UNIVERSITY OF TWENTE.

AsahiKASEI

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

C. Yamada[1,2], A.Yasumoto[2], J.W.M. Noordermeer[1], W.K. Dierkes[1], A. Blume[1]

[1] University of Twente, Dept. of Elastomer Technology and Engineering (the Netherlands)

[2] Asahi Kasei Corp. (Japan)

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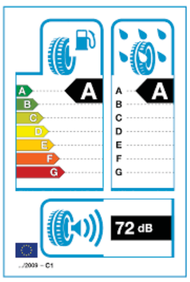
German Rubber Conference

Tire market performance requirements

Tire labeling

EU

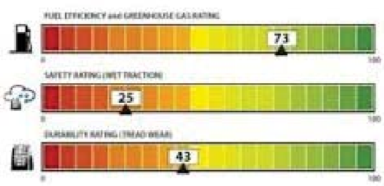


Japan

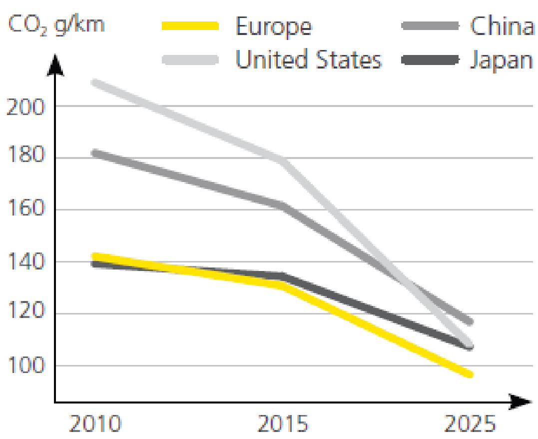
eco tire share in Japan
2010 45% → 2013 70%

Korea

US (planned)



CO2 emission legislation (OE)



High Fuel Efficiency (RR)

Better Wet Grip

Wear Resistance

Strong demand for improving overall performance

Rubber for Tread of Tire

Tread

Performance	Material
● Low-RR ● Grip ● Wear resistance	SBR NR BR Filler (Silica) Oil

E-SBR and S-SBR

S-SBR (Solution SBR) **S**olution-polymerized **S**tyrene **B**utadiene **R**ubber
E-SBR (Emulsion SBR) **E**mulsion-polymerized **S**tyrene **B**utadiene **R**ubber

	E-SBR	S-SBR
Process	Emulsion	Solution
Polymerization	Radical	Anionic
Styrene (%)	0 – 50 %	Controllable (0 ⇔ 90 %)
Styrene Chain	Random	Controllable (Random ⇔ Block)
Vinyl in Butadiene	15 – 18%	Controllable (0 ⇔ 80%)
Functionalization	Introduce 3rd monomer	Chain end
Branching	Multi branched	Controllable (linear ⇔ multi branched)
MW distribution	Wide	Controllable (Wide ⇔ narrow)

Saito, A.: Nippon Gomu Kyokaishi, 71, 41(1998)

How to improve S-SBR?

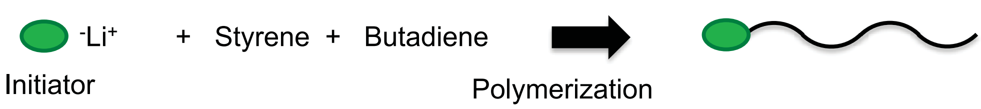
		Advantages	Bad point
Macro structure	High molecular weight (less free chain ends)	Lower tanδ	Lower Processability
	Narrow molecular distribution (less free chain ends)	Lower tanδ	Lower Processability
	Less branch or graft structure (less free chain ends)	Lower tanδ	Lower Processability
Microstructure	Low vinyl content (lower Tg)	Lower tanδ	Lower grip
	Low styrene content (lower Tg)	Lower tanδ	Lower grip and processability
Functionalization	Less free chain ends	Lower tanδ (Good filler dispersion)	Lower processability

Saito, A.: Nippon Gomu Kyokaishi, 71, 41(1998)

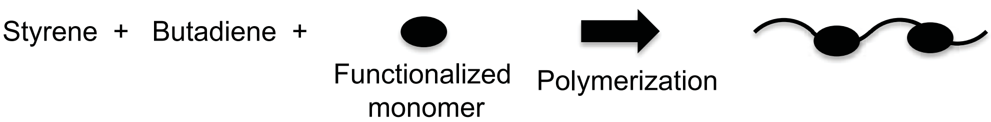
How to introduce functional group in S-SBR?

