DKT 2024
GERMAN RUBBER CONFERENCE
1-4 JULY, NUREMBERG, Germany

INFLUENCE OF ANTIOXIDANTS ON THE SILANIZATION REACTION DURING MIXING OF SILICA-FILLED NR COMPOUNDS

Ammarin Kraibut[1,2], Wisut Kaewsakul[1], Sitisaiyidah Saiwari[2], Kannika Sahakaro[2] and Wilma K. Dierkes[1]

[1] Elastomer Technology and Engineering (ETE), Department of Mechanics of Solids, Surfaces and Systems, Faculty of Engineering Technology, University of Twente, the Netherlands

[2] Polymer Technology, Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Thailand

Elastomer Technology and Engineering
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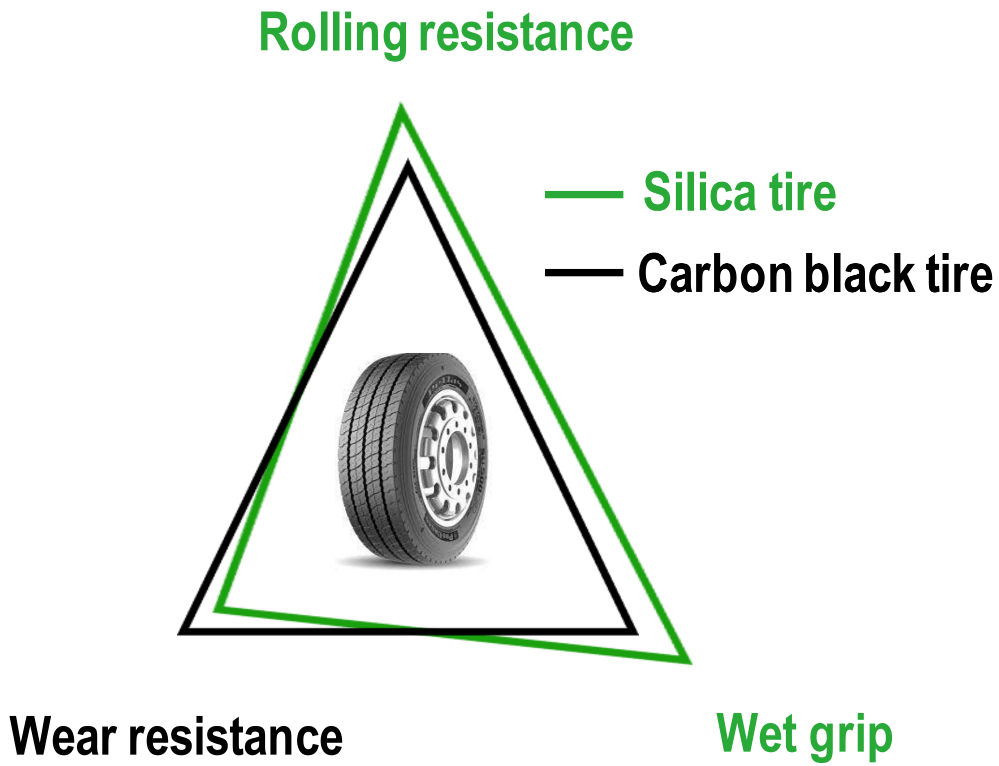
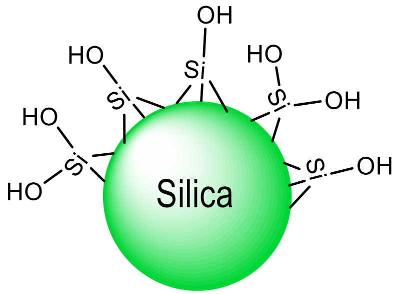
Introduction

Key tire performance indicators and challenges of silica



Magic triangle of tire performance



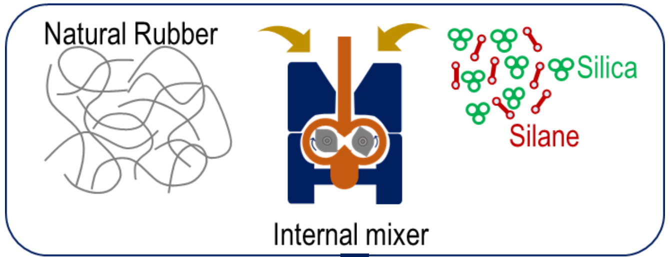
Structure of silica surface *

Silica

Drawback:

High polarity – incompatible with non-polar rubbers (e.g. NR, SBR, BR)

Introduction

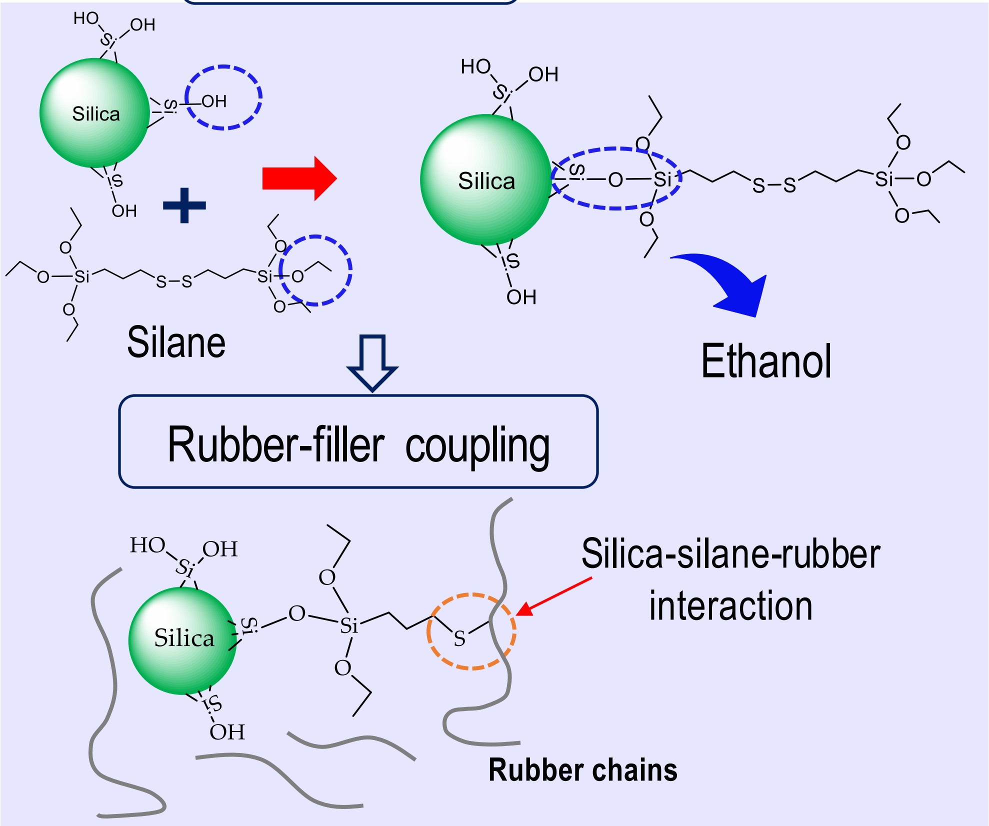


❑ **How to improve the compatibility between silica and rubber?**

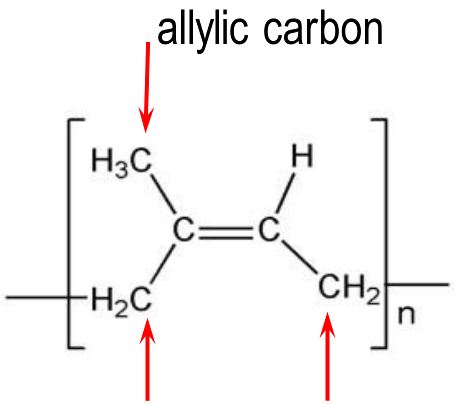
Shearing

Energy dissipation

Silanization



Natural Rubber, NR



Reactive allylic carbon atoms in NR

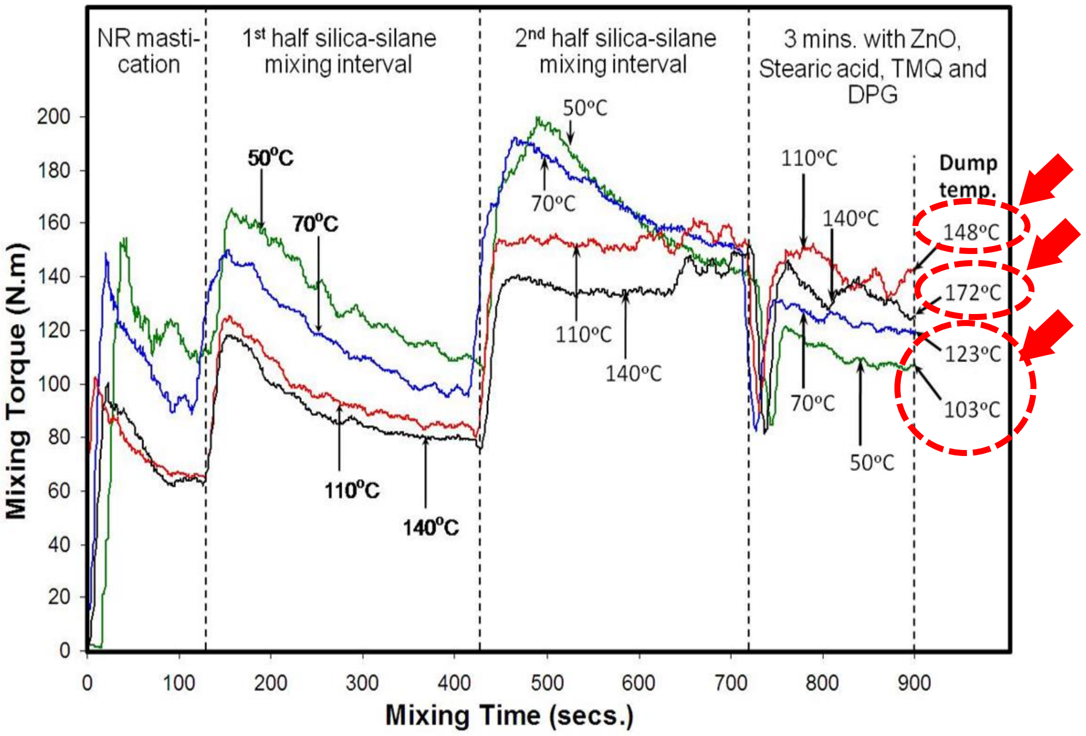
NR is prone to degradation at high temperatures.

