Rubber Curing Systems

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- Over the years three special types of cure systems have been developed. They are:
  - efficient vulcanisation (EV) systems,
  - semi-efficient vulcanisation (SEV) systems and
  - conventional vulcanisation (CV) systems.

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The levels of accelerator and sulfur in CV, SEV and EV systems are shown in **Table 1**

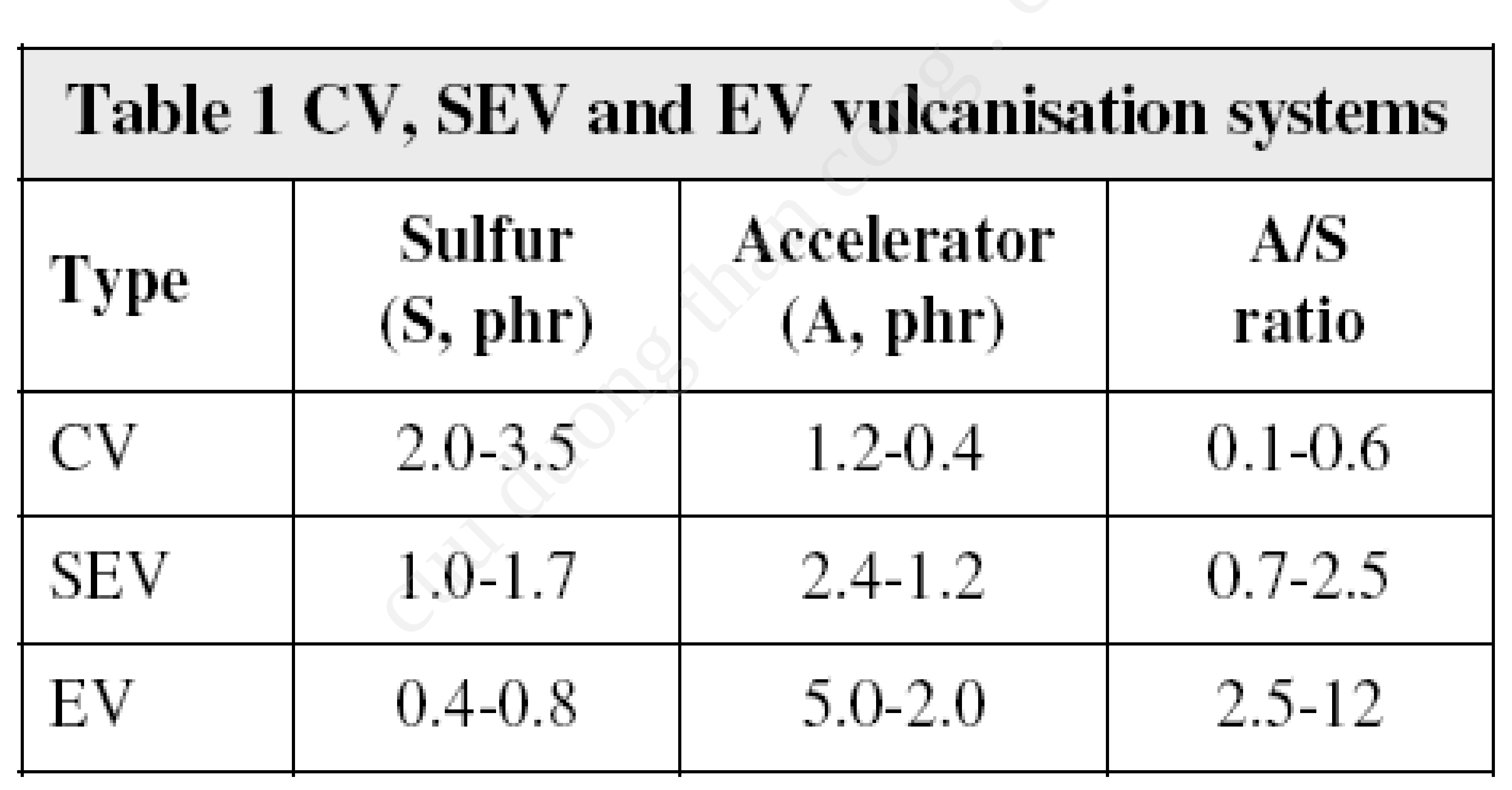

Table 1 CV, SEV and EV vulcanisation systems

Type	Sulfur (S, phr)	Accelerator (A, phr)	A/S ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
SEV	1.0-1.7	2.4-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12

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Measuring Cure

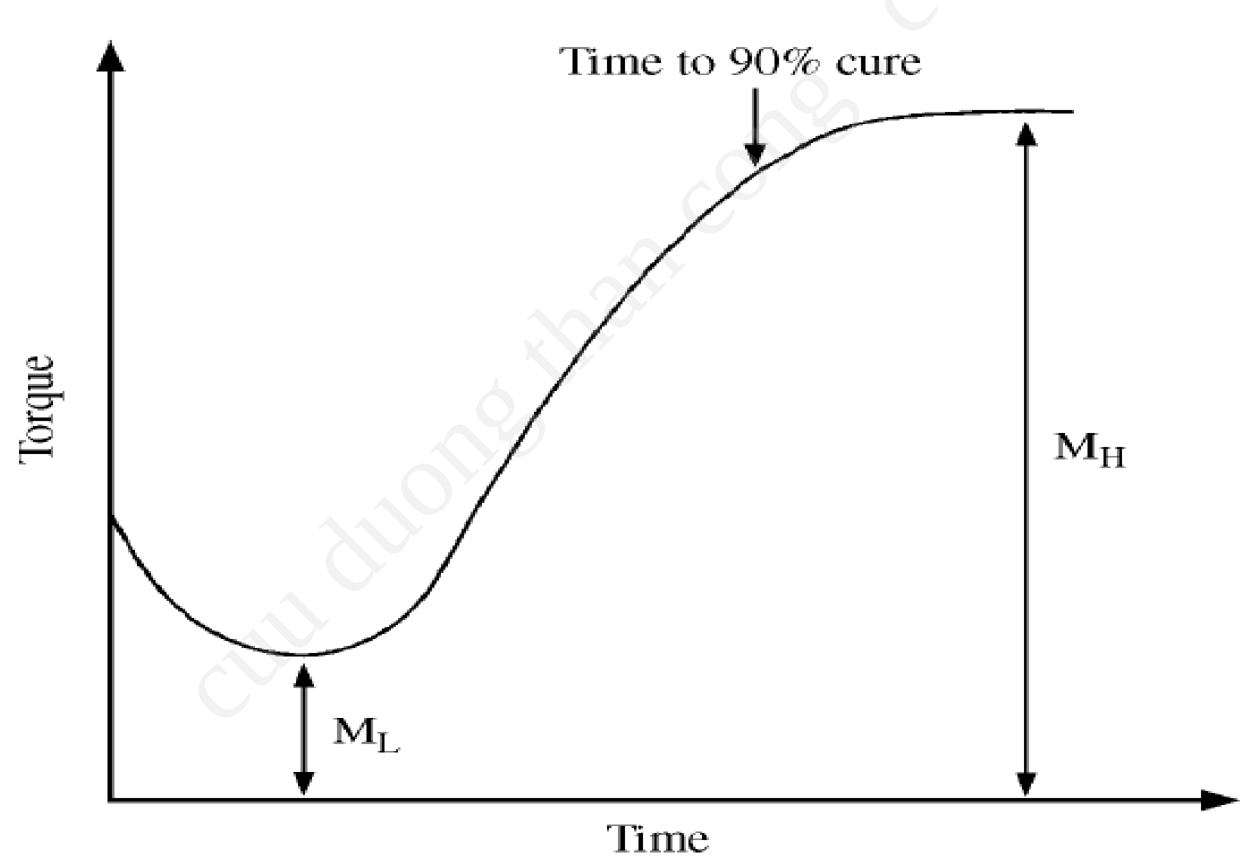

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Table 2 Vulcanisate structures and properties

