

INFLUENCE OF THE WATER AND γ -AMINOPROPYL-TRIETHOXY SILANE ON THE PROPERTIES OF FILLED WITH SiO_2 STYREN BUTADIEN RUBBER

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ABSTRACT

It is known that the water adsorbed on the surface of mineral substances used as fillers in rubber blends influences their properties. In the present paper are summarized results on SBR based vulcanizates filled with SiO_2 (Vulkasil C, product of Bayer). Untreated and treated with ethylene glycol and γ -aminopropyl-3 ethoxy silane SiO_2 were used. A priori, 5 phr of water were added to some of the filler samples. By a capillary tube viscosimeter the rheological properties of rubber blends (in phr): SBR - 100; SiO_2 /containing water/ - 60; ZnO - 4; stearic acid - 1,5) were compared with the properties of SBR based blends, containing SiO_2 without added water. Considerable changes in the coefficient of consistency, flow index and especially in activation energy were found. The changes depend both on the filler treating and the water present in the filler. After adding of 1,5 phr of MBTS (accelerator) and 2 phr of sulfur the vulcanization isotherms of the blends were investigated with a Monsanto rheometer. The formal vulcanization kinetic was studied. It was found that within the extent of conversion in the range 0,1-0,9, the crosslinking may be described by an equation of a first order reaction. This gives an opportunity for rate constant and the activation energy of all blends to be determined. It was found that both the filler treating and the presence of water in it lead to changes in the above mentioned parameters.

The mechanical properties of vulcanizates with SiO_2 containing water were also studied.

Keywords: Aminopropyl-3-ethoxy silane, SiO_2 , water, SBR.

INTRODUCTION

The dispersion of the ingredients in the polymer matrix, as well as the interaction polymer - filler strongly influence the vulcanizates properties of rubber. In SiO_2 filled rubber compounds the absence of polymer - filler interactions leads to absence of bound rubber. In the same time the strong interaction among the SiO_2 particles due to the presence of OH- groups on their surfaces and hydrogen bonds formation leads to the appearance of aggregates filler particles. The aggregates are very strong and it is impossible to destroy them

during compounding [1, 2]. The absence of bound rubber together with the bad filler dispersion lead to lower reinforcing effect, decreased abrasion resistance and increased heat formation in the vulcanizates based on such rubber compounds.

It is well known that the presence of polar compounds or water improves the dispersion of SiO_2 and other mineral fillers in the rubber compounds by blocking the silanol groups on the surface [3, 4]. The presence of water leads to changes in the vulcanization characteristics of the rubber compounds, especially in SiO_2 - filled ones. In the last years for improving of the mechanical

and dynamic properties of the vulcanizates bifunctional organosilanes, which react chemically both with SiO₂ surface and rubber molecules are used. But these reactions have to be carried out under different conditions. The reaction between the silane and the filler have to be carried out during the compounding under the influence of the water, present in the filler. At the compounding temperature of 140°C the silane, methoxy, ethoxy, etc. groups hydrolyze and after that a condensation process with the silanol groups located on the SiO₂ surface may be observed. In some cases (trimethoxisil-1-propaniol) the mercapto group has a strong reactivity and causes a formation of polymer-filler and polymer-polymer bonds. In the above mentioned conditions of compounding this leads to considerable increasing of the compound viscosity. The reaction polymer-filler have to be carried out during the vulcanization process [5, 6].

As one can see from the described above, the water, present in SiO₂ - has an important role for the reaction between its surface and organosilanes during the preparation of the rubber compound.

The purpose of the present paper is to investigate the influence of different amounts of water and diethylene glycol on the properties of SiO₂ filled rubber compounds containing γ -aminopropyl-3-ethoxy silane.

EXPERIMENTAL

The composition of the rubber compounds used are shown in Table 1.

The basic rubber compound composition was as follows /in phr/:

SBR* - 100.0; Zink oxide - 4.0; Stearic acid - 1.5; SiO₂** - 60.0; MBTS - 1.5; Sulphur - 2.0. SBR* – Bulex 1500, Lukoil Bulgaria

SiO₂** - Vulcasil C, Bayer, containing 3% H₂O
 DEG - diethylene glycol
 APTES - γ -aminopropyl-3-ethoxy silane
 MBTS - dibenzothiazylsulfide

The rubber compounds without sulphur and accelerator are prepared with opened laboratory rolls. The prepared compounds are thermally treated in a Brabender Plasticorder at 150°C for 5 min. The purpose of the treatment is to imitate the real industrial compounding conditions and the reactions, running during compounding.

The dependences shear stress τ / - shear rate $\dot{\gamma}$ / at 122°C and 142°C and stresses of 2.11⁵-6.10⁵ Pa were obtained with capillary viscosimeter.

After addition of MBTS and sulphur the kinetic curves of vulcanization were obtained using a Monsanto rheometer. The rate constants and the activation energy of the vulcanization process are determined in accordance with [7].

RESULT AND DISCUSSION

The dependances $\ln \tau - \ln \dot{\gamma}$ may be approximated with straight lines, which gives the possibility to determine “K” and “n” using the Ostwald de Wild law:

$$\tau = k \cdot \dot{\gamma}^n, \quad (1)$$

where:

τ - shear stress

K – consistency coefficient

$\dot{\gamma}^n$ - shear rate

n – flow index,

as well as the activation energy of the viscous flow E_a . The results obtained are shown in Table 2.