1. **Functionalization of the chain end**

2. **Functionalization of initiator**



3. **Functionalization of main chain with functionalized monomer**



4. **Functionalization of side chain**

The aim of this study

Investigate the effect of functional group on silica compounds

Polymers

● Amine group
● Alkoxy amine group

Mw (kg/mol)	240-280
ML (100C)	42-47
Styrene (wt%)	27
Vinyl (wt%)	42-43

Experiments

	Effect	Method
1	Silica micro dispersion	TEM, USAX
2	Flocculation of filler	RPA2000
3	Filler-polymer interaction	Bound rubber, Payne effect

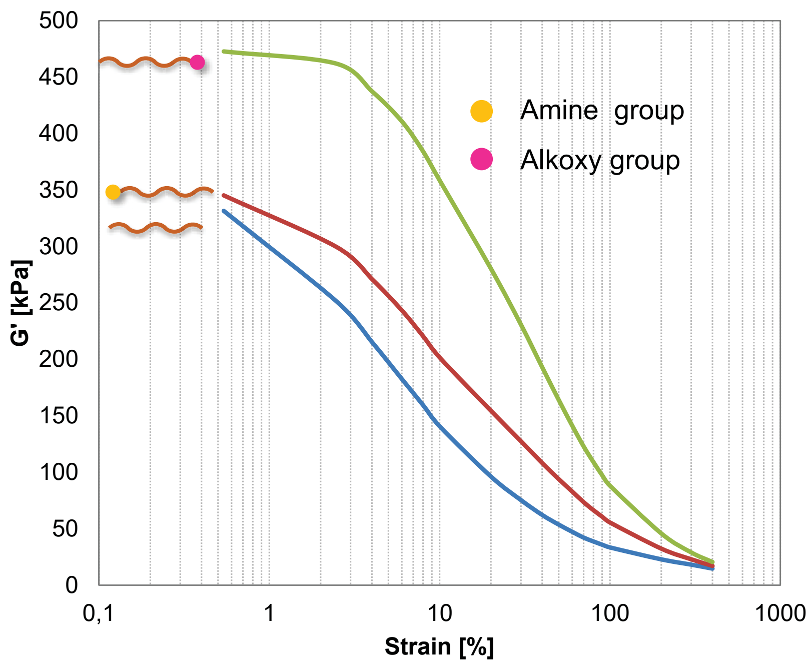
Formulation, mixing procedure and cure condition

Formulation (phr)	
SBR	80
BR (UBEPOL BR150)	20
Silica (ULTRASIL 7000GR)	75
TESPT	5.6
TDAE oil (total)	33
Zinc Oxide	2.5
Stearic Acid	2.0
Antioxidant (6PPD)	2.0
Sulfur	2.2
CBS	1.7
DPG	2.0

Master batch (MB1) Brabender	
Time	
0:00	Add Polymers
0:20	Mix
1:20	1/2 Silica, 1/2 TESPT, Oil
1:50	Mix
2:50	1/2 Silica, 1/2 TESPT, Stearic Acid, Zinc Oxide
3:10	Mix (Control rpm. up to target temp.)
4:10	Ram sweep
6:40	Discharge (145-150 C°)
Master batch (MB2) Brabender	
0:00	Add MB1
4:00	Discharge (145-150 C°)
Final Mix (Productive) Roll (50° C)	
	MB2 + Sulfur and Accelerators

Cure condition	
Temp	160 C°
Time	t90

Payne effect of uncured compounds



✓ The result was opposite to what expected.