Features	Systems		
	CV	SEV	EV
Poly- and disulfidic crosslinks (%)	95	50	20
Monosulfidic crosslinks (%)	5	50	80
Cyclic sulfide (conc.)	High	Medium	Low
Non-sulfidic (conc.)	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat ageing resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat build up	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set (%)	High	Medium	Low

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The curve exhibits a number of features which are used to compare cure:

- Maximum torque M_H.
- t_{S2}, T_2 or T_5 : there is a delay or induction time before the torque or resistance value begins to rise.
- T_{90} : is the time for the torque to increase to:

$$90/100(M_H - M_L) + M_L$$

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Cure rate: A rise in the value of torque with time, the slope of the curve, gives the measure of cure rate. Sometimes cure rates of various cure systems are compared with T90–ts2 data

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Test Equipment and Conditions

- Cure characteristics were determined using an MDR 2000EA rheometer.
- Test specimens were vulcanised by compression molding at temperatures and times indicated.
- Stress-strain properties were determined according to ISO 37

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- tear strength according to ISO 34/1.
- DIN abrasion ISO 4649.
- fatigue to failure ASTM 4482/85.
- hardness according to ISO 48.
- Ageing of the test specimens was carried out in a ventilated air oven at 100 C for 3 days (ISO 188).

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- Heat build up and permanent set after dynamic loading were determined using a Goodrich Flexometer (Load 11 kg or 22 kg; stroke 0.445 cm, frequency 30 Hz, start temperature 100 C) according to ISO 4666/3-1982.
- Dynamic mechanical analysis was carried out using a RDA-700 (prestrain 0.75%, frequency 15 Hz and temperature 60 C) according to ASTM D 2231.

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- Vulcanisate network structure was determined by equilibrium swelling in toluene using the method reported by Ellis and Welding. The volume fraction
- (Vr) obtained was converted into the Mooney-Rivlin elastic constant (C1) and finally into the concentration of chemical crosslinks.

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- The proportions of mono-, di-, and polysulfidic crosslinks in the vulcanisates were determined using thiol amine chemical probes.

- Following the cleavage of the poly- and disulfidic crosslinks, the samples were treated with methyl iodide to distinguish carbon-carbon based crosslinks from monosulfidic crosslinks.

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- The rubber to metal adhesion characteristics were determined according to ASTM 2229-85.

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Curing Systems

Curing systems can be classified into four categories.

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Sulfur Curing Systems

Accelerators

Accelerators may be classified in several ways:

(a) inorganic or organic

(b) acidic or basic

(c) by chemical type or

(d) by speed of the cure, giving rise to the terms slow, medium, semi-ultra and ultra.

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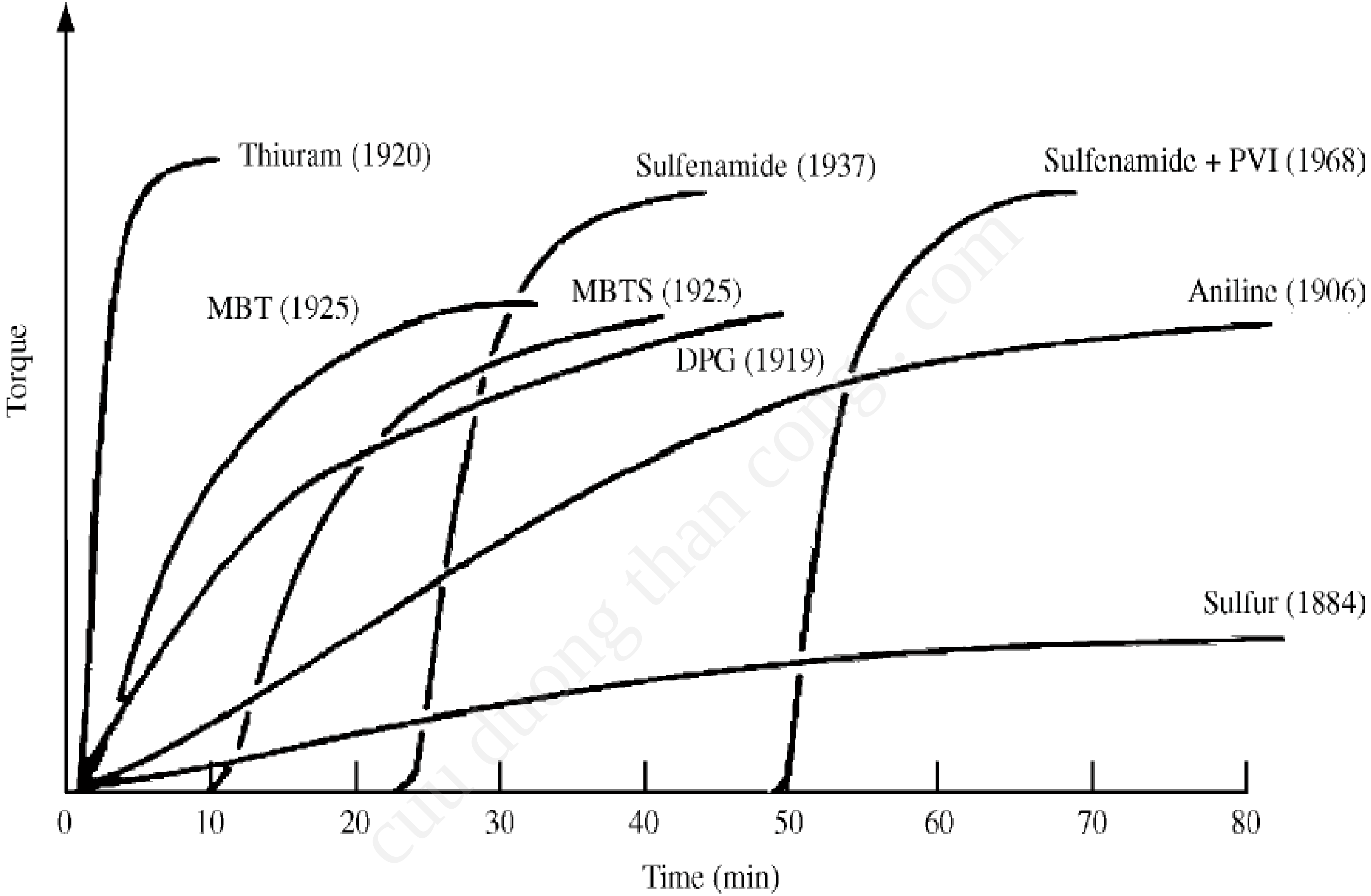

Crosslinking activities of different accelerators in NR at 140 °C. The approximate year of commercial introduction is given in parentheses (405)

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Functionally, accelerators can also be classified into two broad categories:

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Primary accelerators:

Primary accelerators are mercapto based accelerators, generally efficient and confer good processing safety to the rubber compounds, exhibiting a broad vulcanisation plateau with relatively low crosslink density.

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- Secondary accelerators:

Some rubber compounds use only one accelerator but most contain two, a primary at about 1 phr and a secondary (or booster) at 0.1 to 0.5 phr.

