

Compensating extra sulfur to TESPd-silica-filled NR compounds

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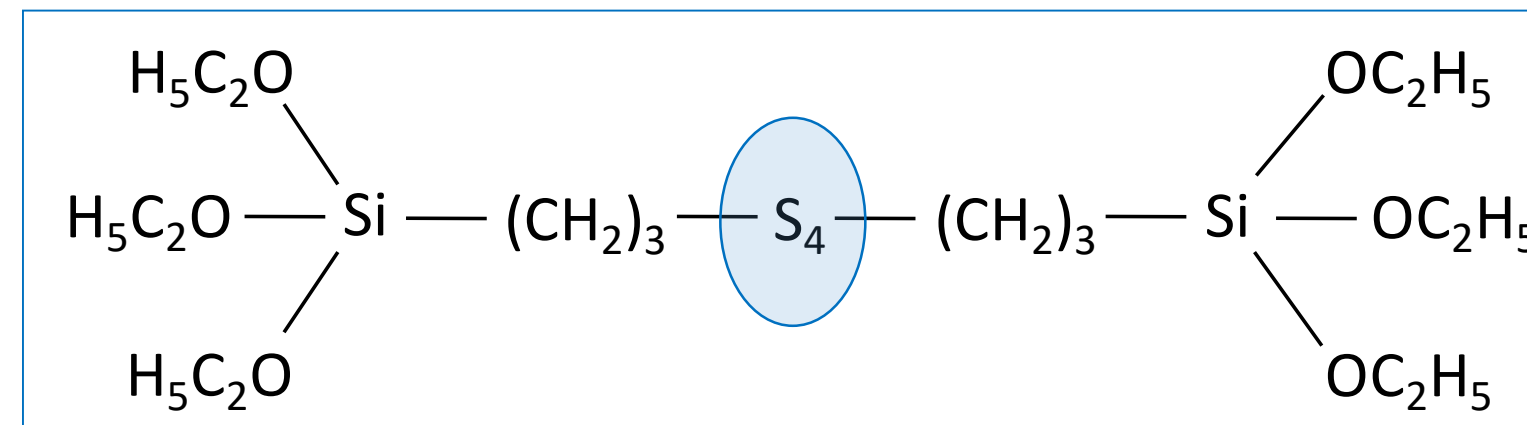
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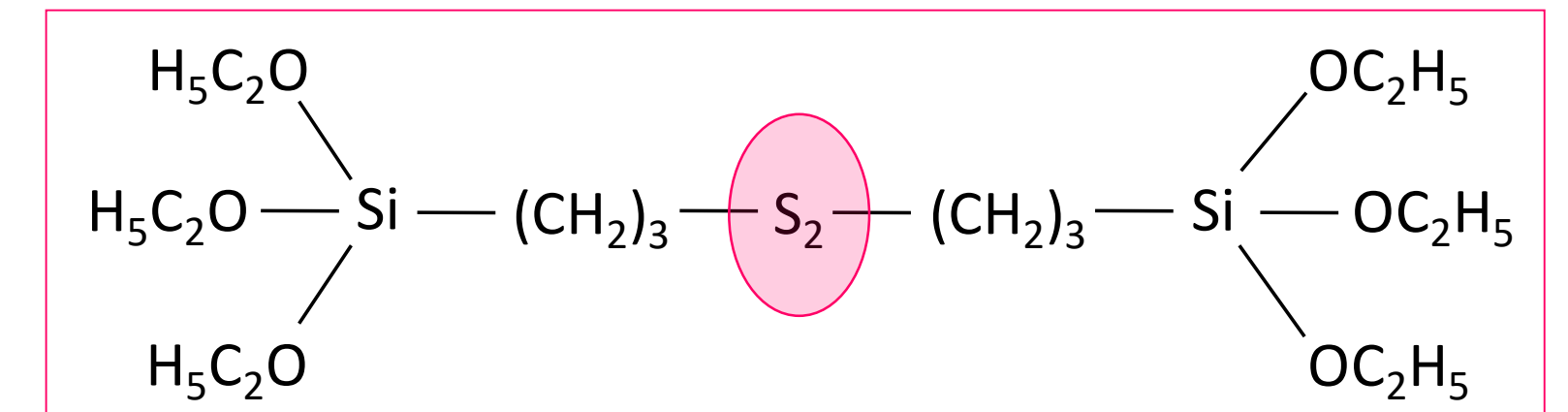
Remark: The results presented in this poster have been published in *Kautschuk Gummi Kunststoffe* 2014, 67 (5), 33-39 or the reference [3].

