

Effect of silanes as crosslinking agent with the NBR rubber

Sunil padhiyar¹, Darshan Shah²

Student of M.E., Department of Rubber Technology, L.D. College of Engineering, Ahmedabad, Gujarat, India¹

M.Tech from IIT kharagpur, Businessmen, India²

Abstract: Silane coupling agent generally use as improve the properties of white filler use in rubber compound for better dispersion. Also silane coupling agent reacts with organic filler & polymer chain as crosslink. Here in this research study the crosslink density & swelling phenomena of silane participate in vulcanization process with Nitrile rubber compound. Also show the comparisons of carbon filled and silica filled NBR rubber compound crosslink density property. Silanes increase the viscosity of compound, crosslink density with low swelling resistance.

Keywords: Use as curative in rubber curing systems.

I. INTRODUCTION

A. The Coupling Agents

There are several types of coupling agents commercially available, including silanes, titanates, zirconates, zircoaluminates, carboxylated polypropylenes, chromates, chlorinated paraffins, organosilicon chemicals, and reactive celluloses. Of these, the organosilanes and titanates are the most widely used for modifying mineral surfaces. The other surface modifiers are more narrowly used where they offer specific advantages in handling or performance.

B. Silanes

Silane coupling agents were first developed for thermoset composites, with organofunctional groups chosen to participate in the crosslinking reaction – amino for melamine or vinyl for unsaturated polyester, for example. In thermoplastics designed to be unreactive under processing conditions, predicting the most appropriate organofunctional group is more complicated.

The general chemical structure of organosilanes is $RSiX_3$,

Where X is a hydrolyzable group, such as methoxy, ethoxy, acetoxy, or chloride, and R is a nonhydrolyzable organofunctional group. Most commercial silanes are alkoxy derivatives, $RSi(OR')_3$, the most common of which follow.

Table 1 Common Commercial Organosilanes

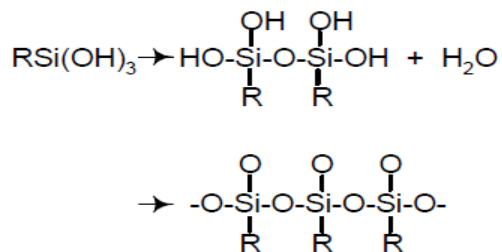
Silane Type	Chemical Name
Amino	Aminopropyltriethoxysilane
Diamino	N-(2-aminoethyl)-3-amino-propyltrimethoxysilane
Methacrylate	3-Methacryloxypropyltrimethoxysilane
Epoxy	3-Glycidoxypropyltrimethoxysilane
Mercapto	3-Mercaptopropyltrimethoxysilane
Vinyl	Vinyltrimethoxysilane
Chloro	3-Chloropropyltriethoxysilane
Alkyl	Methyltrimethoxysilane
Styrylamine	3[2-
Silazane	Hexamethyldisilazane
Triamino	Aminoethylaminoethylaminopropyltrimethoxysilane
Phenyl	Phenyltrimethoxysilane

Hydrolysis of an alkoxy silane forms silanetriol and alcohol.



The rate of hydrolysis depends on the nature of the hydrolyzable group. The most rapid hydrolysis occurs with -Cl, followed by -OOCCH₃, -OCH₃, -C₂H₅, and -OC₃H₇. The formation of the respective acids, hydrochloric and acetic, or alcohols as a byproduct of silane hydrolysis necessitates proper venting in use.

The silanetriol will slowly condense to form oligomers and siloxane polymers.



The -Si-OH groups of the silanetriol or oligomer are believed to initially hydrogen bond with -OH groups on the mineral surface. These -OH groups are from aluminols (e.g., on aluminum trihydrate) or silanols. Since the silicas and silicates that are successfully silane modified generally lack structural silanols, these are ascribed to silanols formed by the reaction of silica surfaces and adsorbed water. This would provide silanol groups in sufficient numbers and distribution to enable uniform silane coating.

The reaction of silanetriol or oligomer with mineral surface -OH may ultimately result in the condensation of siloxane polymer, essentially encapsulating the mineral particle. Silane treatment levels, typically 0.5 to 2.0% on mineral weight, are usually adjusted according to particle size and surface area in order to form a monomolecular layer. This most cost-effectively provides the desired organofunctional surface. If excess silane is present, polymerization results in several molecular layers.

