LODZ UNIVERSITY OF TECHNOLOGY

EDUCATION, RESEARCH, INNOVATION

Low temeprature sulfur vulcanization of diene rubbers

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Motivation & background

Most of the current production standards of rubber goods utilizing sulfur-curing systems are calibrated at **high temperatures** (at least 160 °C), to reduce the curing time and enhance productivity.

Such an approach is, however, **energy-intensive** and may strongly be affected by energy price fluctuations (dependent on **coal** and **oil** commodity prices).

Notice: ETRMA - Rubber Sector Open letter to European Energy Ministers and European Commissioners on the effects on high energy cost*. (Brussels, 30 *September* **2022**)

Motivation: Low-temperature sulfur vulcanization (LTSV)

Challanges:

- Standard curing chemicals are **not reactive enough** to lower the vulcanization temperature;
- Possible **affection** of existing **curing times** (production rates);
- **Risk** of changes in **physical properties** of the final **vulcanizates**.

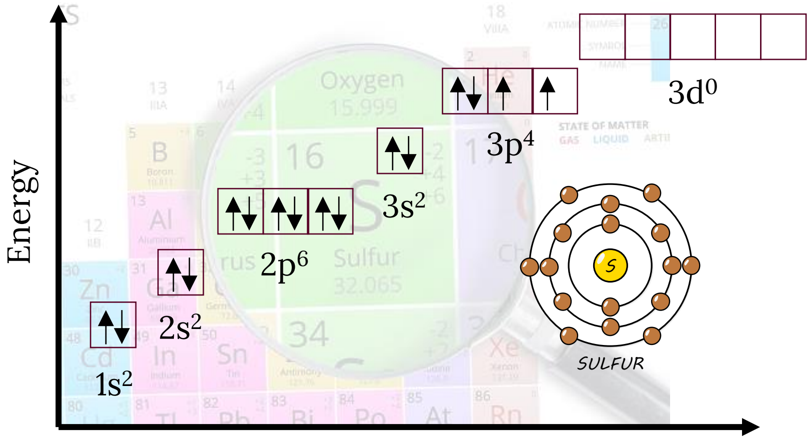
Outcome:

- **Energy efficiency** (cost savings and reduced environmental impact);
- **Safety** (reduced risk of accidents caused by high temperature and volatile compounds emissions);
- Applicability in **low-temperature technologies** like tire retreading or outdoor repairing of rubber goods.

*https://www.etrma.org/news/the-european-rubber-industry-is-dramatically-affected-by-the-high-energy-prices/
https://www.microsoft.com/pl-pl/microsoft-copilot (AI generator for drawings)

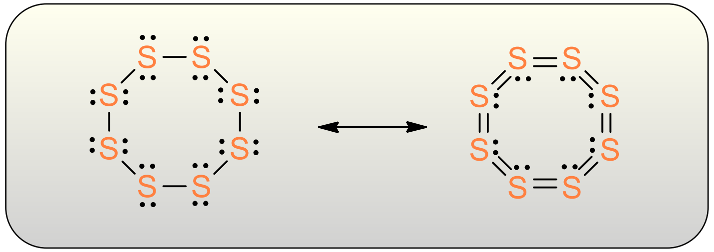
Elemental sulfur and features of *S*-atoms

Electron configuration of sulfur:



Resonance of the cycloocta-S molecule:

- Energy-favored coronal shape
- Each ***S*** atom is equimolar and surrounded by a decet e^-
- This is made possible by e^- delocalization and the presence of empty *d* orbitals
- Strong S-S homomolecular bond (265 kJ/mol)



Average bond enthalpies

C – S – C	285 kJ/mol
C – S – S – C	265 kJ/mol
C – S_x – C	<265 kJ/mol

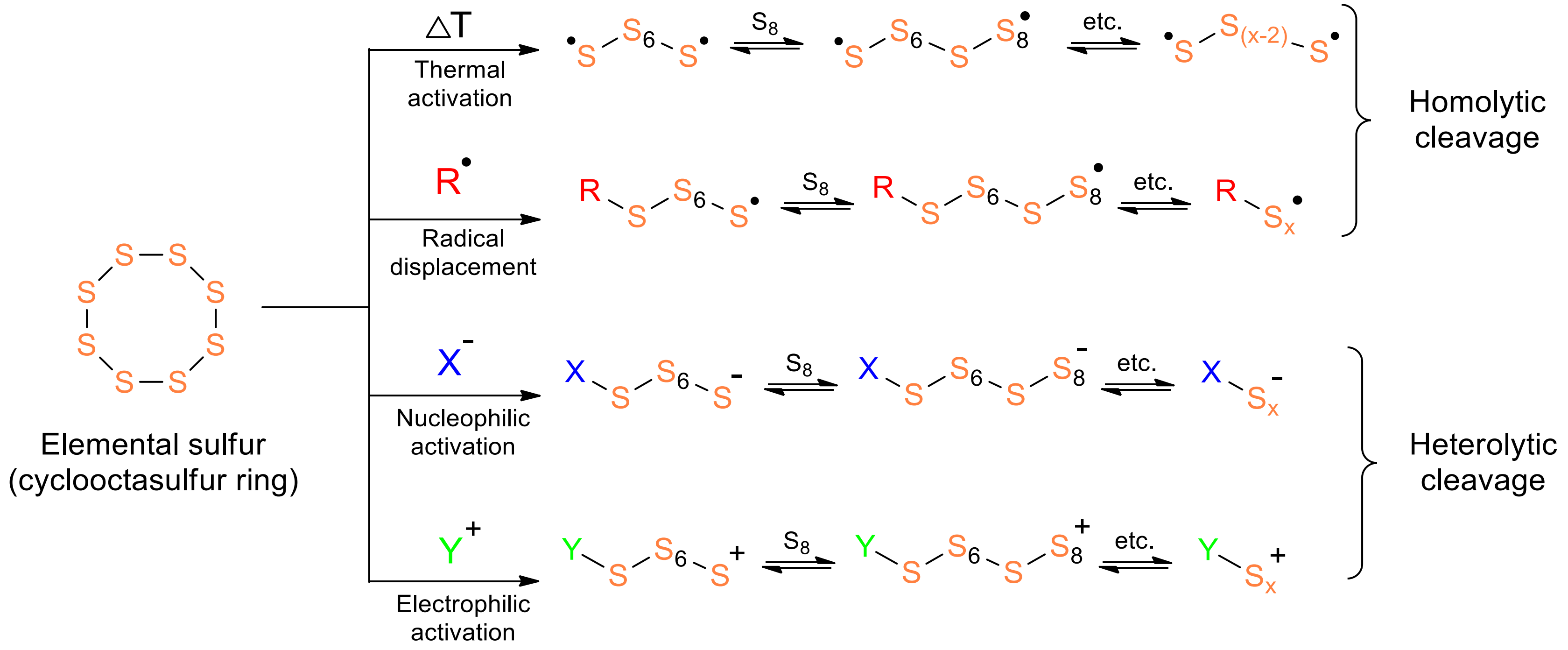
Pauling electronegativity:

Carbon	2.55
Sulfur	2.58

Pryor, W.A. Mechanisms of Sulfur Reactions, McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Company, Inc, **1962**.
Oae, S. Organic Chemistry of Sulfur, 1st ed.; Plenum Press: New York, NY, USA, **1977**.
https://stock.adobe.com/images/sulfur-element-of-mendeleev-periodic-table-magnified-with-magnifying-glass/102967198 (free trial access)

Elemental sulfur and features of *S*-atoms

Activation of S_8 ring – possible pathways of S-S bond cleavage



Nucleophilic agents (Lewis bases):

- Mercaptide ions (RS^-)
- Ammonia and amines ($:NR_3$)
- Phosphines ($:PR_3$)
- Carbanions ($^-CR_3$)
- Cyanide ion (^-CN)
- Halide anions (I^-, Br^-, Cl^-, F^-)
- More...