Background

- TESPT can liberate free sulfur into the system, resulting in an undesired high compound viscosity caused by 'premature scorch' [1].
- An alternative silane: TESPd, has been made available.
- According to the previous study [2], the TESPT-based compounds showed superior overall properties compared to those containing TESPd, mainly attributed to the influence of free sulfur liberated.
- The present study investigates an effect of extra sulfur added to silica-filled NR compounds during non- and productive mixing processes [3].



TESPT – the most commonly used silane coupling agent
Chemical name: Bis-triethoxysilylpropyl tetrasulfide (-S₄-)



TESPD – An alternative to TESPT, preventing a scorch problem
Chemical name: Bis-triethoxysilylpropyl disulfide (-S₂-)

Experimental

Ingredients	Amount (phr)		Components
	TESPT	TESPD + extra sulfur	
NR (BR55)	100.0	100.0	Dose of extra sulfur 1 2 3* 4 5* 6 7* 8 9* phr wt% relative to TESPd content 0 0.02 0.05 0.10 0.15 0.20 0.30 0.45 0.60 0 0.45 1.14 2.27 3.41 5.07 6.82 10.23 13.64
Silica (Ultrasil 7005)	50.0	50.0	
TESPT	5.0	5.0	
TESPD	-	4.4*	
Process oil (TDAE)	8.0	8.0	
Zinc oxide	3.0	3.0	
Stearic acid	1.0	1.0	
TMQ	1.0	1.0	
DPG	1.1	1.1	
CBS	1.5	1.5	
Sulfur	1.5	1.5	
Extra sulfur	-	Variable*	

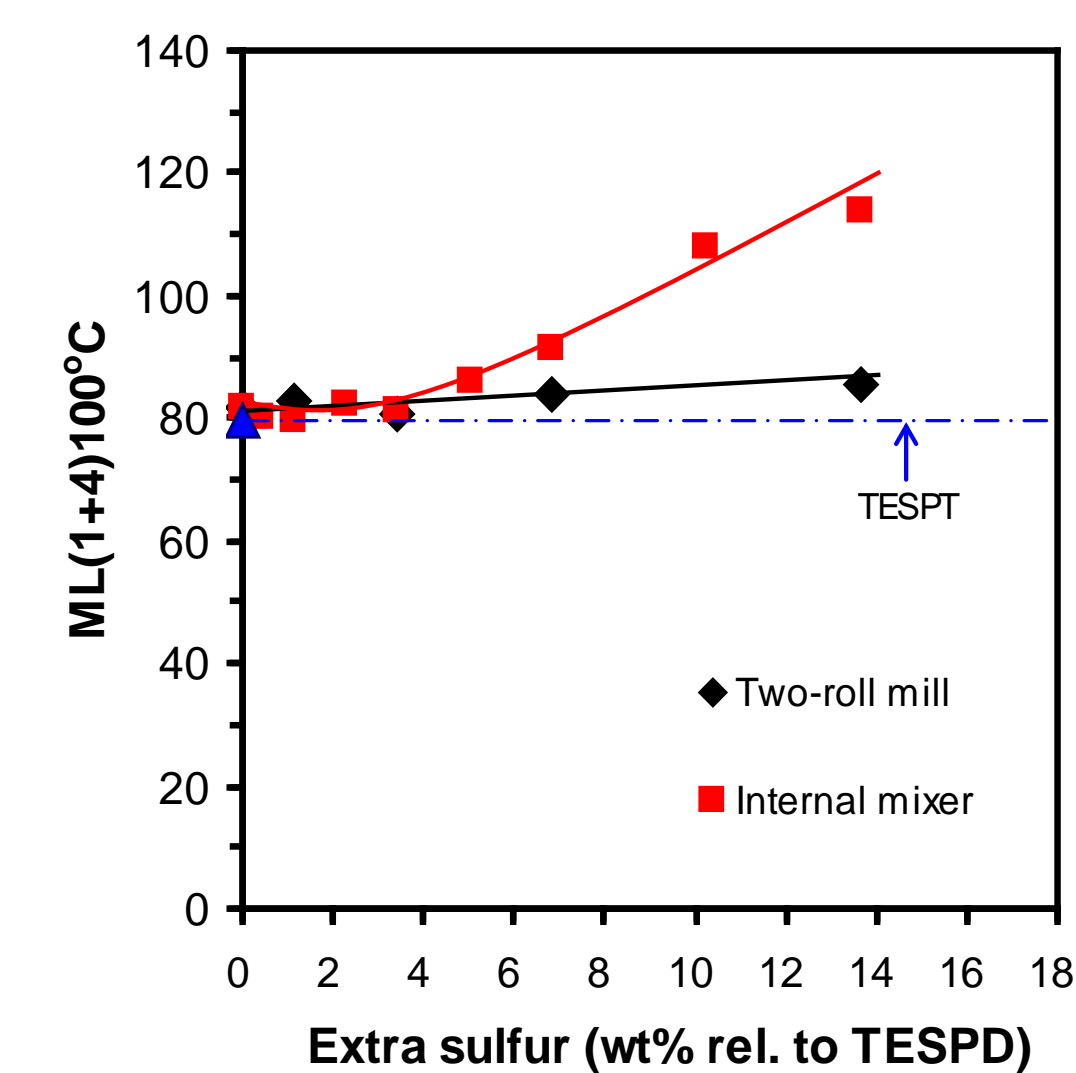
* equivalent nodes in ethoxy functionality, compared to 5.0 phr TESPT