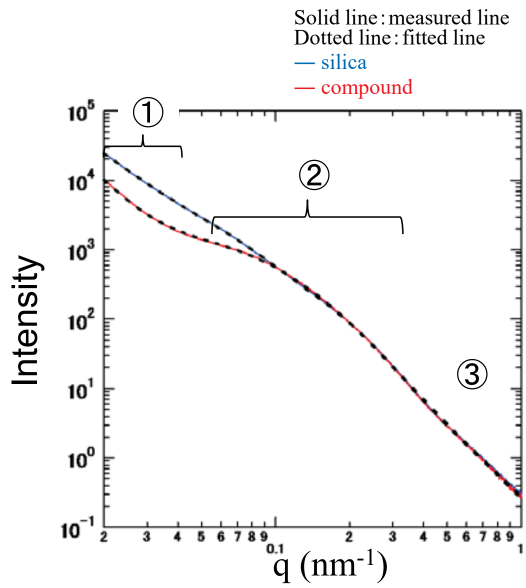
USAX measurement

$$I(q) = n[A\exp\{-q^2(\sqrt{3}r_{2nd})^2/3\}q^{-Dm} + \{I_{2nd}(q) + MI_{silica}(q)\} + B\{erf(qr_{silica}/\sqrt{6})\}^{3(6-Ds)}q^{-(6-Ds)}]$$

①fractal structure at small angle

②Secondary agglomeration

③fractal structure at large angle



A,B: constant

n: Number density of secondary aggregates

M: number of primary particles in the secondary aggregate

r_{2nd}, r_{silica}: secondary aggregate, average primary radius of silica primary particle

D_m, D_s: fractal dimension at small and wide angle

$I_{2nd}(q)$: Scattering equation of the same structure with uniform internal size and secondary aggregates

Electron density difference: $[v*\rho_{silica}+(1-v)*\rho_{polymer})] - \rho^{polymer}$

v: silica volume fraction in the secondary aggregate

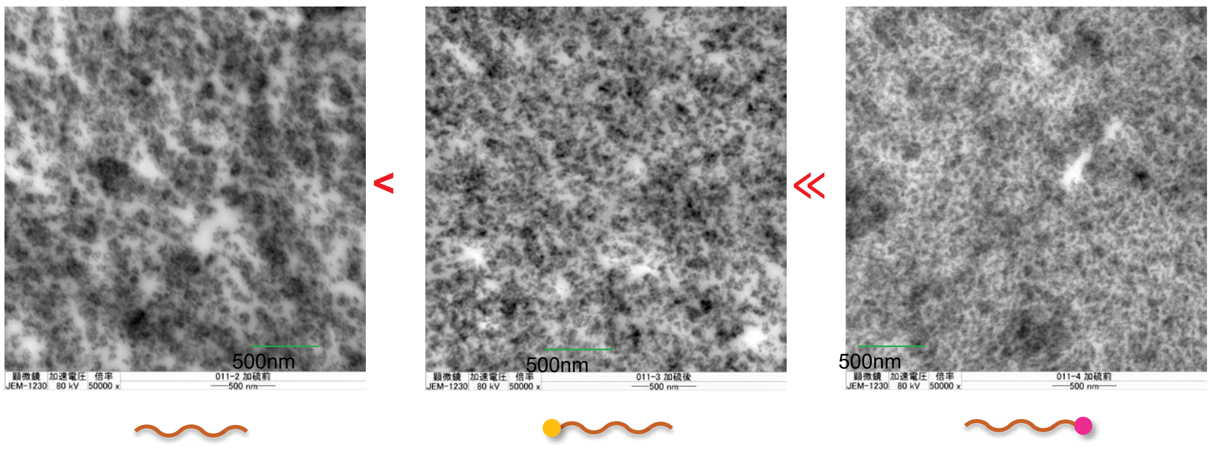
$Isilica(q)$: When the structure in the secondary aggregate is infinitely spread

USAX result and TEM images

Average silica size from USAX profile (nm)