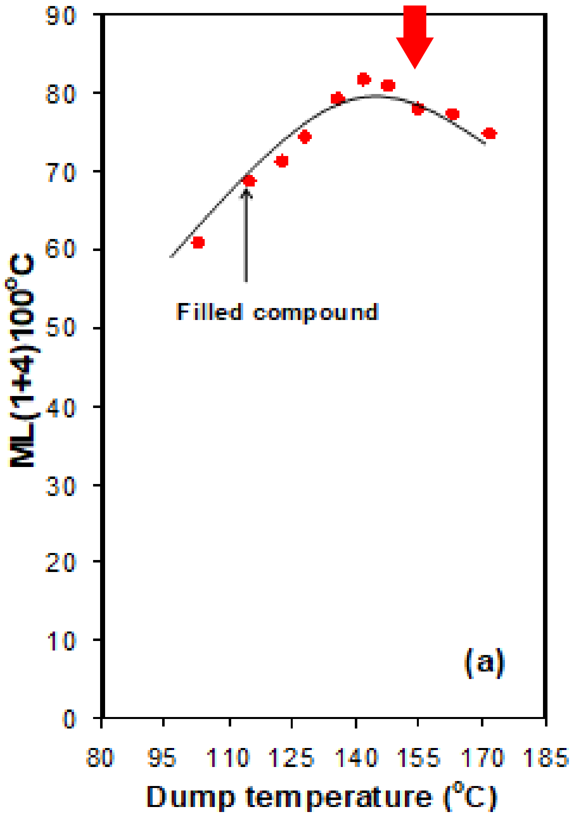
1. Kaewsakul et al., Polym Eng Sci. Vol 55 (4), pp. 836-842 (2015)
2. Kraibut et al., Materials. 73, 347 (2024)
3. https://www.kaohoon.com/breakingnews/407087 accessed on May 3, 2024

Introduction

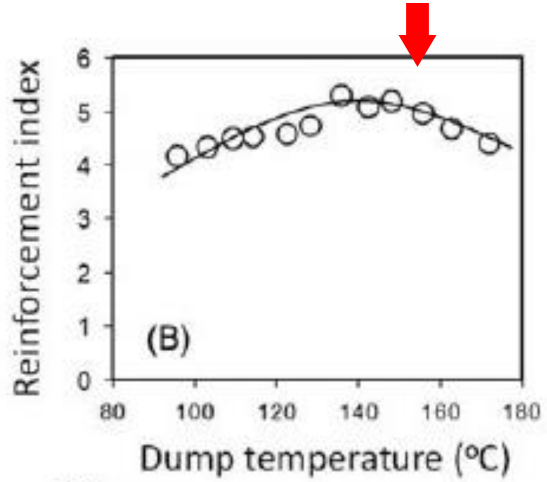
Evidence for degradation during mixing from literature

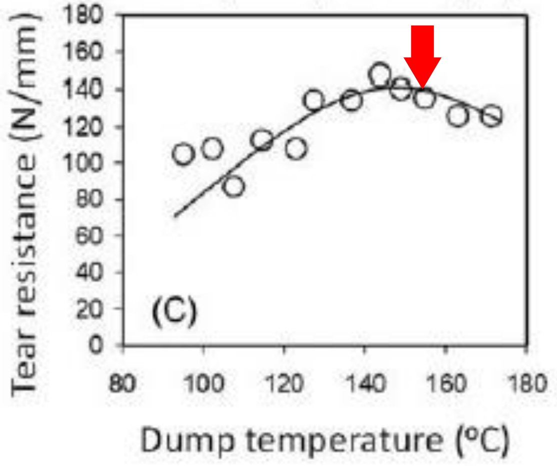
Compound properties





Vulcanizate properties

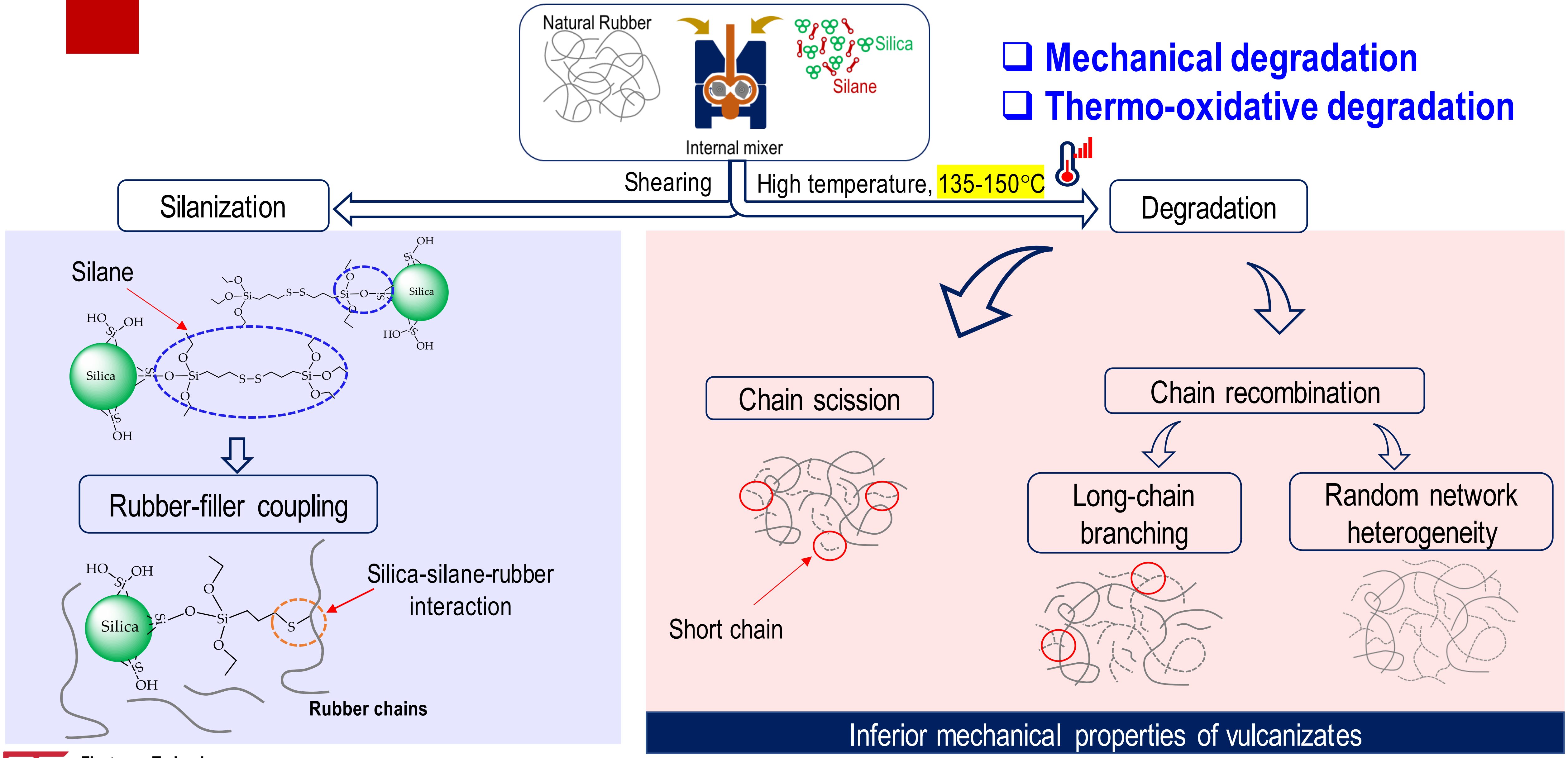




Kaewsakul et al., Rubber Chem. Technol. Vol. 85 (2), pp. 277–294 (2012).