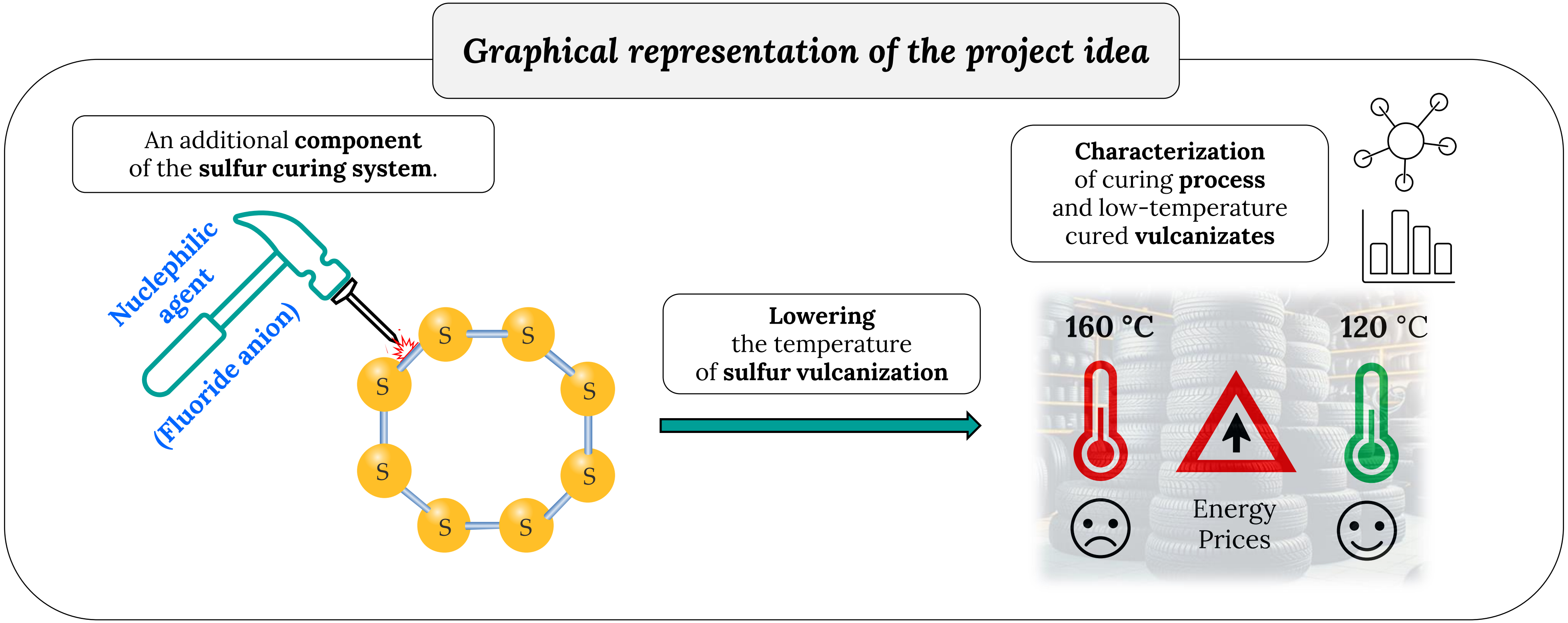
Pryor, W.A. Mechanisms of Sulfur Reactions, McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Company, Inc, **1962**.
Oae, S. Organic Chemistry of Sulfur, 1st ed.; Plenum Press: New York, NY, USA, **1977**.
Parker, A. J.; Kharasch, N. The Scission of Sulfur-Sulfur Bond. *Chemical Reviews* **1959**, 59, 583-628.

Our approach to low-temperature sulfur vulcanization

NATIONAL SCIENCE CENTRE POLAND

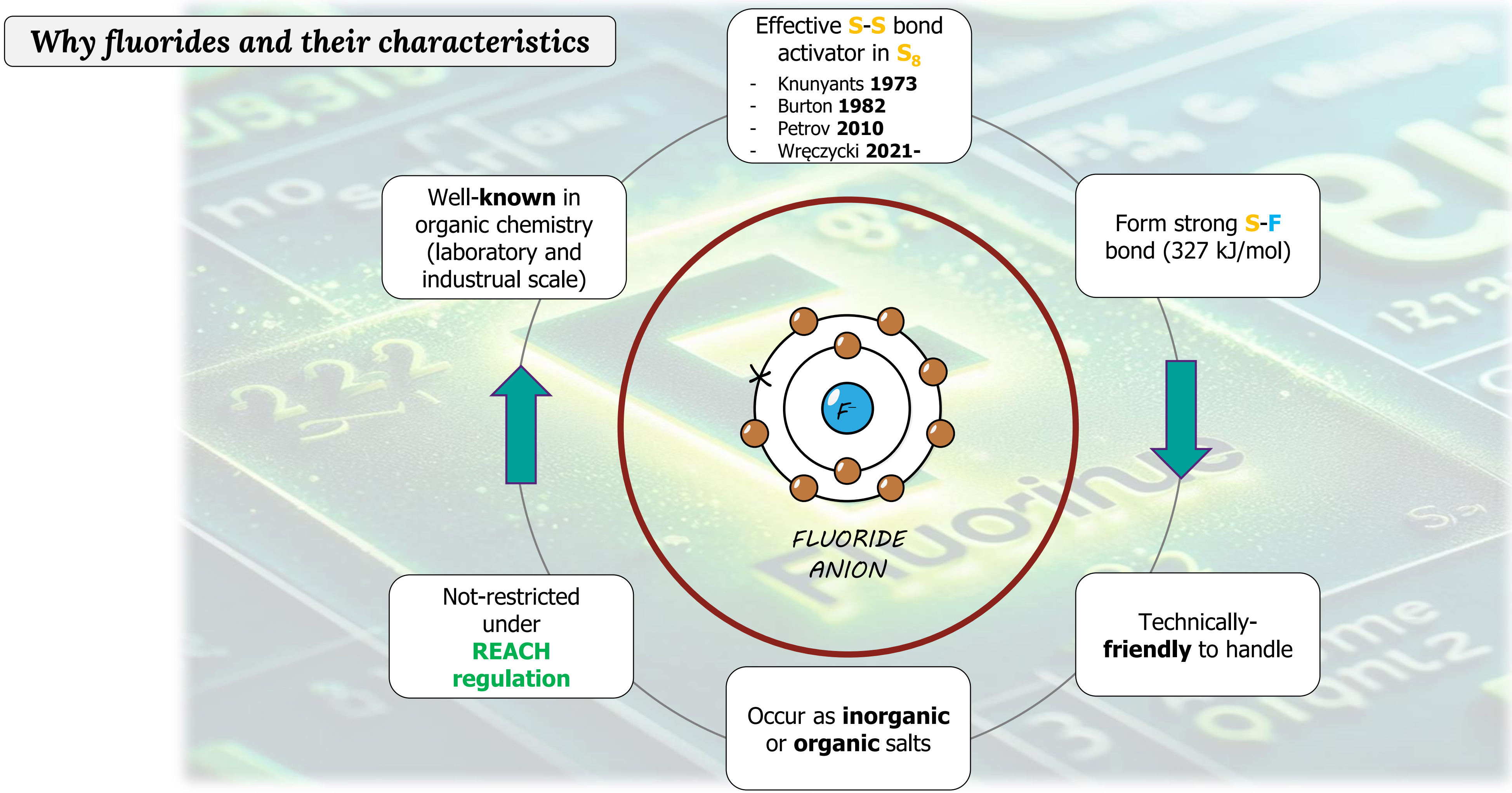
MINIATURA 7

Grant: “MINIATURA 7” (No. 2023/07/X/ST5/00492).