* the quantity of extra sulfur was varied

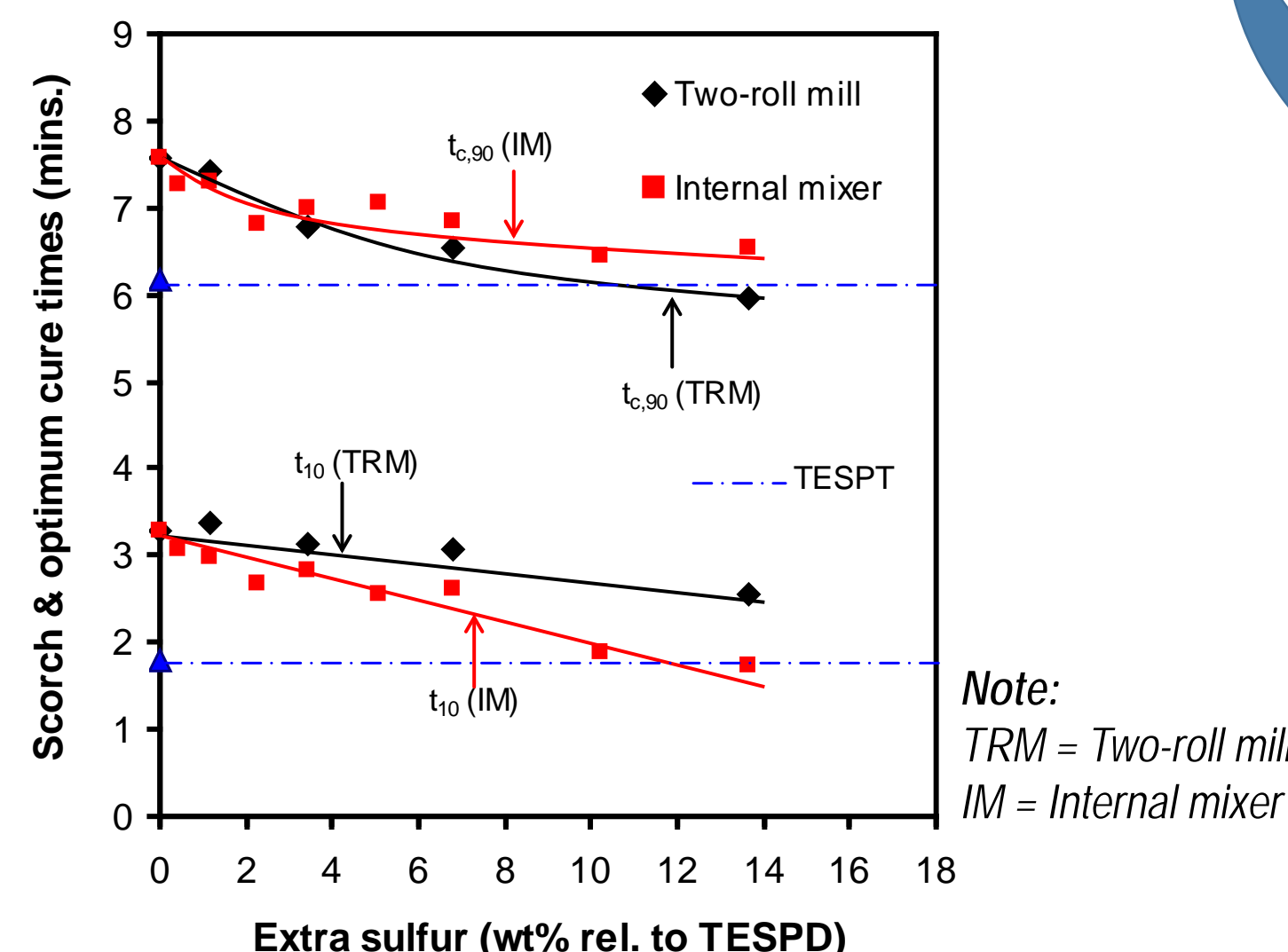
- An internal mixer with fill factor of 70 %, a rotor speed of 60 rpm, starting temperature of 100°C to reach 140-145°C.