Introduction

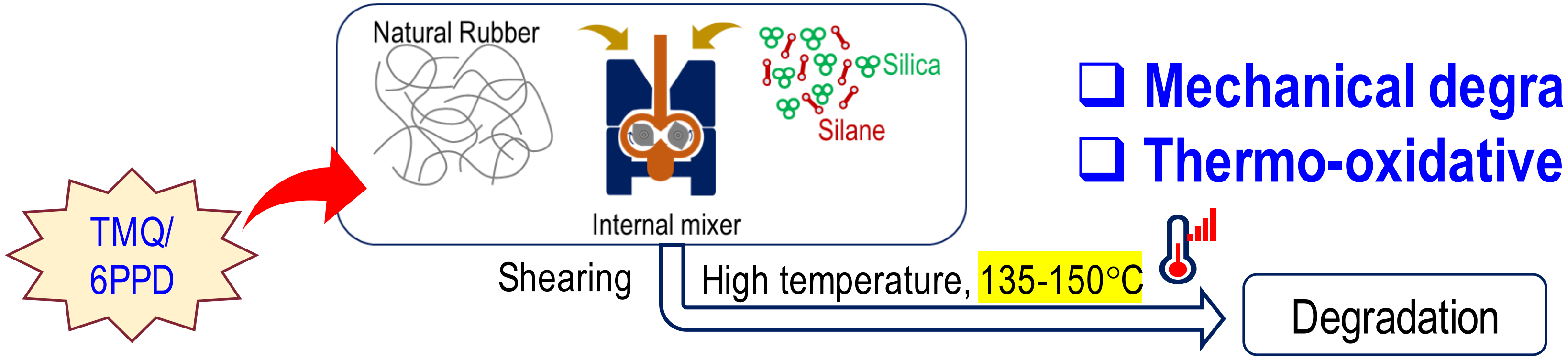
- ❑ **Mechanical degradation**
- ❑ **Thermo-oxidative degradation**



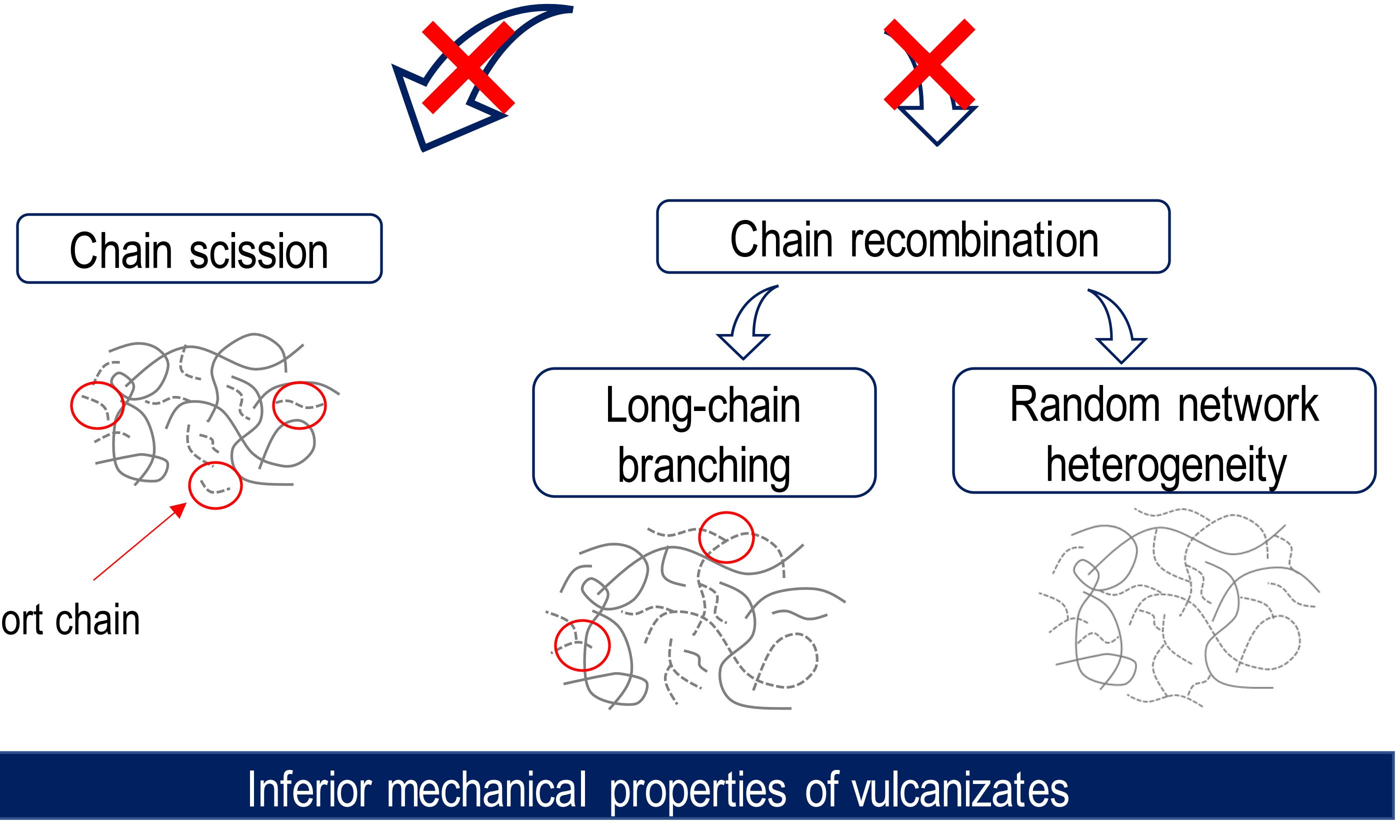
Kraibut et al., Materials. 73, 347 (2024)

Introduction

- ❑ **Mechanical degradation**
- ❑ **Thermo-oxidative degradation**



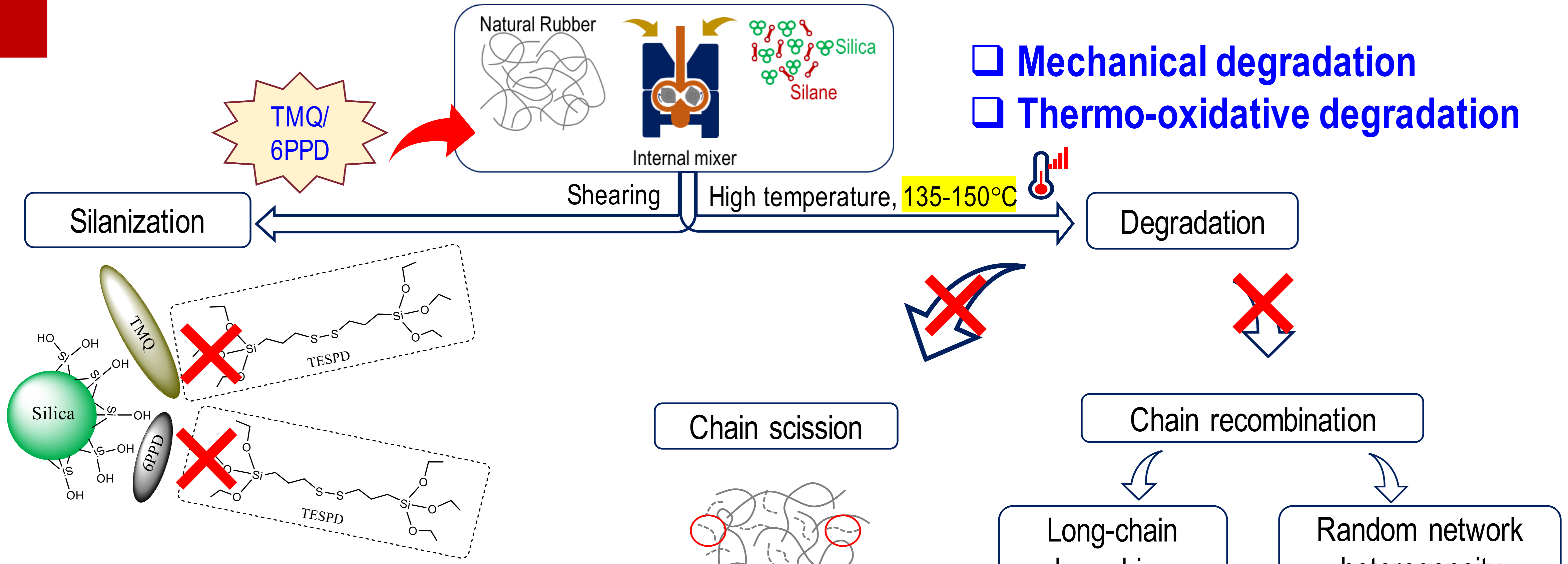
How can these degradation mechanisms be suppressed?



Can TMQ/6PPD suppress the degradation and affect on silanization during mixing of silica-filled NR compounds?

Kraibut et al., Materials. 73, 347 (2024)

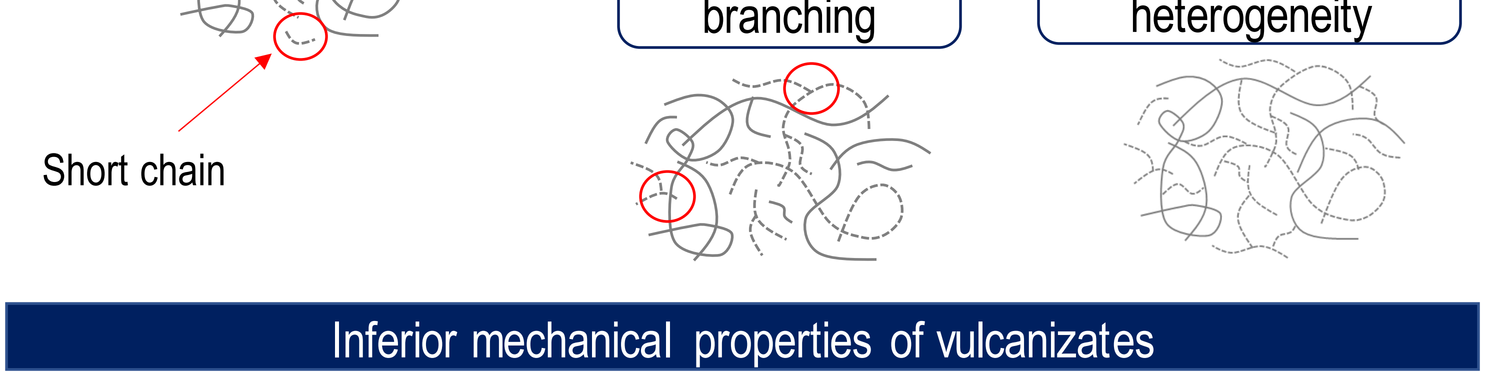
Introduction



Possible effects of TMQ/6PPD:

+ Suppression of degradation of NR

- Effect on silanization efficiency



Kraibut et al., Materials. 73, 347 (2024)

