

Tire Tech expo 2021

Influence of functionalized S-SBR on silica-filled rubber compound properties

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1 University of Twente, 2 Asahi Kasei Europe GmbH

UNIVERSITY
OF TWENTE.

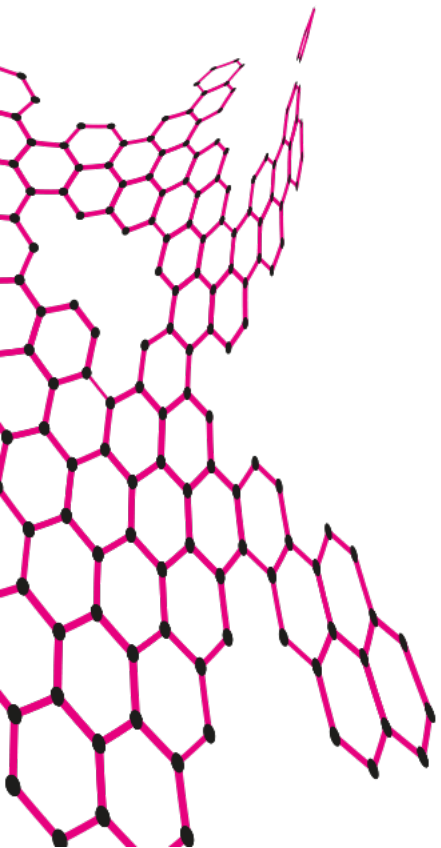
Elastomer Technology and Engineering
Engineering Technology (ET)

AsahiKASEI

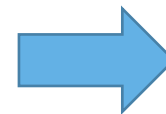
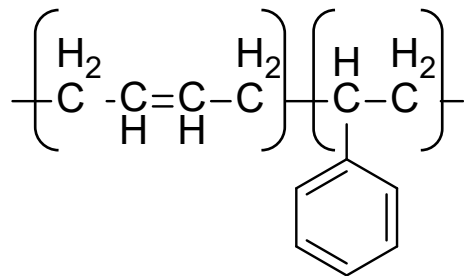
Rubber for Tread of Tire

Tread

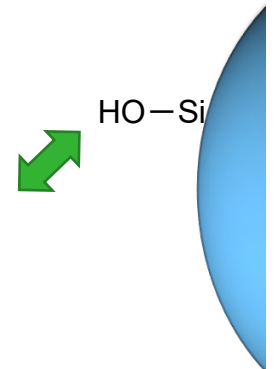
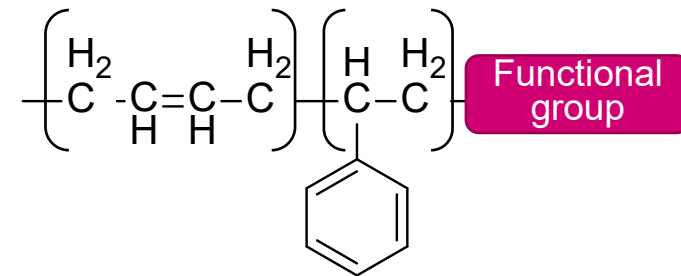
Performance	Material
<ul style="list-style-type: none"> ● Low-RR ● Grip ● Wear resistance 	SBR
	NR
	BR
	Silane
	Filler (Silica)
	Oil Resin



SBR



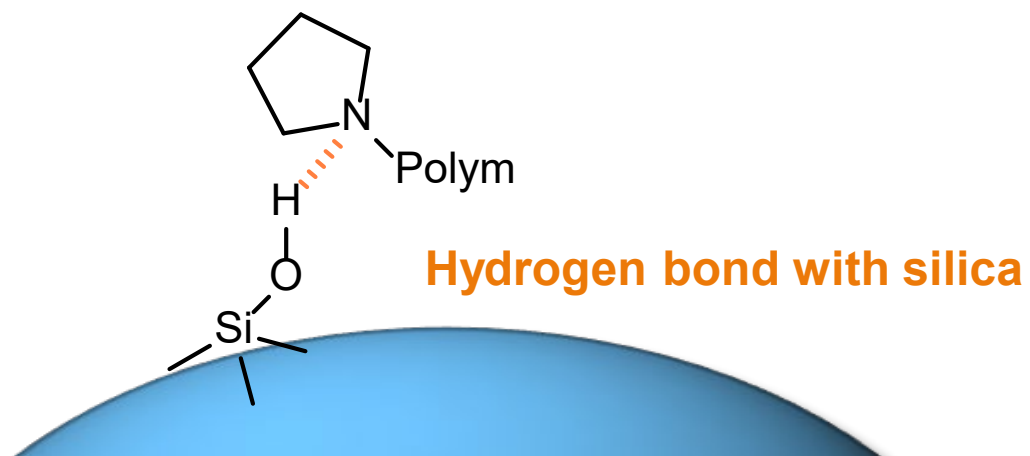
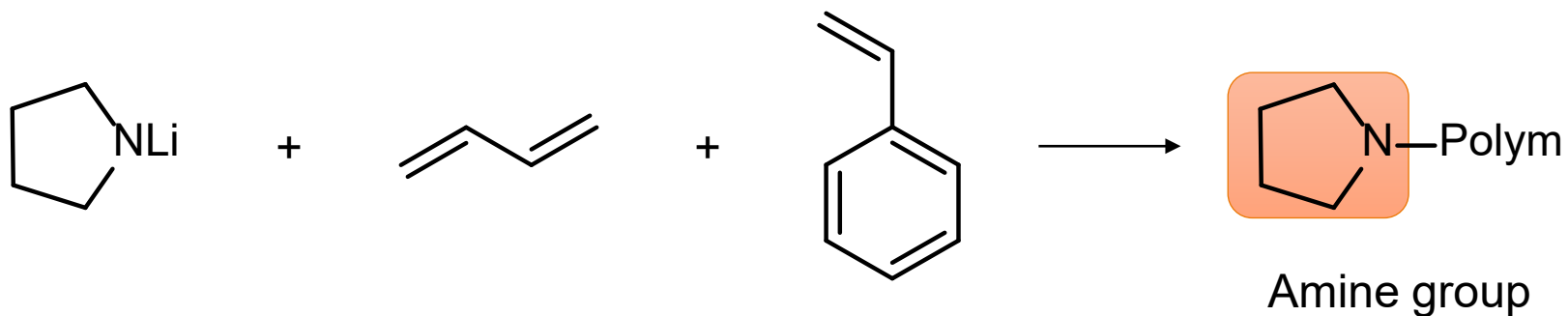
Functionalized SBR



