

# Reinforcement of Styrene-Butadiene Rubber with Silica Modified by Silane Coupling Agents: Experimental and Theoretical Chemistry Study

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**Abstract** The properties of styrene-butadiene rubber (SBR) reinforced by modified silica was investigated according to national standards. Silica was modified by silane coupling agents KH-570, KH-590, and KH-792. The optimized geometries of molecular modified silica reinforced SBR were obtained by using B3LYP calculation of density functional theory with the 6-31+G basis sets. The natural bond orbital analyses were carried out. The Si—O bond length of silica modified by KH-792 was the shortest and the electronegative of O was the highest. It indicated that the connection between silica and KH-792 was the tightest. Higher tensile strength and elongation of reinforced SBR was obtained by silica modified with the KH-792. It was caused by large delocalization of lone pair electrons of the two N atoms in KH-792. The S—C bond length in silica modified by KH-590 was longer than the ordinary S—C bond length. Then the sulfur free radical ( $\cdot S$ ) was produced more easily in vulcanization. The degree of crosslink was increased by the cross-linkage of the rubber molecule and the sulfur free radical. That was why the highest stress and tear strength of reinforced SBR was produced when silane coupling agent KH-590 was used. The calculation results was in accord with experimental data.

**Keywords** silane coupling agent, silica, styrene-butadiene rubber

## 1 INTRODUCTION

Silica is an important filling materials in rubber industry. The application in rubber process was restricted by its less processability compared with carbon black once a time<sup>[1]</sup>. The first application of composite polymer materials silane coupling agents in real process was in 1947 by Ralph<sup>[2]</sup>. He made the polyester complex material from fiberglass cured with propenyl-trimethoysilane. Double intensity of the material was obtained. It was found that the silane coupling agents can enhance the consistency between silica and rubber, and improve processability and mechanical property of rubber. In 1970s, the application of silica in rubber process increased remarkably<sup>[3–5]</sup>. At the same time, the research and development of the silane coupling agents expanded rapidly. The study of mechanism of the silane coupling agents was begun in 1960s. The four step reaction model of the process was put forward by Arkles<sup>[6]</sup>. In this model, there was usually only one bond from each silica to the substrate surface, and the other two silanol groups were present either in condensed or free form<sup>[6]</sup>. The relative stability of the organosilane bonded to silica-surface with Schiffs base

was measured<sup>[7]</sup>. The interaction of triethoxysilane (TES) and bis[3-triethoxysilylpropyl]-tetrasulfane (TESPT) with silica was studied by means of IR spectroscopy<sup>[8]</sup>. The spectral features of Si—O bonded were identified. The IR spectra showed that the treatment of silica with TES (or TESPT) strongly decreased the amount of adsorbed water, whereas two Si—O—Si bridges were formed between TES (or TESPT) and the silica surface. Now, more analytic instrument is brought to get the surface information of material and study the reinforce ageing process of complex material. The chemical bond theory has been put forth to explain the mechanism of the silane coupling agents<sup>[9–12]</sup>.

Quantum chemistry deals with atoms and molecules based on their electronic structure and motion, and unveil the relationship between the property of materials and the strange quantum effects<sup>[13]</sup>. By quantum chemistry, general conclusions can be drawn at the level of electrons. Then the vital prediction of chemical activities can be acted as the guidance for further investigation<sup>[14,15]</sup>. In this paper, quantum chemistry computation is employed to investigate the

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difference of chemical bonds formed by different silane coupling agents, silicon and styrene-butadiene rubber (SBR). The correlation between the mechanical property and the chemical bonds is analyzed on the basis of the differences. The computation results are compared with the experimental results.

## 2 EXPERIMENTAL

Rubber was mixed with all compounding ingredients under the same conditions adopted. The vulcanization of the rubber compounds were carried out at 150°C for the pre-determined optimum cure time. A tensile tester (SANS 4104, Shenzhen) was used for the determination of tensile properties.