Research methodology

Experimental

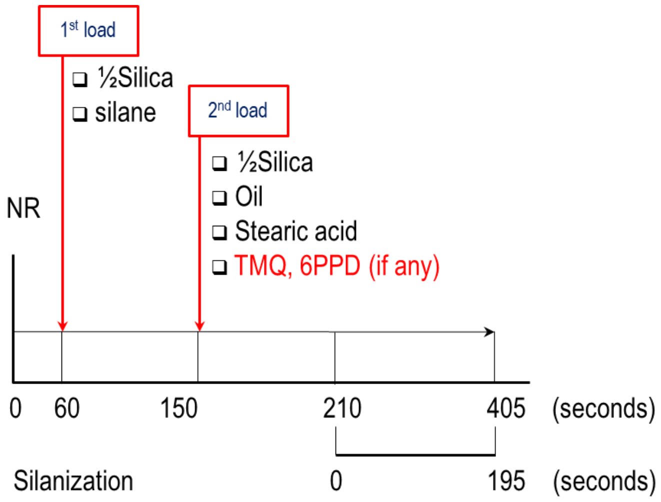
Rubber formulations

Ingredients	Without antioxidants		TMQ/6PPD	
	Gum	Filled NR	Gum	Filled NR
1st step mixing				
NR (SMR-10)	100	100	100	100
Silica (ULTRASIL 7005)	0	55	0	55
TESPD	0	5	0	5
TDAE	0	8	0	8
Stearic acid	1	1	1	1
TMQ	0	0	1	1
6PPD	0	0	2	2
2nd step mixing				
DPG	1.1	1.1	1.1	1.1
ZnO	3.0	3.0	3.0	3.0
CBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

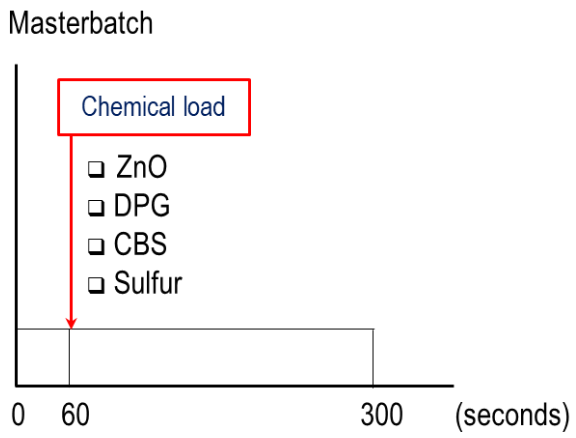
Experimental

Mixing procedure

1st Step Mixing: Gum or Filled NR



2st Step Mixing: Final step of Gum & Filled NR



- Mixer temperature setting 120 °C for Gum and 90 °C for Filled NR
- Fill factor 0.7
- Rotor speed: 50 – 80 rpm to reach dump temperature (i.e.150 °C)

- Mixer temperature setting 70 °C
- Fill factor 0.7
- Rotor speed: 35 rpm

Experimental

Characterization

1) Uncured compounds

Viscoelastic properties

- Mooney viscosity
- Mooney stress relaxation

→ A larger negative stress relaxation slope (a), a higher viscous response

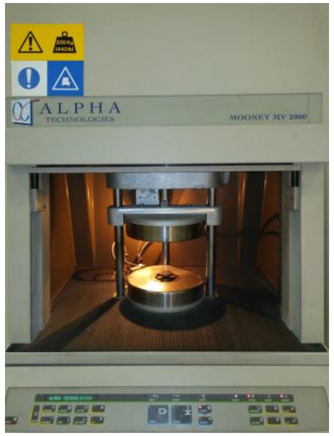
Reinforcing parameter

- Dynamic properties measured as strain sweep

→ Filler-filler interaction

- Bound rubber content

→ Filler-rubber interaction



Mooney viscometer

Rubber Process Analyzer (RPA)

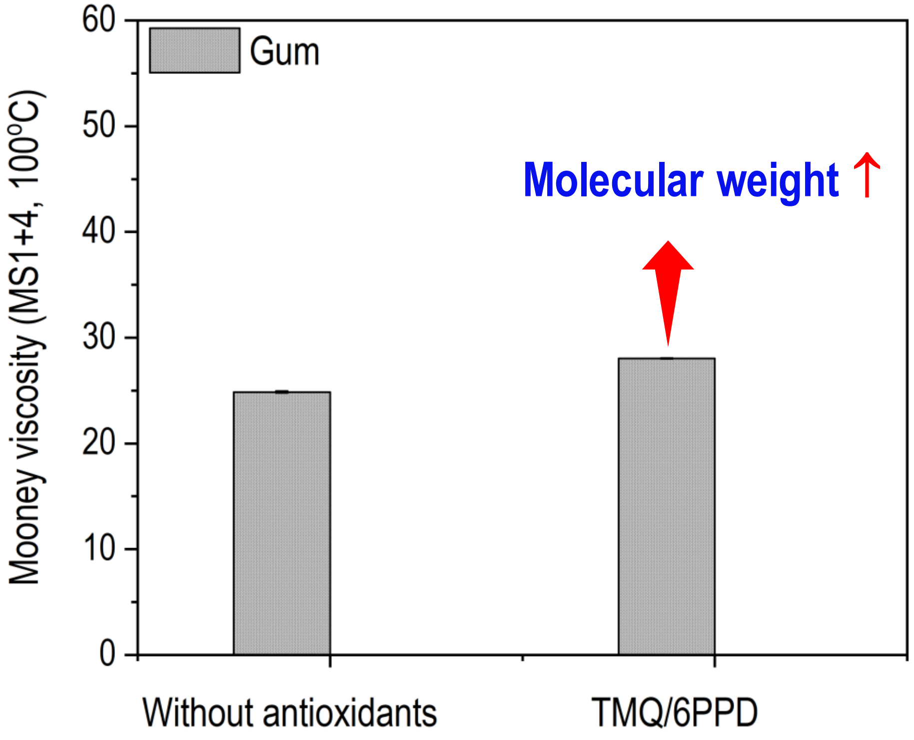
2) Vulcanizates → Mechanical properties

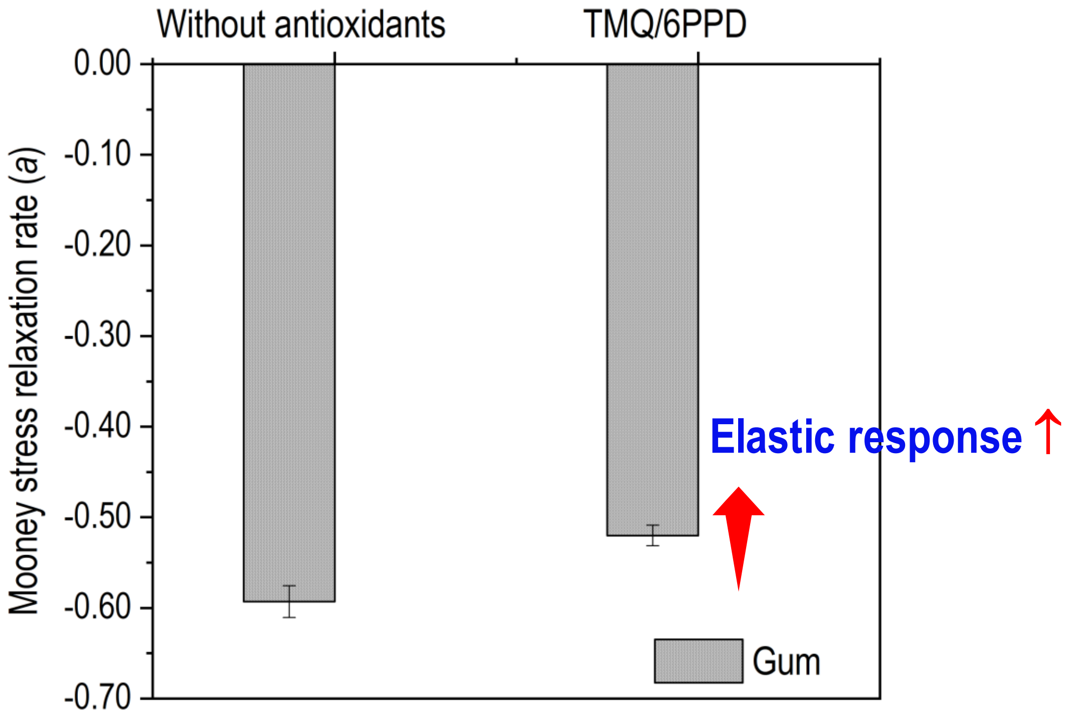
1. https://en.wikipedia.org/wiki/Mooney_viscometer accessed on May 3, 2024
2. https://www.directindustry.com/prod/ta-instruments/product-38477-1795348.html accessed on May 3, 2024