Most commercial silanes are low viscosity liquids with a long shelf life as long as they are kept free of moisture. Exposure to water causes hydrolysis and eventual polymerization, at which point usefulness as a mineral treatment is effectively lost. The exception is aminosilanes, which hydrolyze in water but remain soluble and resistant to polymerization.

Coating or encapsulation of the mineral particle creates a hydrophobic surface from the organofunctional group on the silane. This can range from nonreactive alkyl groups, to reactive epoxy, mercapto, and vinyl groups, among others. The choice of silane organofunctionality is guided by chemical compatibility of silane and matrix, treatment method and conditions, and the particular composite properties targeted for improvement. General recommendations are:

Table 2 Uses of Silane Organofunctional group with polymer

II. EXPERIMENTAL WORKS

A. MATERIALS & FORMULATION

The formulation used in this study is shown in Table 3 given below. The mixing process done in open mixing mill as per standard mixing process, add silane coupling agent at first with rubber. Here with nitrile rubber different proportion of silanes are used & check the crosslink density, swelling immersion, compression set resistance.

	S-1	S-2	S-3	S-4	S-5	S-6
NITRILE 3445	100	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	5	5	5	5	5	5
St. ACID	1	1	1	1	1	1
HAF carbon	50	50	50	0	0	0
Silica	0	0	0	50	50	50
DOP	5	5	5	5	5	5
DEG	0	0	0	2	2	2
Si -69	0	2	4	0	2	4
SP 1068	4	4	4	4	4	4
MBTS	1.5	1.5	1.5	1.5	1.5	1.5

Table 3. Formulation

Above in table mention all ingredients are standard & fresh it mix on open mixing mill add silane Si 69 with polymer so it mix uniformly in polymer chain. Here formulation silane affected carbon black filled compound & same proportion with silica filled compound which property it improve. Mixing mill temp is 70 Degree C curing done in hand press for 15 min at 150 degree C. with silane coupling agent rubber filler mixing time is less & good dispersion shown on mill.

B. RESULTS AND TESING

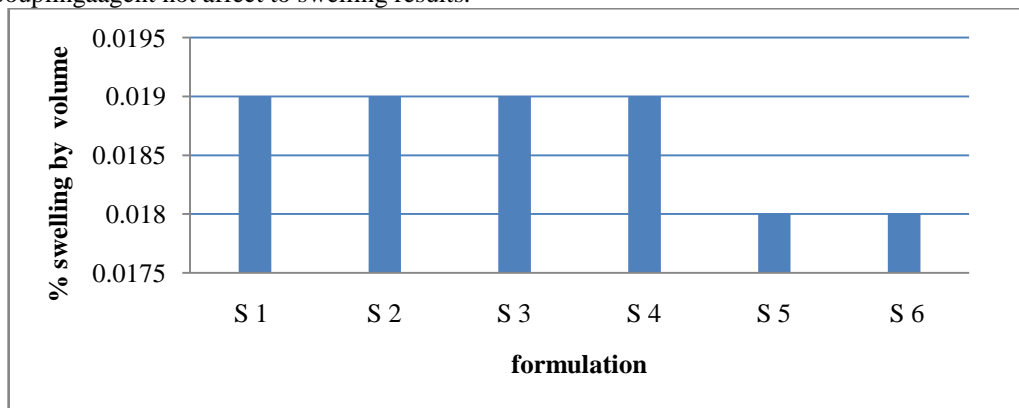
For the crosslink density check further test which is mention blow table & graphs.

- Rheometer results: as shown in below table 4. Here with the increasing the silane dosage cure rate reduces. It means silane work as curative in this compound. Also minimum torque ML and maximum torque MH is reduced with silane Si -69add, because of the silane is also work as tackifier so it reduces the viscosity. Scorch time is increase with the silane Si-69.