Interact or react with silica surface to reduce filler-filler interaction

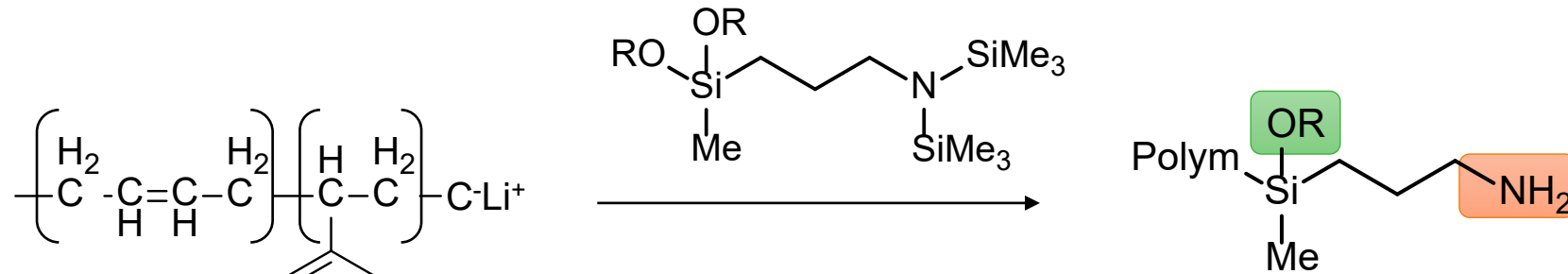
How to polymerize functionalized SBR

Initiator with functional group



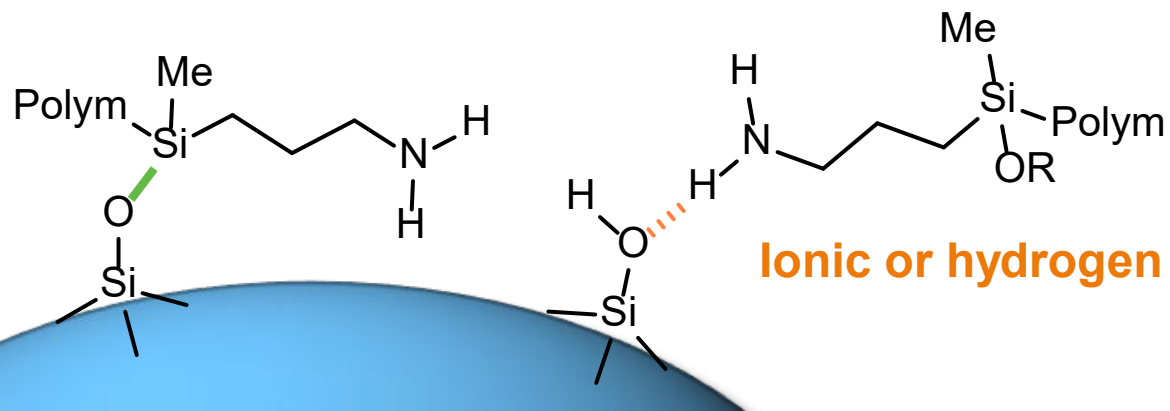
How to polymerize functionalized SBR

Termination with functional group



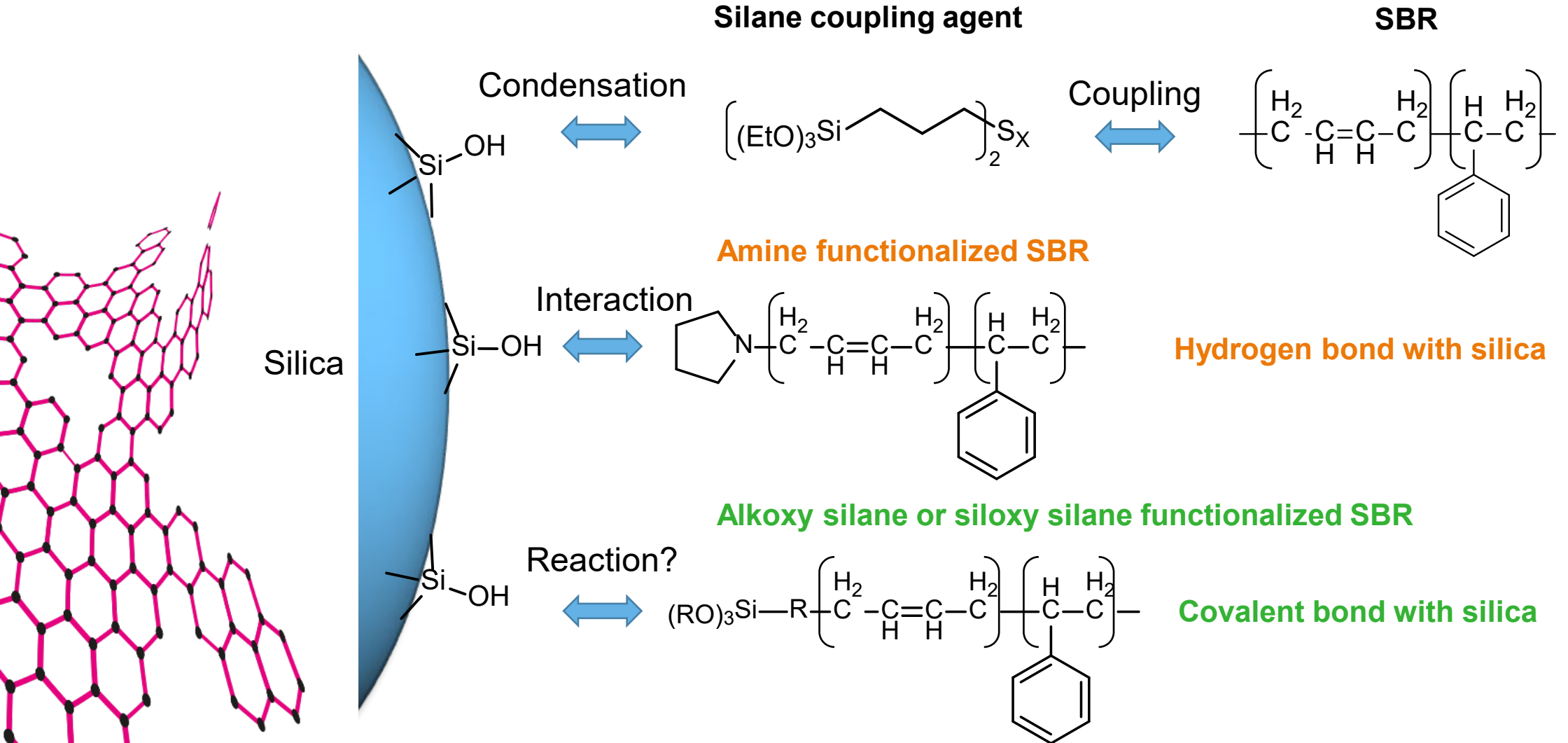
Alkoxy silane or siloxy group and amine

Covalent bond

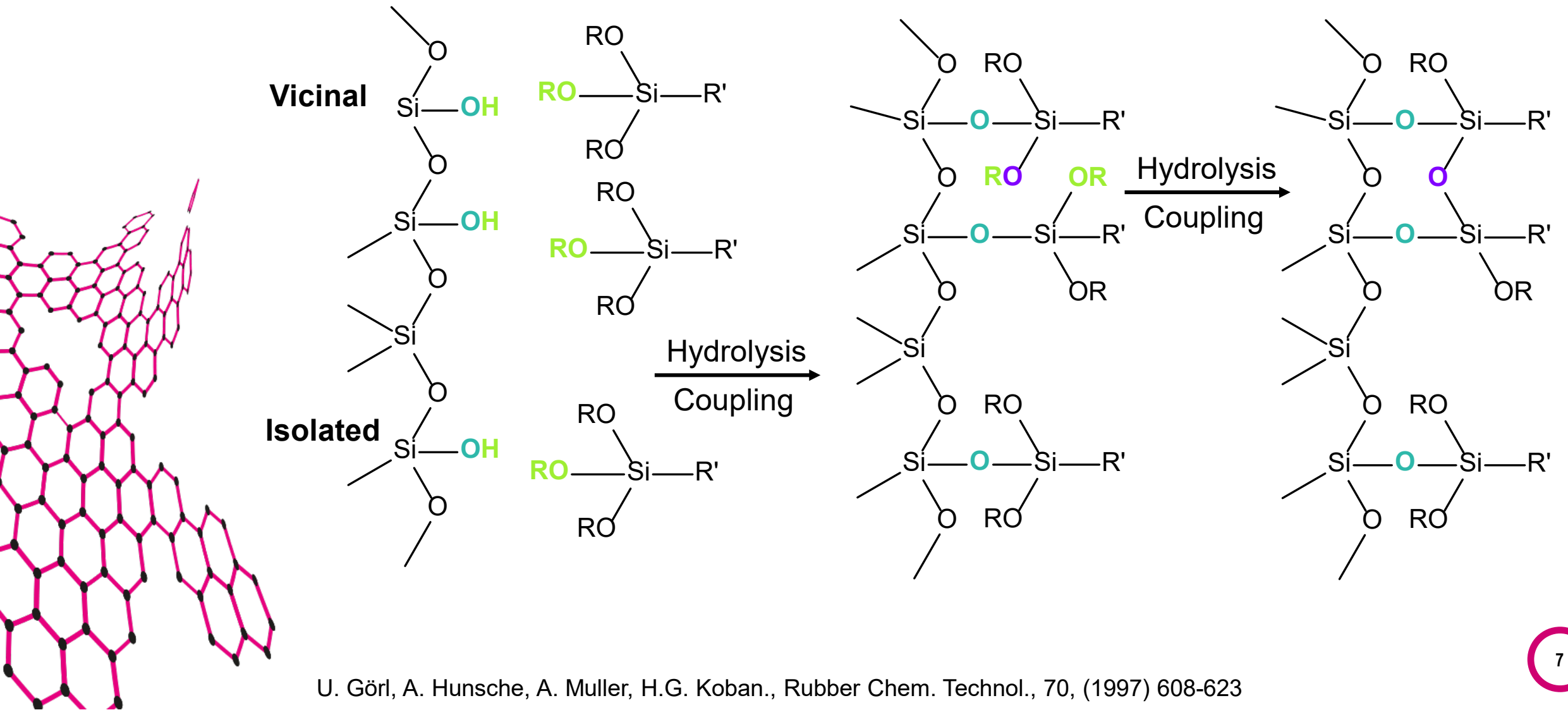


Ionic or hydrogen bond

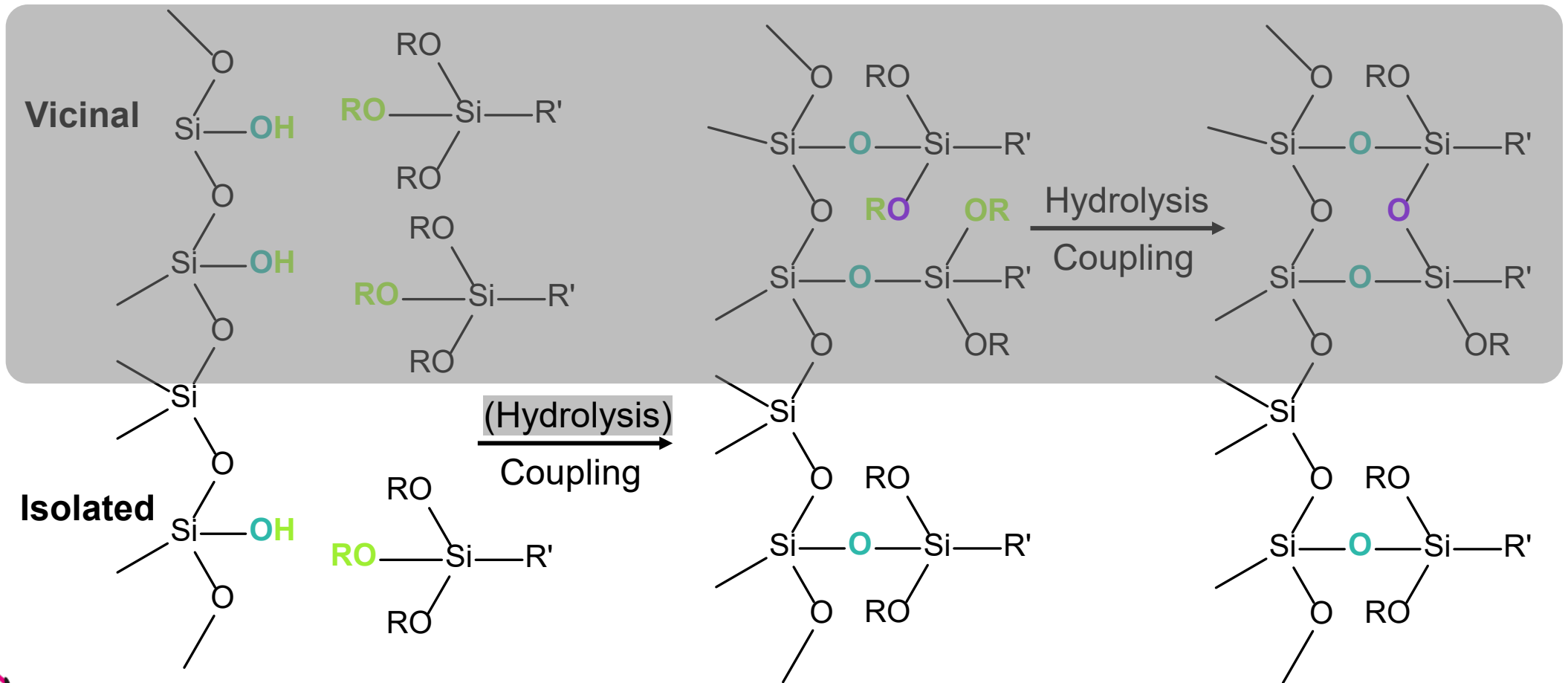
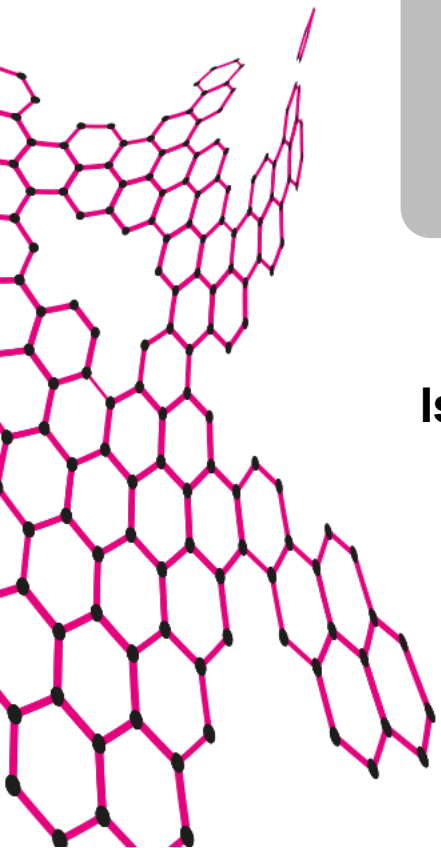
Reaction in the silica compound



