „a" is the activity parameter of fillers. The mechanical properties of the vulcanizates were determined according to ISO 37 using dumbbell type 2 (ASTM D412) specimens. The stress relaxation was measured at room temperature. The samples were extended by 100% and stress drop was measured during 1800 s. The rate of relaxation was given by $n = -d(\ln\sigma)/d(\ln t)$ where σ - is the stress and t is the time. Hysteressis and Mullins effect were calculated by integration of the area under stress-strain curves of the samples extended to 300% elongation.

The content of sol fraction in the vulcanizates was determined at the temperature of 25°C, first extracting the samples with acetone for 4 days, in order to remove non-rubber substances; then the samples were extracted with toluene for 2 weeks in nitrogen atmosphere. The sol content in the samples with filler S^F was calculated according to Ahagon [8] from the formula:

$$S^F = S^O * W_P \qquad (2)$$

where S^O is the content of sol, and W_P is the weight fraction of polymer in the sample.

RESULTS

From our study it follows that the polar substances stronger interact with the surface of silica, than saturated hydrocarbons. On the other hand, ΔG_A of unsaturated hydrocarbons is located above the line of dispersive interactions. Therefore, one cannot exclude the possibility of specific interactions between silica functional groups and π electrons of unsaturated e.g. aromatic hydrocarbons. Benzene is capable to stronger specific interactions with silica than the alcanes. Pohle [9] has observed a shift of isolated -OH group wave number, in the following order: toluene > benzene > chlorobenzene. It is coincident with electron density of the aromatic hydrocarbons.

The wetting energy of fumed silica A 200 with hexane is equal to 64 mJ/m^2 (8.33 J/g, tab. 1). This value is comparable to the given in the literature. The heat of immersion in isooctane, determined by Sanders and Kewashan, is equal to 55 mJ/m^2 [10]. The wetting heat of solids depends on the degree of their hydration, and it is smaller e.g. if the surface of silica is covered by monomolecular layer of water. Considerable difference in the wetting heats of squalene and squalane was detected. The molecule of squalene contains 6 π bonds, so from this reason it interacts stronger with active centres of silica.

It seemed interesting to prove whether alkanes adsorbed on the silica surface e.g. hexane, can be displaced by hydrocarbons of greater molecular weight, as well as substances of donor or acceptor character. To solve the problem the heats of hexene-1, squalane, squalene, chloroform and butanone-2 adsorption on silica wetted with n-heptane were determined. From the data collected in Table 1 it could be assumed, that only hexene-1, squalene and butanone-2 can displace hexane from the surface of silica. The heat of wetting with chloroform, which is of acceptor character, is small in relation to amphoteric substances (ethyl ether), or substances of donor character (butanone-2).

Table 1. Heat of wetting of silica Q [J/g].

Adsorbate	Q	Adsorbate	Q
n-hexane	8,32 (5,04)*	chloroform	2,63
hexene-1	13,47	diethyl ether	12,42
squalane	2,12	ethyl acetate	14,59
squalene	10,21	butanone-2	15,15

* - concerns silica covered by monolayer of water at $p/p_0 = 0,52$

It seemed interesting to prove whether alkanes adsorbed on silica surface (e.g. hexane) can be expelled by hydrocarbons of larger molecular weight, as well as substances exhibiting a donor or acceptor character.

To solve the problem the heats of adsorption of squalane, squalene, chloroform and butanone-2 on silica, previously wetted with n-hexane, were determined. From the data collected in Table 2 it can be seen that substances which could displace n-hexane from the surface of silica are: hexene-1, squalene and butanone-2. The heat of wetting with $CHCl_3$, which is of electro-acceptor character, is small compared to amphoteric compounds (e.g. diethyl ether) or substances exhibiting electro-donor character, such as butanone-2.

However it appeared that small quantities of squalane and $CHCl_3$ as well are retained on the silica surface, that was wetted with hexane (Table 2).

Table 2. Heat of displacement of n-hexane from the silica surface by various adsorbates.

Concentration of a probe applied (solution in n-hexane)	Adsorption heat [mJ/g]	Desorption heat [mJ/g]	Amount of adsorbed probe	
			c_a [%]	a_a [μmol/g]
squalane(20%)	45	-36	2.8	10.0
squalene (20%)	1196	-691	5.5	21.3
hexene-1(20%)	369	0	70.0	910.6
chloroform (1%)	26	-17	7.4	7.3
butanone-2 (1%)	3183	-1836	22.4	21.0
butanone-2 (1%) *	2770	-1000	19.4	20.4
butanone-2 (1%) + squalene (20%)	3777	-2135	---	---

* - on the silica surface was previously adsorbed 56.4 μmol/g of squalene,
Triple adsorption of the probes dissolved in hexane
Desorption – by means of hexane,
the amount of adsorbed probe c_a = number of adsorbed μmoles of the probe /number of μmoles in the solution,
a_a = number of μmoles/g $Si0_2$.