Viscosity and viscoelastic properties

Viscosity and viscoelastic properties

Mooney viscosity and stress relaxation: Gum compound



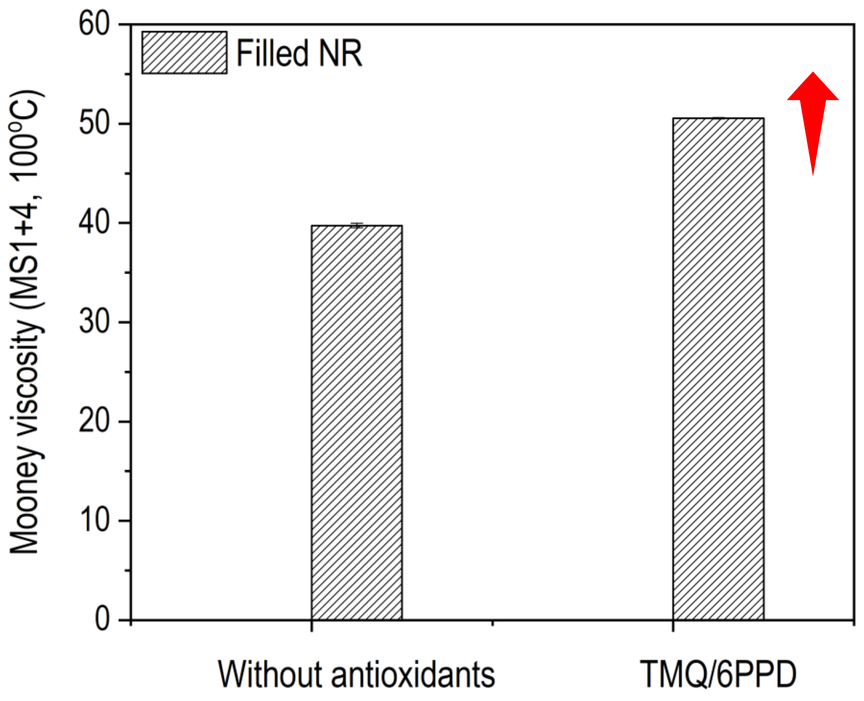


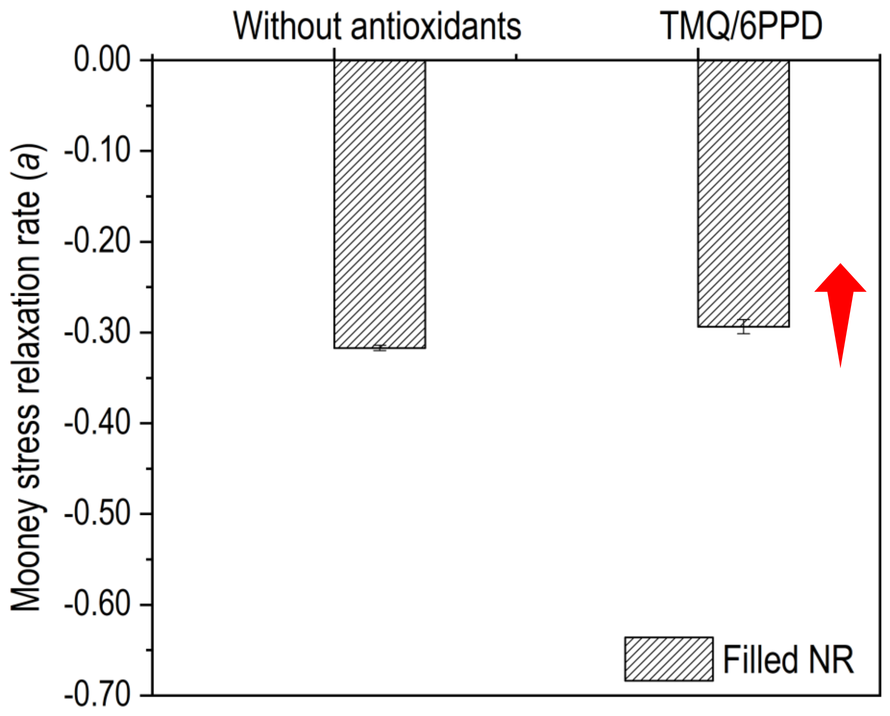
Mooney viscosity ↑ → Rate of Mooney stress relaxation ↓

Antioxidants can reduce chain scission, confirmed by a higher viscosity and elasticity of the compound.

Viscosity and viscoelastic properties

Mooney viscosity and stress relaxation





Higher compound viscosity can be due to:

- **Higher molecular weight ✓**
- **Higher filler-rubber interaction?**
- **Higher filler-filler interaction?**

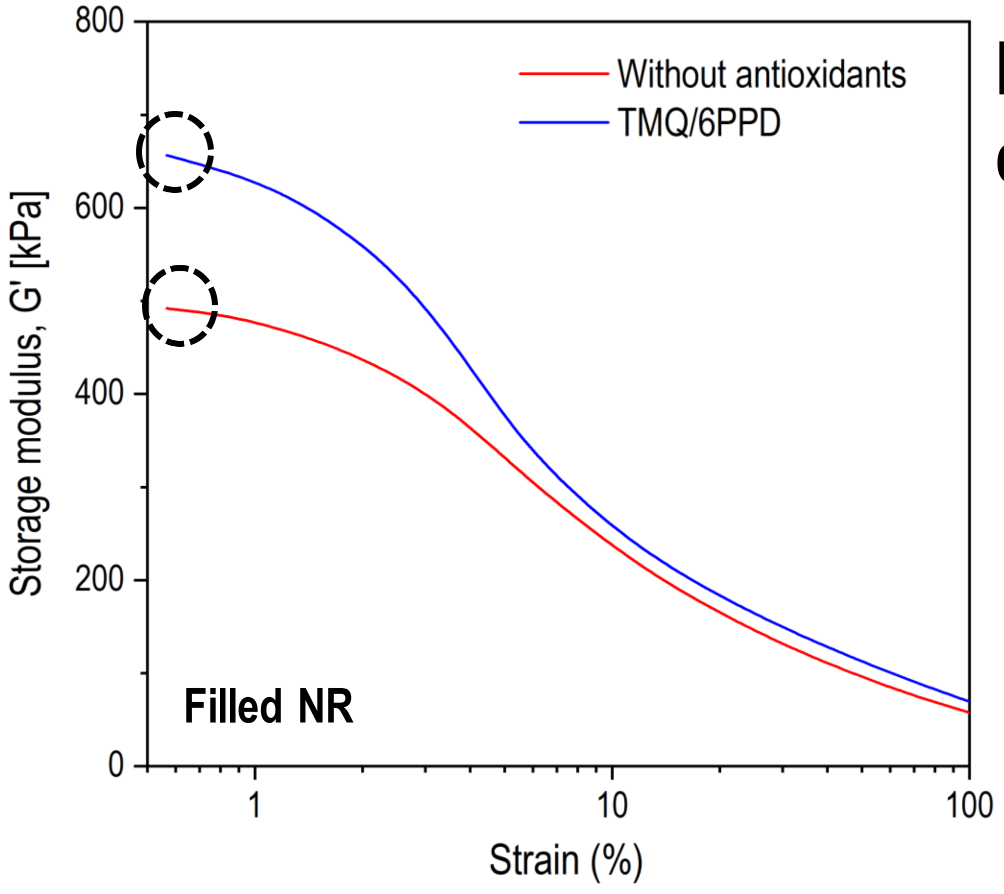
Do antioxidants interfere with the silanization and coupling reactions??

Reinforcing parameter

Filler-filler interaction

Silica dispersion

Filler-filler interaction



Higher Payne effect = more filler-filler interaction due to:

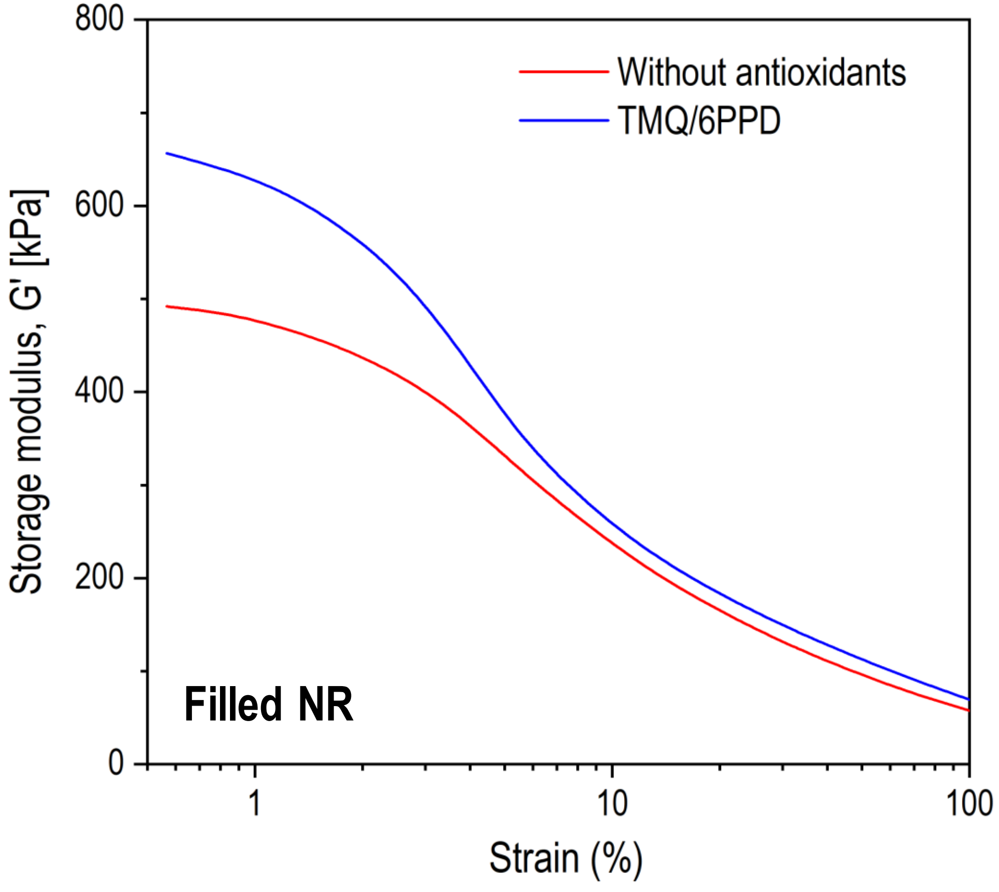
- **Higher Mw → higher initial modulus?**
- **Interference of antioxidants with silanization?**

A systematic proof is required!

ΔG′ at low-high strain indicates filler-filler interaction.