Reaction between silane and silica

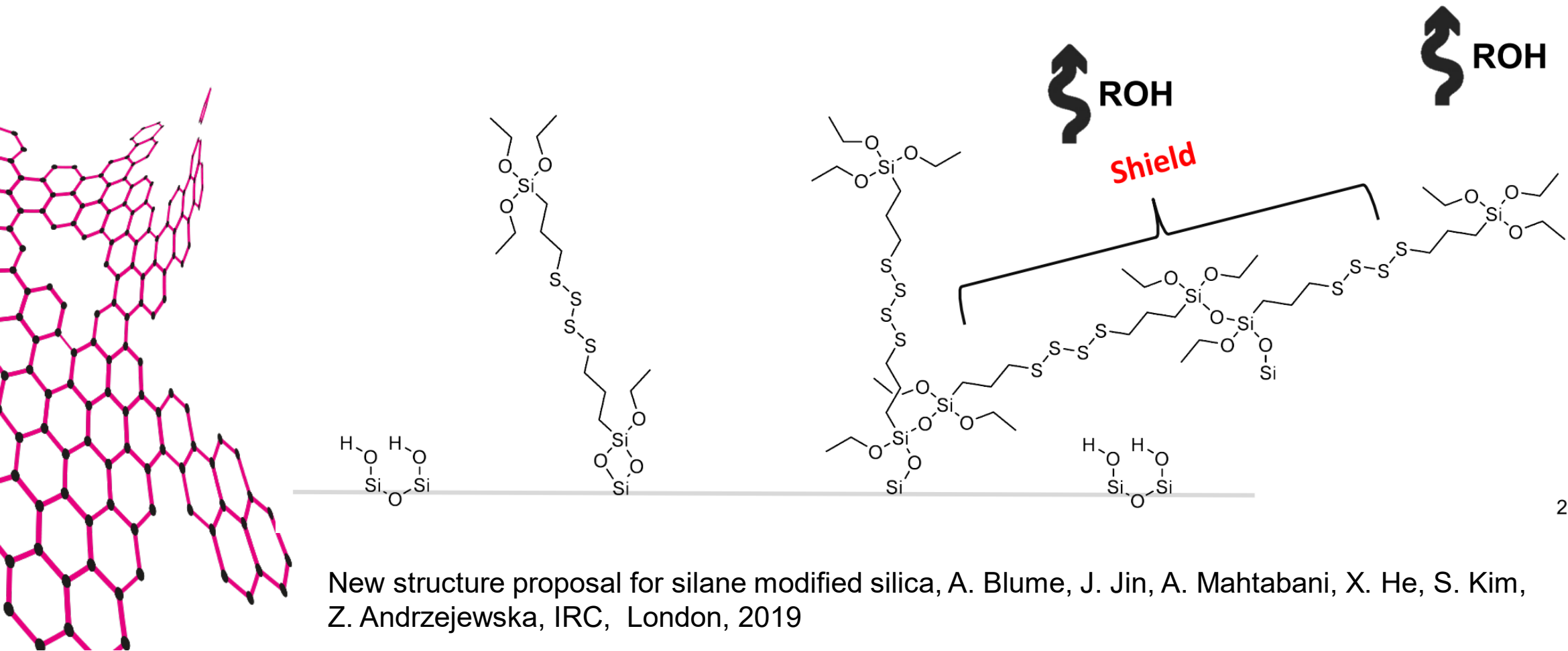


Reaction between silane and silica

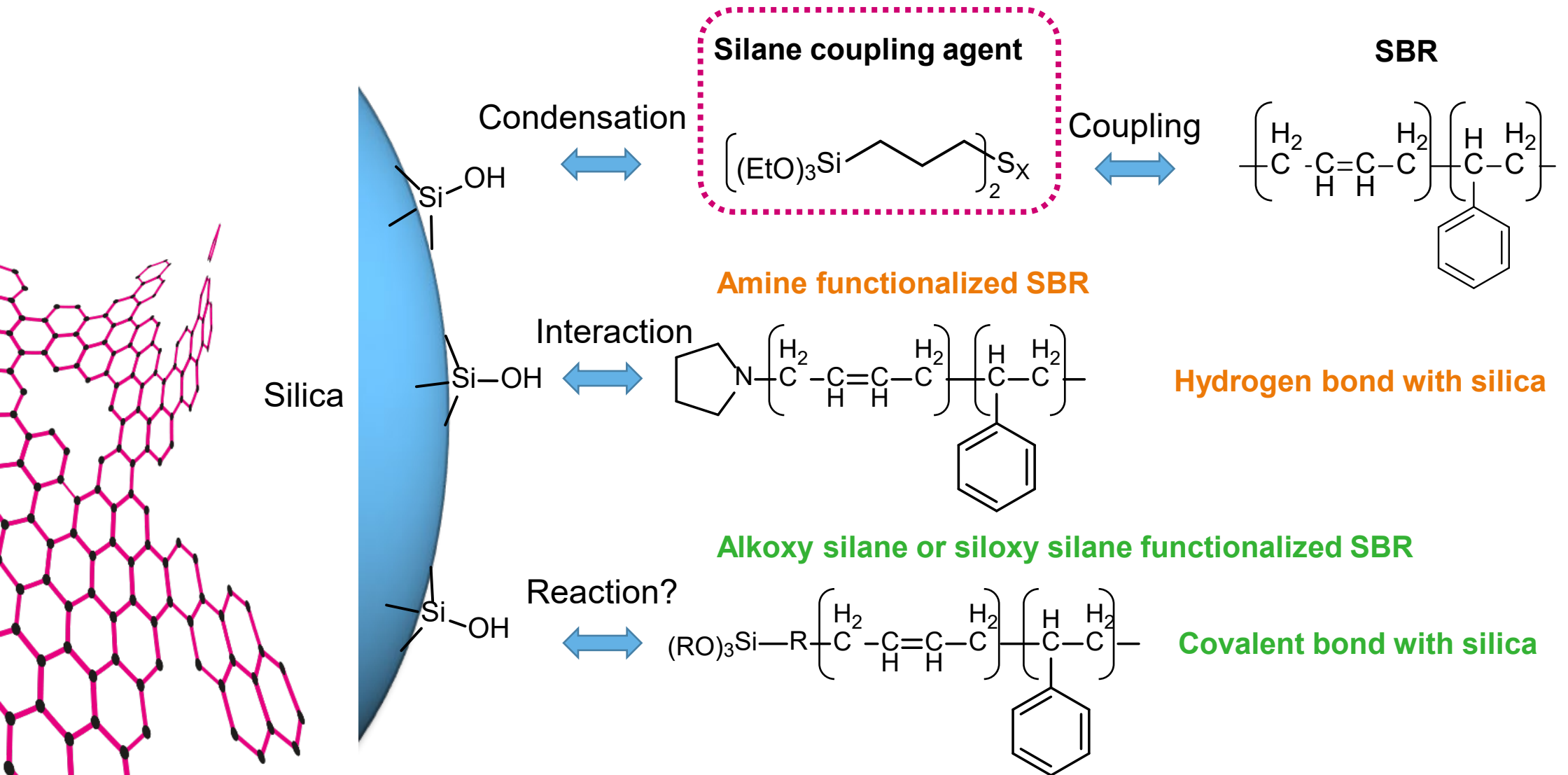


New proposal for silane reaction

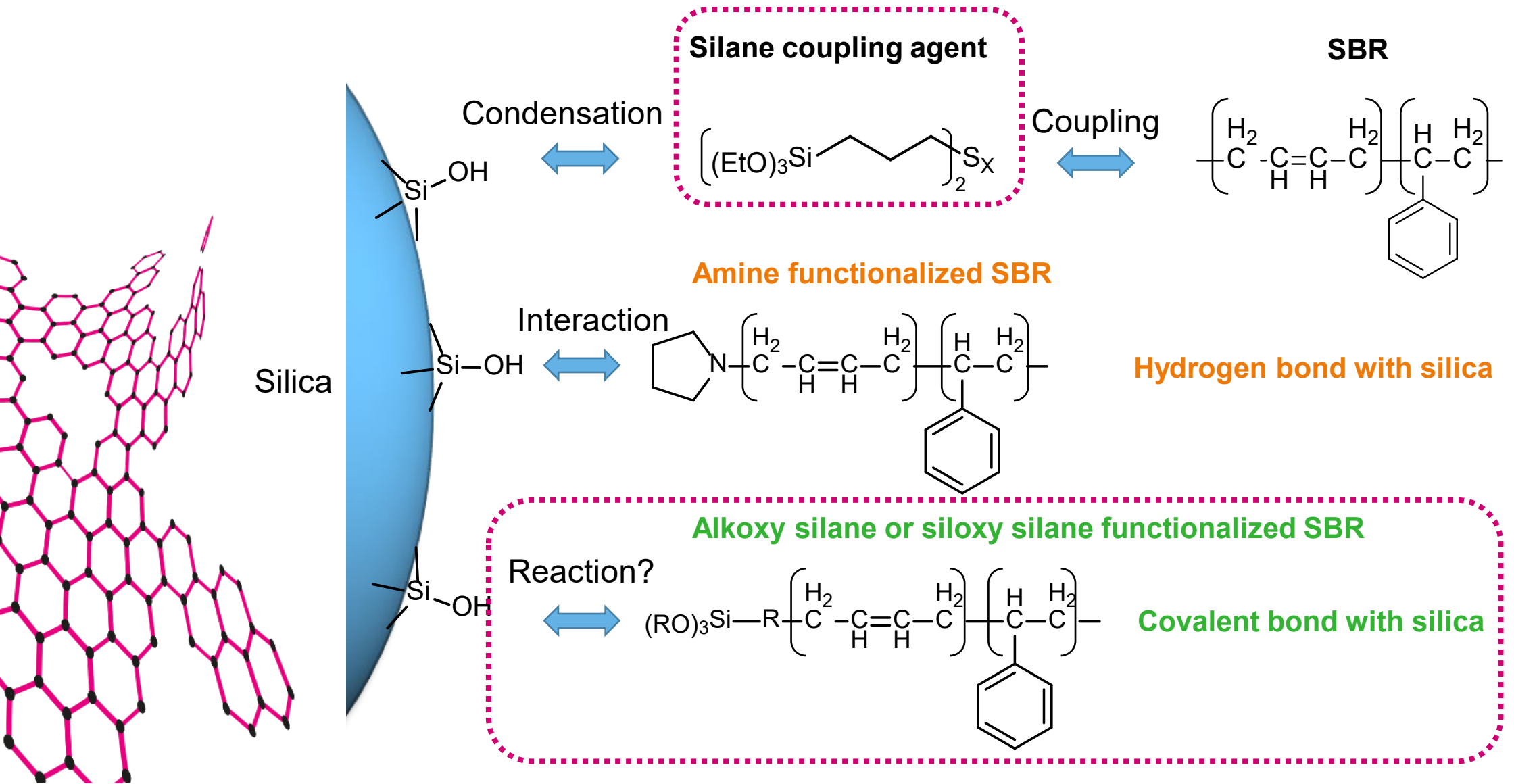
- 75% Si-OHs remain
- Two silane molecules can only react with two Si-OHs with a distance higher than 0.4 nm (=4 Å)



Reaction in the silica compound



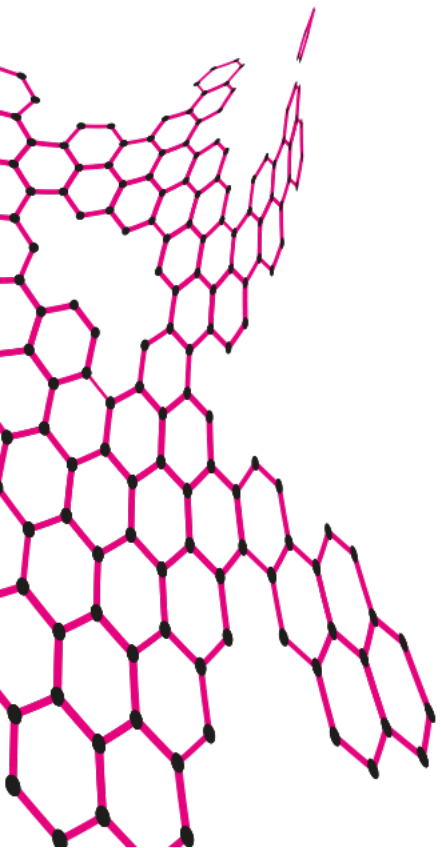
Reaction in the silica compound



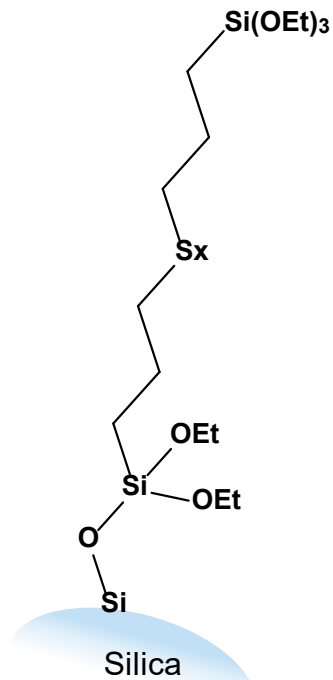
Possible reaction in the compound

Possible reaction in the normal compound

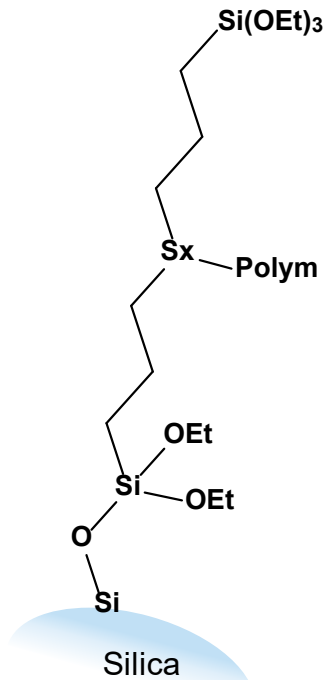
Possible reaction in the functionalized SBR compound



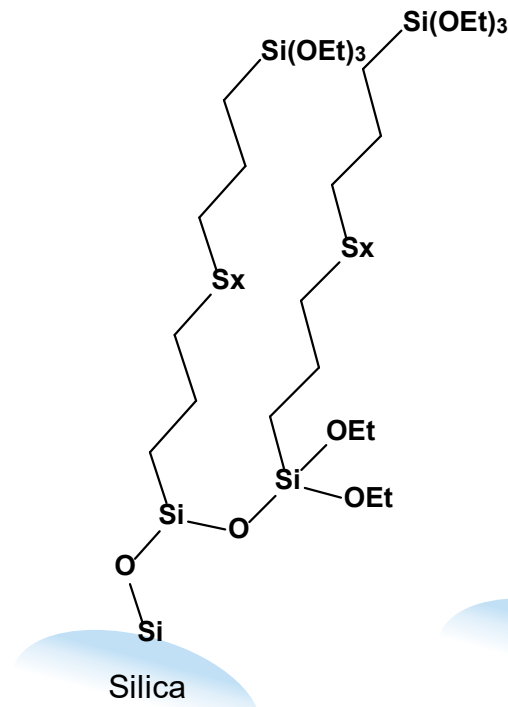
Silane and silica
(silanization)



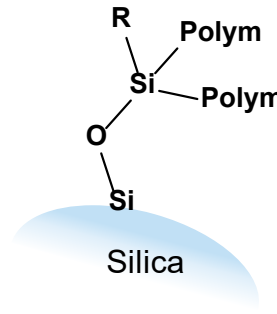
Silane modified
silica and SBR
(sulfur coupling)