Unsaturated hydrocarbons displace n-hexane and are adsorbed on the silica surface with considerable thermal effects. Butanone-2, due to its donor character, is also easily adsorbed.

Squalene, present on the silica surface or in hexane solution, does not prevent the adsorption of polar substance. Squalene and butanone-2 used in common displace n-hexane from the silica surface; the corresponding adsorption heat is larger, than that of both compounds used separately.

The results suggest that the silica surface is energetically strongly heterogeneous and is able to adsorb simultaneously both polar and non-polar substances. It can be concluded that substances of electro-donor character interact more strongly with the silica surface, than hydrocarbons.

As it can seen n-hexane is easily desorbed by electrodonor probes. In accordance with these data we stated that activity of silica toward ethylene-propylene rubber depends on surface parameters of a peroxide applied. It decreases in the order : EPM + DCP > EPM + DBP > EPM + DCBP. This relation correlates fairy well with the values of solubility parameters and surface energy of the components, calculated from group contributions and values of energy of adhesion between silica and the elastomer or peroxide [2].

It is known, that silica-elastomers interactions depend not only on the filler surface structure and activity but are also influenced by the presence of polar compounding ingredients. To clear this particular point the adsorption of accelerators and curatives was investigated. It was found that diphenyloguanidine (DPG) is easily adsorbed on silica from solution in toluene. An accelerator with more acidic character than DPG, e.g. mercaptobenzothiazole disulphide (MBTS), is adsorbed on the silica surface in quantity that is about ten times smaller (Table 3).

Table 3. Adsorption (particles/nm^2) of accelerators and curatives on the silica surface.

Accelerator	A	Curative	A
DPG	3,10	DCP	2,00
MBT	0,92	DBP	2,11
CBS	1,20	DCBP	1,46
TMTD	0,94	DTBP	0,54
MBTS	0,34	S_8	0,37

Polar compounding ingredients adsorb on the silica surface and change the filler surface properties. From our studies it follows that crosslinking system adsorption on the silica surface results in a decrease of viscosity of the filler suspensions in paraffin oil – analogue of ethylene-propylene rubber (Table 4). Treatment of the silica surface with the ingredients of crosslinking system leads to a decrease in ϕ value – the filler ability to form its own network in a liquid, modelling the elastomer matrix, is reduced. Compounds adsorbed on the filler surface cause deactivation of its active sites.

Table 4. Silica effect on the rheological properties of paraffin oil.

Symbol	ϕ	ϕ / ϕ_0	k	n
Z	0,26	3,82	13,04	0,42
S_8 / Z	0,24	3,53	6,44	0,52
S_8 + DPG / Z	0,18	2,65	1,57	0,71
crosslinking system / Z	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 from the equation formulated by Ostwald and de Waele

Z – silica Zeosil 175 MP

S_8 / Z – silica treated with sulphur from the solution in toluene

It was disclosed that the activity of silica towards EPDM depends to a large extent on the type of crosslinking system used. Table 5 shows the crosslink density and mechanical properties of EPDM vulcanizates, containing various types of silica.

Table 5. Crosslink density and mechanical properties of ethylene-propylene vulcanizates, containing SiO_2.

Rubber	Curative	$\nu_E * 10^5$ [mol/ cm^3]	$\Delta\nu_{NH3} * 10^5$ [mol/ cm^3]	ν^F / ν^0	s^F/s^O	$\sigma^F_{100} / \sigma^0_{100}$	σ_{100}, [MPa]	TS [MPa]	E_B, %
EPDM	S_8+ MBTS	7.30	2.02	0.86	1.70	2.95	3.45	11.2	540
EPDM	S_8+ DPG	4.86	1.34	0.50	3.41	2.12	2.69	8.8	740
EPM	DCP	10.80	3.71	0.85	2.40	1.73	1.73	12.1	792
EPM	DBP	6.15	3.11	1.17	1.34	1.44	1.40	7.4	862
EPM	DCBP	5.07	0.44	1.48	1.01	1.30	1.30	4.5	941

ν_E - crosslink density, $\Delta\nu_{NH3}$ - decrease of crosslink density under influence of ammonia, ν^F/ν^O - the ratio of crosslink density of vulcanizate with and without filler, s^F/s^O - sol content (in nonfilled vulcanizates S_8+ MBTS - 3.3%, S_8+ DPG - 3.2%), $\sigma^F_{100}/\sigma^0_{100}$ - ratio of the stress at 100 % elongation of filled vulcanizates to those not containing fillers, σ_{100} - stress at elongation 100 %, TS - tensile strength, E_B - elongation et break.