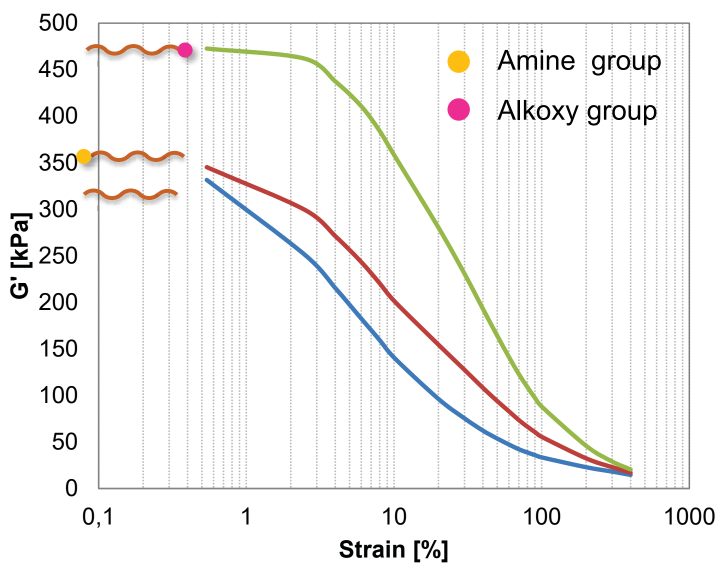
● Amine group
● Alkoxy group

54 < **52** ≪ **48**



- ✓ **The results of USAX and TEM do not correlate with Payne effect (ΔG′).**
  - Amine group slightly affects the silica dispersion
  - Alkoxy group improves the silica dispersion

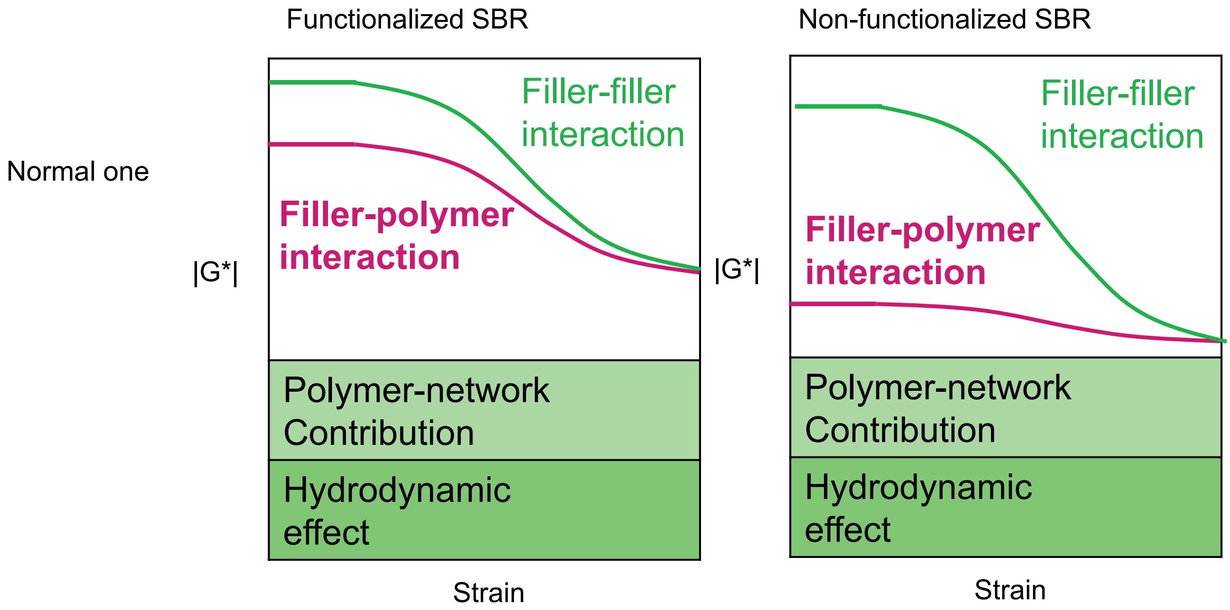
Payne effect of uncured compounds



- ✓ Higher G′ at high strain in functionalized SBR
- ✓ Plateau curve in alkoxy SBR compounds