It is obvious (Table 2) that the presence of an additional amount of water in SiO₂ leads to increasing of the consistency coefficient and the flow index of the rubber compounds; the addition of DEG decreases

Table 1. Compositions of the rubber compounds used.

Ingredients	Compound No					
	1	2	3	4	5	6
DEG	-	5	-	-	5	-
Water	-	-	5	-	-	5
APTES	-	-	-	5	5	5

Table 2. Rheological characteristics.

Characteristics	Compound No					
	1	2	3	4	5	6
Consistency coefficient, K						
122 °C	6,3.10 ⁶	5,4.10 ⁶	6,5.10 ⁶	6,0.10 ⁶	5,5.10 ⁶	5,25.10 ⁶
142 °C	5,6.10 ⁶	4,9.10 ⁶	6,0.10 ⁶	5,5.10 ⁶	4,8.10 ⁶	4,9.10 ⁶
Flow index, n						
122 °C	0,15	0,17	0,12	0,19	0,21	0,21
142 °C	0,14	0,16	0,11	0,18	0,21	0,21
E _a , kJ/mol	29,0	19,0	22,0	21,0	24,0	20,0

Table 3. Vulcanization characteristics.

Characteristics	Compound No					
	1	2	3	4	5	6
160 °C						
ΔM, dN.m	32	30	34	45	46	36
T ₉₀ , min	47	7,2	23	21	3,6	5,5
tg φ	0,21	0,13	0,16	0,20	0,14	0,18
180 °C						
ΔM, dN.m	39	36	29	41	39	36
T ₉₀ , min	11	2,6	5	8	2,2	2,5
tg φ	0,19	0,15	0,19	0,19	0,15	0,20
E _a , kJ/mol	140	91	116	58	51	110

these characteristics. Probably this may be explained with different mechanisms of interaction of these substances with the silanol groups located on the SiO₂ surfaces. The addition of both substances leads to decreasing of E_a. The presence of APTES also leads to increasing of E_a. APTES interacts chemically with the silanol groups on SiO₂ surface and thus the particles surface becomes hydrophobic. DEG and water do not change K, n and E_a of the rubber compounds, containing APTES, because it is impossible for them to have an influence on a hydrophobic surface.

The most important vulcanization characteristics obtained with the Monsanto rheometer are shown in Table 3. It is obvious that SiO₂ filled rubber compounds without other additives have an increased optimum vulcanization time (47 min), due to adsorption of

the accelerator and sulphur on the SiO₂ surface. The addition of DEG decreases the optimum vulcanization time. Its adsorption on the filler surface makes more difficult the adsorption of the accelerators and sulphur on this surface. The results obtained confirm this assumption. Water has a similar action, but its influence is not so strongly expressed. E_a decreases from 140 kJ/mol to 91 kJ/mol in the presence of DEG and to 116 kJ/mol in the presence of water. ΔM (we accept that it is a measure for the vulcanization net density) does not change significantly. Rubber compounds containing APTES have T₉₀ similar to the compounds, containing water (23 min), but shorter than the compounds, containing DEG (7 min). ΔM has a considerably higher value, but the activation energy of the vulcanization is lower. This may be explained with the action of the amino group as a secondary vulcanization accelerator and with the possibility for formation of polymer-filler bonds by

aminosilane.

The addition of DEG to rubber compounds, containing APTES leads to decreasing of optimum vulcanization time, but does not change the vulcanization net density and activation energy. The presence of water in the rubber compounds, containing APTES also leads to decreasing of T₉₀, but in the same time to decreasing of ΔM and increasing of E_a. The latter may be due to the water action, especially by blocking the activity of amino groups.

The mechanical characteristics of the vulcanizates are shown in Table 4. The addition of DEG and water in the rubber compounds leads to decreasing of M₃₀₀ (modulus at 300 % of deformation). This may be due to decreased interaction forces among the filler particles and their better dispersion in the rubber matrix. As a result

Table 4. Mechanical characteristics of the vulcanizates investigated.

Characteristics	Compound No					
	1	2	3	4	5	6
Modulus at 300 % of deformation, MPa	6,0	3,7	5,0	8,0	7,7	7,5
Tensile strength, MPa	20,0	24,0	23,0	24,7	26,5	24,6
Relative elongation ϵ_1 , %	760	780	760	680	640	660
Residual elongation ϵ_2 , %	50	50	40	30	30	30
Hardness, Shore A	75	70	75	71	68	74
Abrasion resistance, mm ³	160	133	108	56	76	90

the tensile strength and abrasion resistance increase. The presence of APTES leads to increasing of M_{300} , the tensile strength and the abrasion resistance. APTES decreases the interactions among the filler particles, improves their dispersion and forms polymer-filler bonds. The presence of DEG and water in the rubber compounds, containing APTES does not change significantly the tensile strength, but decreases the abrasion resistance. Probably these substances make more difficult the formation of polymer - filler bonds.

CONCLUSIONS

The presence of 3 % of water is enough for hydrolization of the APTES ethoxy groups and their reaction with silanol groups located on SiO₂ surface. The presence of APTES in SiO₂ filled rubber compounds improves their vulcanization characteristics and vulcanizates' mechanical properties. The presence of an additional amount of water in SiO₂ filled rubber compounds containing APTES does not lead to improving both of the rheological and vulcanization characteris-

tics as one can see in SiO₂ filled samples without APTES. The addition of water in SiO₂ filled rubber compounds containing APTES decreases some of their mechanical properties.

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