https://ncn.gov.pl/o-ncn/multimedia/logotyp-ncn
https://www.ncn.gov.pl/ogloszenia/konkursy/miniatura7

Our approach to low-temperature sulfur vulcanization



Blazejewski, J. C.; Diter, P.; Warchol, T.; Wakselman, C. *Tetrahedron Letters* **2001**, 42, 859-861.
Petrov, V.A.; Marshall, W. *Journal of Fluorine Chemistry* **2010**, 131, 1144–1155.
See, Y.Y.; Morales-Colón, M.T.; Bland, D.C.; Sanford, M.S. *Accounts of Chemical Research* **2020**, *53*, 2372–2383.
https://www.microsoft.com/pl-pl/microsoft-copilot (AI generator for drawings)

Results – Section 1: Optimization of the additives and curing parameters

*The influence of the **fluoride salt type** and its **physical form** on curing parameters of **NBR rubber***

Rubber formulations	F1 (25%)	F2 (25%)	F3 (25%)
Compound		[phr]	
Acrylonitrile-butadiene rubber (NBR)		100	
Zinc oxide (ZnO)		3	
Stearic acid (ST)		1	
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)		1	
Elemental sulfur (S_8)		2	
F1: TBAF 1.0M in THF (solution)	**0.51**	**–**	**–**
F2: TBAF · $3H_2O$ (solid)	**–**	**0.61**	**–**
F3: CsF (solid)	**–**	**–**	**0.30**

* The percentage value of fluorides are equal to the addition of 25% of the molar amount of pure fluoride calculated on elemental sulfur (S_8) used to prepare the rubber mix. Differences in the amount of fluorides are due to different molar masses.

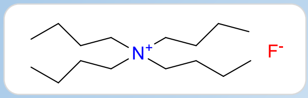
Mixing conditions	Laboratory micromixer (60 cm³)
Temperature	60 °C
Temperature rise	60 °C → 90 °C
Order	NBR, ST, ZnO, **Fluoride**, CBS, S_8
Time	10 min
Rotor speed	20 rpm (incorporation) 40 rpm (homogenization)
Final step: Rolling into sheets (two-roll open mixing mill)	
Vulcanization conditions	120 °C (**L**ow) 160 °C (**H**igh) – **Reference**

Fluorides

Terta-n-butylammonium fluoride (TBAF)

F1: Solution of 1.0M in THF (yellowish liquid)

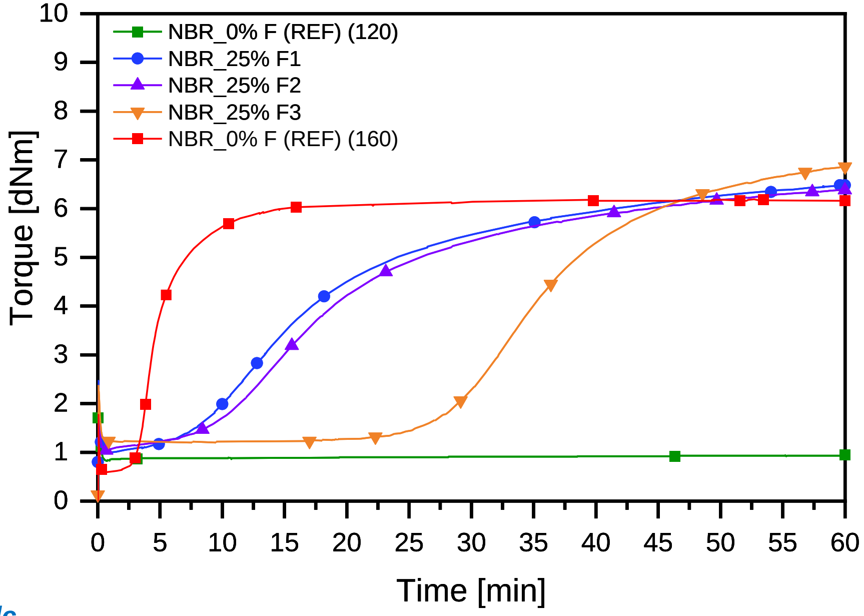
F2: Solid, trihydrate (·$3H_2O$) (colorless solid)



Caesium fluoride

F3: Solid, anhydrous (white powder)

Cs^+ F^-



Vulc. temp. [°C]	160 °C	120 °C		
% Fluoride	–	25%		
Fluoride	–	F1	F2	F3
t_{90} [min]	10	36.5	37.5	47
M_{MAX} [dNm]	6.19	6.48	6.38	6.87
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm³]	1.78	1.78	1.65	1.83

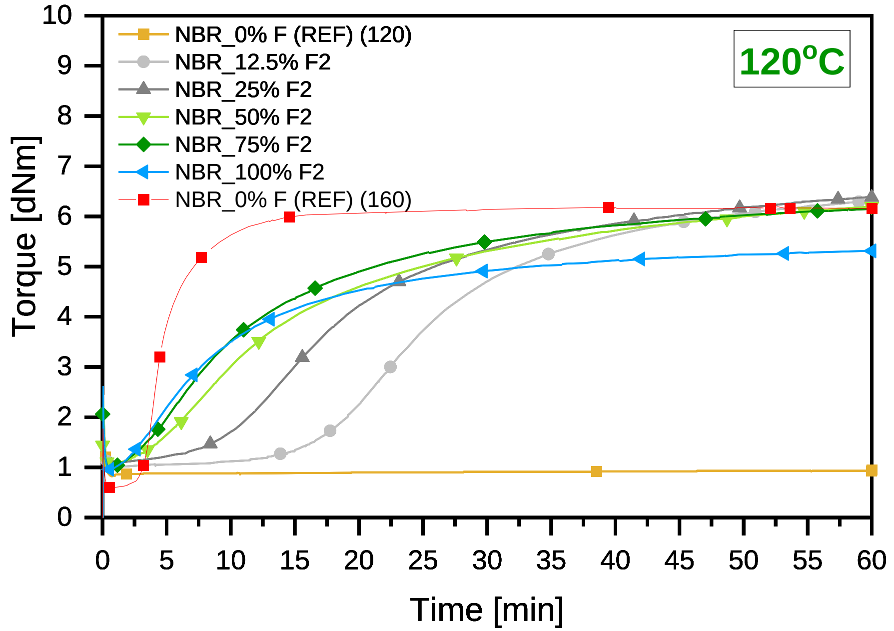
Results – Section 1: Optimization of the additives and curing parameters

*The influence of the **fluoride salt amount** on curing parameters of **NBR rubber***

Rubber formulations	F2 (12.5%)	F2 (25%)	F2 (50%)	F2 (75%)	F2 (100%)
Compound			[phr]		
Acrylonitrile-butadiene rubber (NBR)			100		
Zinc oxide (ZnO)			3		
Stearic acid (ST)			1		
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)			1		
Elemental sulfur (S_8)			2		
	0.31	**–**	**–**	**–**	**–**
	–	**0.61**	**–**	**–**	**–**
F2: TBAF · $3H_2O$ (solid)	**–**	**–**	**1.23**	**–**	**–**
	–	**–**	**–**	**1.84**	**–**
	–	**–**	**–**	**–**	**2.46**

* The percentage value of fluorides are given as molar amount of pure fluoride calculated on elemental sulfur (S_8) used to prepare the rubber mix.