Because of higher filler-polymer interaction

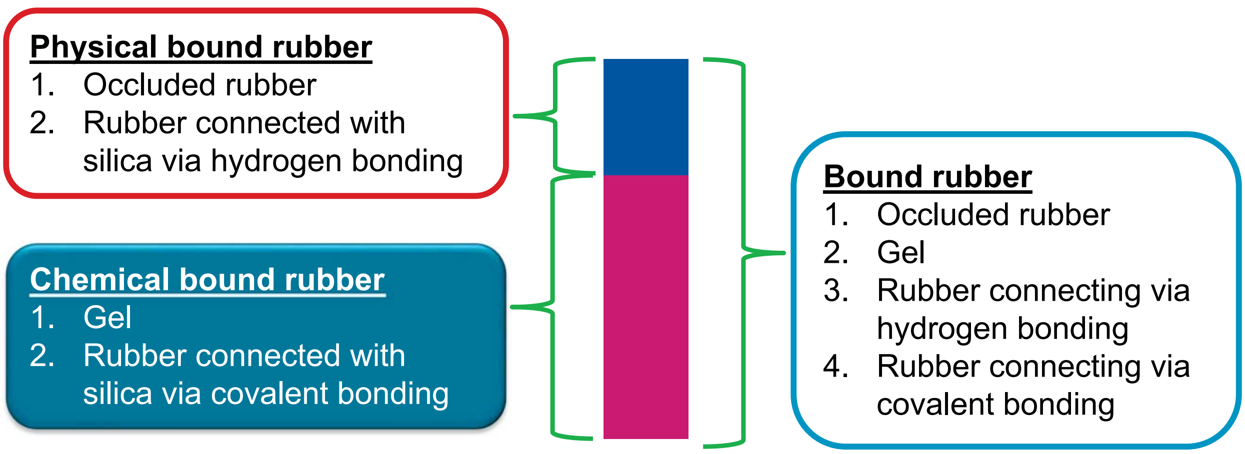
Comparison the result of payne effect and USAX



✓ Possibility that filler-polymer interaction can be dependent on strain as various bonding styles exist between rubber and silica

Measurement bound rubber

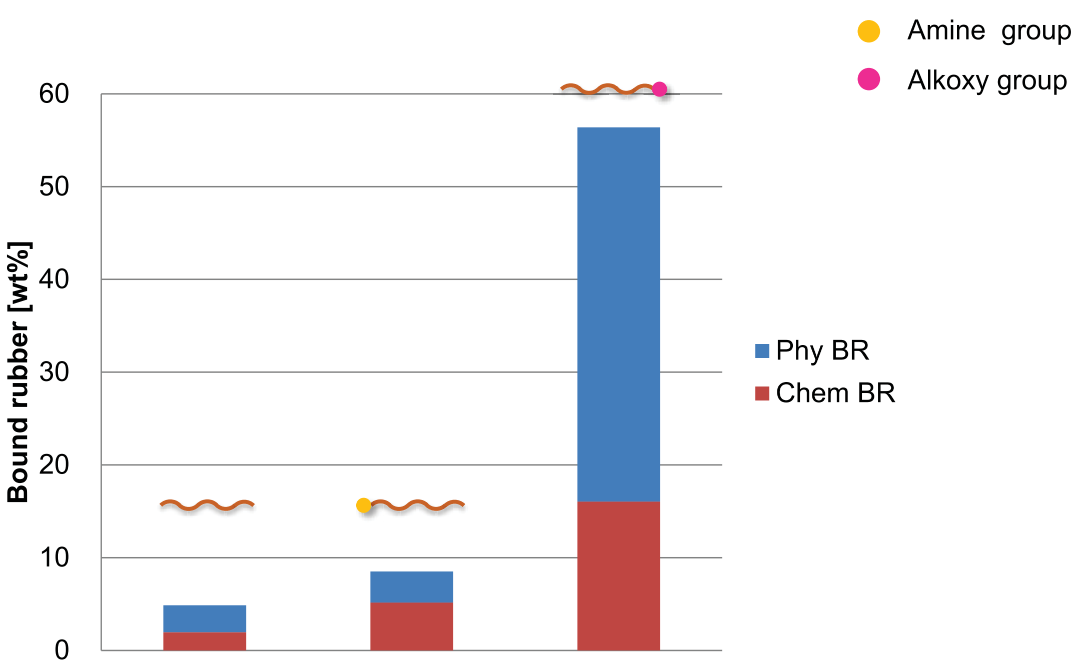
Phy BR Rubber weekly connected to silica
Chem BR Rubber strongly connected to silica