- Mixing sequence: NR for 2 min, ½ silica+silane (+ ½ extra sulfur) for 5 min, ½ silica+silane+TDAE oil (+ ½ extra sulfur) for 5 min, ZnO+stearic acid+TMQ+ ½ DPG for 3 min, and discharged.
- Sulfur (+extra sulfur)+accelerators+ ½ DPG were added on two-roll mill.
- The measurement methods are described in [3].

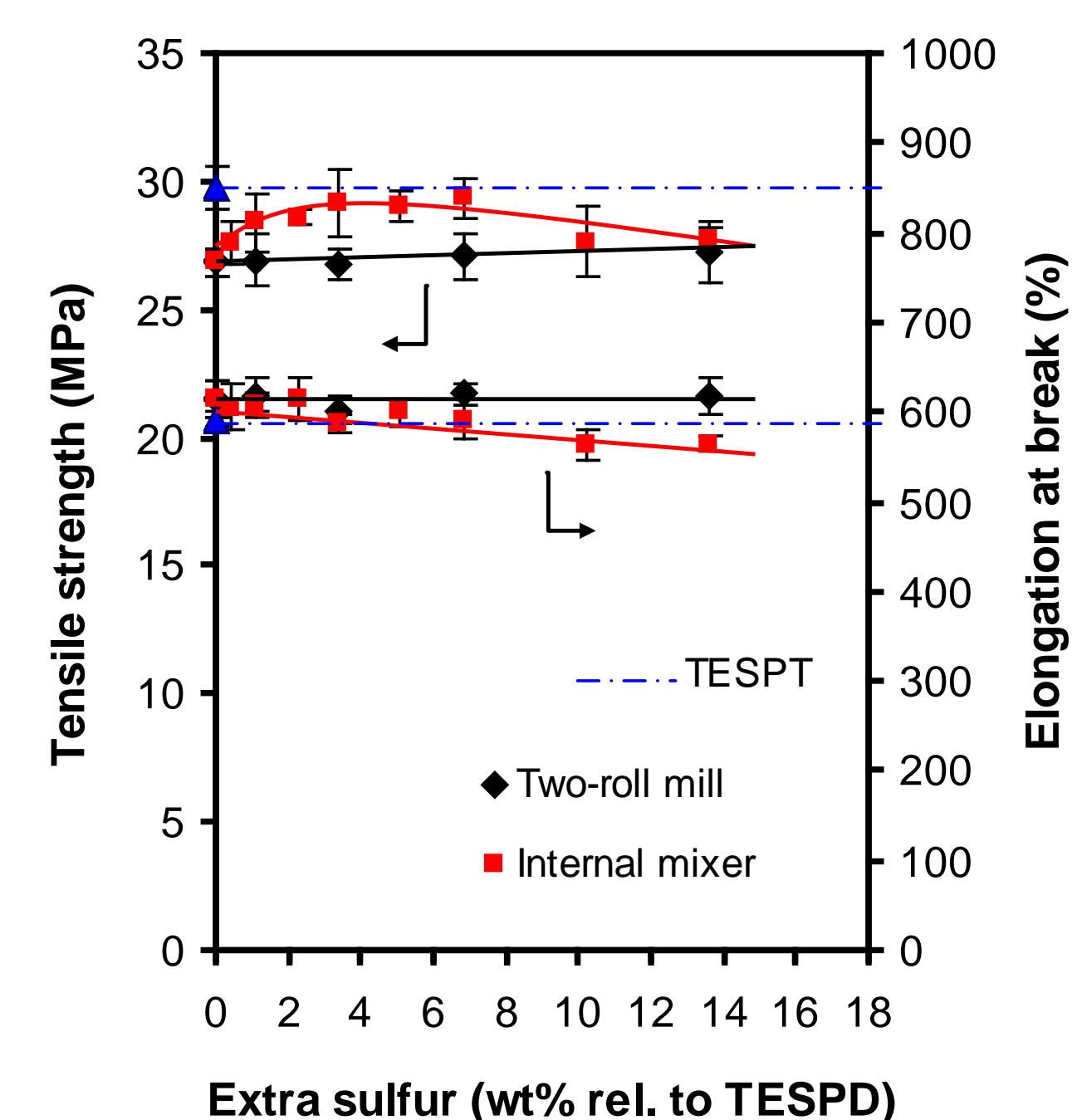
Results



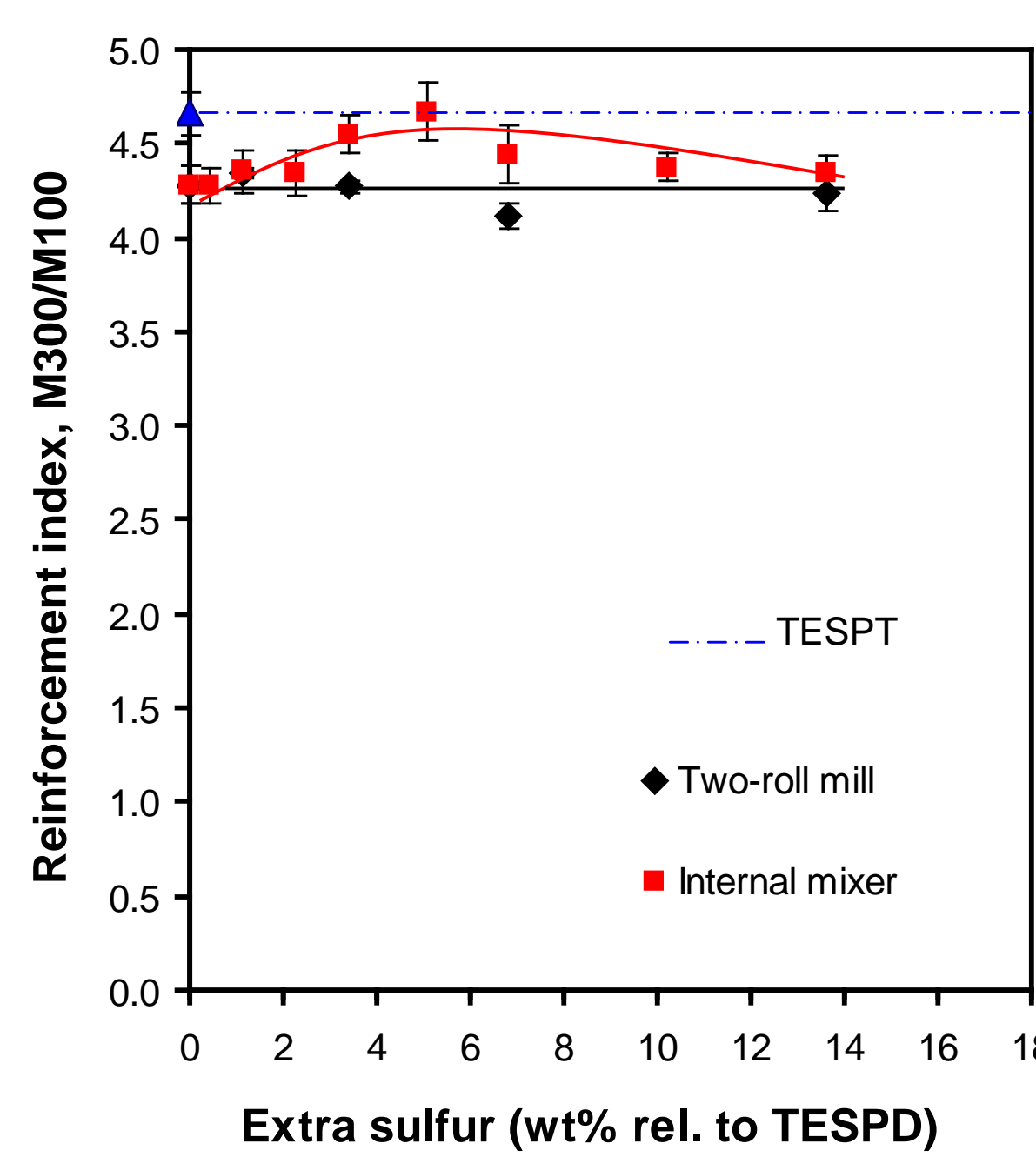
Compound viscosity and cure properties



Note: TRM = Two-roll mill, IM = Internal mixer

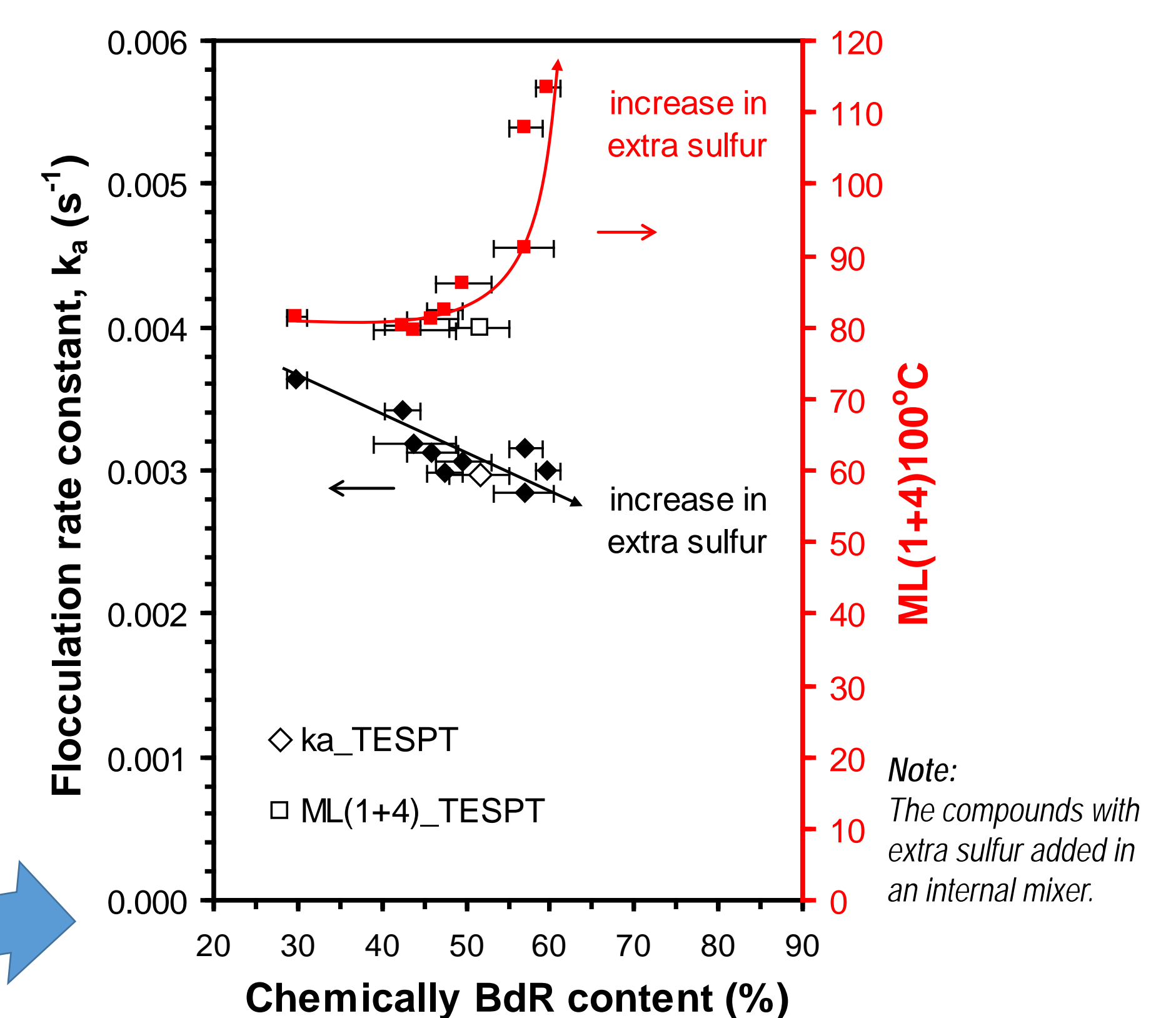


Mechanical properties of vulcanizates