Mixing conditions	Laboratory micromixer (60 cm³)
Temperature	60 °C
Temperature rise	60 °C → 90 °C
Order	NBR, ST, ZnO, **Fluoride**, CBS, S_8
Time	10 min
Rotor speed	20 rpm (incorporation) 40 rpm (homogenization)
Final step: Rolling into sheets (two-roll open mixing mill)	
Vulcanization conditions	120 °C (**L**ow) 160 °C (**H**igh) – **Reference**

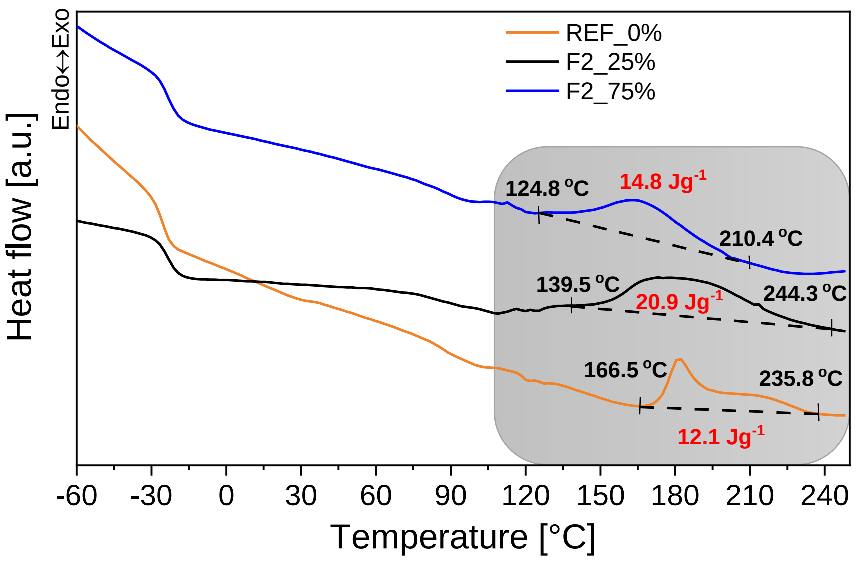


Vulc. temp. [°C]	160 °C	120 °C				
Fluoride	–	F2: TBAF · $3H_2O$ (solid)				
%Fluoride	–	12.5%	25%	50%	75%	100%
t_{90} [min]	10	41	37.5	36	31	26
M_{MAX} [dNm]	6.19	6.31	6.38	6.20	6.15	5.32
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm³]	1.78	1.60	1.65	1.60	1.71	1.09

Results – Section 1: Optimization of the additives and curing parameters

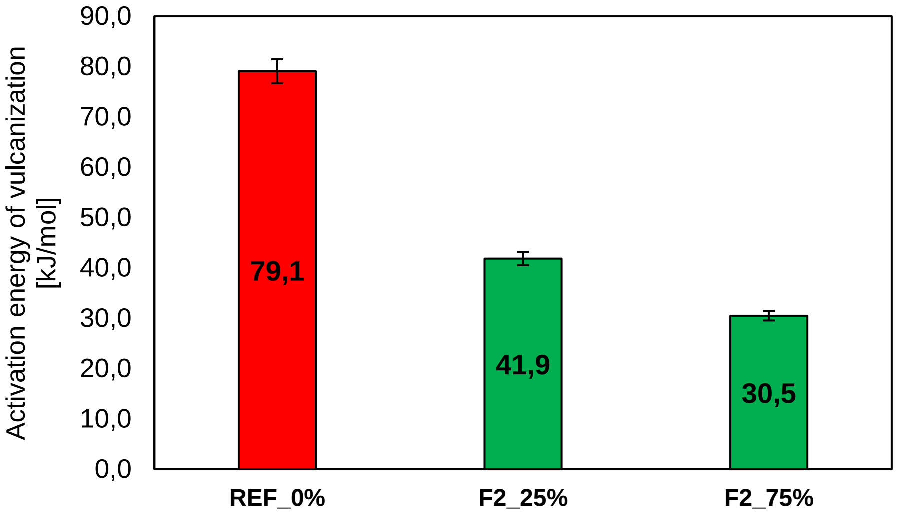
The fluoride anion supported sulfur vulcanization of **NBR rubber** *followed by* **DSC** *and* $\mathbf{E_a}$

Differential scanning calorimetry (DSC)



F2: TBAF, solid, trihydrate ($\cdot 3H_2O$)

Activation energy of vulcanization (Kamal-Sourour model)



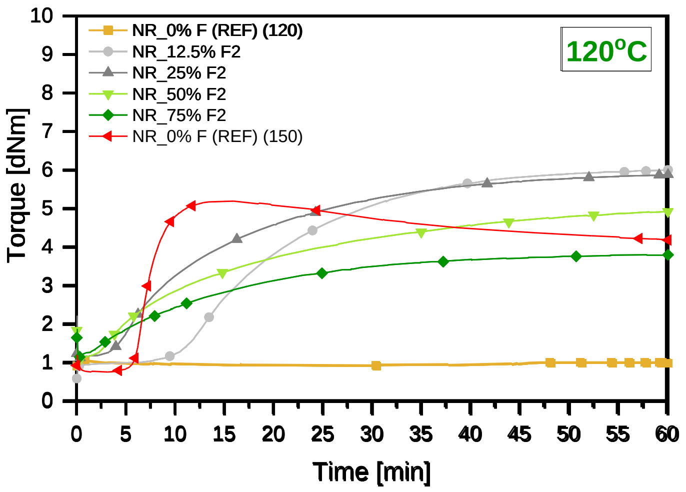
Results base on rheometric curves measured in three different temperatures:

- ***120 °C***, ***130 °C***, ***140 °C*** for samples containing fluoride
- ***140 °C***, ***150 °C***, ***160 °C*** for reference sample – without fluoride

Results – Section 1: Optimization of the additives and curing parameters

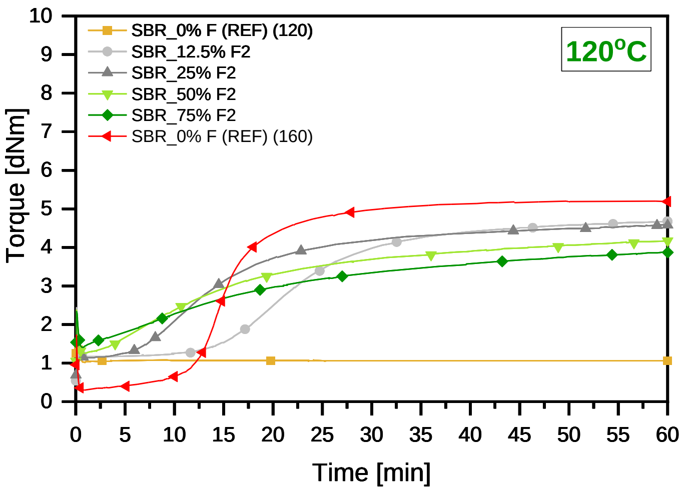
*The efficiency of the fluoride anion supported sulfur vulcanization on the other **diene rubbers***