These combinations cause faster vulcanisation than each product separately and a considerable activation of cure which is positive for the general property spectrum of the vulcanisates.

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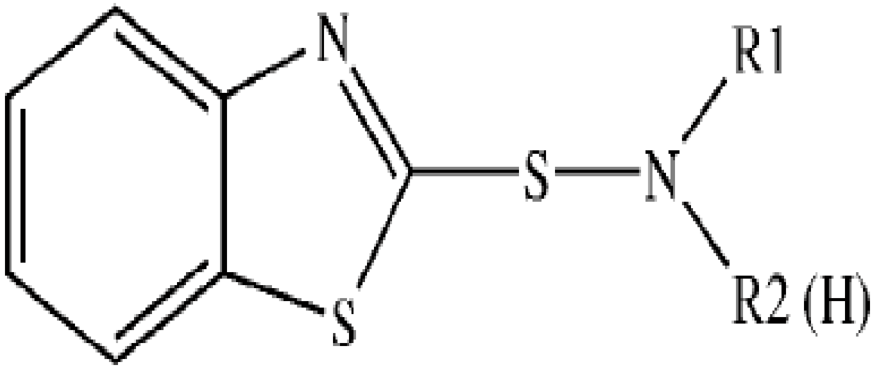
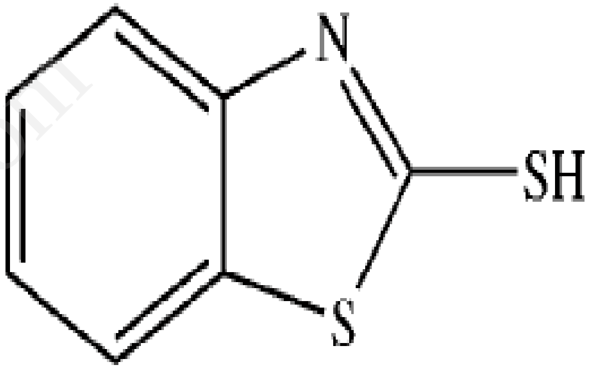
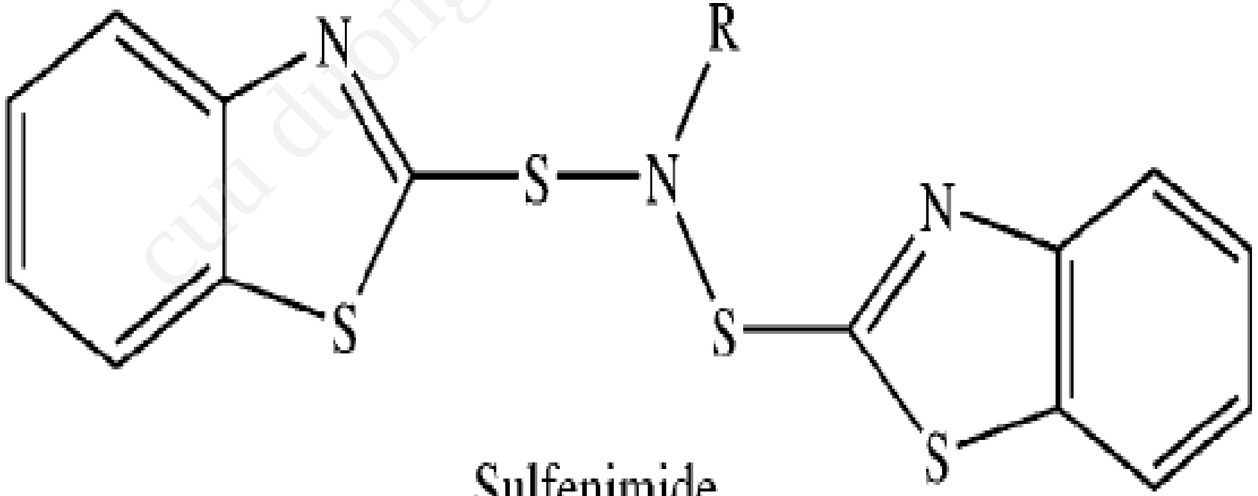
Primary



Sulfenamide



Thiazole



Sulfenimide

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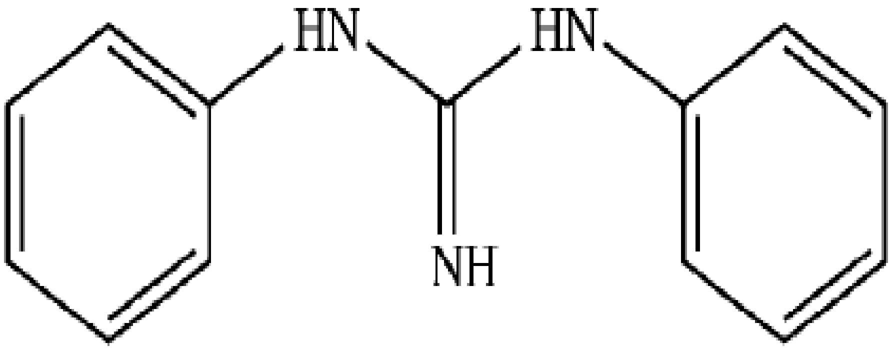
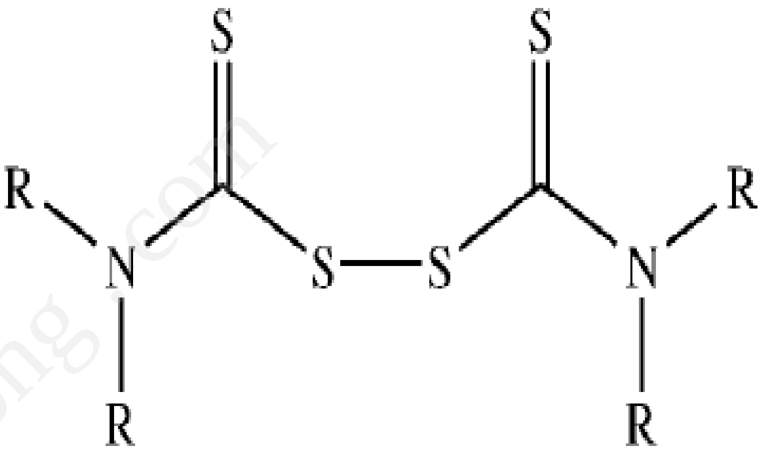
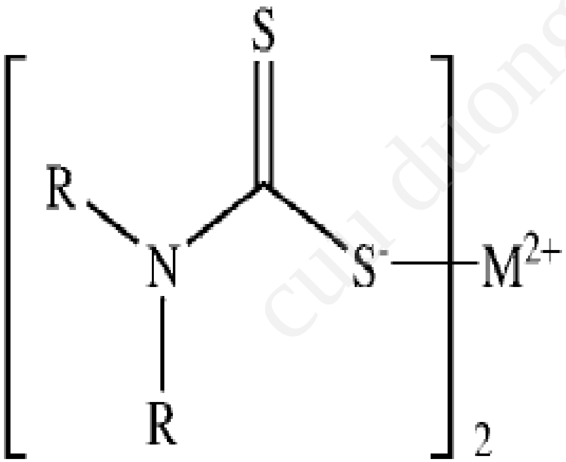
Secondary