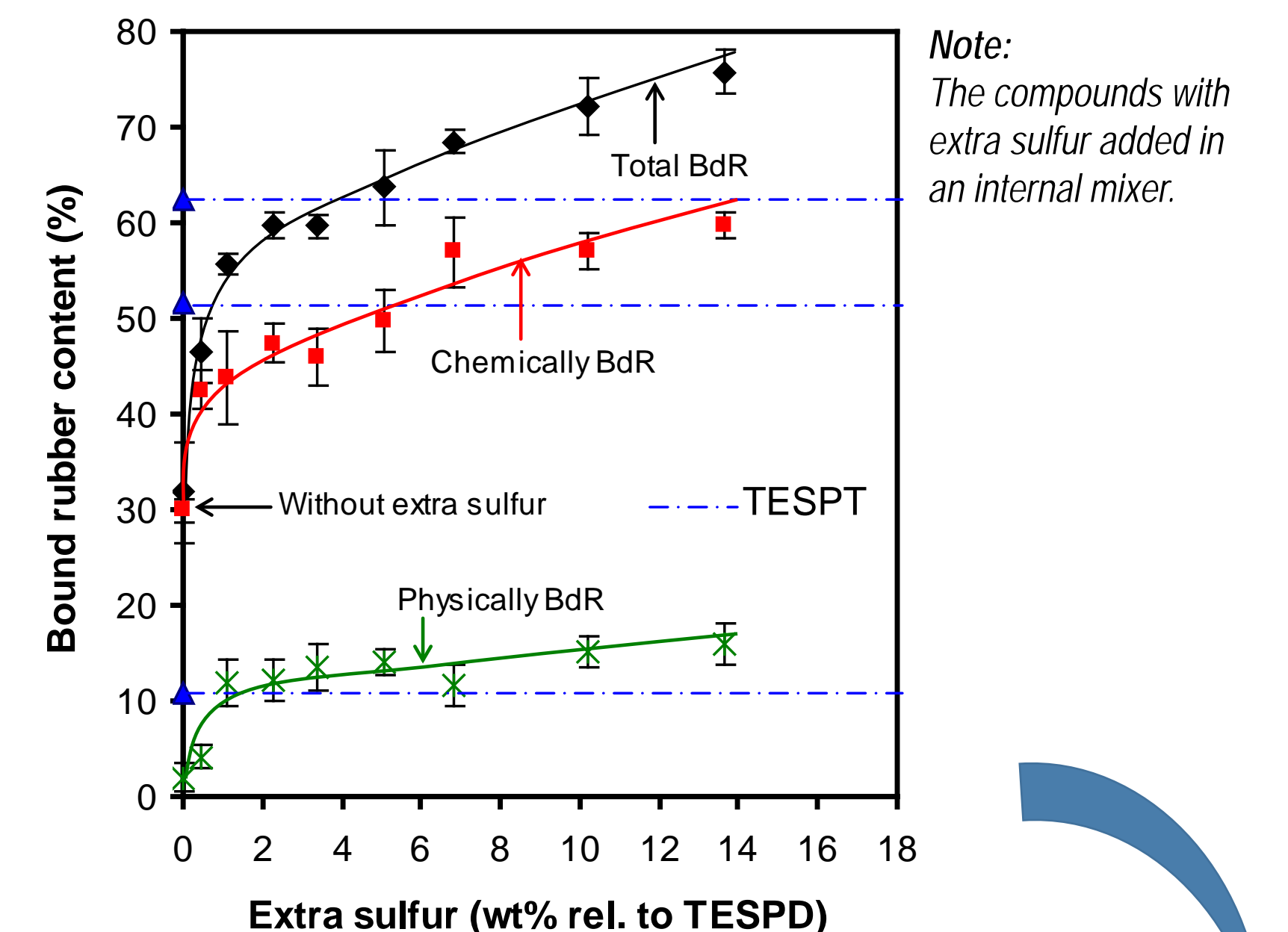


Conclusions

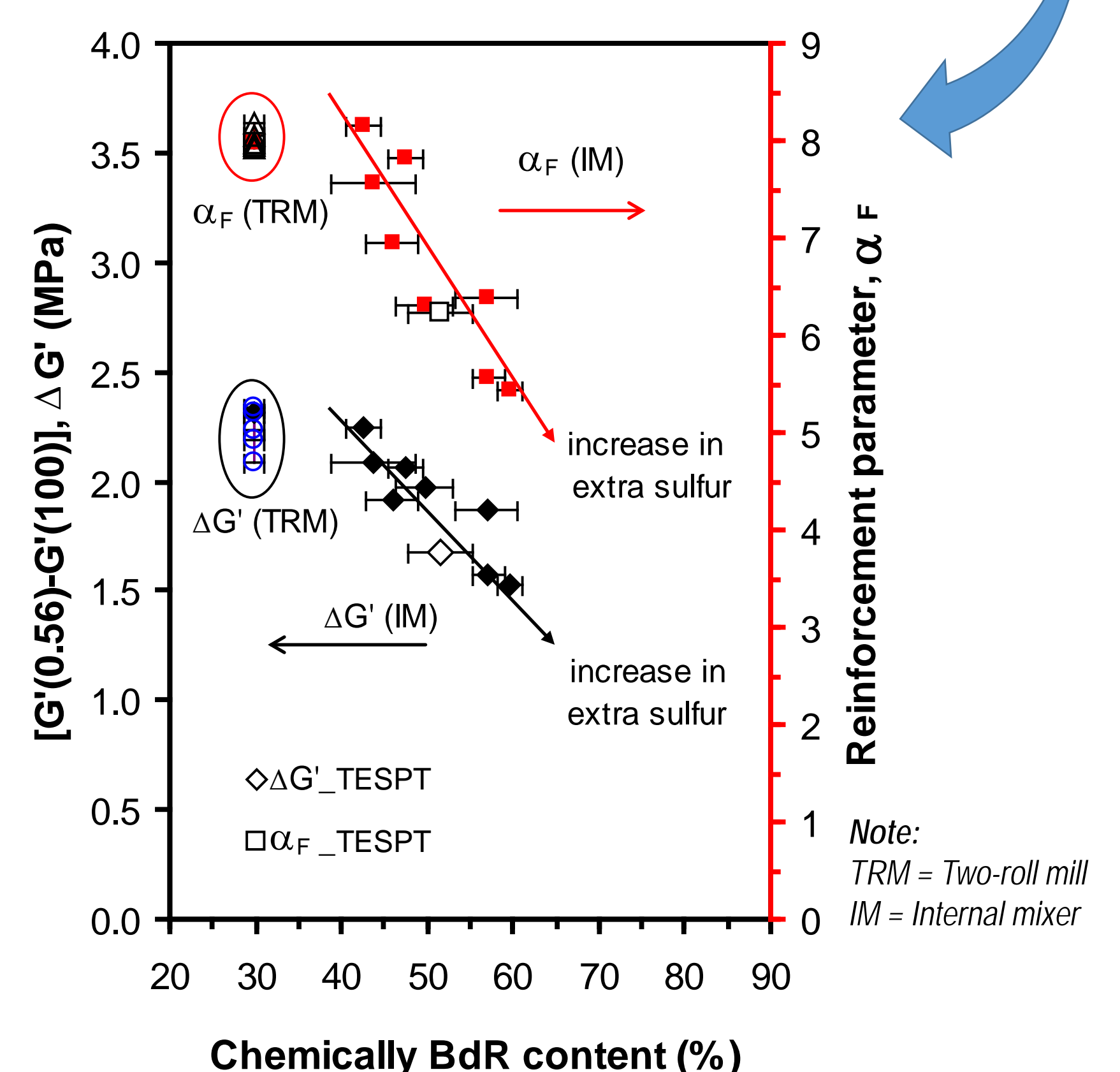
- The addition of extra sulfur in an internal mixer during non-productive step gives a positive contribution towards improved silica dispersion, and hence final properties.
- Adding extra sulfur during productive mixing on a two-roll mill has practically no effect.
- Extra sulfur at 3.4-5.1 wt% relative to the TESPd amount (0.15-0.20 phr), added during mixing of TESPd-silica-NR in an internal mixer is an optimal amount.



Extra networks can suppress the mobility of silica clusters but give undesired high viscosity at a certain content of extra sulfur added.



Indicators of filler-rubber interactions and lightly crosslinked rubber networks.



Adding extra sulfur during non-productive mixing gives a significant impact on filler-filler interaction or Payne effect & reinforcement.