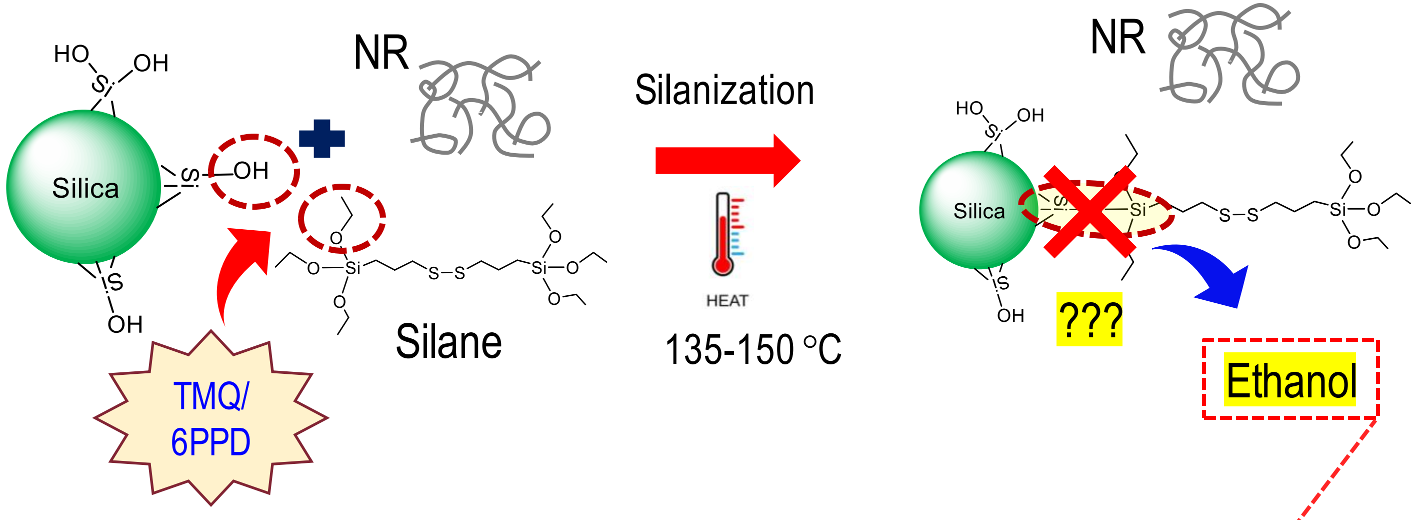
Silica dispersion

Filler-filler interaction



ΔG′ at low-high strain indicates filler-filler interaction.

Interference of antioxidants with silanization?



- Investigation of the effect of TMQ/6PPD using a model compound
- Observation of released ethanol as measurement of the degree of silanization

Model compound study

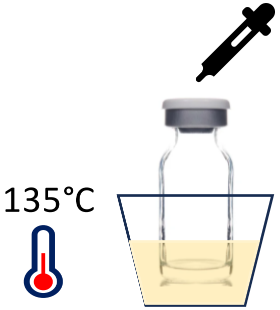
Influence of antioxidants on the silanization

Influence of antioxidants on the silanization?

Model compound study

Influence of antioxidants on the silanization

135°C



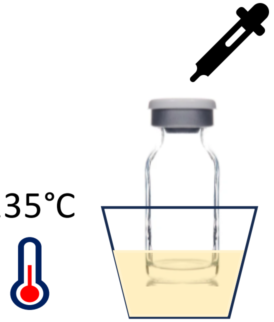
1) N-Decane
2) Silica
3) TESPD
4) TMQ or 6PPD (if any)

GC Analyzer

Quantify the ethanol released from the silanization reaction

Effect of antioxidants in the presence of DPG as a silanization booster

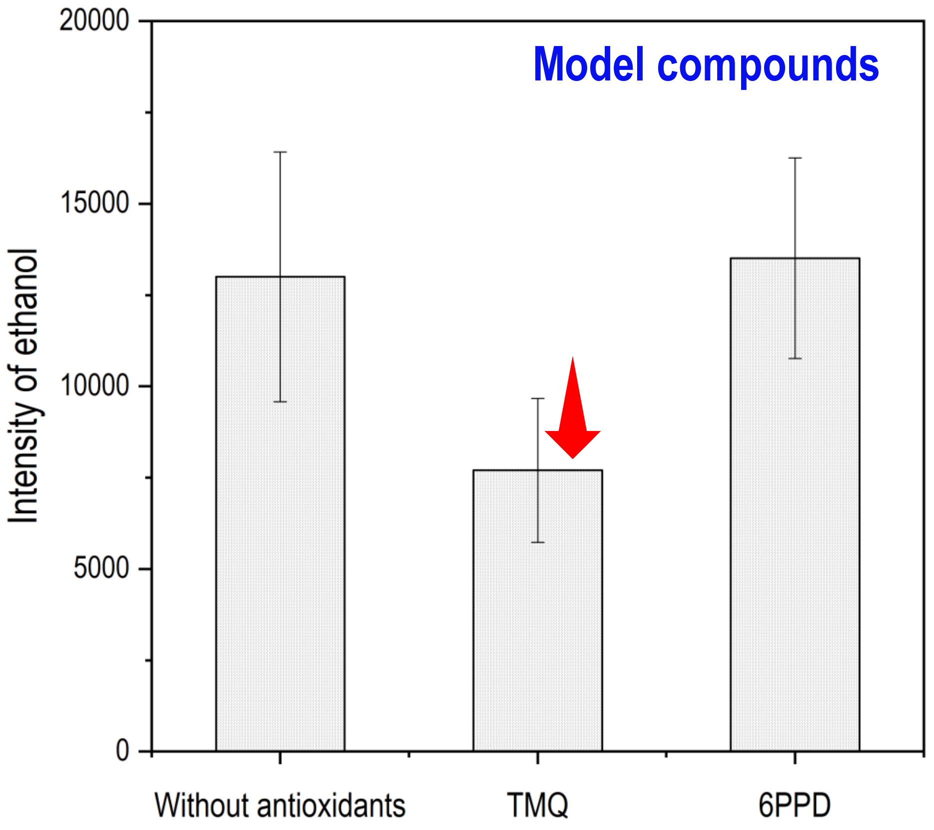
135°C



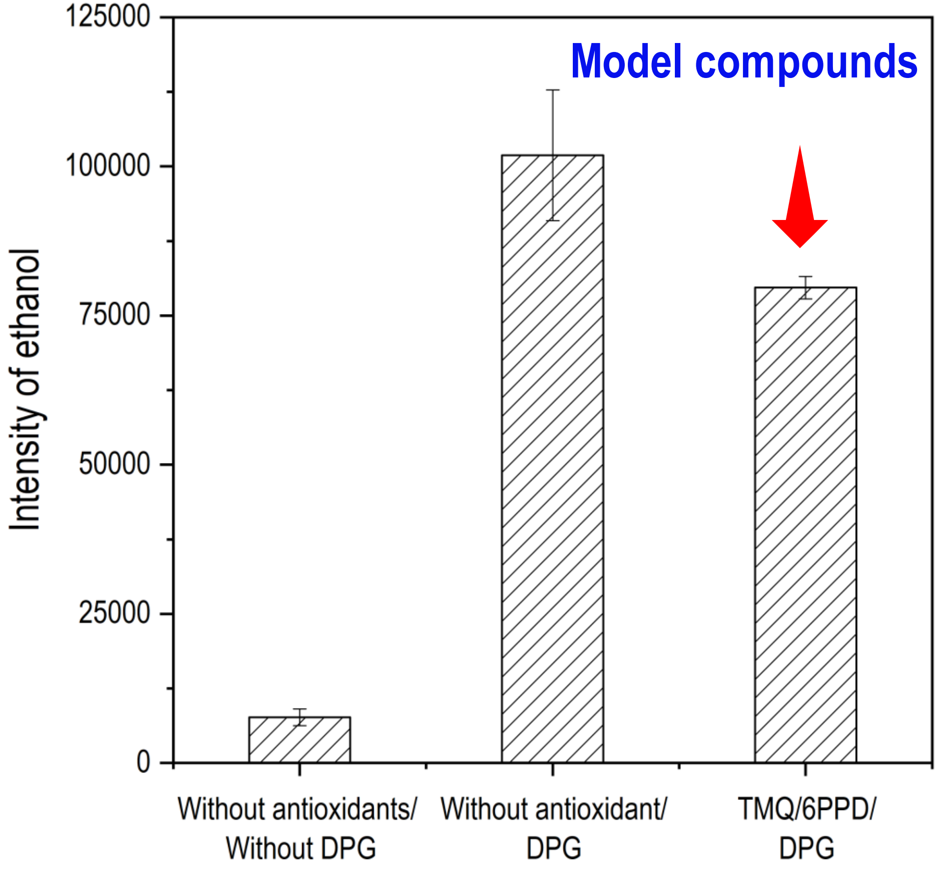
1) N-Decane
2) Silica
3) TESPD
4) DPG (if any)
5) TMQ/6PPD (if any)