Natural rubber (NR)



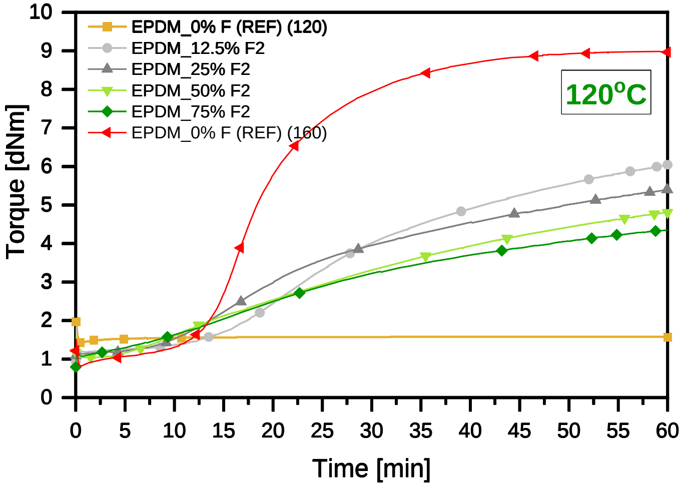
Parameter					
Vulc. temp. [°C]	150 °C	120 °C			
Fluoride	–	F2: TBAF · $3H_2O$ (solid)			
%Fluoride	–	12.5%	25%	50%	75%
t_{90} [min]	9.5	34.5	31	35	27.5
M_{MAX} [dNm]	5.2	6.01	5.89	4.95	3.82
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm^3]	1.27	1.18	1.00	0.79	0.68

Styrene-butadiene rubber (SBR)



Parameter					
Vulc. temp. [°C]	160 °C	120 °C			
Fluoride	–	F2: TBAF · $3H_2O$ (solid)			
%Fluoride	–	12.5%	25%	50%	75%
t_{90} [min]	23	34	28	32	36.5
M_{MAX} [dNm]	5.20	4.68	4.59	4.17	3.88
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm^3]	1.17		0.53		

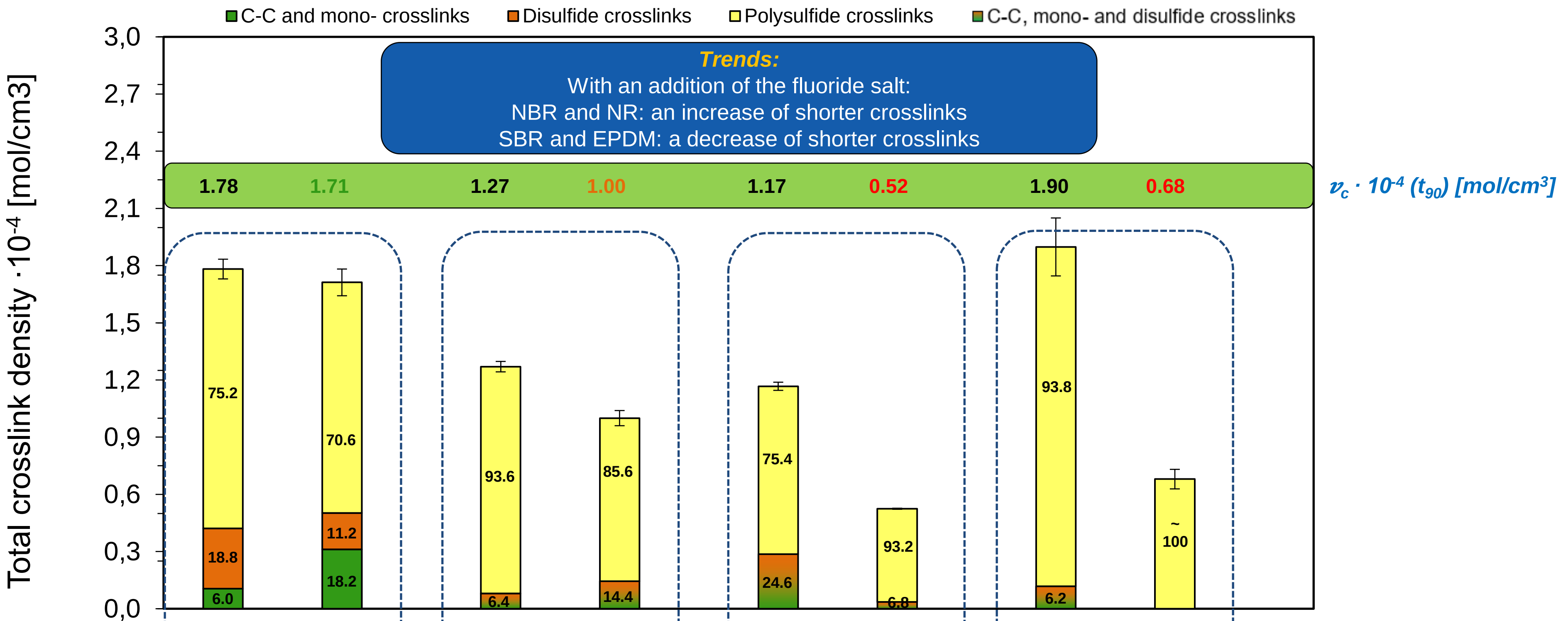
Ethylene-propylene-diene rubber (EPDM)



Parameter					
Vulc. temp. [°C]	160 °C	120 °C			
Fluoride	–	F2: TBAF · $3H_2O$ (solid)			
%Fluoride	–	12.5%	25%	50%	75%
t_{90} [min]	31.5	48	47	47	45
M_{MAX} [dNm]	8.99	6.05	5.41	4.81	4.36
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm^3]	1.90		0.67		

Results – Section 1: Optimization of the additives and curing parameters

Crosslink density and structure – unfilled compounds; ***comparison of rubbers***



Rubber	NBR		NR		SBR		EPDM	
Fluoride	REF	F2	REF	F2	REF	F2	REF	F2
% Fluoride	0%	75%	0%	25%	0%	25%	0%	25%
Vulc. temp. [°C]	160 °C	120 °C	150 °C	120 °C	160 °C	120 °C	160 °C	120 °C

Summary – Section 1: Optimization of the additives and curing parameters

Primary effect:
Vulcanization enabled at 120 °C
(regardless of the ***fluoride type***, its ***physical form***, ***amount*** and ***rubber type***)

Impact of fluoride salt type and its physical form:
Organic fluorides (TBAF) are more effective than inorganic (CsF)

Impact of fluoride salt amount:
Higher amount improve curing parameters to a certain level
(**NBR**: 75% mol./S_8, **NR**, **SBR**, **EPDM**: 25% mol./S_8)

The efficiency of the curing system on different diene rubber type:
Strongly depends on the rubber type (solubility, polarity)
(***Efficiency trend***: : *NBR → NR → SBR → EPDM)*

Results – Section 2: Performance of the low-temperature cured vulcanizates

*The efficiency of the fluoride anion supported sulfur vulcanization on **filled NBR rubber***

Rubber formulations	SiO_2	*s*-SiO_2	CB
Compound	[phr]		
Acrylonitrile-butadiene rubber (NBR)	100		
Zinc oxide (ZnO)	3		
Stearic acid (ST)	1		
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)	1		
Elemental sulfur (S_8)	2		
F2: TBAF · $3H_2O$ (solid)	**1.84** (NBR)		
Silica (SiO_2)	**10**	**–**	**–**
Silanized silica (s-SiO_2)	**–**	**10**	**–**
Carbon black (CB)	**–**	**–**	**10**

* The percentage value of fluorides are equal to the addition of 25% (NR, SBR, EPDM) or 75% (NBR) of the molar amount of pure fluoride calculated on elemental sulfur (S_8) used to prepare the rubber mix.