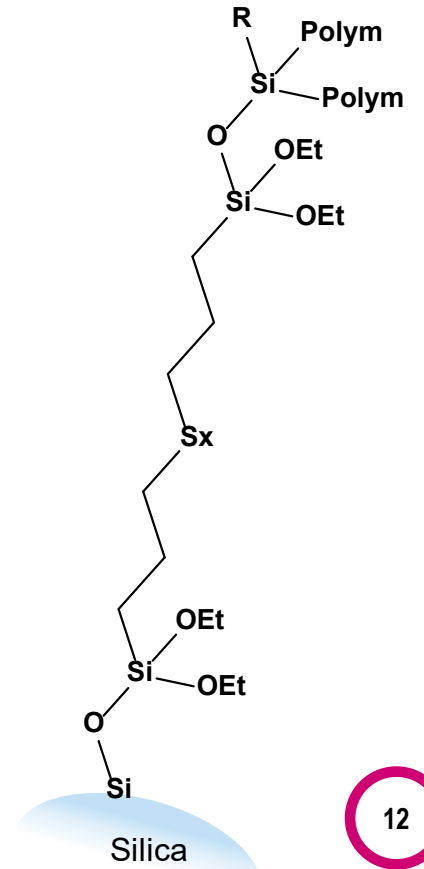
Silane modified
silica and silane



Functional group
in SBR and silica



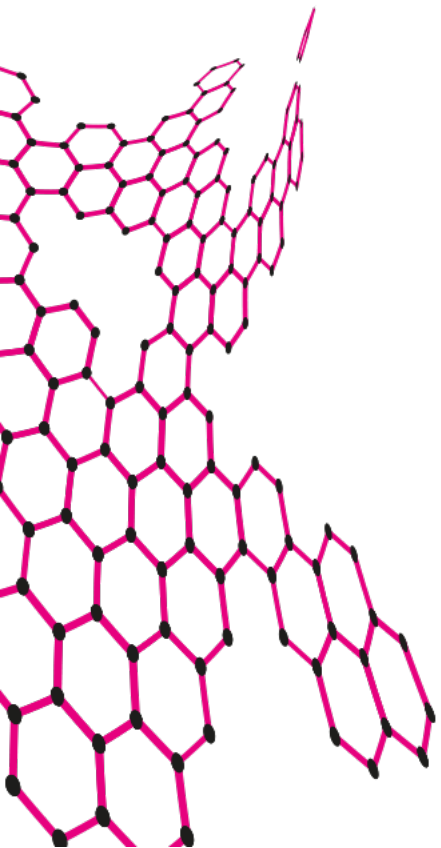
Functional group in
SBR and silane



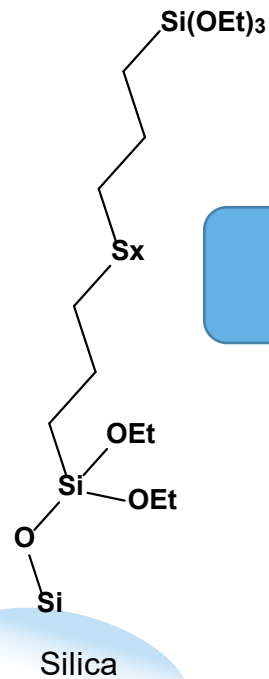
Possible reaction in the compound

Possible reaction in the normal compound

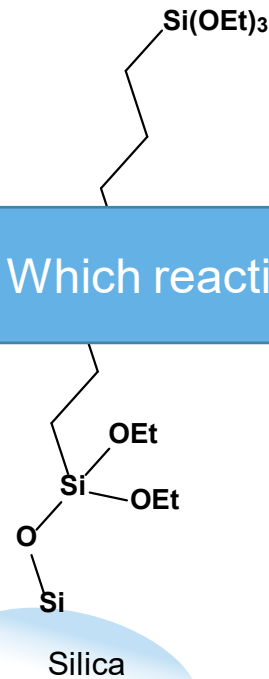
Possible reaction in the functionalized SBR compound



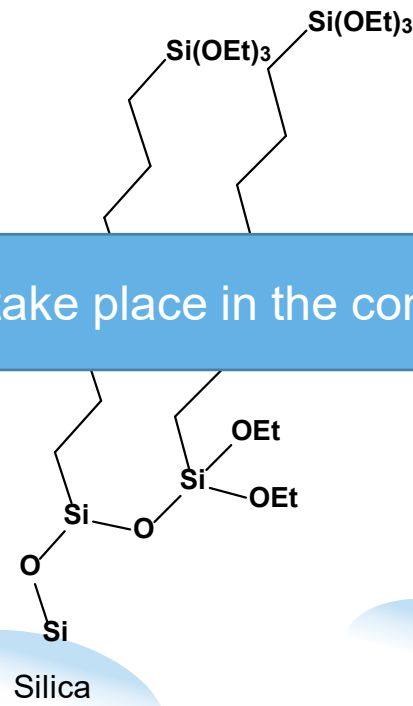
Silane and silica
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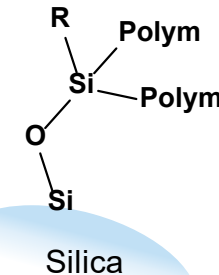
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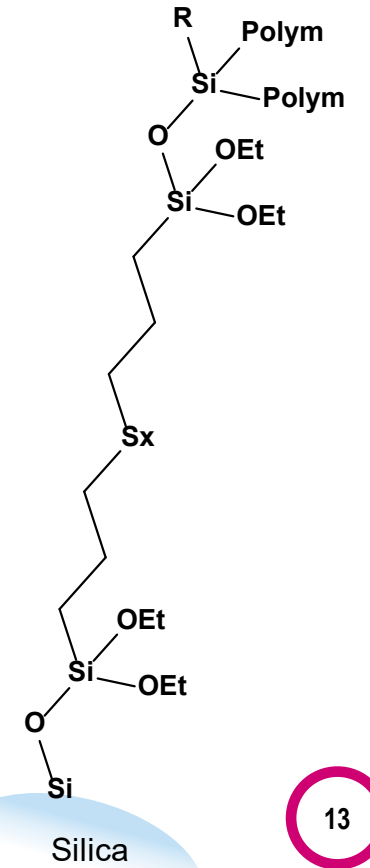
Silane modified
silica and silane



Functional group




Functional group in
SBR and silane

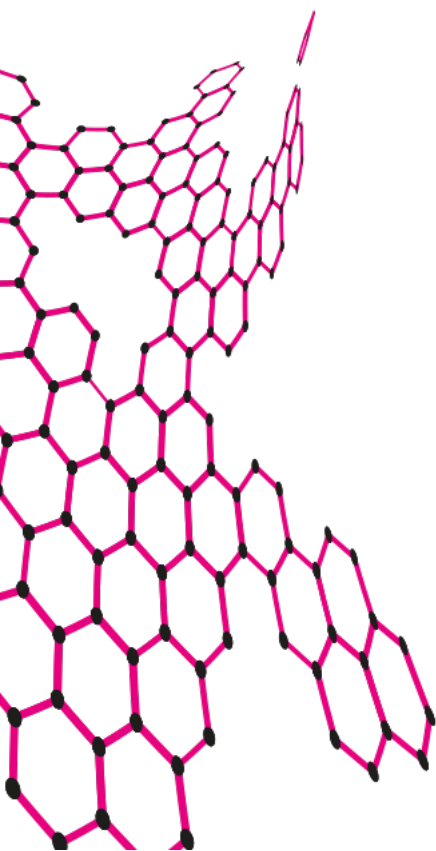


Which reactions take place in the compound?

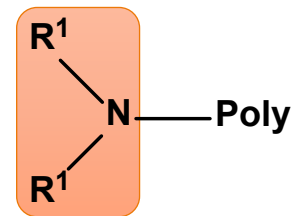
SBRs for this study

Clarify the reaction mechanism in the compound by combination of functionalized SBRs and different types of silanes

	SBR1	FSBR2
Structure	 Buna VSL50252HM	$n \left(\text{yellow circle} - \text{wavy orange line} - \text{pink circle} \right)$
Styrene / %	25	35
Vinyl in Bd / %	65	40
Mw (kg / mol)	600	800

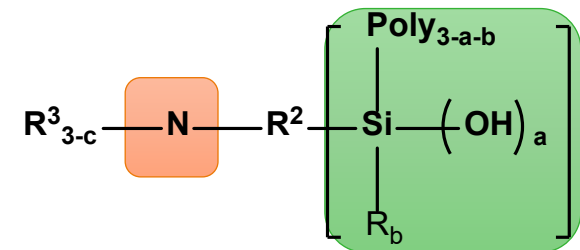


 **Amine group**



Hydrogen or ionic bond

 **Functional group**

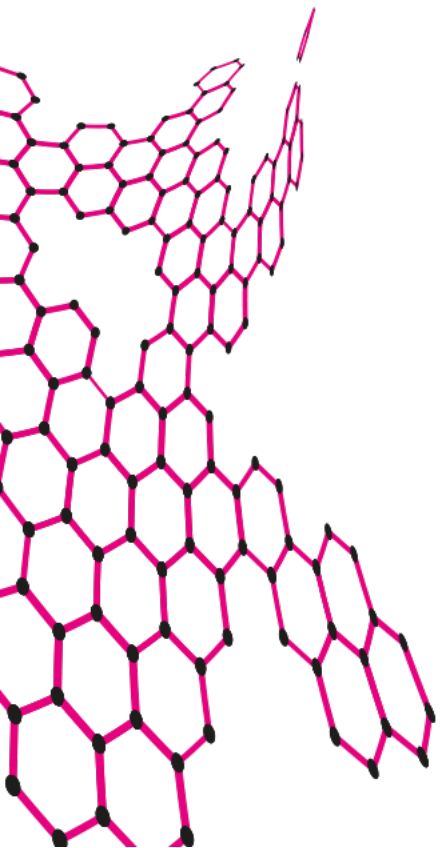


Covalent bond
Hydrogen bond

Silane coupling agent

Can silane also couple chemically to the functional group of the polymer?

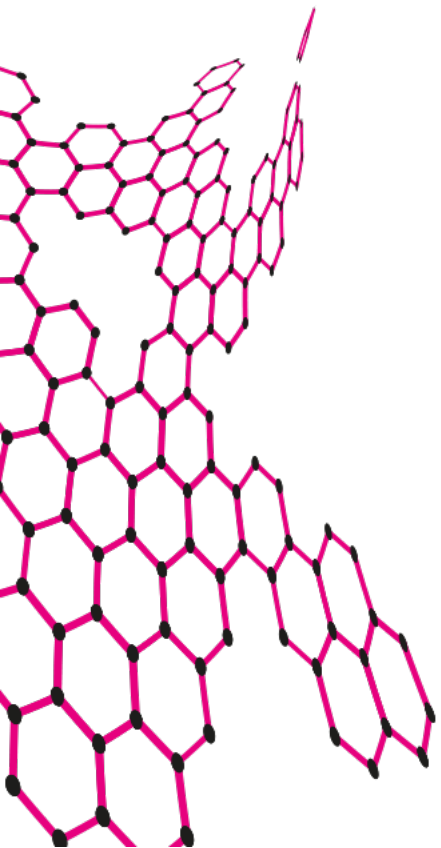
	Structure	Possible reaction		
		silanization	Coupling with SBR	Reaction with functional group
PTEO	$(\text{EtO})_3\text{Si}-(\text{CH}_2)_2\text{CH}_3$	✓		✓
TESO	$(\text{EtO})_3\text{Si}-(\text{CH}_2)_8-\text{Si}(\text{OEt})_3$	✓		✓
TESPD	$(\text{EtO})_3\text{Si}-(\text{CH}_2)_3-\text{S}_x-(\text{CH}_2)_3-\text{Si}(\text{OEt})_3$ $x = 2.2$	✓	✓	✓
TESPT	$(\text{EtO})_3\text{Si}-(\text{CH}_2)_3-\text{S}_x-(\text{CH}_2)_3-\text{Si}(\text{OEt})_3$ $x = 3.7$	✓	✓	✓



Formulation

- The sulfur content of the TESPT compound is adjusted considering the free sulfur generated from TESPT
- The number of ethoxy groups of silane is kept constant in each compound

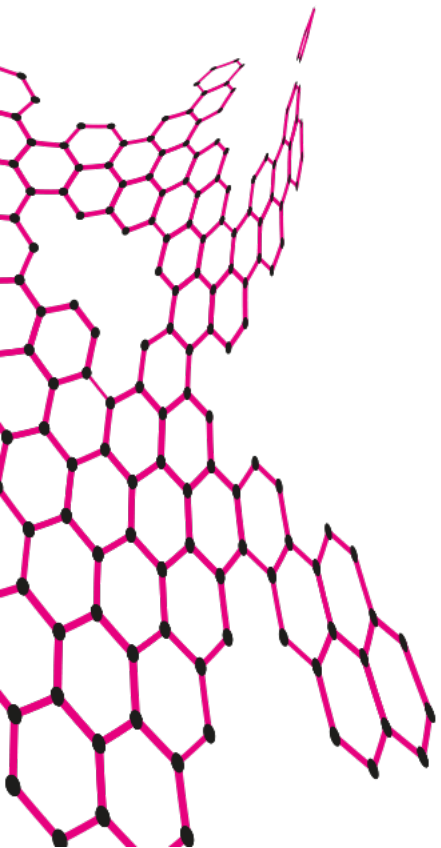
Materials (in phr)	1	2	3	4	5
SBR	100	100	100	100	100
Silica (ULTRASIL 7000 GR)	75	75	75	75	75
Silane	-	PTEO	TESO	TESPD	TESPT
	-	4.7	4.9	5.4	5.6
TDAE oil (total)	37.5	37.5	37.5	37.5	37.5
Zinc Oxide	2.5	2.5	2.5	2.5	2.5
Stearic Acid	2	2	2	2	2
Antioxidant (6PPD)	2	2	2	2	2
Sulfur	2.2	2.2	2.2	2.2	1.7
CBS	1.7	1.7	1.7	1.7	1.7
DPG	2	2	2	2	2



How to detect polymer-filler reaction?