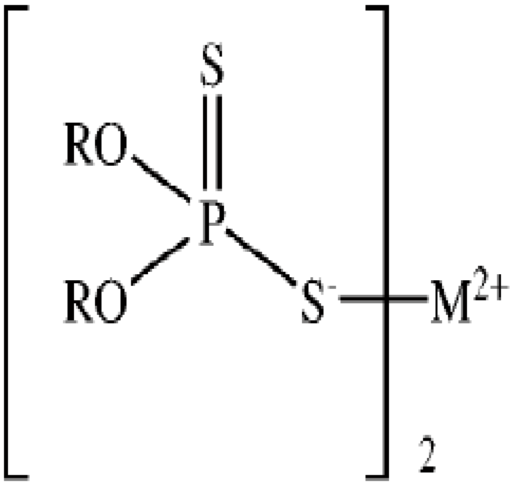
Guanidine



Thiuram



Dithiocarbamate



Dithiophosphate

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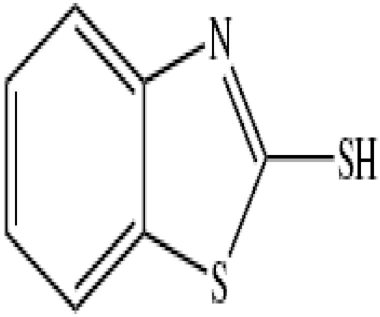
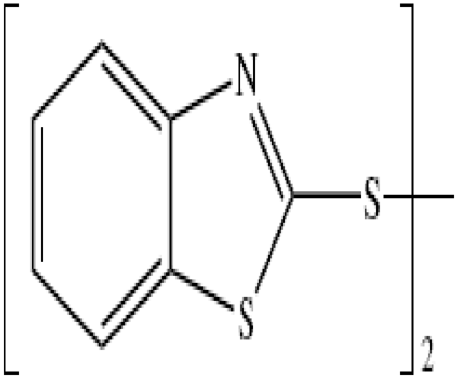
Table 3 Accelerators for sulfur vulcanisation

Compound	Abbreviation	Structure
Benzothiazole		
2-mercaptobenzothiazole	MBT	
2,2´-dithiobenzothiazole	MBTS	

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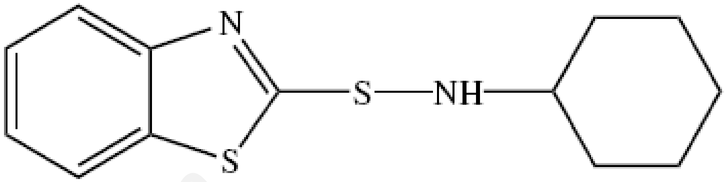
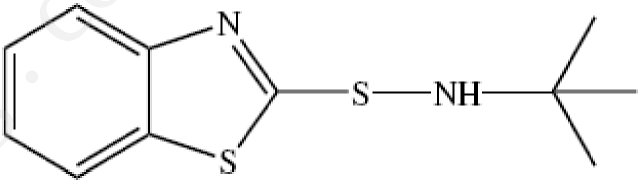
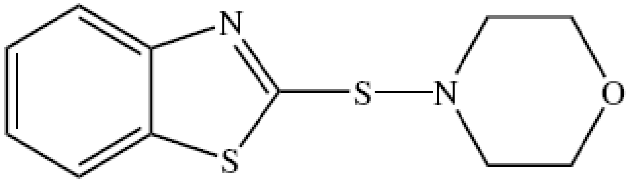
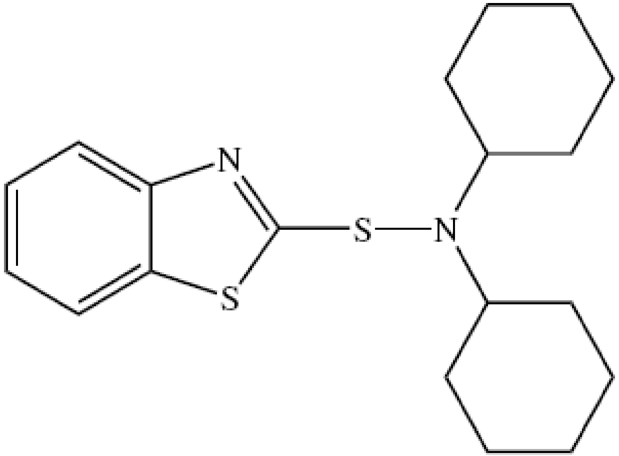
Benzothiazolesulfenamide		
N-cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-butylbenzothiazole-2-sulfenamide	TBBS	
2-morpholinothiobenzothiazole	MBS	
N-dicyclohexylbenzothiazole-2-sulfenamide	DCBS	

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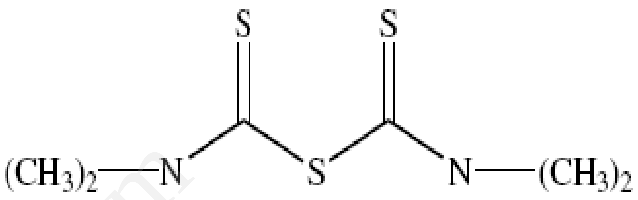
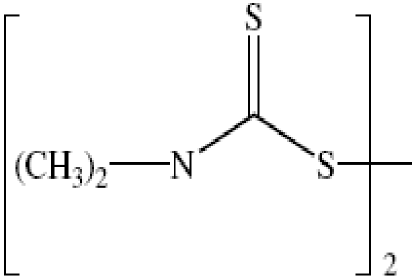
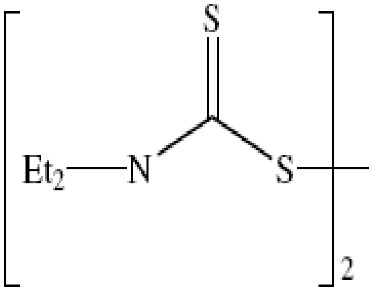
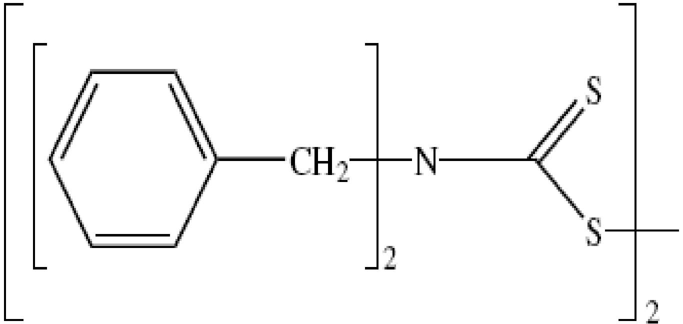
Thiuram		
tetramethylthiuram monosulfide	TMTM	
tetramethylthiuram disulfide	TMTD	
tetraethylthiuram disulfide	TETD	
tetrabenzylthiuram disulfide	TBzTD	