The elastomer was crosslinked with sulphur, and MBTS or DPG were used as accelerators. In table 5 we also provide data concerning changes in the crosslink density of the vulcanizates ($\Delta\nu$), when swelling measurements are performed in the presence of ammonia. It is commonly assumed that ammonia induces hydrogen bond rupture at the rubber silica interface [11]. Therefore the value of $\Delta\nu$ could be related to the activity of the silica, although in our opinion ammonia can also disrupt hydrogen bonds between the associated silanol groups of the silica itself and, to some extent, polysulphide crosslinks, which usually is not taken into account. Examination of the data given in Table 5 leads to the conclusion that silica displays greater activity in rubber crosslinked with sulphur and MBTS than with sulphur used in conjunction with DPG. We are of the opinion that the differences in the behaviour of silica in elastomer, depending on the type of crosslinking system used are connected with the adsorption of accelerators on its surface. Diphenylguanidine, which is readily and permanently adsorbed on the silica surface, results in a deactivation of the latter, it hampers contact between the active surface sites of the silica and the elastomer and the formation of hydrogen bonds between Si-OH groups. It is probably for this reason that the $\Delta\nu_{NH3}$ value of the vulcanizates, obtained in the presence of DPG is much lower (1.34×10^{-5} mole/cm^3) than that obtained in the case of MBTS (2.02×10^{-5} mole/cm^3).

Silica causes a considerable (up 50 %) reduction in the degree of crosslinking of the elastomer by sulphur if DPG is applied, but only by 14 % in the case of S_B + MBTS.

It can be concluded that during vulcanisation (160°) only a small fraction of the accelerator can be desorbed, it results that the reactions leading to the crosslinking of the rubber take place mainly in the vicinity of the filler particles. As a consequence the distribution of the crosslinks in the elastomeric matrix should be non-uniform. Higher sol contents of vulcanizates, obtained when a large amount of accelerator is adsorbed on the filler surface, e.g. in S_8 + DPG samples are in agreement with this hypothesis.

It was also shown that silica has a higher reinforcing effect if dicumyl peroxide is used as crosslinking substance toward EPM than di-2,4-chlorobenzoil peroxide (DCBP) or di-tert-butyl peroxide (DTBP) (Table 5). DCP was expected to exhibit the highest tendency to adsorption amongst the studied peroxides. Its solubility parameter is higher than that of DTBP. Dichlorobenzoil has the highest polarity of these peroxides. However, it was shown that halogen derivatives, e.g. $CHCl_3$ adsorb only in small quantities onto the silica surface. Based on this observation dichlorobenzoil peroxide is expected to follow the same tendency. It can thus be concluded that the use of dicumyl peroxide should result in the most heterogeneous vulcanizates to be produced. This was confirmed by the ratio of sol content for filled to unfilled vulcanizates, it is the largest when DCP is used. Silica exhibits the highest reinforcing activity in such vulcanizates. In this part of work activity of silica toward ethylene-propylene copolymer (EPM) crosslinked by different peroxides, also in the presence of coagents allyl maleate (AM) and methacrylamide (MA) was investigated.

It was established that in the peroxide-cured ethylene-propylene rubber only C-C crosslinks are present, whereas addition of monoallyl maleate salt resulted in the formation of two types of crosslinks: covalent C-C crosslinks and cluster-like ionic crosslinks [12]. Curing of rubbers in presence of unconventional crosslinking agents leads to obtaining vulcanizates of heterogeneous structure [13]. Their poor solubility in elastomer matrix makes the system microheterogeneous. Coagent of peroxide crosslinking used with ethylene-propylene rubber (ethylene glycol dimethacrylate) produced inclusions of several tens nanometers of dimensions in the elastomer matrix [14]. Two coagents of peroxide crosslinking, allyl maleate and acrylamide have been applied, expecting vulcanizates of more heterogeneous structure, in comparison to the pure peroxide ones, to be obtained.