	Direct/Indirect	Comment
NMR	Direct	Molecular weight of polymer should be less than 50,000 to detect functional group
FTIR	Direct	Functional group in the compound is 6.0×10^{-5} mol in 100 g compound. It cannot be detected.
Bound rubber	Indirect	Influenced by filler-polymer interaction
Payne effect	Indirect	Influenced by many factors
Swelling test	Indirect (Cured)	Influenced by the filler-filler interaction
Mooney-Rivlin	Indirect (Cured)	Influenced by the filler-filler interaction

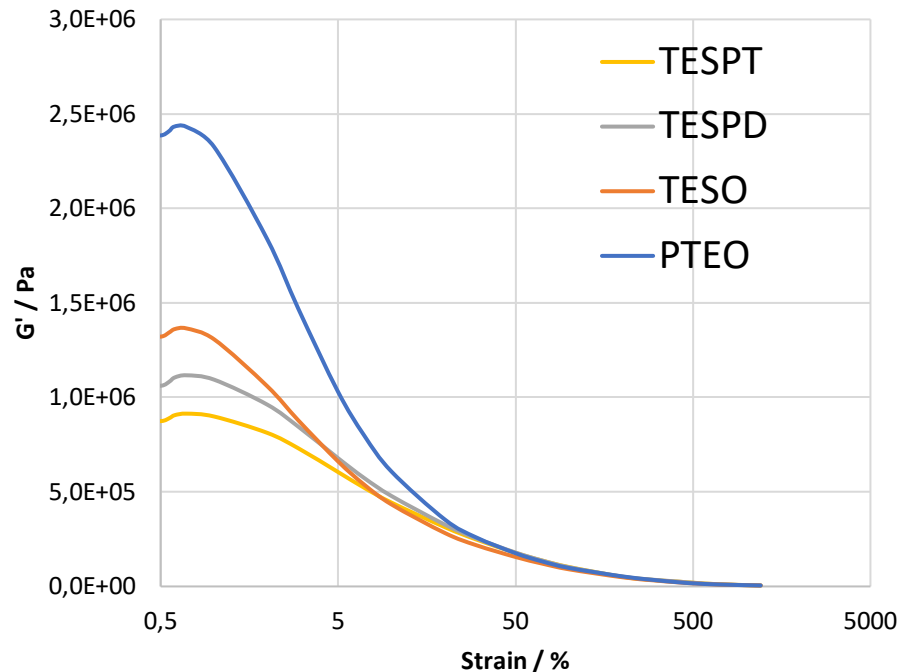
In progress



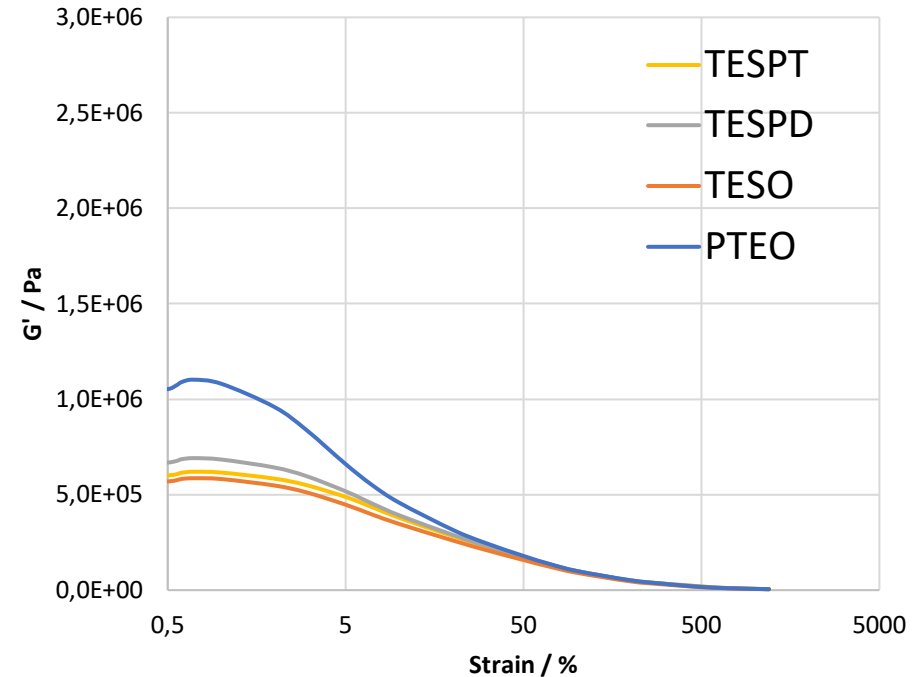
Payne curve of uncured compound

Measurement condition: 100 °C, 0.5 Hz

SBR1 non-functionalized



FSBR2 Both-ends-functionalized



Payne effect

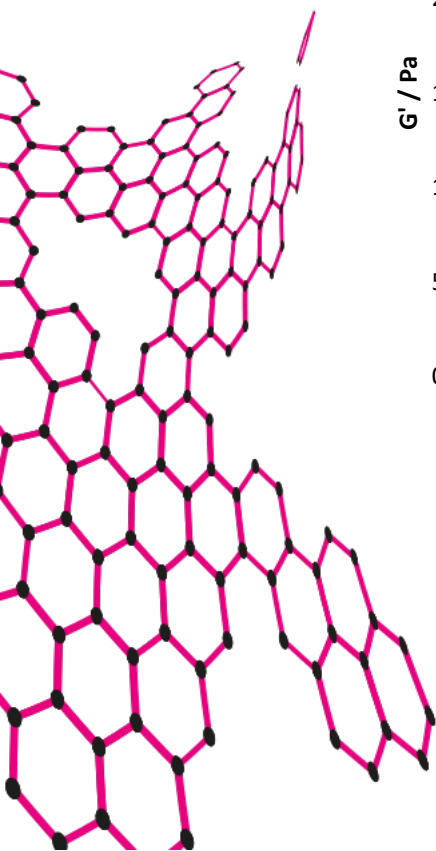
PTEO >> TESO > TESP > TESPT

High shielding effect of TESO
Polymer-filler interaction of sulfur silane

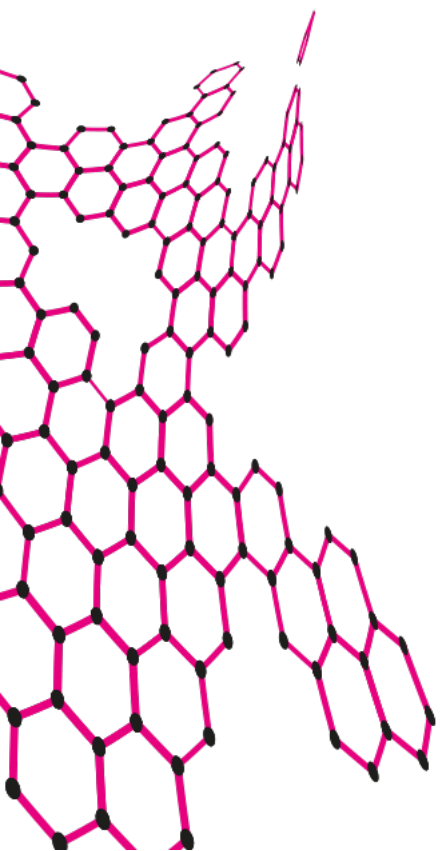
Payne effect

PTEO >> TESP > TESPT ≈ TESO

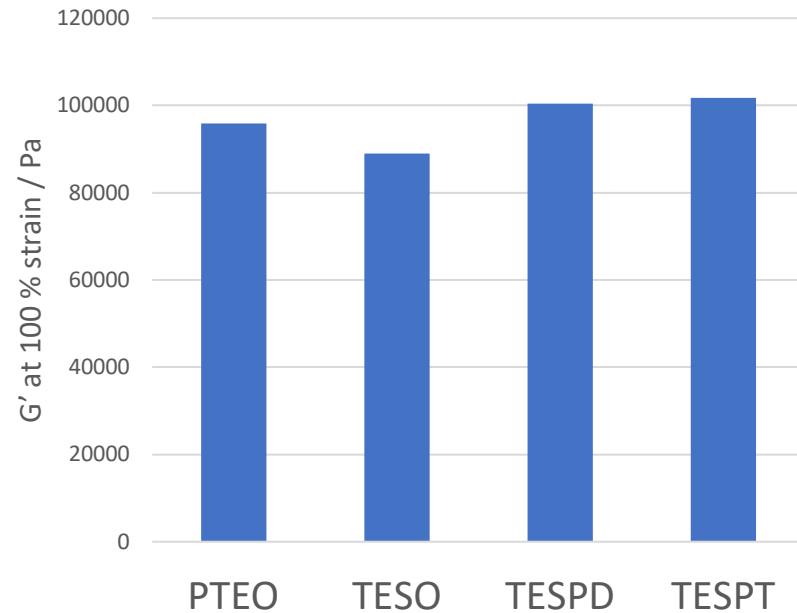
Combination of polymer-filler interaction by functional group and shielding effect of TESO



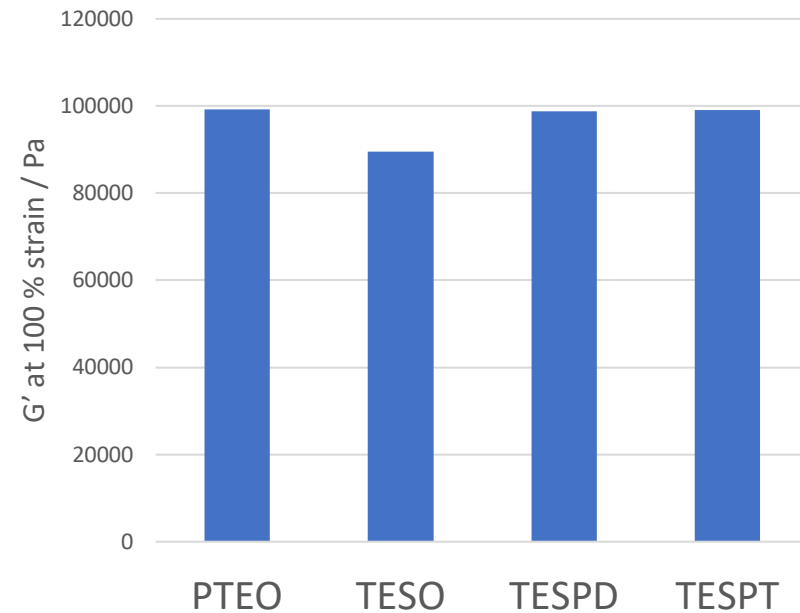
Storage moduli at high strain



SBR1 non-functionalized



FSBR2 Both-ends-functionalized



No difference between two SBRs

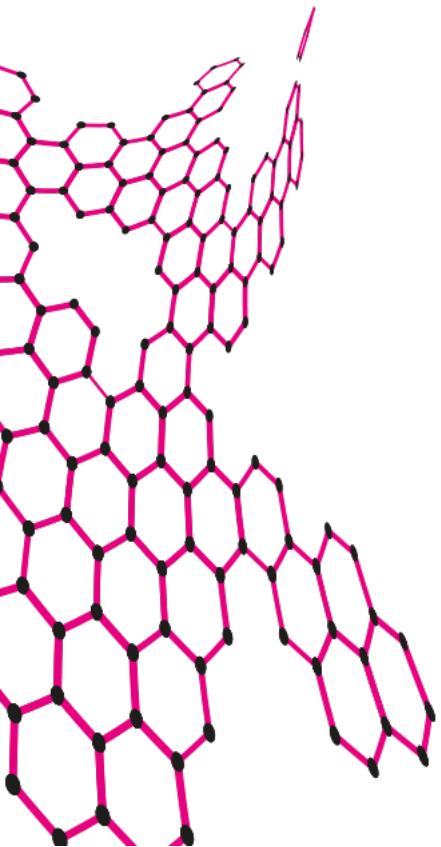
Difficult to detect the polymer-filler interaction from Payne curve