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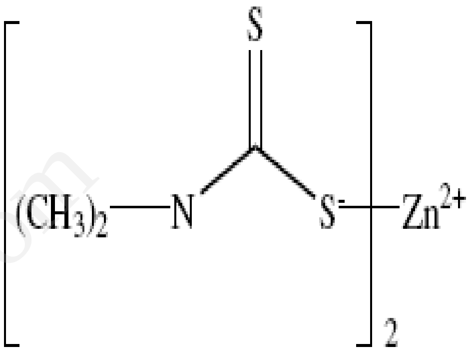
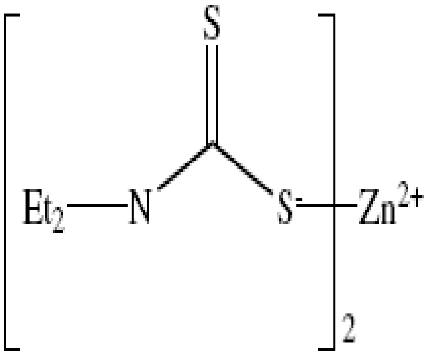
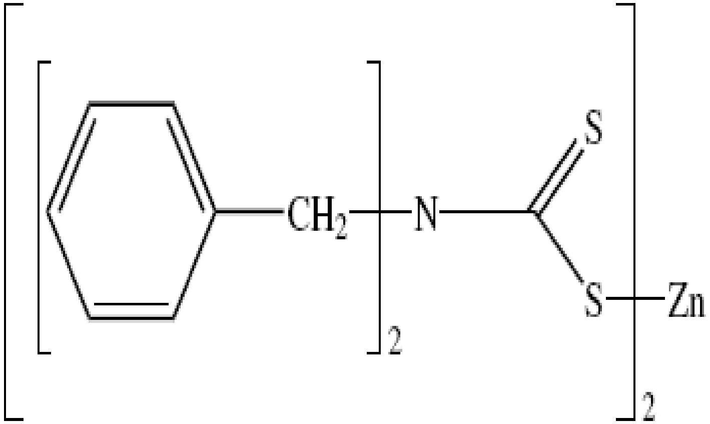
Dithiocarbamate		
zinc dimethyldithiocarbamate	ZDMC	
zinc diethyldithiocarbamate	ZDEC	
zinc dibenzyldithiocarbamate	ZBEC	

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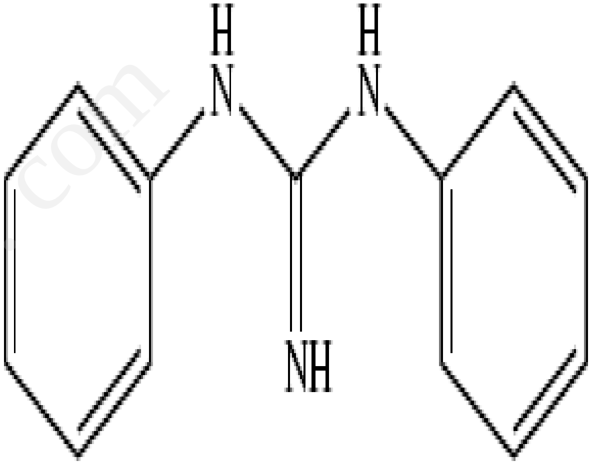
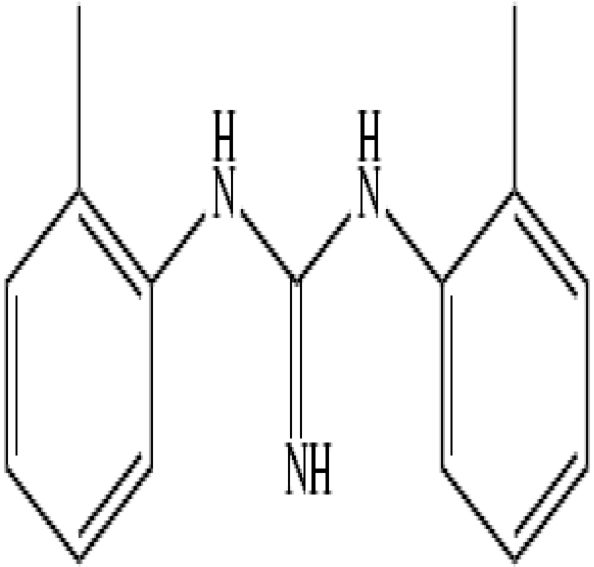
Guanidines

diphenyl guanidine	DPG	
di-o-tolylguanidine	DOTG	

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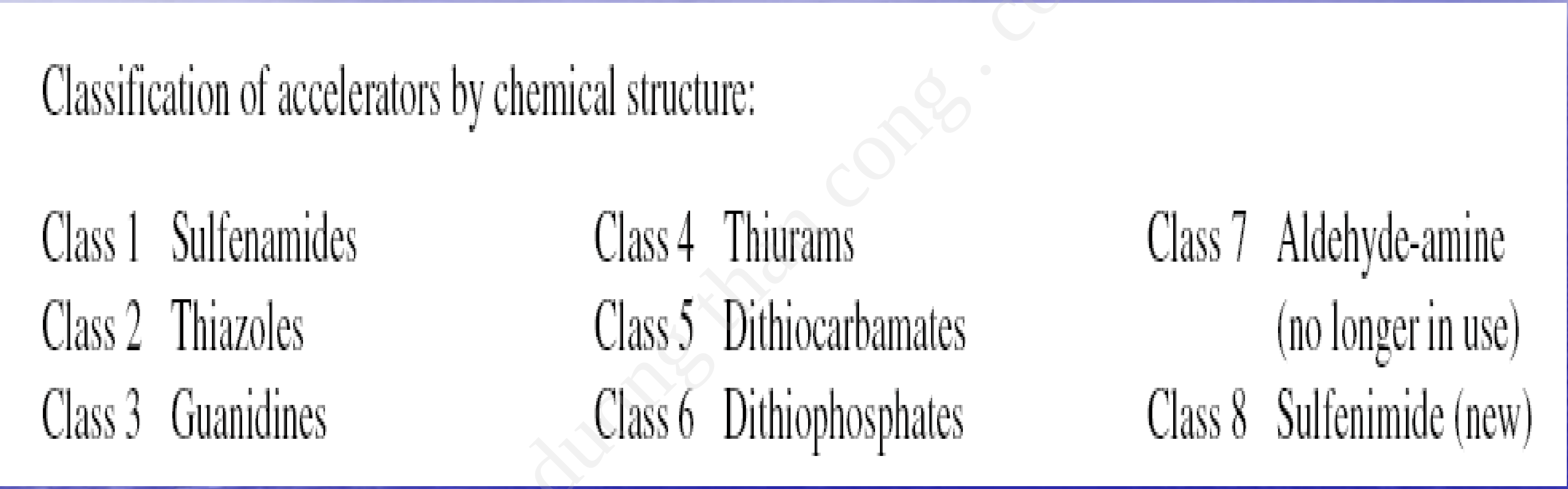

Classification of accelerators by chemical structure:

Class 1 Sulfenamides
Class 2 Thiazoles
Class 3 Guanidines
Class 4 Thiurams
Class 5 Dithiocarbamates
Class 6 Dithiophosphates
Class 7 Aldehyde-amine (no longer in use)
Class 8 Sulfenimide (new)

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Table 4 Comparison of different classes of accelerators (a.11)

Class	**Vulcanisation rate**
Aldehyde-amine	Slow
Guanidines	Medium
Thiazoles	Semi-fast
Sulfenamides	Fast-delayed action
Sulfenimides	Fast-delayed action
Dithiophosphates	Fast
Thiurams	Very fast
Dithiocarbamates	Very fast