## 3 CALCULATION METHOD

The representation structures of silica modified with silane coupling agents was simplified. Atom Si of silica connects with silane coupling agent by only one Si—O—Si bond, and the other three bonds of Si are saturated by a hydroxyl group respectively<sup>[16]</sup>. Only one unit of structure of SBR was involved in calculation. With the organic groups of silane coupling agents, SBR can be bonded to modified silica. Density functional theory (DFT) calculations were carried out using Becke-Lee-Yang-Parr's three-parameter hybrid function<sup>[17]</sup> (referred as B3LYP). The geometry optimizations were obtained with B3LYP/6-31+G basis set. Then the natural bond orbital (NBO) computations at the optimized structures were done subsequently. All calculations were performed with the GAUSSIAN 98 program suite on a SGI1450 workstation.

## 4 RESULTS AND DISCUSSION

### 4.1 Experimental results

Table 1 shows the effect of silica modified by silane coupling agents on the properties of reinforced SBR. The maximum 100% stress, 300% stress and

tear strength of reinforced SBR were obtained by silica modified by KH-590. On the other hand, more excellent tensile strength and elongation of cured SBR were expressed when silica was modified by KH-792.

### 4.2 Geometry optimization and NBO analysis of silica modified with silane coupling agents

Figures 1, 2 and 3 schematically depict the

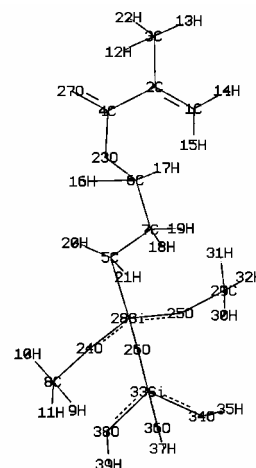


Figure 1 Configuration of KH-570 grafted on the surface of silica

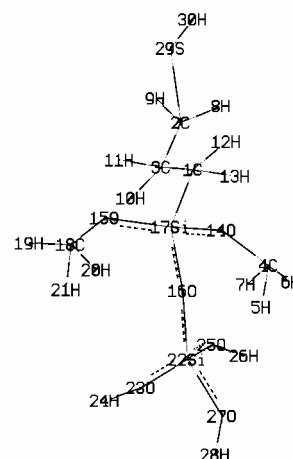


Figure 2 Configuration of KH-590 grafted on the surface of silica

Table 1 The effects of silica modified by silane coupling agents on the properties of reinforced SBR

Properties	Silica	Silica (KH-590)	Silica (KH-792)	Silica (KH-570)
hardness (Shore A)	55	57	57	58
100% stress, MPa	1.04	1.25	1.07	1.18
300% stress, MPa	2.1	3.18	2.34	2.58
tensile strength, MPa	6.3	10.8	13.0	7.8
elongation, %	574	550	652	555
permanent set	12	8	8	8
tear strength, kN·m <sup>-1</sup>	20.9	21.4	19.4	19.5