Chemical bound rubber

Chemical bound rubber is measured under ammonia atmosphere

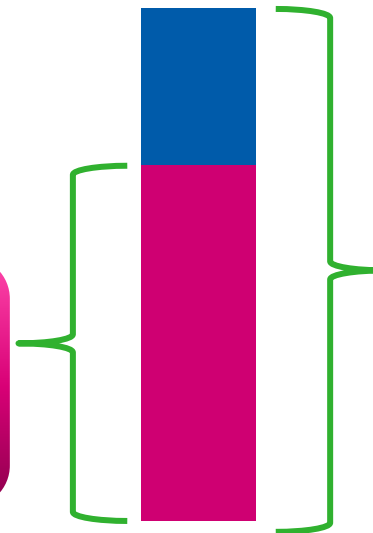
- Polymer chains weakly attached to the silica surface will be detached
- Occluded rubber is released

Polymer strongly bounded to silica remains



Chemical bound rubber

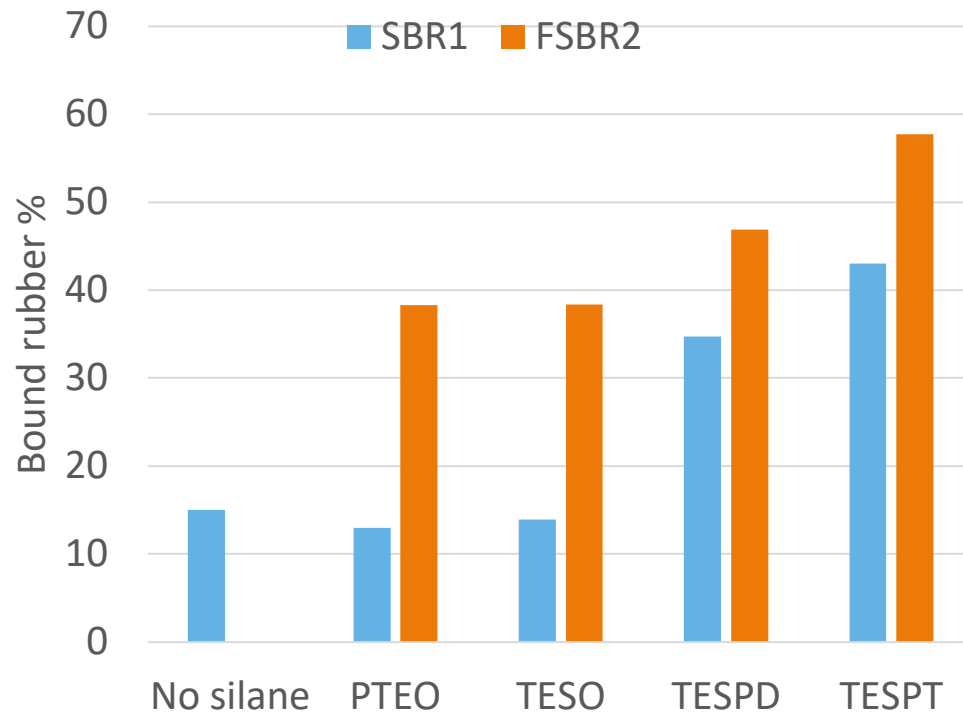
1. Gel
2. Rubber coupled to silica via covalent bonding



Bound rubber

1. Occluded rubber
2. Gel
3. Rubber weakly attached to the silica surface
4. Rubber bounded via covalent bonding

Chemical bound rubber content



For SBR1, the bound rubber content is around 15% in the compounds without silane and with non-sulfur silane

- Strong interaction of 1,2-butadiene unit with silica

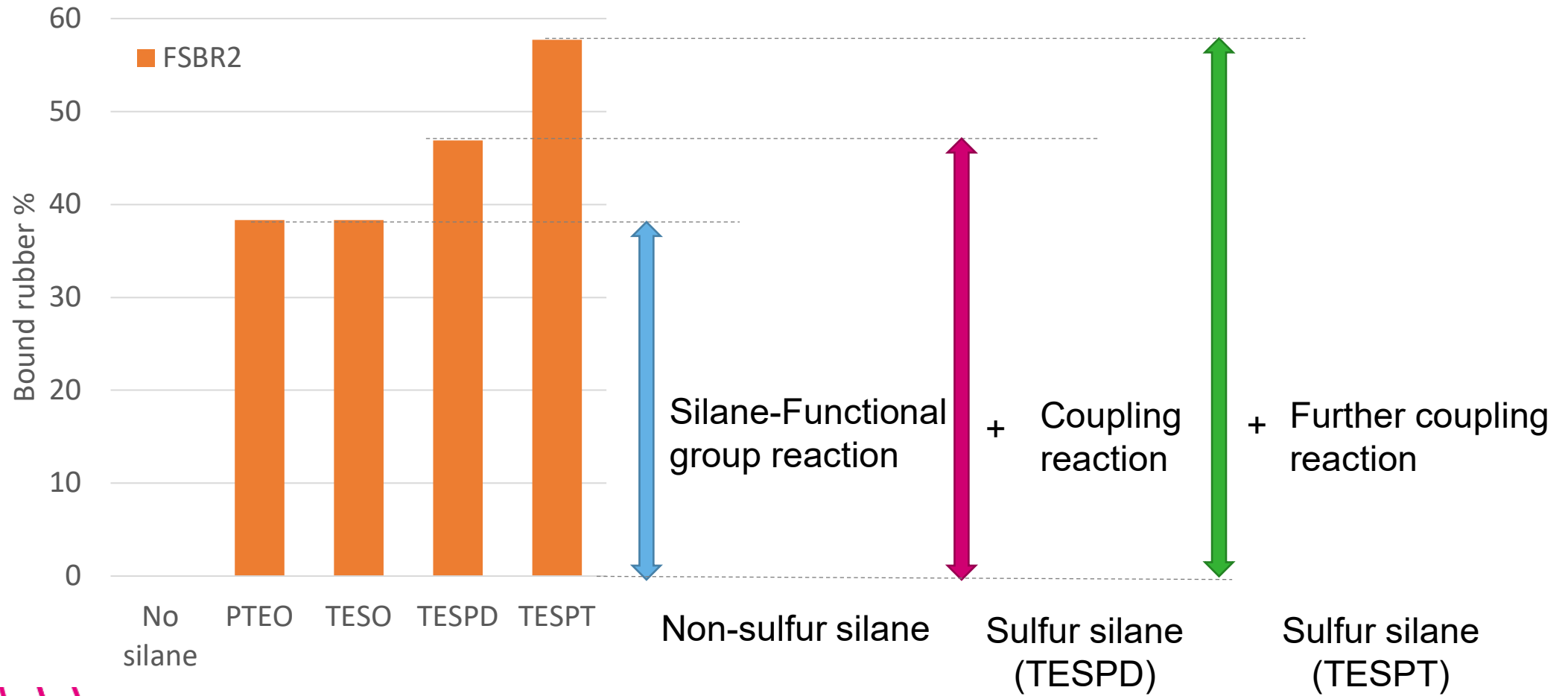
The bound rubber increases significantly in the presence of PTEO or TESO in FSBR2 compounds

- Indicating reaction between non-sulfur silanes and functional groups in SBR

More bound rubber was observed with sulfur-silanes

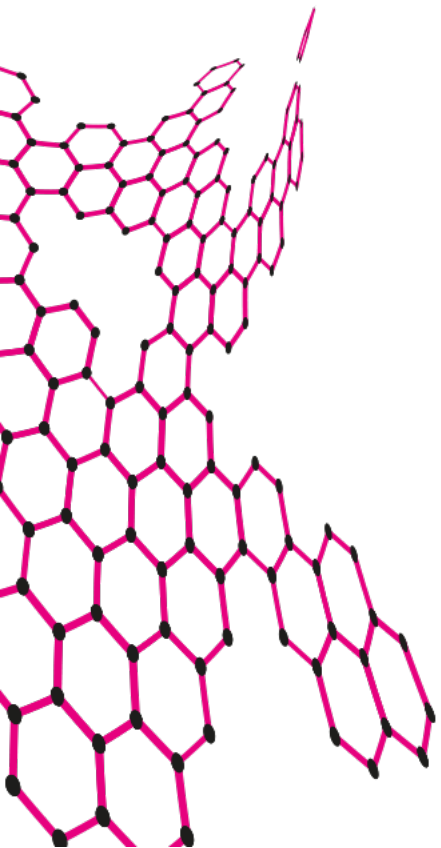
- Due to silane coupling and reaction between silane and functional group in SBR

Chemical bound rubber content

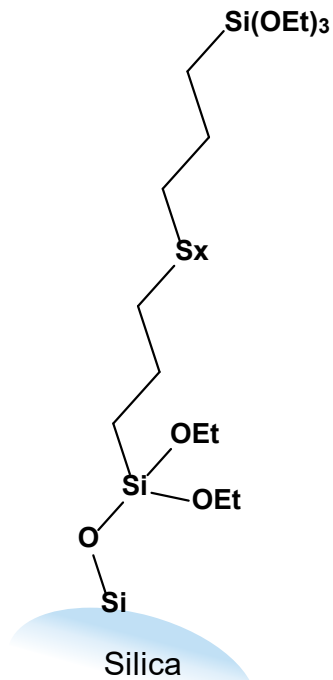


Reaction in the compound

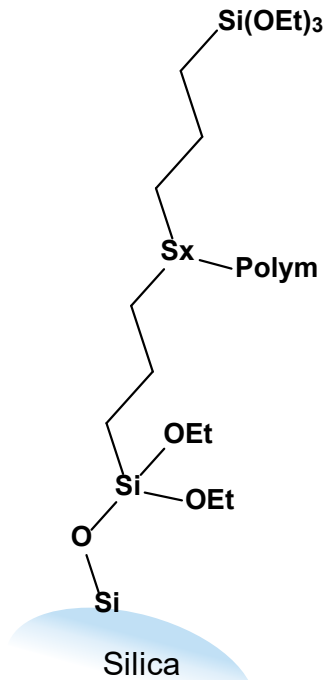
Possible reactions in the unmodified SBR compound



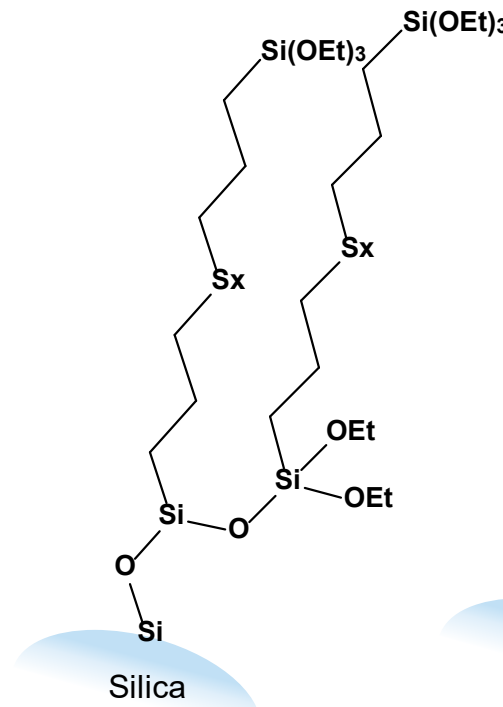
Silane and silica
(silanization)



Silane modified
silica and SBR
(sulfur coupling)