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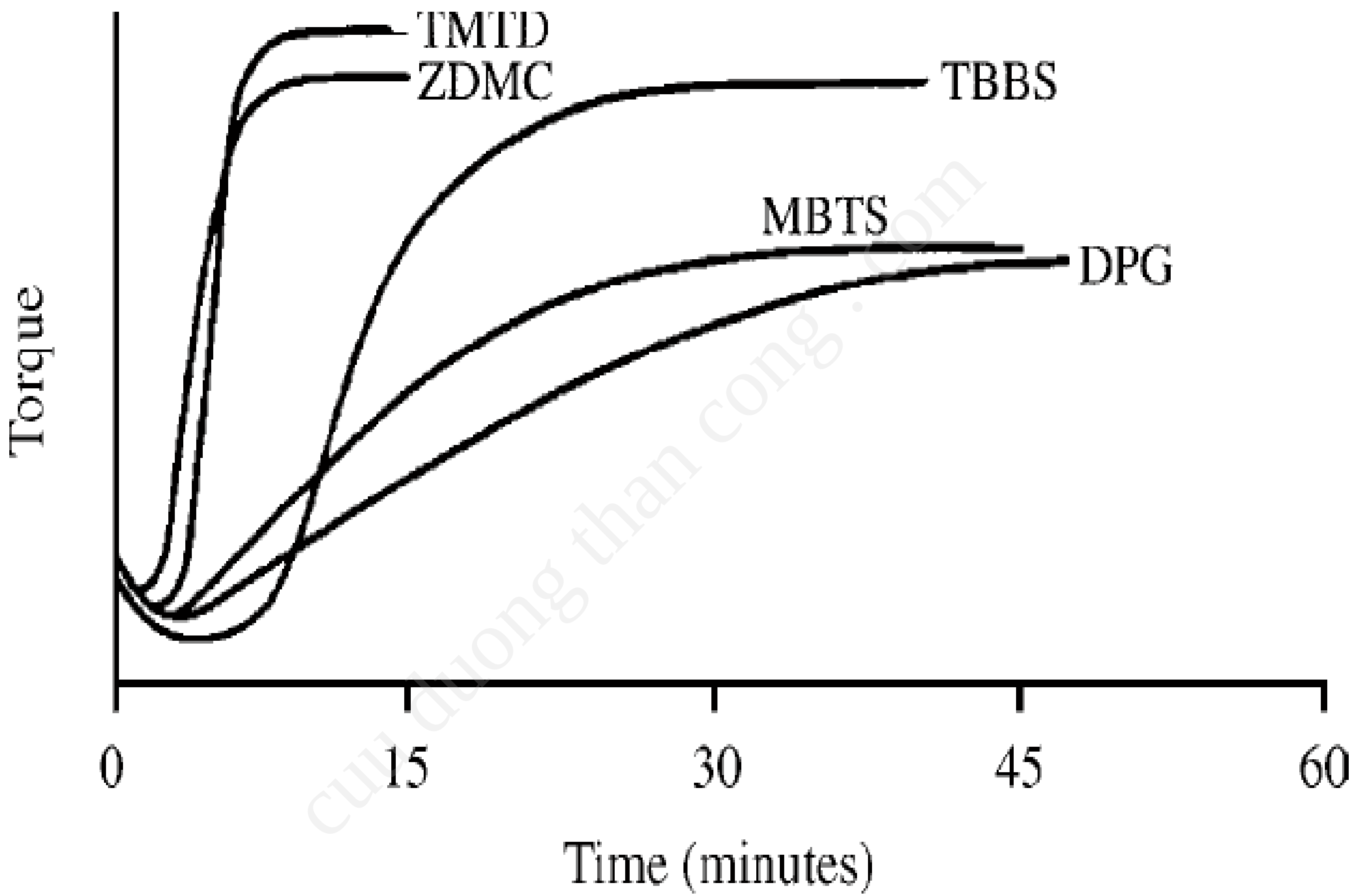

Figure 4 Comparison of accelerators/sulfur (0.5/2.5 phr) in NR (a.11)

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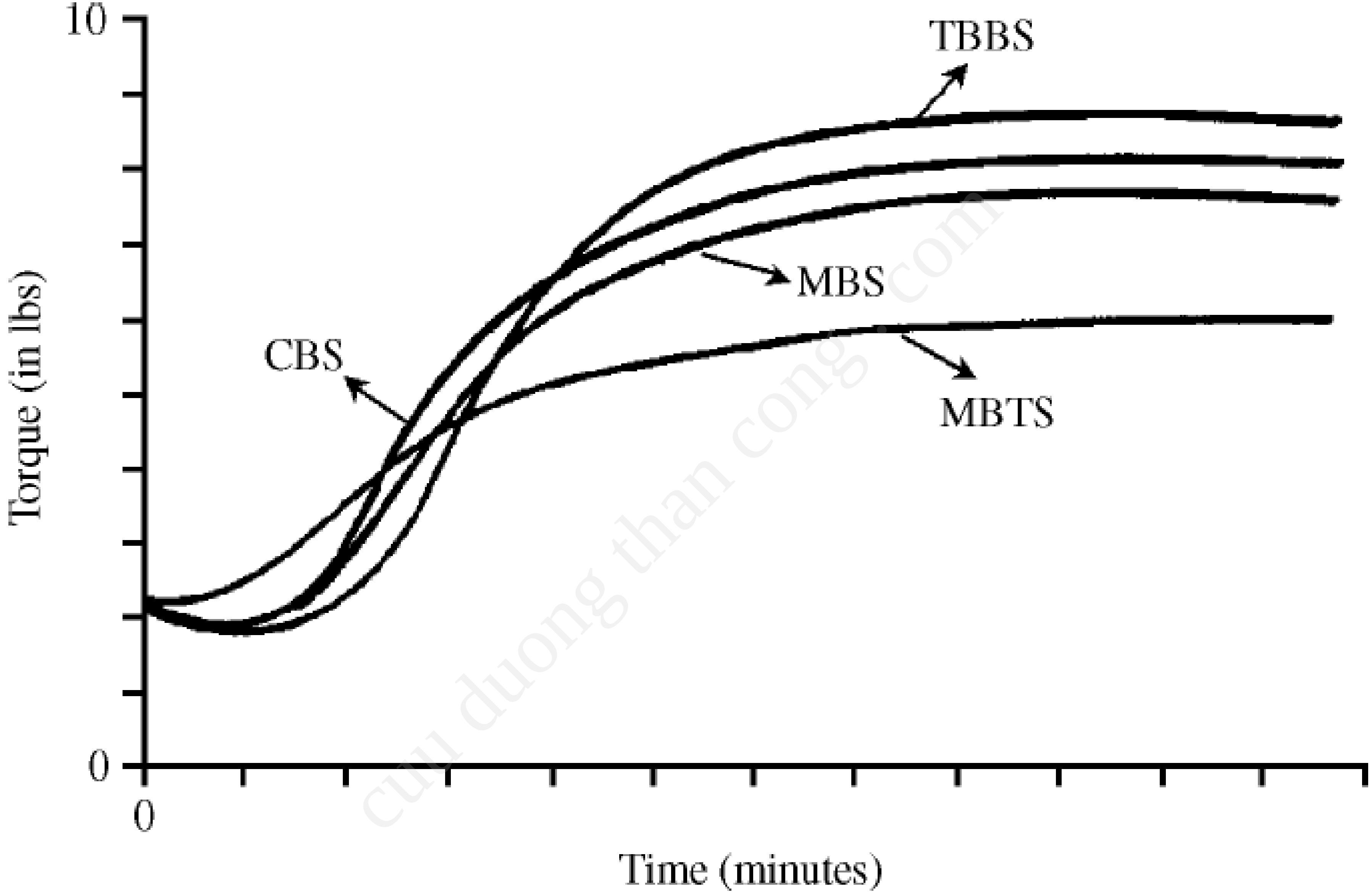

Figure 5

Comparison of primary accelerators/sulfur (0.5/2.5 phr) in NR at 144 °C (a.11)