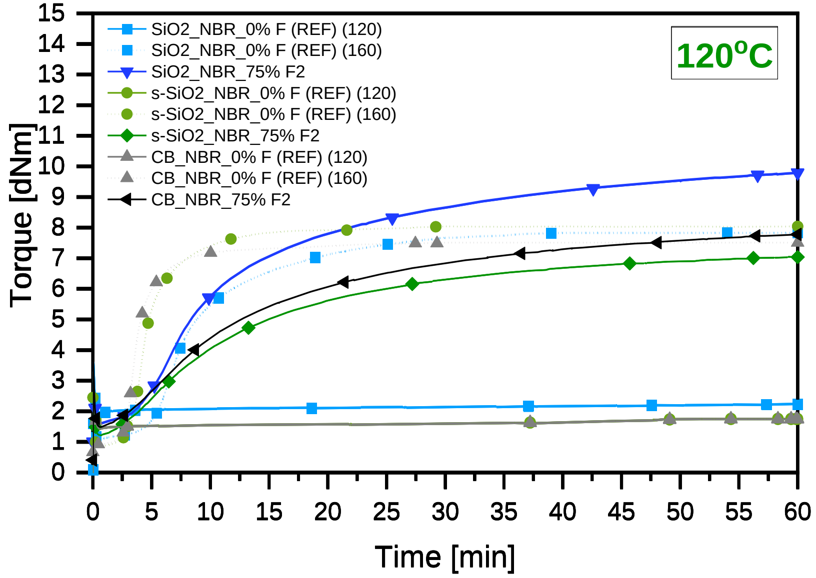
Mixing conditions	Laboratory micromixer (60 cm^3)
Temperature	60 °C
Temperature rise	60 °C → 90 °C
Order	NBR, ST, ZnO, **Filler**, Fluoride, CBS, S_8
Time	10 min
Rotor speed	20 rpm (incorporation) 40 rpm (homogenization)
Final step: Rolling into sheets (two-roll open mixing mill)	
Vulcanization conditions	120 °C (**L**ow) 160 °C (**H**igh) – **Reference**

Fillers

Silica (SiO_2)
Tradmark: **Aerosil® 380**
Manufacturer: Evonik GmbH

Silanized silica (s-SiO_2)
After treatment with dimethyldichlorosilane
Tradmark: **Aerosil® R972**
Manufacturer: Evonik GmbH

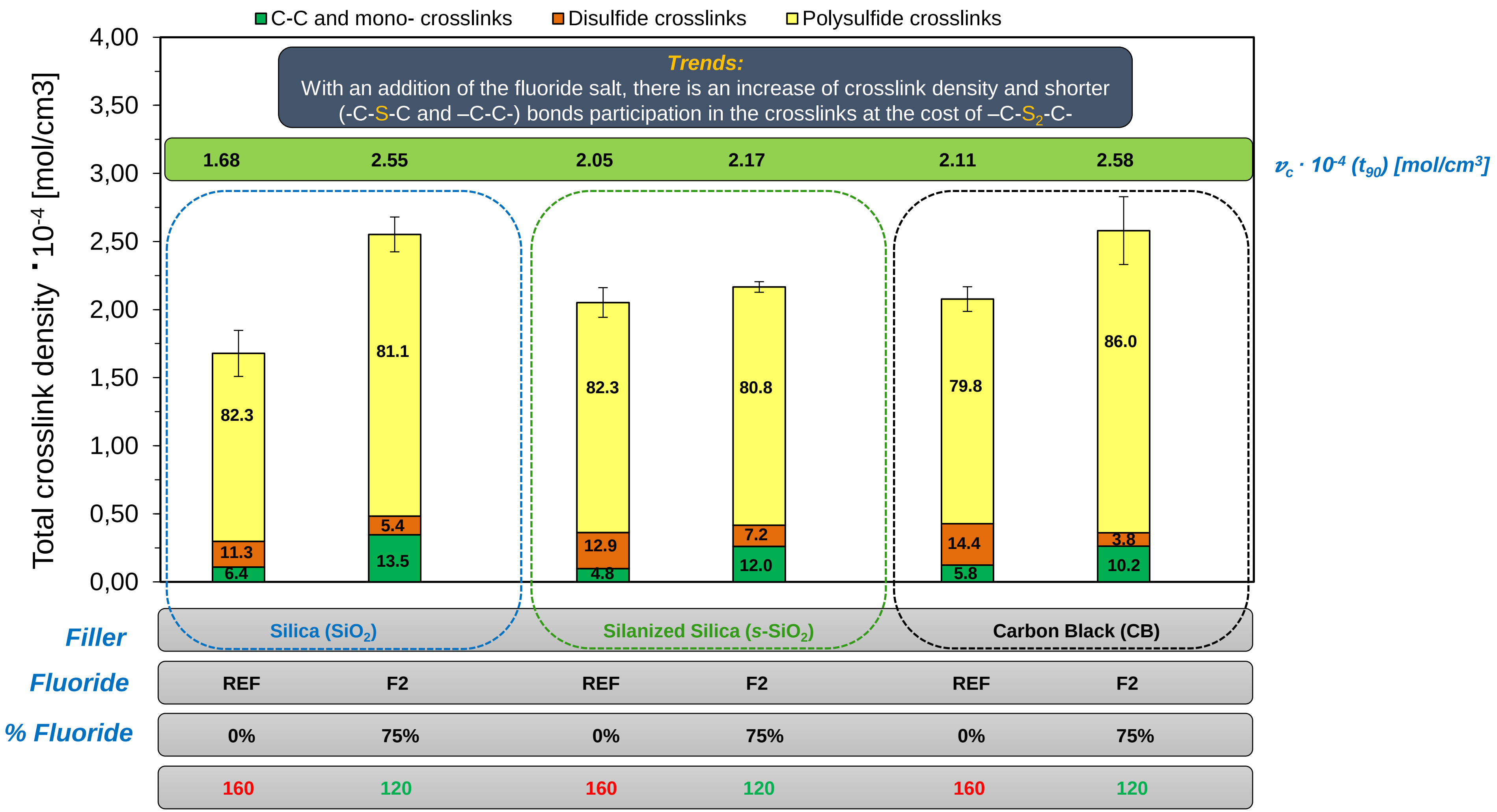
Carbon black (CB)
Tradmark: **Humex N-339 HAF**
Manufacturer: Hules Mexicanos S.A. de C.V



Filler	SiO_2		*s*-SiO_2		CB	
Vulc. temp. [°C]	160 °C	120 °C	160 °C	120 °C	160 °C	120 °C
%Fluoride	0%	75%	0%	75%	0%	75%
t_{90} [min]	19	32	9	31.5	7	33.5
M_{MAX} [dNm]	7.05	9.79	8.05	7.07	7.52	7.80
$\nu_c \cdot 10^{-4}$ (t_{90}) [mol/cm³]	1.68	2.55	2.05	2.17	2.11	2.58