**Table 2** The bond lengths (nm) of silane coupling agents grafted on the silicon optimized by B3LYP/ 6 31+G

No.	Silica modified with KH-590				Silica modified with KH-792				Silica modified with KH-570			
	atom	bond	bond length	PCN	atom	bond	bond length	PCN	atom	bond	bond length	PCN
1	C	R(1,2)	0.1346	-0.4748	C	R(1,3)	0.1544	-1.1908	C	R(1,2)	0.1544	-0.3915
2	C	R(1,14)	0.1086	0.6366	C	R(1,12)	0.1096	-0.9093	C	R(1,35)	0.1105	-0.2439
3	C	R(1,15)	0.1085	-0.8104	C	R(1,13)	0.1099	-0.1316	C	R(1,36)	0.1097	-1.2539
4	C	R(2,3)	0.1510	0.0537	C	R(1,17)	0.1884	-0.4210	C	R(1,37)	0.1471	-0.8192
5	C	R(2,4)	0.1500	-1.3528	H	R(2,3)	0.1532	0.2462	C	R(2,31)	0.1467	0.1422
6	C	R(3,12)	0.1098	-0.7517	H	R(2,8)	0.1094	0.1813	C	R(2,33)	0.1096	-0.4203
7	C	R(3,13)	0.1094	0.1361	H	R(2,9)	0.1093	0.1929	H	R(2,34)	0.1100	0.2435
8	C	R(3,22)	0.1096	-0.4293	H	R(2,29)	0.1918	0.2309	H	R(3,5)	0.1542	0.1796
9	H	R(4,23)	0.1384	0.2462	H	R(3,10)	0.1100	0.2339	H	R(3,14)	0.1096	0.1910
10	H	R(4,27)	0.1235	0.1831	H	R(3,11)	0.1097	0.21157	H	R(3,15)	0.1100	0.1839
11	H	R(5,7)	0.1543	0.1939	H	R(4,5)	0.1095	0.2506	H	R(3,19)	0.1880	0.1721
12	H	R(5,20)	0.1096	0.2150	H	R(4,6)	0.1096	0.2558	H	R(4,5)	0.1543	0.1899
13	H	R(5,21)	0.1099	0.1913	H	R(4,7)	0.1093	0.2216	H	R(4,10)	0.1098	0.2163
14	H	R(5,28)	0.1884	0.1794	O	R(4,14)	0.1456	-0.7850	H	R(4,11)	0.1108	0.2746
15	H	R(6,7)	0.1525	0.1932	O	R(14,17)	0.1704	-0.7539	H	R(4,31)	0.1471	0.2149
16	H	R(6,16)	0.1096	0.2140	O	R(15,17)	0.1702	-1.2187	O	R(5,12)	0.1100	-0.7895
17	H	R(6,17)	0.1093	0.2111	Si	R(15,18)	0.1455	2.3109	O	R(5,13)	0.1098	-0.7701
18	H	R(6,23)	0.1483	0.2065	C	R(16,17)	0.1702	-0.3713	O	R(6,7)	0.1095	-1.2201
19	H	R(7,18)	0.1100	0.2338	H	R(16,22)	0.1652	0.1957	Si	R(6,8)	0.1097	2.3279
20	H	R(7,19)	0.1096	0.2763	H	R(18,19)	0.1092	0.2060	C	R(6,9)	0.1093	-0.3876
21	H	R(8,9)	0.1095	0.2236	H	R(18,20)	0.1095	0.1978	H	R(6,16)	0.1455	0.2064
22	H	R(8,10)	0.1096	0.2432	Si	R(18,21)	0.1096	2.4841	H	R(16,19)	0.1708	0.19661
23	O	R(8,11)	0.1092	-0.2130	O	R(22,23)	0.1697	-1.0712	H	R(17,19)	0.1705	0.1920
24	O	R(8,24)	0.1456	-0.7894	H	R(22,25)	0.1705	0.4784	Si	R(17,20)	0.1454	2.5106
25	O	R(24,28)	0.1703	-0.7771	O	R(22,27)	0.1702	-1.0647	O	R(18,19)	0.1703	-1.0657
26	O	R(25,28)	0.1703	-1.1973	H	R(23,24)	0.0970	0.4728	H	R(18,24)	0.1650	0.4752
27	O	R(25,29)	0.1455	-0.3758	O	R(25,26)	0.0969	-1.0843	O	R(20,21)	0.1095	-1.0686
28	Si	R(26,28)	0.1702	2.4365	H	R(27,28)	0.0970	0.4954	H	R(20,22)	0.1097	0.4727
29	C	R(26,33)	0.1652	-0.3964	S	R(29,30)	0.1380	0.0904	O	R(20,23)	0.1092	-1.0801
30	H	R(29,30)	0.1095	0.2095	H			0.0459	H	R(24,25)	0.1699	0.4937
31	H	R(29,31)	0.1096	0.1975					N	R(24,27)	0.1706	-0.3901
32	H	R(29,32)	0.1092	0.1943					H	R(24,29)	0.1702	0.3716
33	Si	R(33,34)	0.1698	2.4660					H	R(25,26)	0.0970	0.1889
34	O	R(33,36)	0.1705	-1.0683					H	R(27,28)	0.0969	0.1847
35	H	R(33,38)	0.1702	0.4782					H	R(29,30)	0.0970	0.1711
36	O	R(34,35)	0.0970	-1.0655					H	R(31,32)	0.1016	0.1894
37	H	R(36,37)	0.0969	0.4730					N	R(37,38)	0.1012	-0.7751
38	O	R(38,39)	0.0907	-1.0865					H	R(37,39)	0.1014	0.3444
39	H			0.4961					H			0.3421

Note: PCN—pure charge number obtained by Mulliken population.