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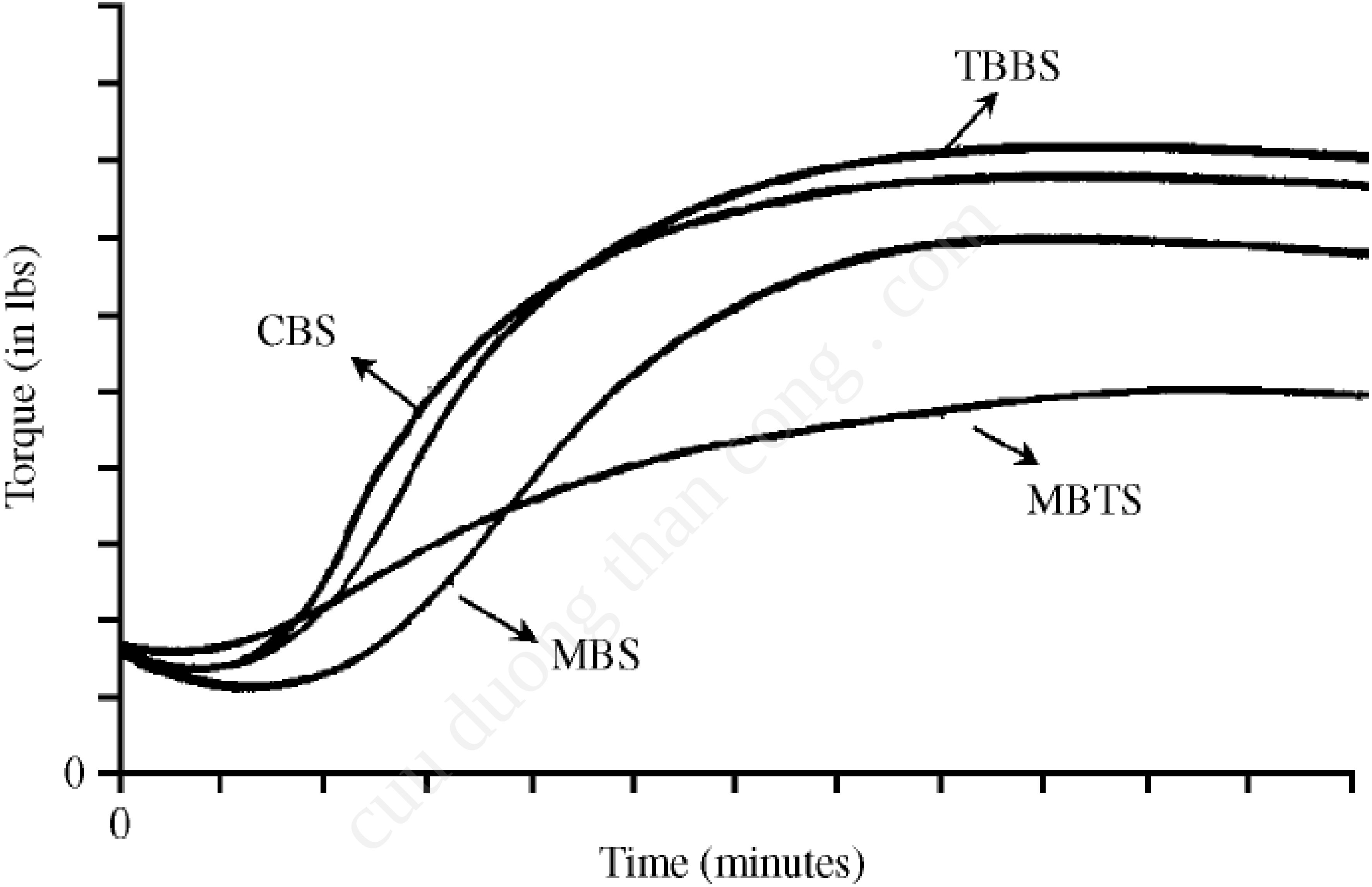

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Figure 6

Comparison of primary accelerators/sulfur (1.2/1.5 phr) in SBR (a.11)

Table 5 Comparison of secondary accelerators in NR (a.11)

Ingredients/stocks	1	2	3	4	5	6	7	8
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS	1.2	0	0	0	0	0	0	0
DPG	0.4	0	0	0	0	0	0	0
TBBS	0	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0	0.4	0	0	0	0	0	0
TMTM	0	0	0.4	0	0	0	0	0
TETD	0	0	0	0.4	0	0	0	0
ZDMC	0	0	0	0	0.4	0	0	0
ZDEC	0	0	0	0	0	0.4	0	0
ZDBC	0	0	0	0	0	0	0.4	0
DOTG	0	0	0	0	0	0	0	0.4
Mooney scorch at 120 °C, T5 (minutes)	7.2	16.8	21.5	23.5	13.7	16.7	20.2	21.7
Rheometer at 145 °C								
T90 (minutes)	9.2	7.5	9.5	9.8	7.0	7.8	9.3	16.5
Modulus at 100% elongation (MPa)	2.6	3.4	3.5	3.0	3.1	2.9	2.8	2.8
Elongation at break (%)	550	450	430	480	470	500	510	510

Formulation: NR 100; FEF Black 40; aromatic oil 10.0; zinc oxide 5.0; stearic acid 1.5; 6PPD 2.0

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Table 6 Comparison of secondary accelerators in SBR (a.11)

Ingredients/stocks	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Sulfur	1.8	1.8	1.8	1.8	1.8	1.8	1.8
MBTS	1.2	0	0	0	0	0	0
DPG	0.4	0	0	0	0	0	0
TBBS	0	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	0	0.3	0	0	0	0	0
TMTM	0	0	0.3	0	0	0	0
TETD	0	0	0	0.3	0	0	0
ZDMC	0	0	0	0	0.3	0	0
ZDBC	0	0	0	0	0	0.3	0
ZBPD	0	0	0	0	0	0	0.3
Mooney scorch at 135 °C, T5 (minutes)	10.4	12.3	22.0	14.5	13.2	18.7	24.4
Rheometer at 160 °C							
T90 (minutes)	9.2	7.4	9.3	8.6	8.7	12.0	21.3
Modulus at 100% elongation (MPa)	2.0	2.1	2.1	2.0	1.9	1.9	1.6
Elongation at break (%)	450	430	420	430	470	470	500

Formulation: SBR-1500 100; N-330 50; aromatic oil 10; zinc oxide 4; stearic acid 2; 6PPD 2

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- NR and SBR compounds with MBTS/DPG as the control. The secondary accelerators also change the network structures. The polysulfidic crosslinks are converted to monosulfidic exhibiting heat stability.

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Sulfur Donors

- Aside from the sulfur itself, sulfur bearing compounds that liberate sulfur at the vulcanisation temperature can be used as vulcanising agents.