Model compound study

Influence of antioxidants on the silanization



Effect of antioxidants in the presence of DPG as a silanization booster



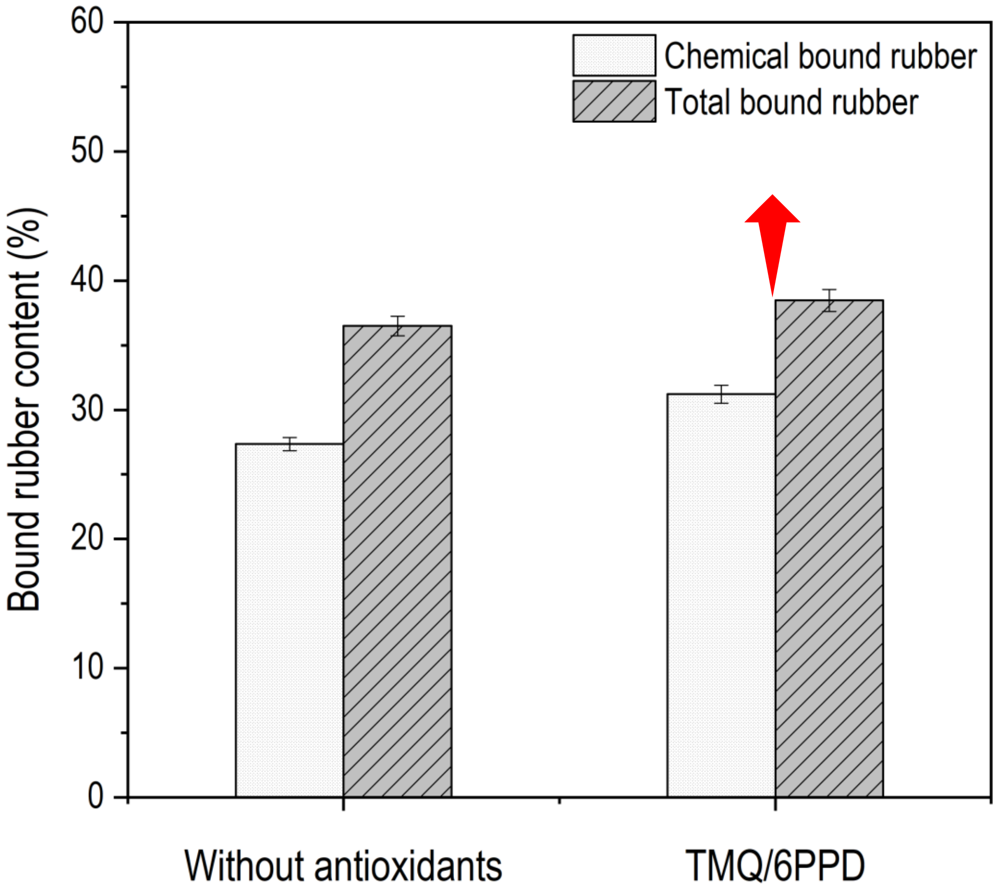
☑ Only TMQ is the one interfering with the silanization reaction.

Reinforcing effect

Filler-rubber interaction

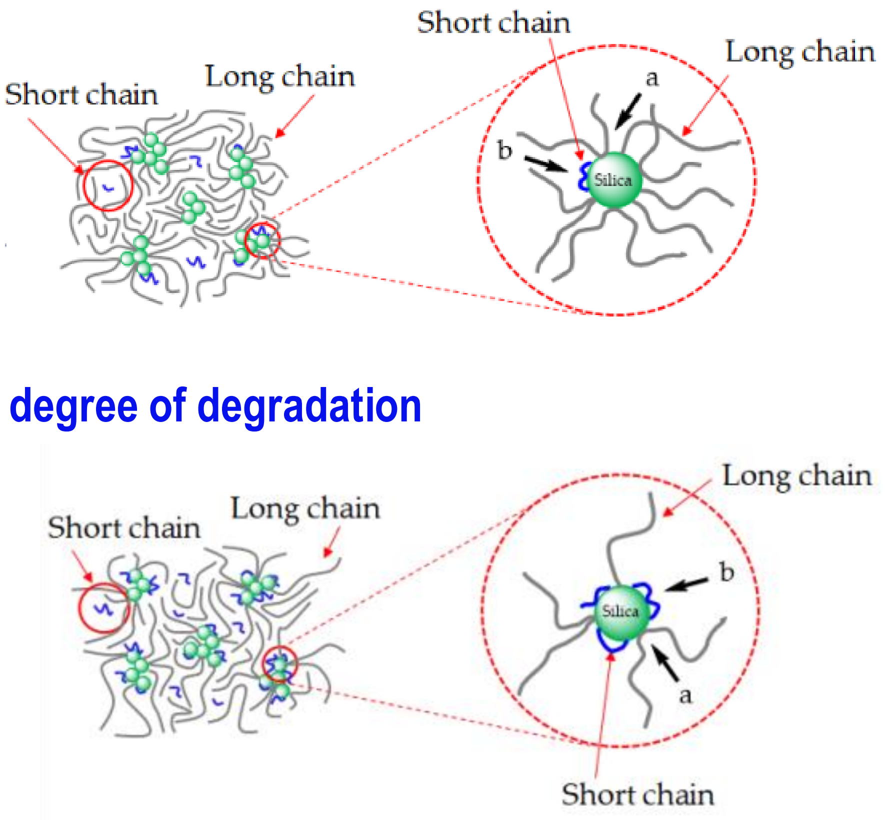
Reinforcing effect

Filler-rubber interaction



Low degree of degradation

High degree of degradation

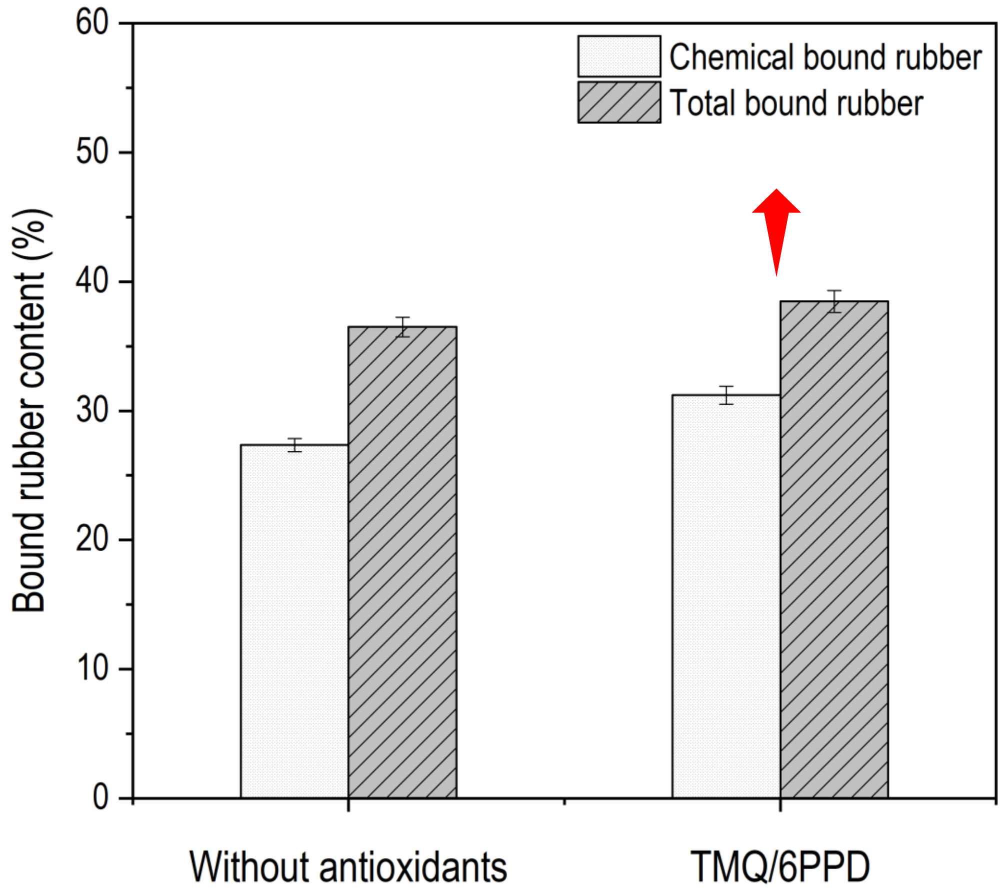


- ☑ Interference of TMQ on the silanization seems to be negligible.
- ☑ The higher molecular weight of antioxidants-compound causes the higher filler-rubber interaction

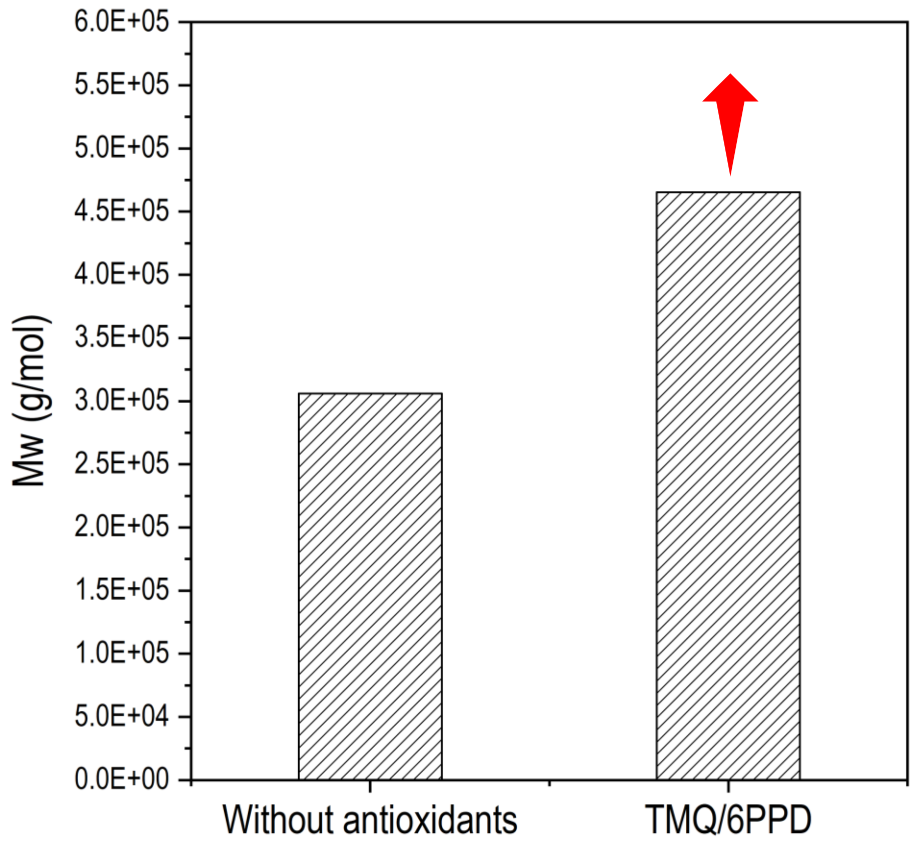
Kraibut et al., Materials. 73, 347 (2024)

Reinforcing effect

Filler-rubber interaction



GPC analysis of the sol fraction of silica-filled NR



- ☑ TMQ/6PPD suppresses the degradation resulting in higher Mw of rubber chains.
- ☑ Higher Mw of NR chains causes higher bound rubber content (filler-rubber interaction).