The ratio of specific to covalent crosslinks in EPM vulcanizates containing AM and MA is approximately 10-20% (Table 6). Introduction of coagents into a mixture containing silica causes an increase of the concentration of bonds formed at the rubber-filler interphase crosslinks is on a level of 30-40%. Vulcanizates of EPM containing coagents display greater susceptibility to physical stress relaxation at room temperature than purely peroxide vulcanizates. It can therefore be postulated that the crosslinks arising with participation of coagents and SiO_2 are of a „slippery" nature. In such a case dissipation of critical stresses is facilitated, leading in consequence to increase of the tensile strenght of the vulcanizate. The activity of silica depend on the structure of the crosslinks in the elastomers. Specific crosslinks probably interact with the surface of the fillers. The carboxyl and amido groups can also be adsorbed on the surface of silica as a result of formation of hydrogen bonds. Calcium carbonate is a filler of a small specific surface area, it is inert and "not prone to adhesion" and its interactions with hydrocarbon elastomers are weak. It is undoubtedly the reason for the small influence created by the crosslinking system on the filler reinforcing activity in this particular case. It can be stated that the activity of calcium carbonate does not depend on the crosslinking system applied (Fig. 1).

Table 6. Crosslink density and mechanical properties of EPM vulcanizates.

Filler+ coagent	ν_E 10^5 mole/cm^3	$\Delta\nu_E$ 10^5 mole/cm^3	s,%	$\sigma^N_{100}/\sigma^0_{100}$	σ_{100} MPa	TS, MPa	E_B,%	n x10^3	R_H,%	H, %
none, none	5.48	0.13	8.2	-	1.0	2.3	416	46.0	36.2	16.4
none, AM	4.24	0.45	10.3	-	0.9	4.7	776	55.3	32.3	23.5
none, MA	10.17	2.42	7.4	-	1.1	3.8	500	57.4	32.7	24.8
none, AM+MA	5.56	1.47	11.3	-	1.0	6.2	782	62.4	32.4	31.2
SiO_2,none	10.80	3.71	9.4	1.7	1.7	12.1	792	84.2	20.7	61.3
SiO_2,AM	15.17	5.44	13.7	2.4	2.4	16.7	834	103.2	20.2	72.3
SiO_2,MA	21.61	9.19	4.3	2.4	2.4	17.9	705	124.1	20.3	84.7
SiO_2, AM+MA	14.64	4.80	8.7	2.3	2.3	19.0	794	136.2	18.4	84.7

n = -dlns/dlnt - relaxation rate, $R_H = H_5/H_1$ - Mullins effect, H - hysteresis losses.

Table 7. Activity of carbon black toward NR crosslinked with different crosslinking substances.

Curative system	Crosslink type, %			"a" coefficients[1)]			
	C-Sx-C x>3	C-S_2-C, C-S-C	C-C	N-221	N-330	N-550	N-990
S+DPG	90	8	2	2.52	2.42	2.33	1.91
S+DBTS	21	74	5	2.41	2.12	2.03	1.79
TMTD	-	22	78	2.08	1.85	1.75	1.70
DCP	-	-	100	1.80	1.79	1.73	1,65

1) Coefficient "a" from equilibrium swelling in Parks-Lorenz equation.

Influence of the crosslinking system on the surface activity of carbon black has also been studied. Relation between the activity of carbon black and the kind of crosslinks present in natural rubber (NR) is demonstrated in Table 7. Carbon black exhibits higher activity in vulcanizates with polysulphide than covalent (C-C) crosslinks. Adsorption of the components of the crosslinking system on the surface of carbon black could be demonstrated. It is likely to result in the change of elastomer-filler interactions, as well as the network structure and distribution of crosslinks. More distinct changes in filler activity, observed for carbon blacks of higher specific surface area i.e. of stronger reinforcing character are also worth mentioning. The higher the content of active carbon blacks in the compounded rubber, the lower the sulfidity of the crosslinks [1]. Such a