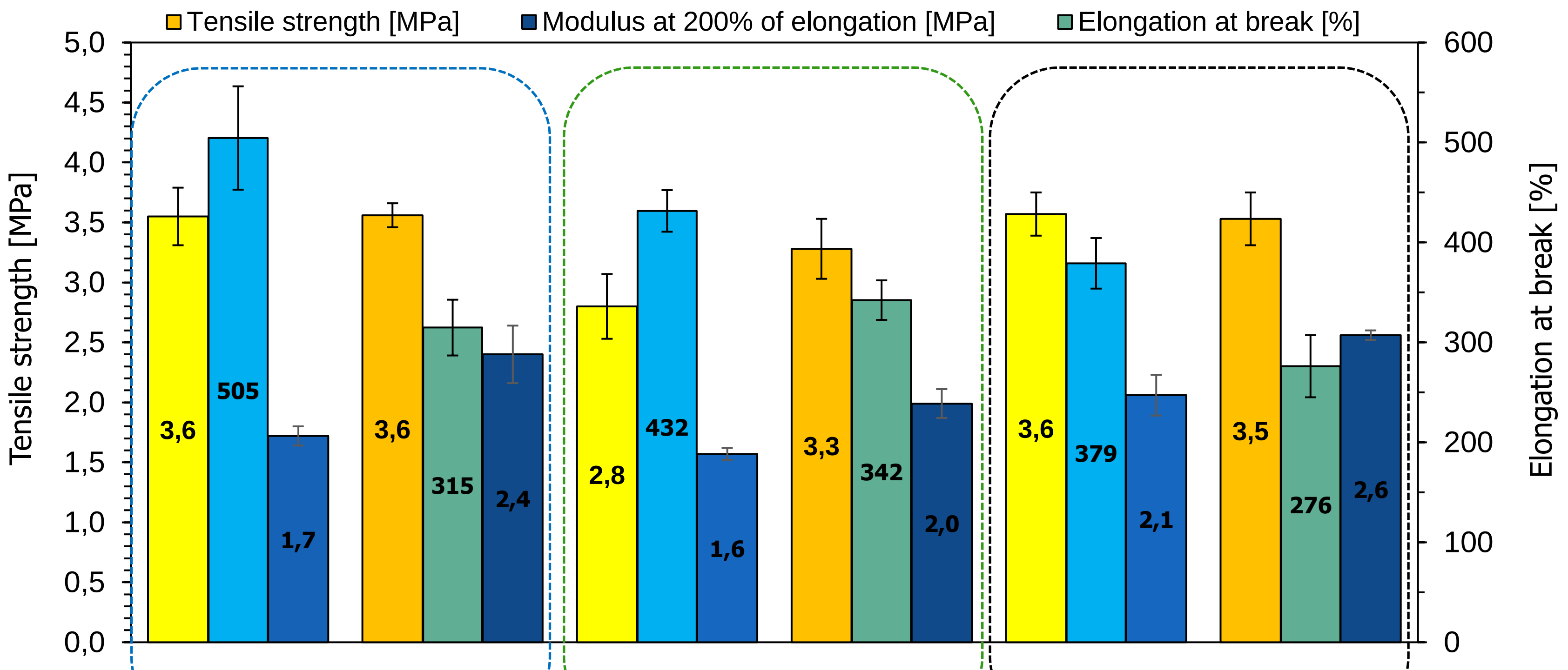
Results – Section 2: Performance of the low-temperature cured vulcanizates

Crosslink density and structure – filled **NBR** *compounds;* ***comparison of fillers***



Results – Section 2: Performance of the low-temperature cured vulcanizates

Mechanical parameters under static conditions – filled ***NBR*** *compounds;* ***comparison of fillers***

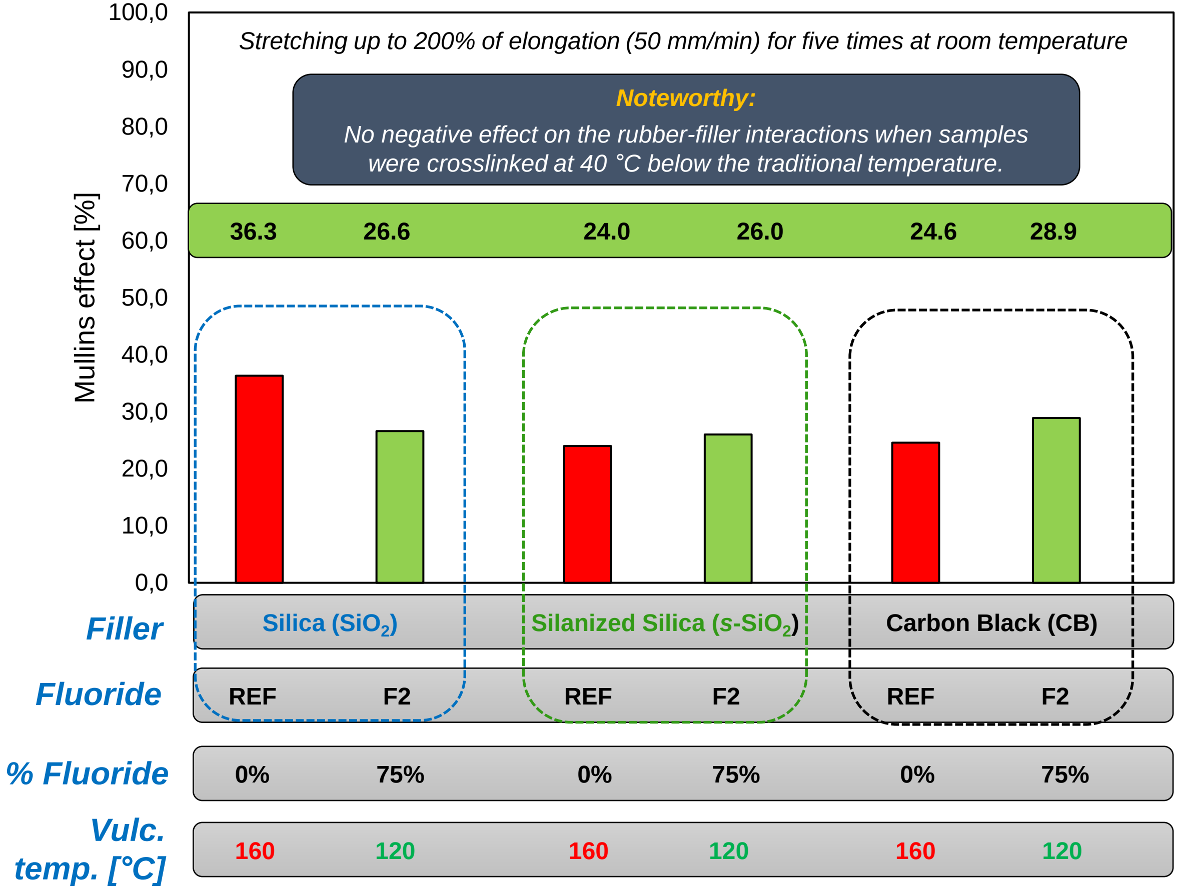


Filler	Silica (SiO_2)		Silanized Silica (s-SiO_2)		Carbon Black (CB)	
Fluoride	REF	F2	REF	F2	REF	F2
% Fluoride	0%	75%	0%	75%	0%	75%
Vulc. temp. [°C]	160	120	160	120	160	120