Influence of antioxidants

Intermediate sum up

Adding TMQ/6PPD during mixing of silica, silane and rubber:

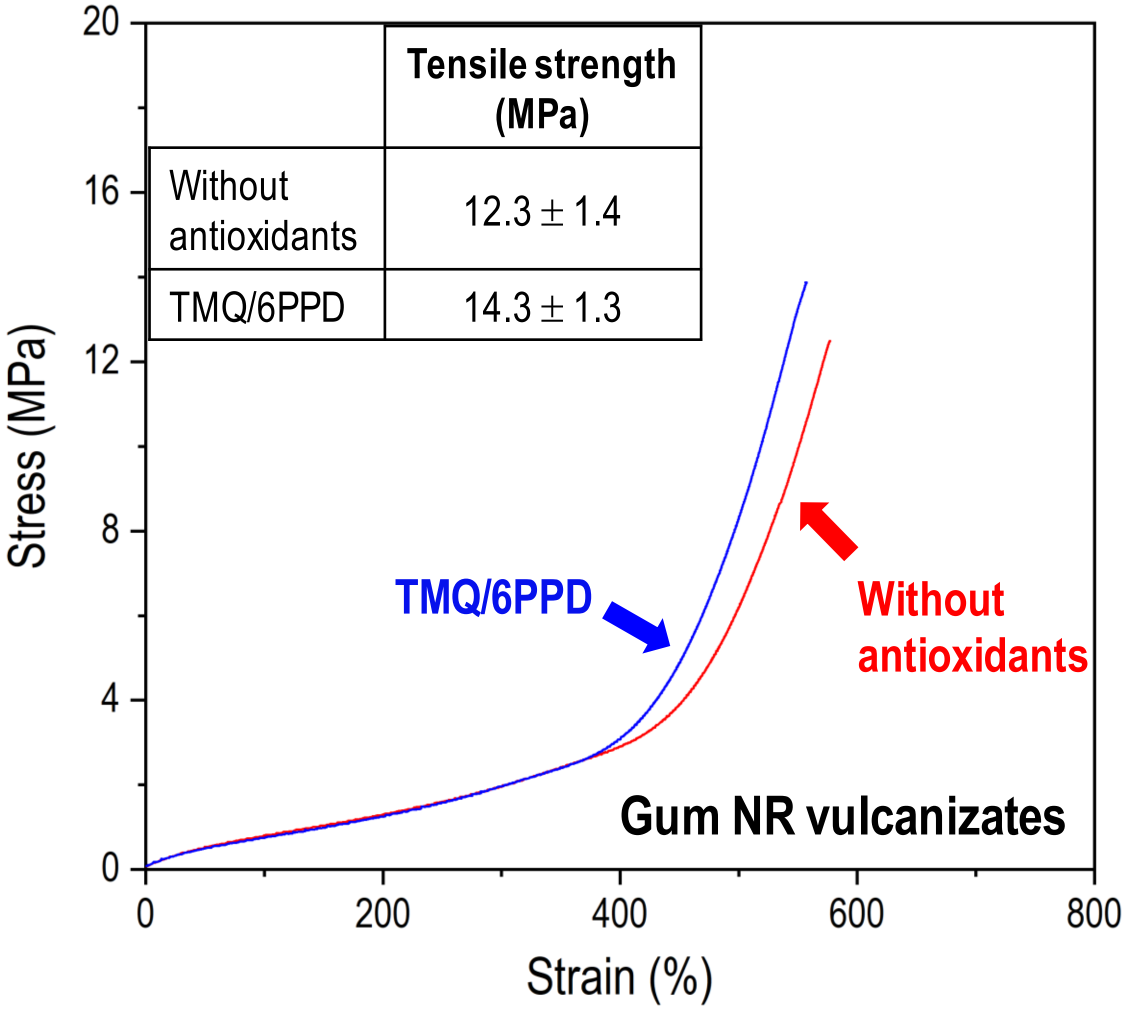
1) Positive effect: Suppressing chain scission →
☑ Higher molecular weight
☑ Higher elastic response
☑ Higher bound rubber (rubber-filler interaction)

2) Negative effect: Interfering with silanization, particularly TMQ →
☒ Higher filler-filler interaction

How do these competitive effects influence the final vulcanizate properties?

Vulcanizate properties

Mechanical properties

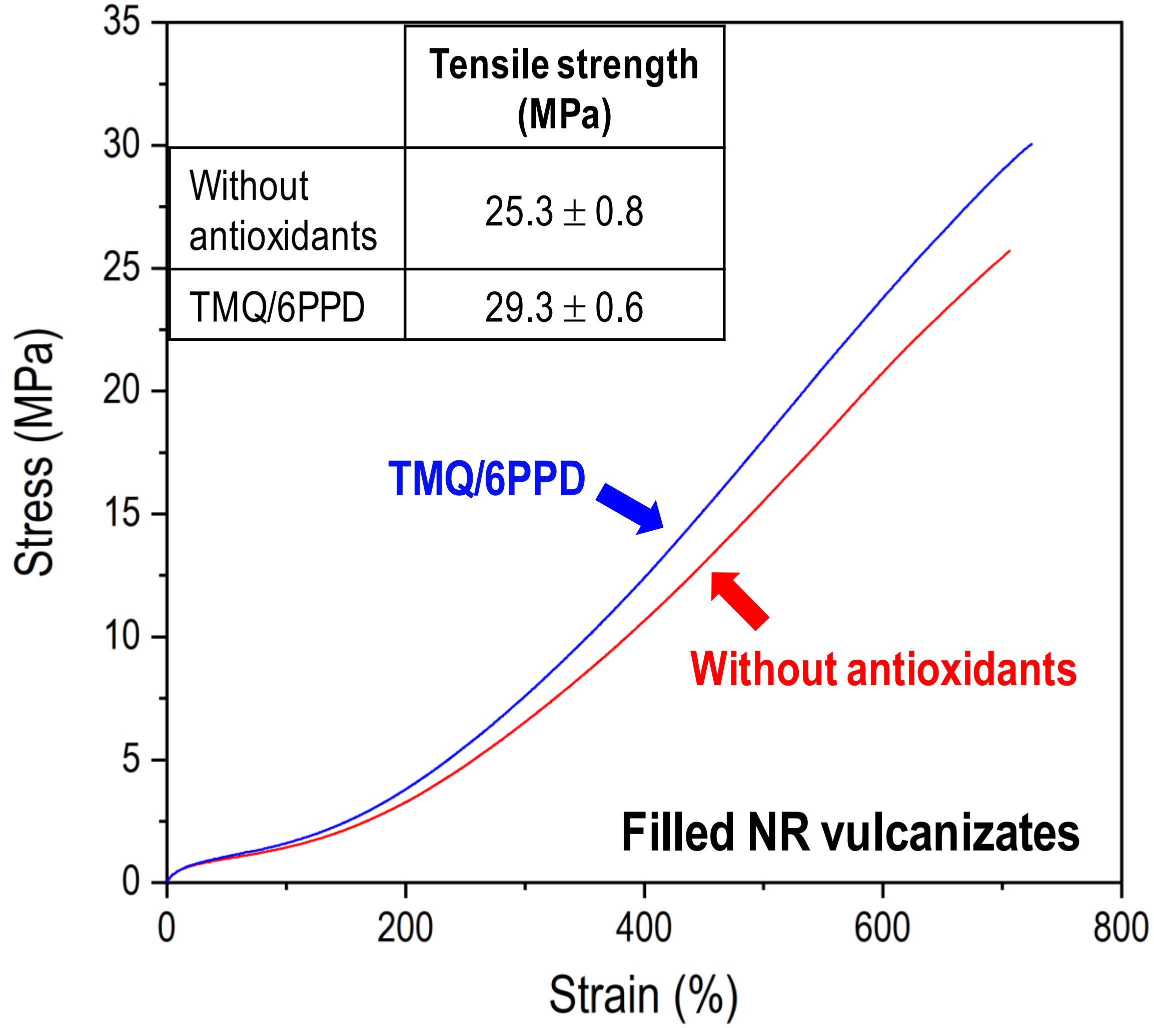


Gum NR vulcanizates

With TMQ/6PPD:

- ❑ Viscoelastic properties
  - → Higher number of long chains
  - → Higher average Mw
  - → More entanglements

Mechanical properties



	Tensile strength (MPa)
Without antioxidants	25.3 ± 0.8
TMQ/6PPD	29.3 ± 0.6

Filled NR vulcanizates

With TMQ/6PPD:

❑ Viscoelastic properties
→ Higher number of long chains
→ Higher average Mw
→ More entanglements

❑ Reinforcing parameters
→ Increase of bound rubber (filler-rubber interaction)

Conclusions

Conclusions

Competitive reactions during mixing of silica, silane and natural rubber at high temperatures:

- ⊕ Silanization/coupling reactions
- ⊖ Rubber degradation

Adding TMQ/6PPD during silica-silane-rubber mixing:

- ❑ results in a higher molecular weight of rubber → dominant effect on the final properties
- ❑ shows interference of TMQ with the silanization reaction → higher filler-filler interaction
  - ➢ effect negligible for the final properties

TMQ/6PPD suppress rubber degradation during mixing of silica-filled NR compounds

→ improves the final properties of the vulcanizates

Thank you for your kind attention

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