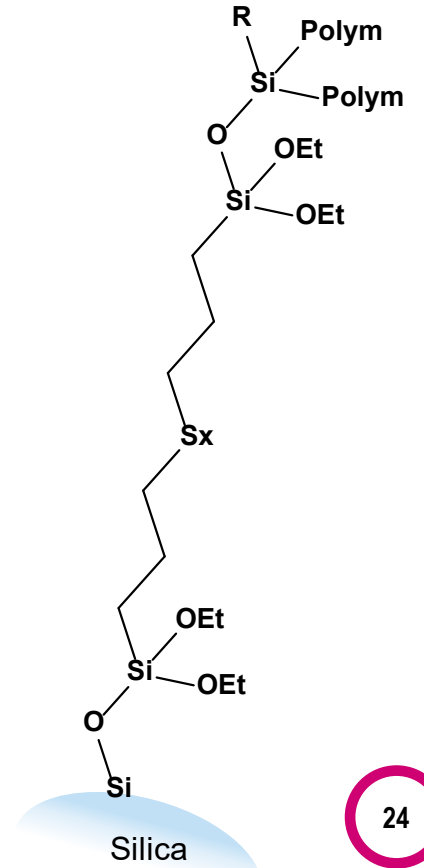


Silane modified
silica and silane

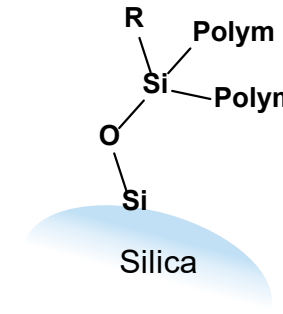


Possible reactions in the functionalized SBR compound

Functional group in
SBR and silane

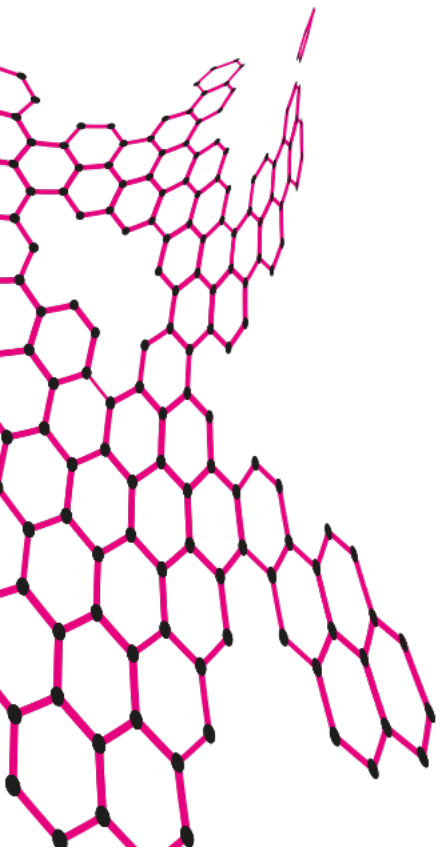


Functional group
in SBR and silica

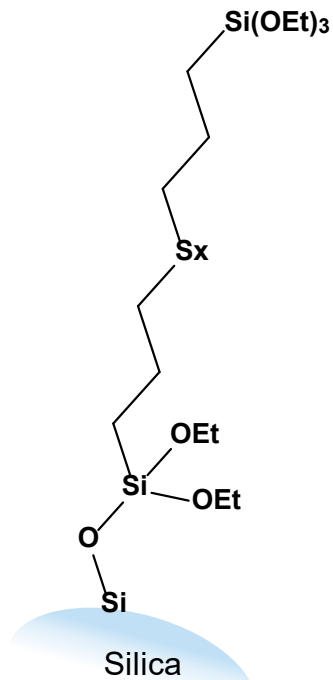


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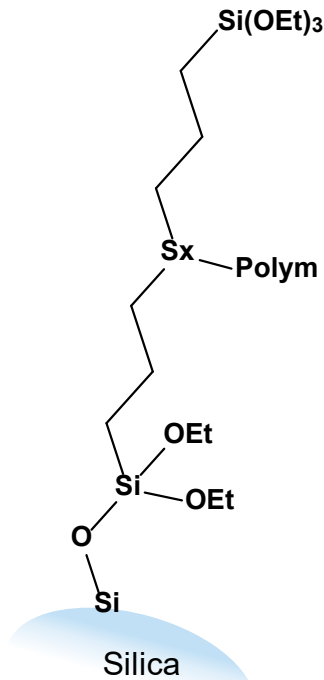
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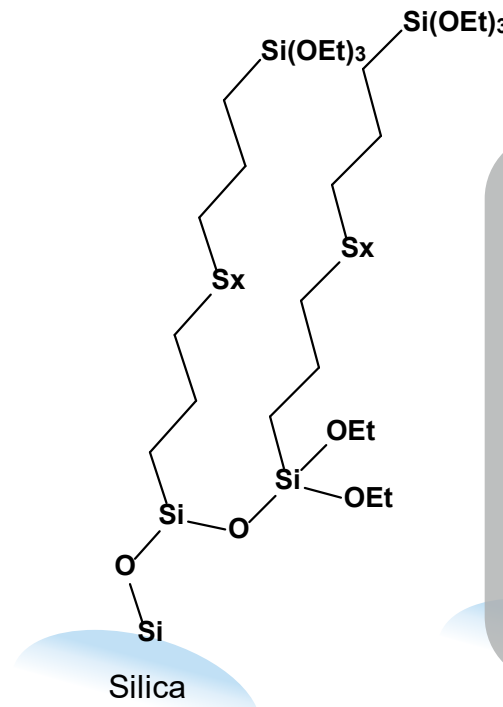
Silane and silica
(silanization)



Silane modified
silica and SBR
(sulfur coupling)

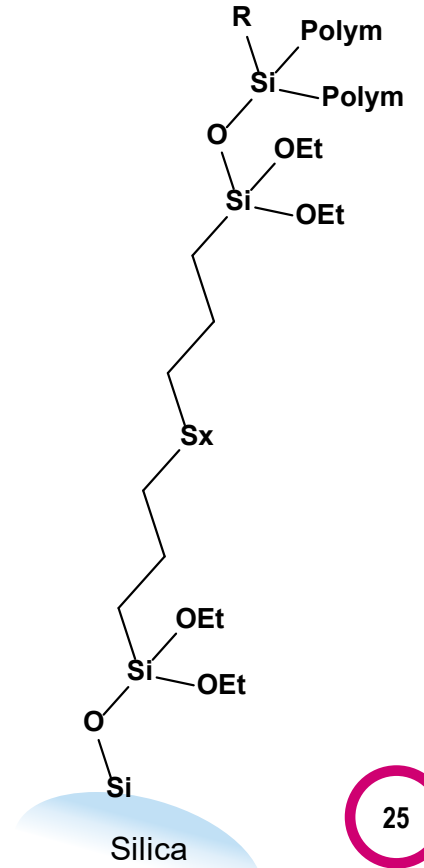
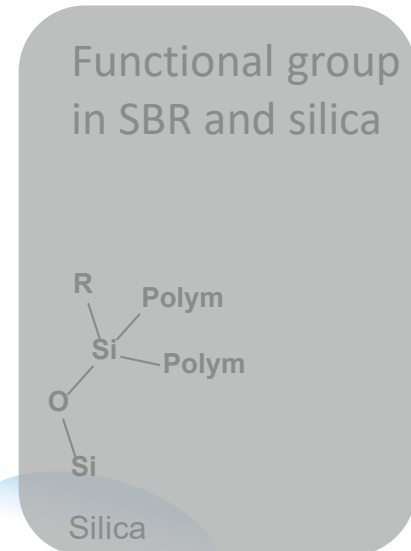


Silane modified
silica and silane



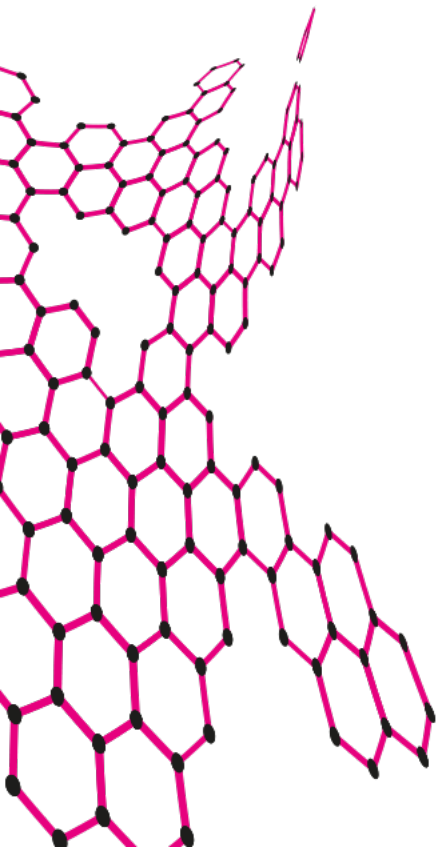
Possible reactions in the functionalized SBR compound

Functional group in
SBR and silane

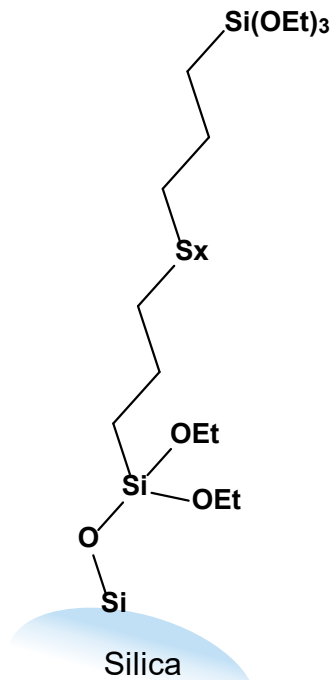


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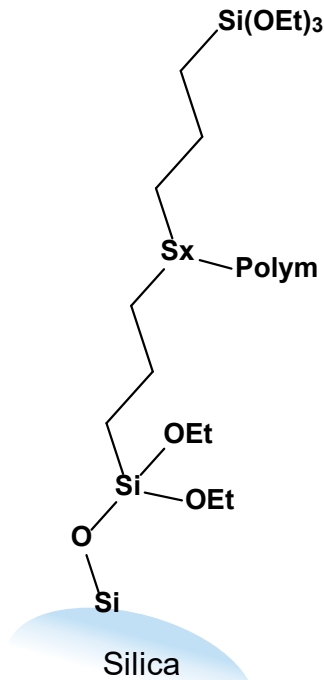
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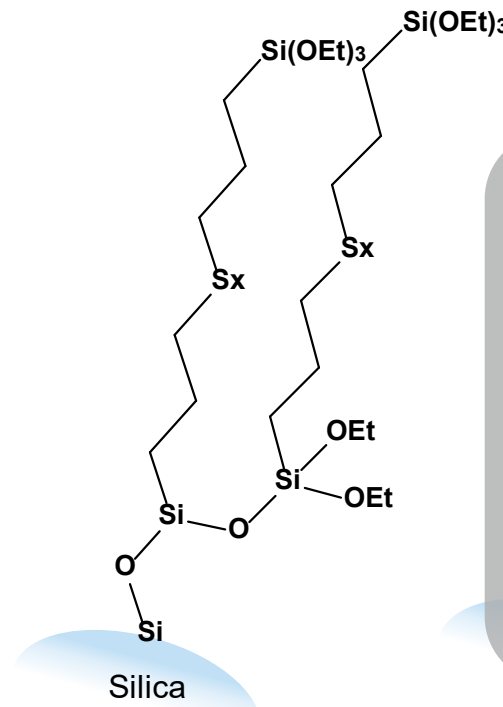
Silane and silica
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Silane modified
silica and SBR
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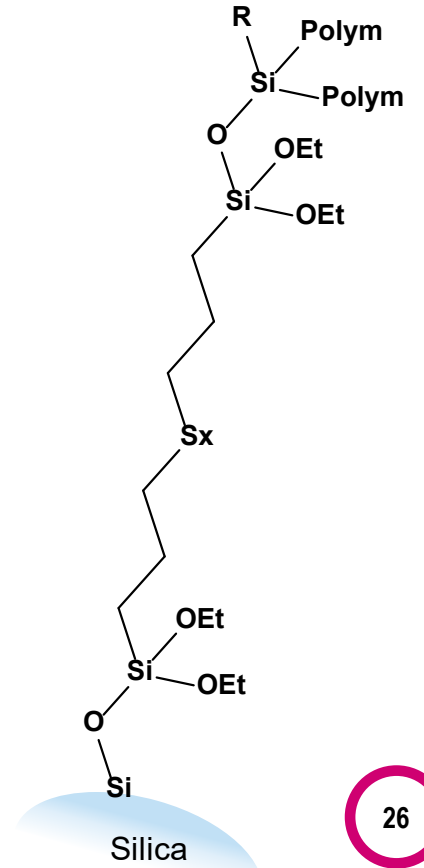
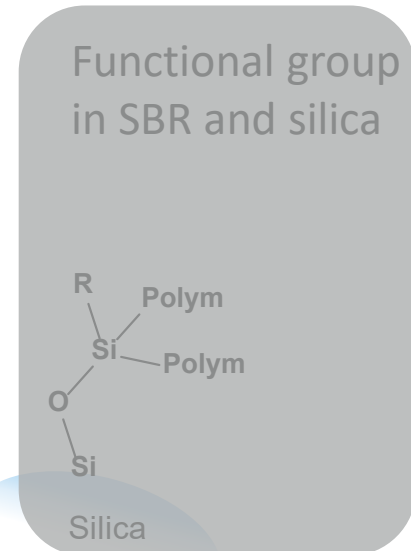