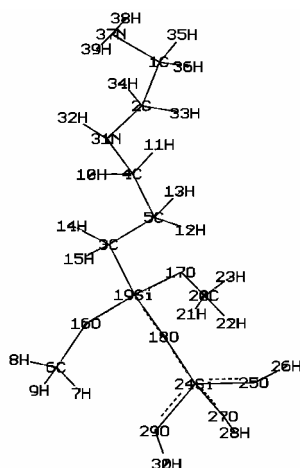


Figure 3 Configuration of KH-792 grafted on the surface of silica

structures of silica modified by silane coupling agents. The optimized geometric parameters are listed in Table 2. The NBO results of silica bond to silane coupling agents are shown in Table 3.

All the Si—O bonds joining the silica with silane coupling agents showed double-bond property in the three optimized structures. However, differences occurred in bond length and Mulliken population. The shortest bond length of Si—O was formed by silica and KH-792. It was 1.650. The charge of O atom obtained by Mulliken population had the largest number, 1.220. It implied that higher electronegativity of O atom was gained. The Si—O bond lengths connecting KH-590 and KH-570 with silica were almost the same. A difference occurred in electronegativity of O atom. The values were 1.219 and 1.197 respectively. NBO results revealed that all the Si—O bonds were composed by  $sp$  hybridization of O atom and  $sp^3$  hybridization of Si, but the occupancies were different. The largest orbital occupancy of Si—O bond was also gained by KH-792 grafted on silica, it was 1.9856. The other two orbital occupancies of Si—O bond were 1.9850 and 1.9849. Both results of optimization and NBO suggested that linkage of silica and KH-792 was the tightest.

It was worth noted that the S—C bond length of KH-590 grafted on silica in the optimized structure was longer than ordinary S—C bond length. We can deduce that the bond is broken more easily in vulcanization. Otherwise, the delocalization of atom N34 of KH-792 grafted on silica was notable. The calculated result of highest occupied molecular orbital (HOMO) is shown in Fig.4 (The structure was optimized and the corresponding geometric parameters are listed in Table 2. The atoms numbers were omitted to display the electronic cloud more clearly. The atoms have to the same numbers as shown in Fig.3. There was a large electronic sharing region between atom N34 and adjacent atom C. Delocalization make the chemical bond between the KH-792 and SBR form more easily.

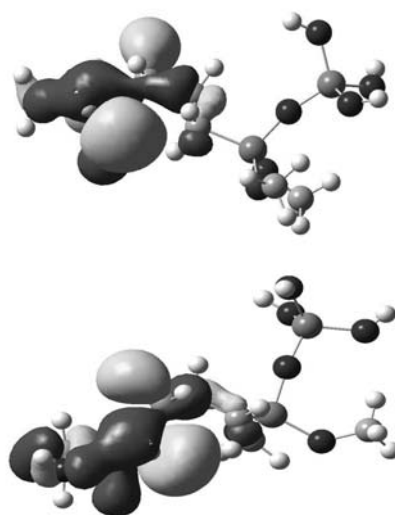


Figure 4 The HOMO of silica bonding with KH-792

#### 4.3 Calculation results of reinforced SBR with silica modified by silane coupling agents

The silica modified by silane coupling agents was filled in SBR as reinforcement. In calculations, the silane coupling agents connected to SBR through the organic groups. Then NBO calculations for the optimized structures were carried out. The NBO results of organic

Table 3 NBO results of modified silica connected SBR by organic group of silane coupling agents

Coupling agent	Atoms	Type of bond	Composed of bond	Orbital occupancies
KH-570	O26-Si33	BD	$\sigma_{\text{SiO}}=0.926(sp1.24)\text{O} + 0.377(sp2.91)\text{Si}$	1.9850
KH-590	O16-Si22	BD	$\sigma_{\text{SiO}}=0.926(sp1.24)\text{O} + 0.377(sp2.92)\text{Si}$	1.9849
KH-792	O18-Si24	BD	$\sigma_{\text{OSi}}=0.926(sp1.22)\text{O} + 0.378(sp2.91)\text{Si}$	1.9856

Note: BD—2-center bond.