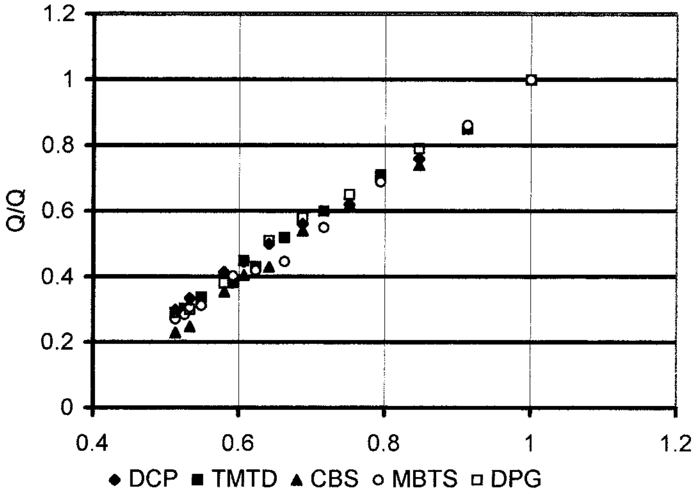

Figure 1. Influence of calcium carbonate content by weight (z) on the ratio of the equilibrium swelling (Q^F/Q^O) of NR vulcanizates.

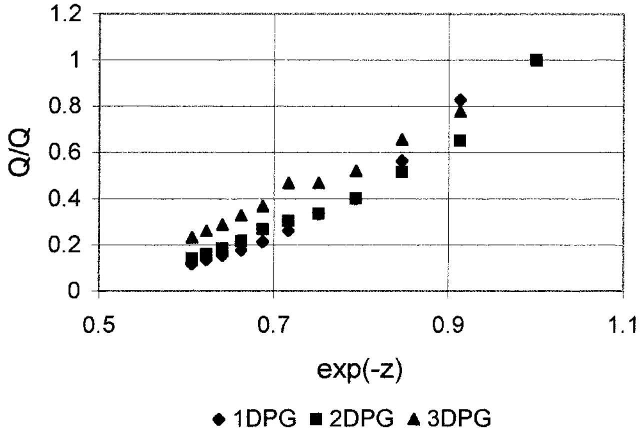

Figure 2. Influence of N 330 carbon black content by weight (z) on the ratio of the equilibrium swelling (Q^F/Q^O) of NR vulcanizates. The curatives contents (S/DPG) 1.1.8/1.5, 2. 2.0/2.4, 3. 3.6/3.0 phr.

result is likely to be the consequence of a higher concentration of crosslinking agent around filler. The evolution of the equilibrium swelling of the vulcanizates, as a function of filler content according to the formula of Parks & Lorentz [7], is linear for most of the samples studied. However, in the case of active carbon blacks, low concentrations of curing agents (S + DPG) result in a break of the linear character of Q_W at comparatively high content of the filler, in the range of 70-100 phr (Figure 2).The relation is again linear for higher concentrations of the curing agents. In our opinion the observed change in the Q_W behaviour results from the adsorption either of the whole curing system or of only the basic accelerator (DPG) onto the filler surface. In the case of highly filled vulcanizates almost the entire accelerator is probably adsorbed onto the filler surface. For higher amounts of the accelerator, changes in its distribution in the elastomer matrix are not significant. Changes in the linear relationship between Qw and filler loading are not observed if lewer adsorbatle accelerators are used. From the data illustrated in Figure 2 it can be concluded that the activity of the filler in sulphur vulcanizates depends on the crosslink density. Such effect is not observed in the case of peroxide crosslinking. For sulphur vulcanizates of low crosslinks density carbon black generally exhibits higher activity, which seems likely to be a result of a heterogeneous distribution of the crosslinks in the elastomeric matrix. It cannot be excluded, however, that for higher concentrations of crosslinking agent, the possibility of interactions between the filler particles, i.e. the ability to form the so-called "structure" is limited.

Conclusion

Silica interacts more strongly with polar substances than with aliphatic hydrocarbons, e.g. general-purpose rubbers.

Diphenylguanidine is readily adsorbed on silica. An accelerator with a more acid character than DPG, i.e. di(2-benzothiazolyl) disulphide, is adsorbed on the surface of silica in quantity that is about ten times lower. Adsorption of DPG leads to changes in the surface properties of silica, its capacity for forming three-dimensional „structure" is lowered. As a consequence the hydrodynamic effect, i.e. the influence of silica on the viscosity of the dispersion medium decreases.

Reinforcing action of active fillers depends on the kind of crosslinking system applied. It is very distinct in the case of carbon black of the high specific surface or silica. Activity of calcium carbonate does not depend on crosslinking system applied.

In our opinion, crosslinking agents adsorb on the filler surface, which leads to changes in elastomer-filler interactions. Adsorption of the crosslinking agents onto the filler surface results in a heterogeneous distribution of the crosslinks. Instead of being statistically distributed their distribution in elastomer matrix is probably bimodal. It positively affects the properties of the system.

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