Silane modified
silica and silane



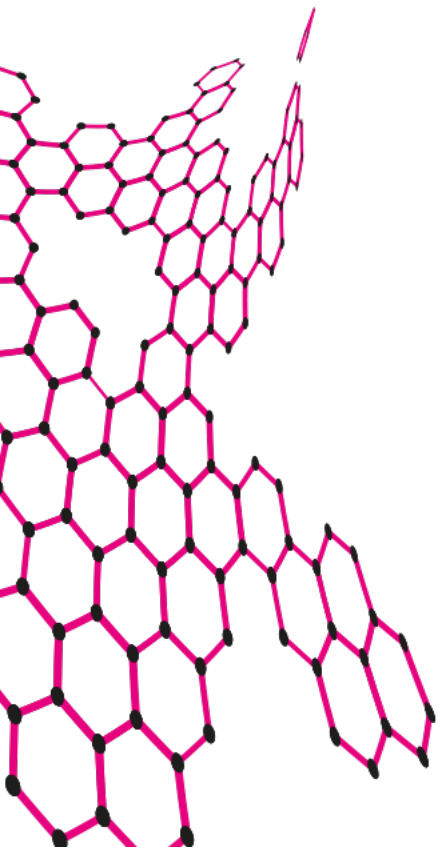
Possible reactions in the functionalized SBR compound

Functional group in
SBR and silane

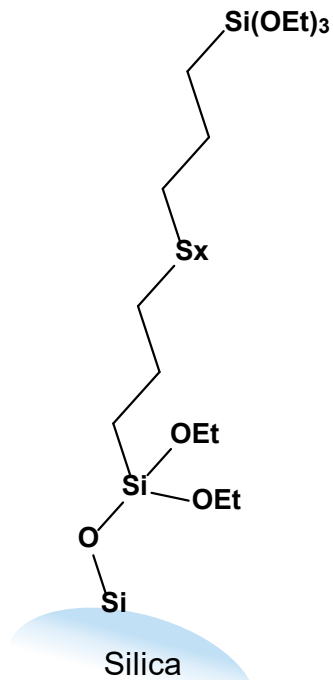


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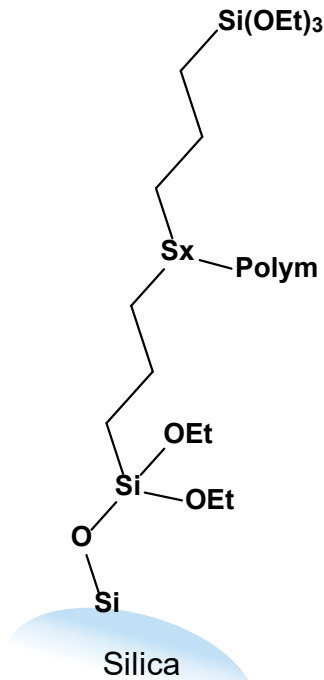
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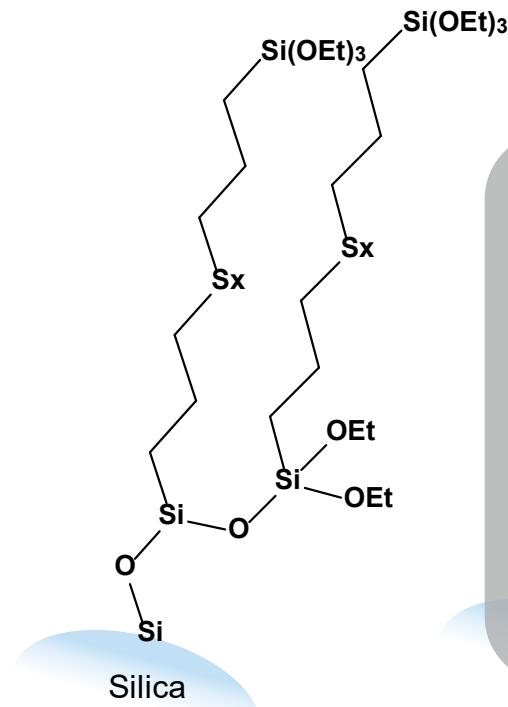
Silane and silica
(silanization)



Silane modified
silica and SBR
(sulfur coupling)

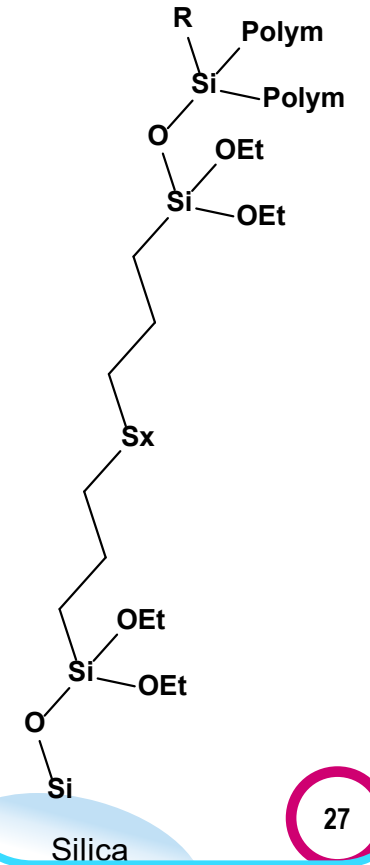


Silane modified
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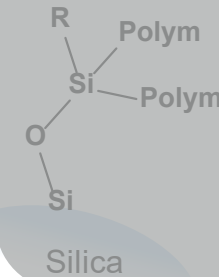


Possible reactions in the functionalized SBR compound

Functional group in
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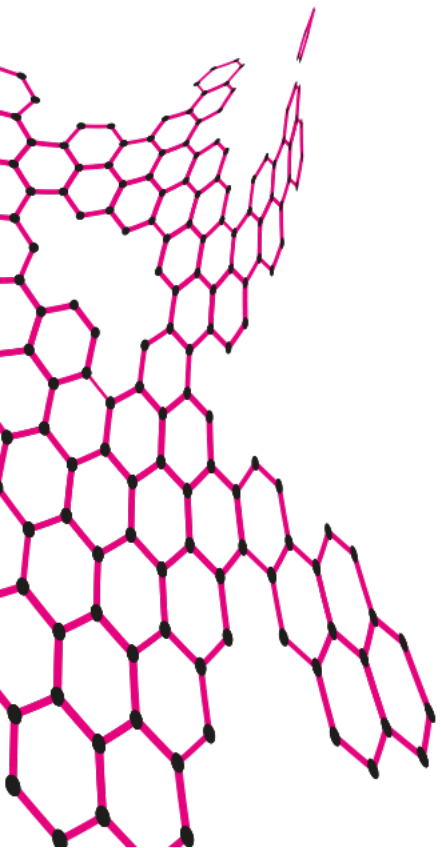
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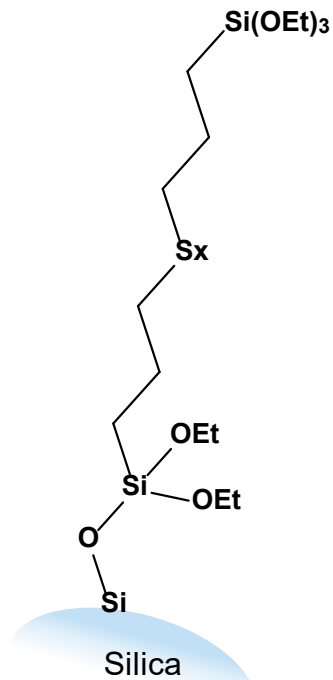
Reaction in the compound

Possible reactions in the unmodified SBR compound

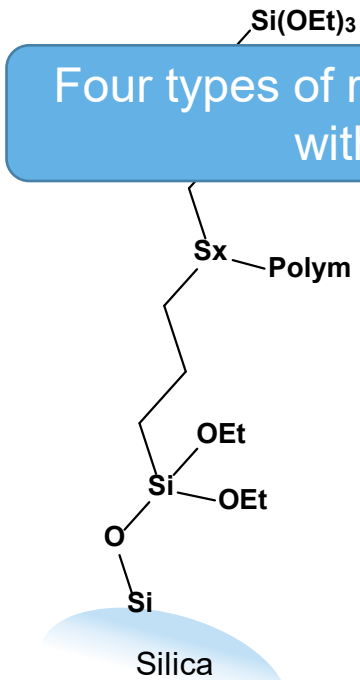
Possible reactions in the functionalized SBR compound



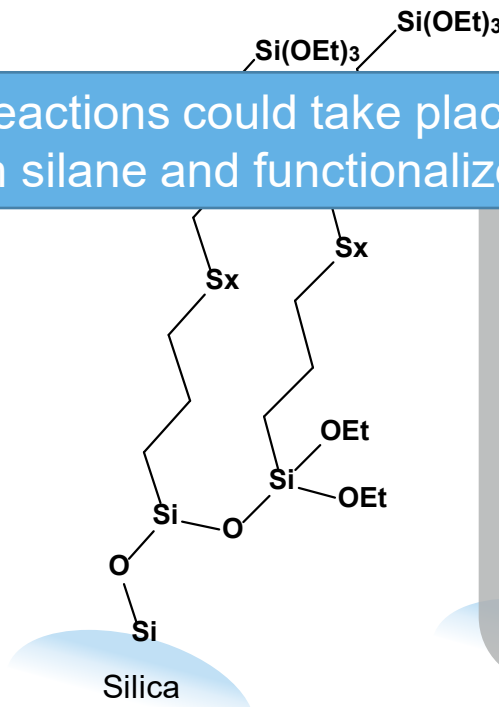
Silane and silica
(silanization)



Silane modified
silica and SBR
(sulfur coupling)

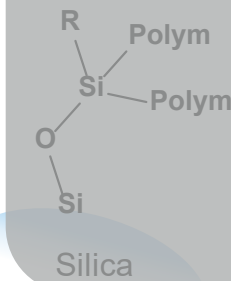


Silane modified
silica and silane

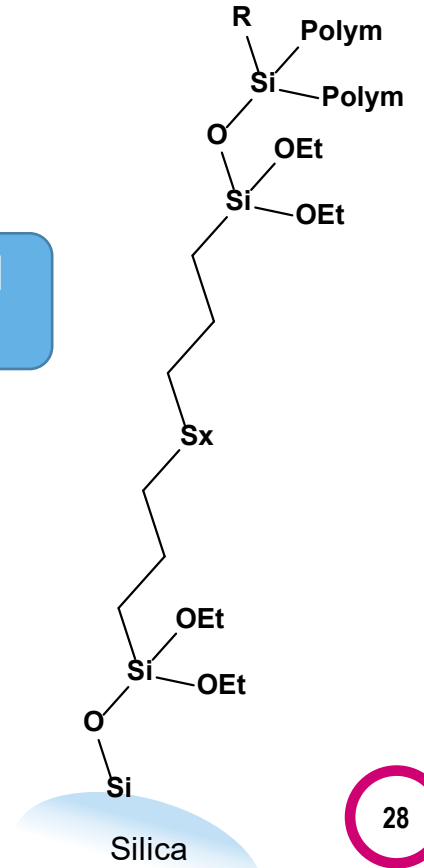


Four types of reactions could take place in the compound with silane and functionalized SBR

in SBR and silica



Functional group in
SBR and silane





**THANK YOU FOR
YOUR KIND ATTENTION!**