connected with silica via hydrogen bonding

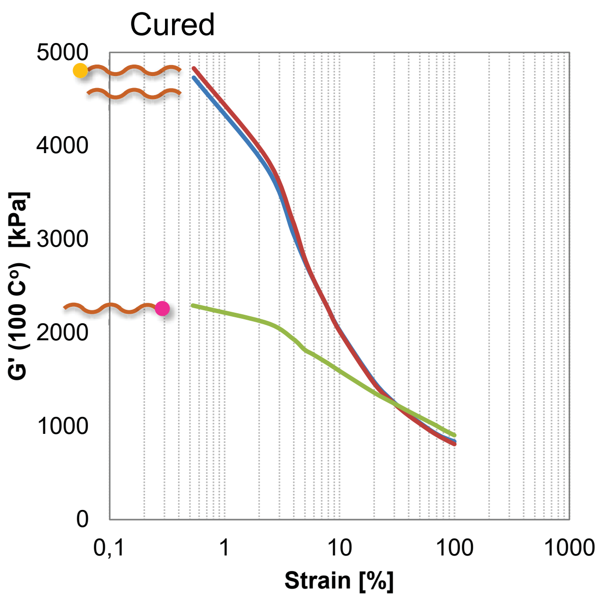
connected with silica via covalent bonding