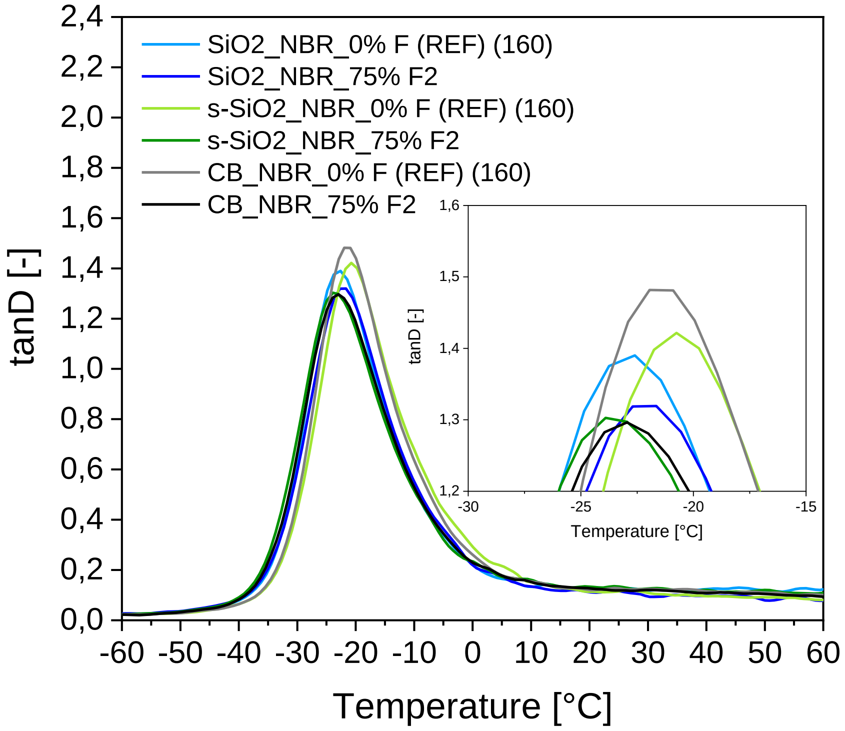
Results – Section 2: Performance of the low-temperature cured vulcanizates

Mechanical parameters - filled ***NBR*** *compounds;* ***comparison of fillers***

Mullins effect:



DMTA (tanD)



Noteworthy:

Glass transition temperatures slightly shifted into lower values for low temperaturd cured vulcanizates filled with s-SiO_2 and CB.

Section 2 summary: Performance of the low-temperature cured vulcanizates

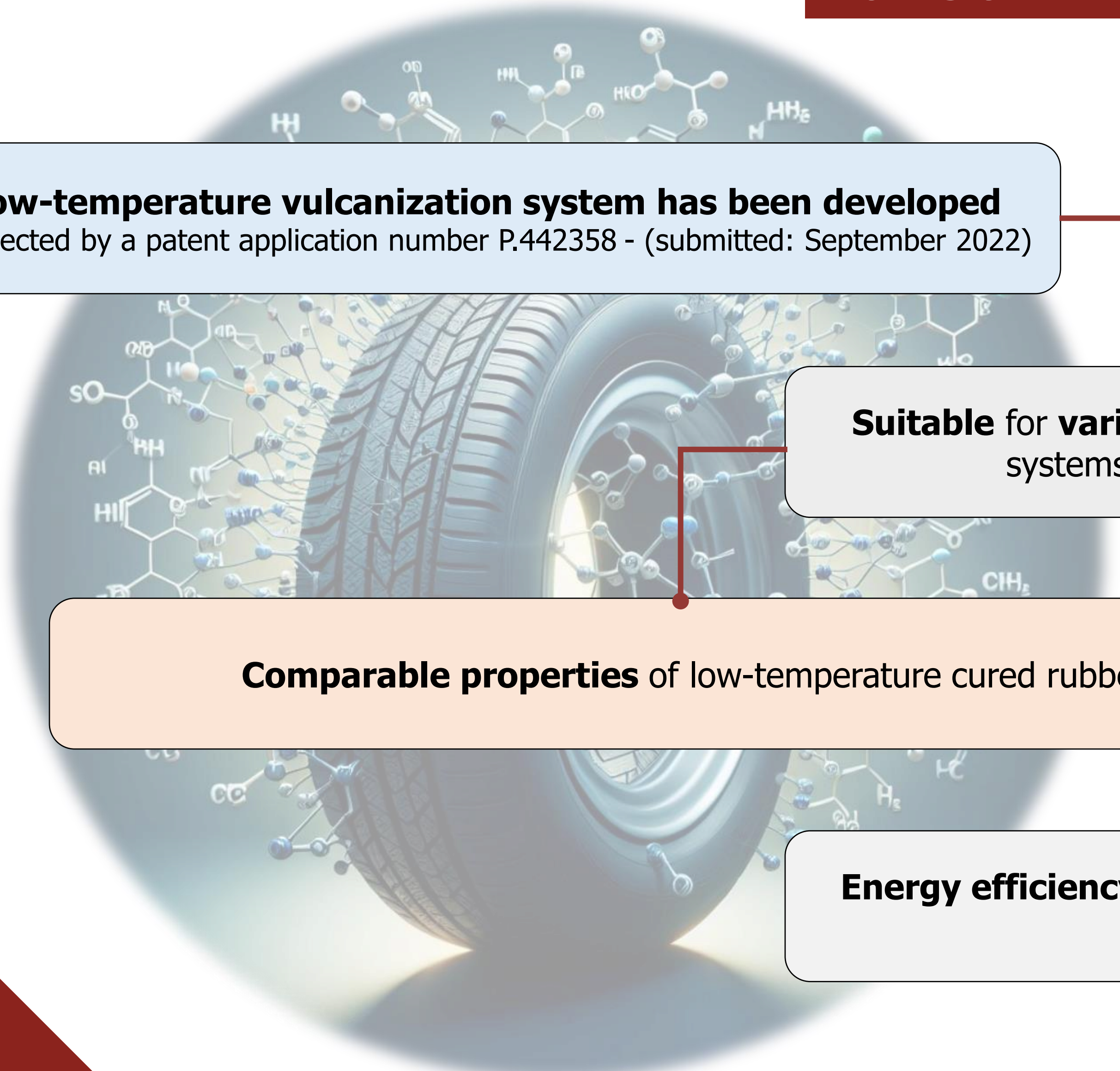
Primary effect:
Vulcanization enabled at 120 °C
(***fillers*** generally do not interfere with the vulcanization process)

Impact of the filler type:
In nitrile rubber (NBR) the effectiveness of the low-temperature curing system was highest for **SiO_2**, then **CB** and **s-SiO_2** filled compounds.

Static mechanical parameters of low-temperature cured rubbers:
Static mechanical properties can be at the **same level** as for vulcanizates cured at **conventional** temperature (160°C).

No negative effect on the **rubber-filler interactions** as well as **dynamic parameters** when samples cured at 120°C.

Summary: Low-temperature sulfur vulcanization



Low-temperature vulcanization system has been developed
(protected by a patent application number P.442358 - (submitted: September 2022)

Potential aaplication in low-temp. rubber technologies
such as tire retreading or outdoor repairing of conveyor belts

Suitable for **various diene rubbers** and can be used with **different filler** systems and **various** organic **accelerators (*versatile*)**

Comparable properties of low-temperature cured rubbers

Energy efficiency in the industrial scale may be achieved due to significantly lower vulcanization temperature

https://www.microsoft.com/pl-pl/microsoft-copilot (AI generator for drawings)

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