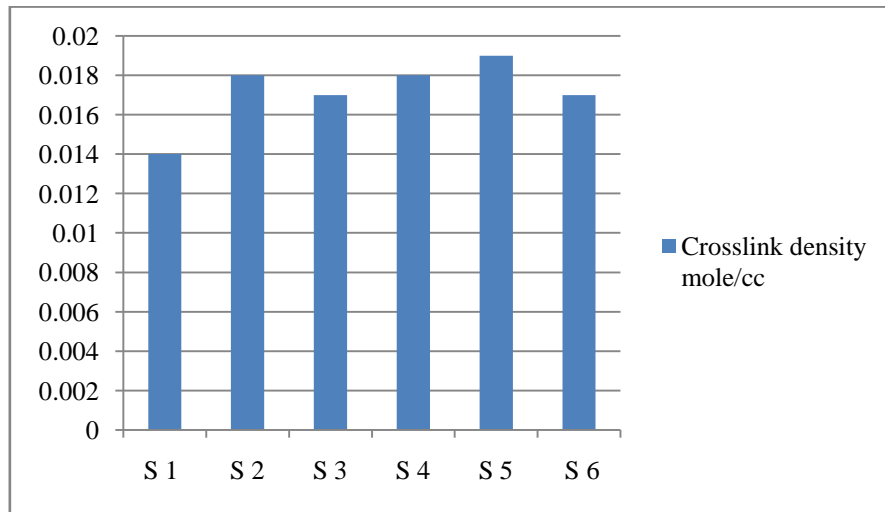
Formulation on C.B.	S 1	S 2	S 3	S 4	S 5	S 6
Rheometer property	(Arc 3, temp - 150 C, time 15 min.)					
Minimum torque ML	10.78	9.55	8.55	21.44	16.44	14.33
Maximum torque MH	55.56	43.11	35.89	48.22	42.22	41.66
Induction time Ts2	2.52	3.15	3.53	6.35	6.19	5.46
Scorch time Ts5	3.28	4.14	5.08	7.25	7.35	7.09
Optimum cure time Tc90	9.59	11.51	12.21	12.31	13.23	13.29
Cure rate	14.14	11.96	11.52	16.78	14.2	12.77

Table 4. Rheometer properties

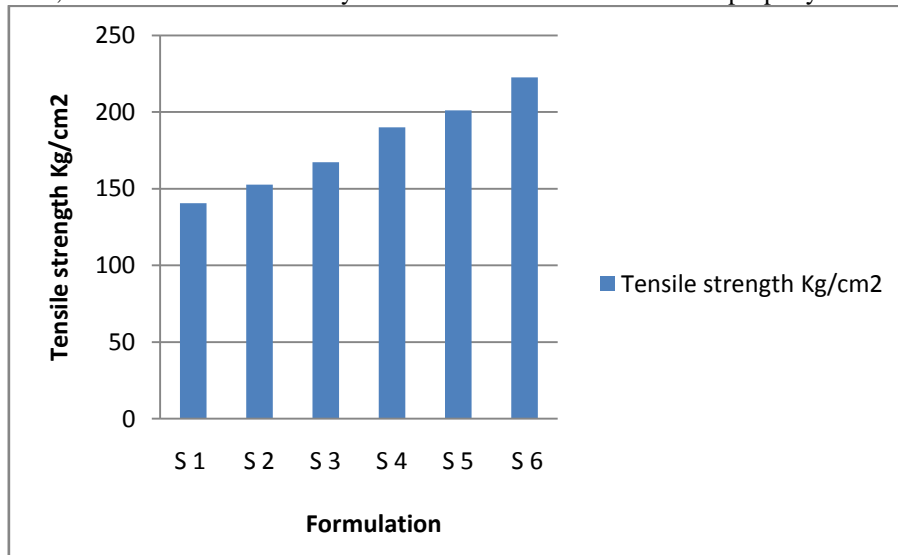
- Swelling phenomena: In this test NBR rubber not shows as much in toluene solvent. But comparison with silane percent swelling is less in formula S 3 & S 6 with the dosage of silane is 4% is optimum value. Silane coupling agent not affect to swelling results.



- Crosslink density: Crosslink density is measure by use the florry huggins equation with the swelling data. Also in graph shows crosslink density increase with silane Si-69 uses.



➤ Tensile strength: With the increase the silane percent increase the tensile strength. So it means that crosslink density is increase, Also increase the viscosity of rubber with abrasion resistance property.



III. CONCLUSION

A conclusion is by using 4 % silane coupling agent we get better physical & rheometric properties also increase crosslinking density of polymer with sulfur vulcanization as well as peroxide vulcanization. Silane coupling agent basically work as catalyst in curing process it does not work alone with polymers. Here only mercapto base silane Si-69 use so for further types of silanes I say that it also depends on their structure & properties.

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