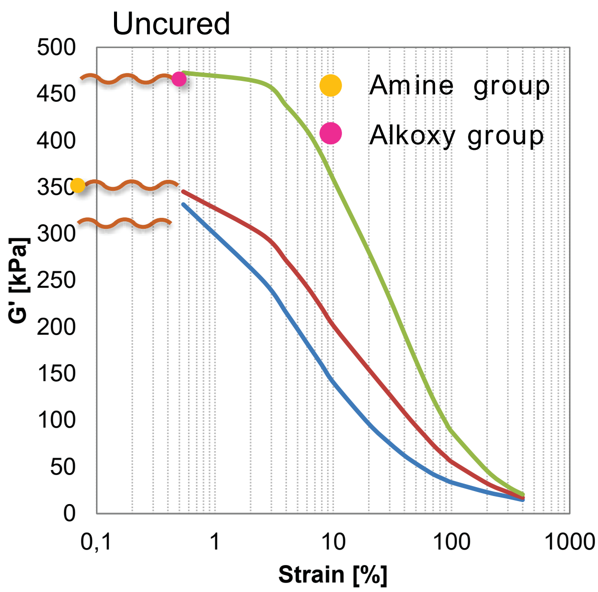
Bound Rubber of uncured compound



- ✓ Alkoxy group : More chem BR and phy BR
- ✓ Amine group : Small effect on BR

Payne Effect After Cure

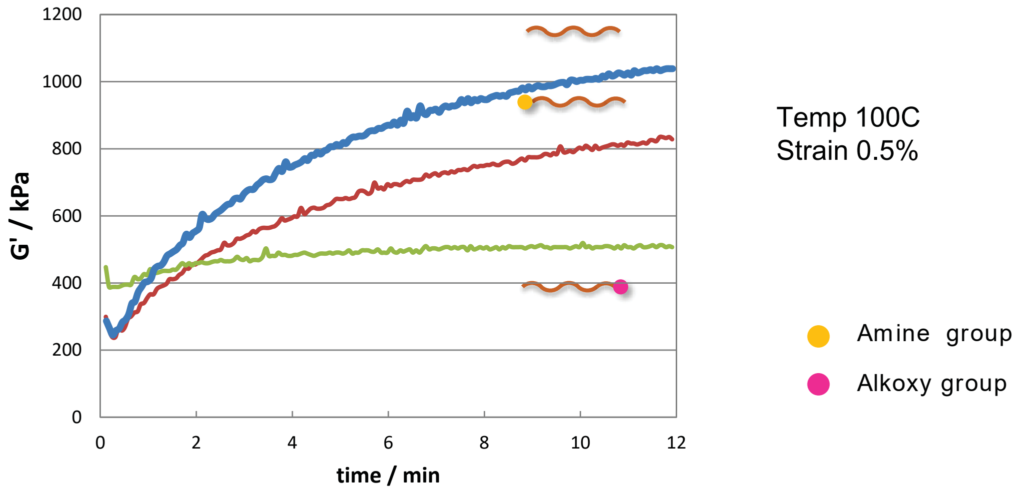




- ✓ Alkoxy functionalized SBRs : Lower G′ at low strain
  → opposite behavior to uncured G′

Flocculation

Flocculation is re-agglomeration of silica during curing process

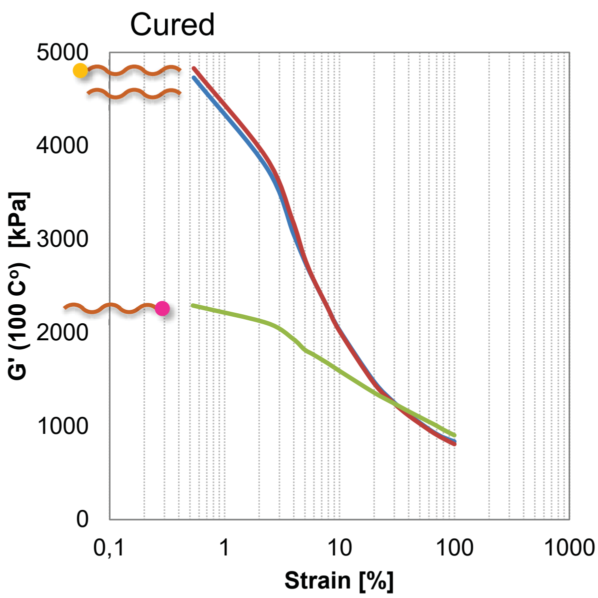


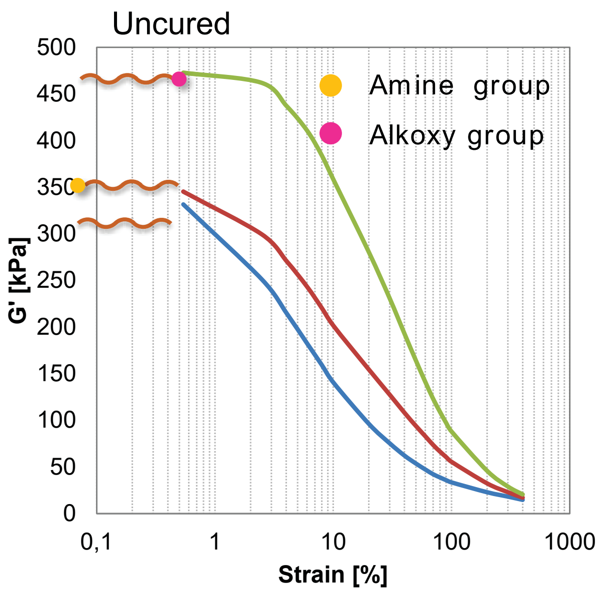
- ✓ Alkoxy group : Significant effect for reducing flocculation
- ✓ Amine group : Some effect for reducing flocculation