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**Table 4** NBO results of modified silica connected SBR by organic group of silane coupling agents

Coupling agent	Atoms	Type of bond	Composed of bond	Occupancies of the orbital	$E(2)$ kJ·mol <sup>-1</sup>
KH-570	C—C	BD	$\sigma_{CC}=0.715(sp1.57)C + 0.699(sp1.54)C$	1.9903	9.33
	C—C	BD	$\pi_{CC}=0.699(2p)C + 0.715(2p)C$	1.9764	12.64
KH-590	C—S	BD	$\sigma_{CS}=0.721(sp4.34)C + 0.693(sp5.61)S$	1.9843	7.91
	S	LP		1.9673	14.91
KH-792	C—C	BD	$\sigma_{CC}=0.704(sp2.82)C + 0.710(sp2.66)C$	1.9857	6.36
	C—N	BD	$\sigma_{CN}=0.628(sp3.68)C + 0.779(sp2.19)N$	1.9891	10.09
	N	LP		1.9673	35.54

Note: BD—2-center bond;

LP—1-center valence lone pair ;

$E(2)$ —stabilization energy, estimated by means of second-order perturbation theory, which associates with the interactions of electronic donor-acceptor in molecule. Larger value suggests stronger delocalization tendency of electronic donor.

groups bond to SBR are shown in Table 4.

In addition, both lone pair electrons of N atoms in filler silica modified by KH-792 exhibited extremely strong delocalization tendency. Except the N atoms bonded to SBR, the lone pair electrons of another N atom also had large  $E(2)$  value, 40.62kJ·mol<sup>-1</sup>.

The experimental and calculation results indicated that silane coupling agents affected properties of reinforced SBR. The effects were caused by the differences of bonds between silica, silane coupling agents and SBR.

The molecular formula of KH-590 grafted on silica can be written as HS—(CH<sub>2</sub>)<sub>3</sub>—Si—O—Si(OH)<sub>3</sub>. The bond length of S—C in the optimized geometry was 1.97, longer than the ordinary bond length. More over, atom S appeared strong electron donor features. All these resulted in that sulfur free radical ( $\cdot S\cdot$ ) can be released easily in vulcanization. The degree of crosslink of rubber was increased by the linkages of sulfur free radical and rubber. The excellent stress and tear strength were the result of increased crosslink. However, high crosslink was an obstacle of stretch, so the tensile strength and elongation were not so good.

Compared the NBO result of SBR filled by silica modified by KH-570 with that by KH-792, higher electronic density occurred in silica modified by KH-570. The occupancy of valance bond  $\sigma_{CC}$ , bonding the silica modified by KH-570, was 1.9903, while the occupancy of valance bond  $\sigma_{CN}$ , bonding the silica modified by KH-792, was only 1.9843. That was the reason why the SBR with silica modified by KH-570 had larger stress strength.

At the same time, both lone pair electrons of N atoms in KH-792 exhibited extremely strong delocalization tendency to the carbon chain between them, which means that the lone pairs moved in this large region. The extra tensile strength and elongation came from that.

From the analysis, the calculation results agree with experimental results very well.

## 5 CONCLUSIONS

The properties of SBR reinforced by modified silica was measured. Quantum chemistry computation was employed to investigate the difference of chemical bond formed by different silane coupling agents, silicon and SBR. The main conclusions are drawn as follows:

(1) Silane coupling agents affect the properties of SBR reinforced by modified silica. The greatest stress and tear strength of reinforced SBR was obtained when the filler was modified by KH-590. Excellent tensile strength and elongation were exhibited when the filler was modified by KH-792.

(2) Calculation results indicate that the bonding between silica and KH-792 is the tightest. Large delocalization of lone pair electrons of the N atoms in KH-792 is responsible for the highest tensile strength and elongation of reinforced SBR. The longer S—C bond make the sulfur free radical ( $\cdot S\cdot$ ) produce easily in vulcanization. That is the reason why SBR has excellent exhibition in stress and tear strength when KH-590 is used in the system.

The effect of silane coupling agents on the prop-

erties of SBR is relied on the different bond formed by silica, silane coupling agents and SBR. The insight into the relationship is discovered from the point of microcosmic view. The calculation results are in agreement with experimental data.

## NOMENCLATURE

$E(2)$	stabilization energy, $\text{kJ}\cdot\text{mol}^{-1}$
$\sigma_{ab}$	$\sigma$ valence bond between atoms $a$ and $b$
$\pi_{ab}$	$\pi$ valence bond between atoms $a$ and $b$

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