Higher filler-polymer interaction → Lower flocculation

Compound with alkoxy SBR shows lower cured G′ despite of higher uncured G′

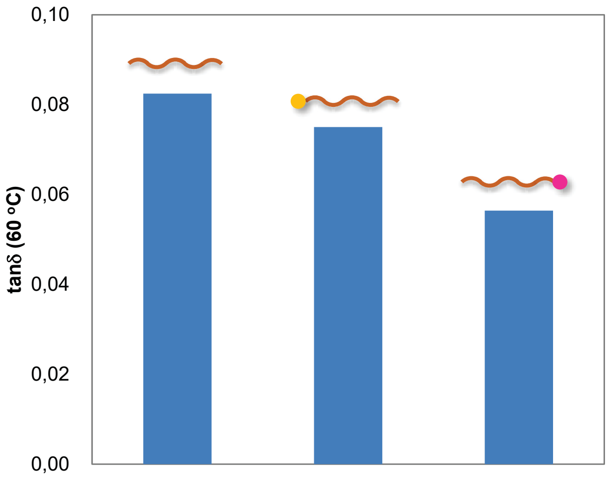
Payne Effect After Cure

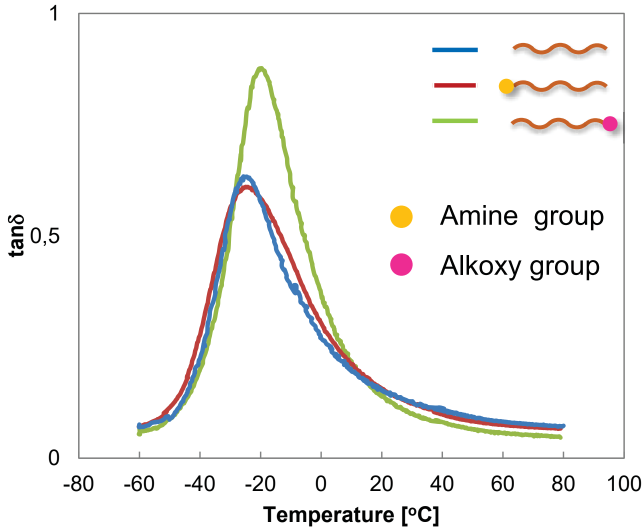




✓ Cured G′ shows opposite behavior as uncured G′
→ Flocculation occurs during curing process

tanδ

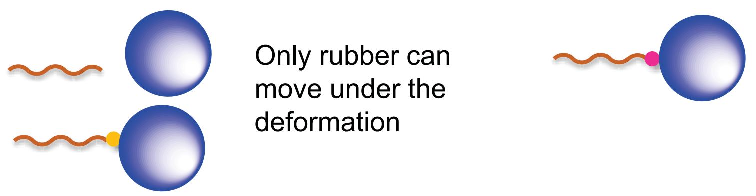




- ✓ Alkoxy functional group : more effect on improving tanδ
- ✓ Amine group : slight effect on tanδ
- ✓ Alkoxy functional group : Higher peak of tanδ

Why tanδ peak is higher in functionalized SBR compound?

1. Strong filler-polymer interaction changes silica to act rubber-like



Only rubber can move under the deformation

Silica particle can move with rubber under the deformation

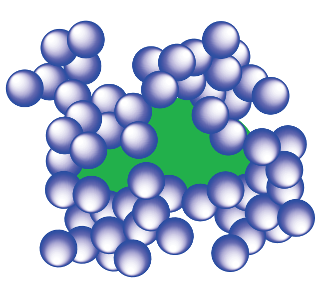
No or week interaction with silica

Strong interaction with silica

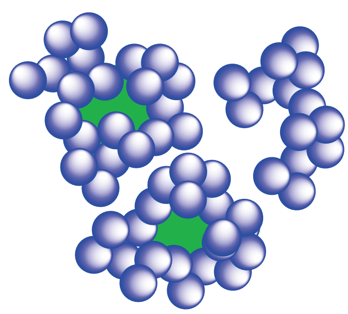
2. There is less occluded rubber because of better dispersion

Amine group

Alkoxy group



Worse dispersion
→More occluded rubber



Better dispersion
→less occluded rubber

The Summery

- ✓ Alkoxy group can improve silica dispersion and filler-polymer interaction, and reduce flocculation, on the other hand, effect of amine group is smaller.
- ✓ Payne effect does not always relate to silica dispersion and dependent of filler-polymer interaction on strain is suggested.
- ✓ High tanδ peak of functionalized SBR compound can be explained by rubber-like acting silica which has strong interaction with rubber.

Effect	How to analyze	Amine group 	Alkoxy group 
Silica dispersion	TEM, USAX	+	+++
Flocculation of filler	RPA2000	+	+++
Filler-polymer interaction	Bound rubber Payne effect	+	+++