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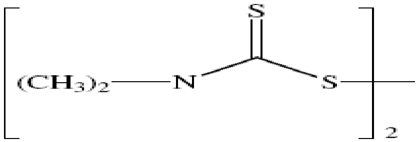
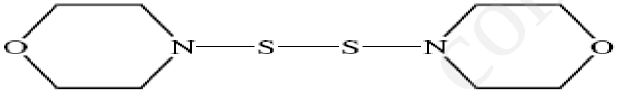
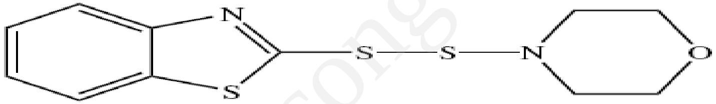
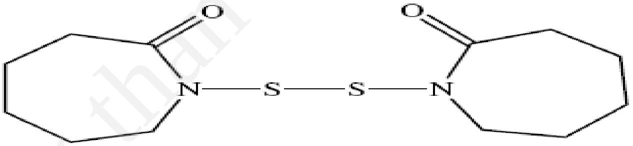
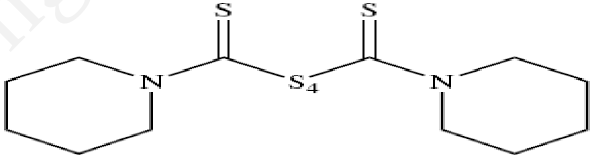
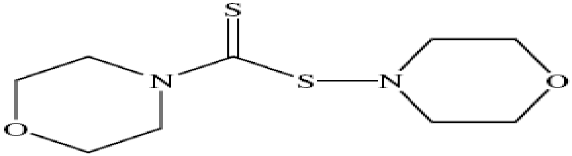
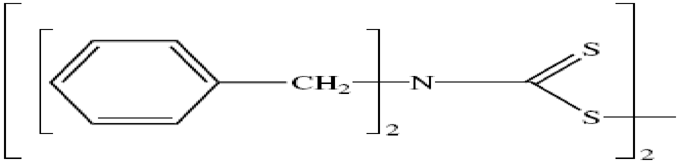
Table 7 Sulfur donors

Material	Structure	Active sulfur (%)	M.P. (°C)
TMTD		13.3	124
4,4´-dithiodimorpholine (DTDM)		13.6	125
2-morpholino-dithio-benzothiazole (MBSS)		28.4	129
caprolactam disulfide (CLD)		28.8	131
Dipentamethylenethiuram tetrasulfide (DPTT)		16.6	120
N-oxydiethylene thiocarbamyl-N´-oxydiethylenesulfenamide (OTOS)		12.9	136
TBzTD*		5.8	124

**TBzTD acts as sulfur donor only at very high concentration*

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Cures for Speciality Elastomers

- The curing systems used to vulcanise speciality elastomers such as EPDM, CR, IIR and NBR are different than those used to cure NR, SBR, BR and its blends
- The former elastomers are less unsaturated and therefore need a high ratio of accelerator to sulfur

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Cure Systems for EPDM

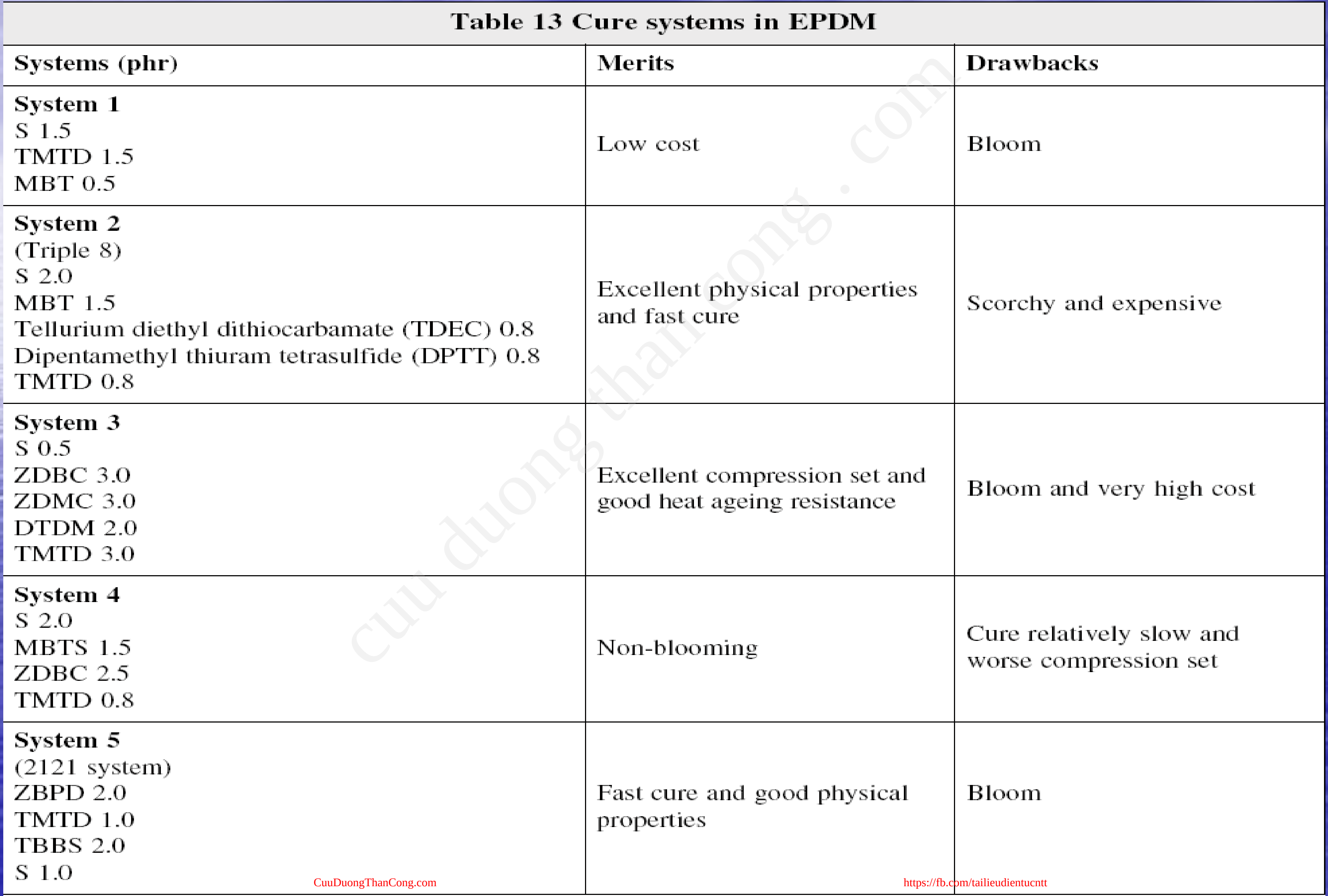

Table 13 Cure systems in EPDM

Systems (phr)	Merits	Drawbacks
System 1 S 1.5 TMTD 1.5 MBT 0.5	Low cost	Bloom
System 2 (Triple 8) S 2.0 MBT 1.5 Tellurium diethyl dithiocarbamate (TDEC) 0.8 Dipentamethyl thiuram tetrasulfide (DPTT) 0.8 TMTD 0.8	Excellent physical properties and fast cure	Scorchy and expensive
System 3 S 0.5 ZDBC 3.0 ZDMC 3.0 DTDM 2.0 TMTD 3.0	Excellent compression set and good heat ageing resistance	Bloom and very high cost
System 4 S 2.0 MBTS 1.5 ZDBC 2.5 TMTD 0.8	Non-blooming	Cure relatively slow and worse compression set
System 5 (2121 system) ZBPD 2.0 TMTD 1.0 TBBS 2.0 S 1.0	Fast cure and good physical properties	Bloom

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Cure Systems for Nitrile Rubber

- Cure systems for nitrile rubber are somewhat analogous to those of NR, SBR or BR except that magnesium carbonate (MC) treated sulfur is usually used to aid sulphur dispersion into the polymer.

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Table 18 High sulfur cure systems for nitrile rubber

Curatives/stocks	1	2	3
MC treated sulfur	1.5	1.5	1.5
TMTM	0.4	0	0
MBTS	0	1.5	0
TBBS	0	0	1.2
TMTD	0	0	0.1
Processing and curing properties			
Mooney scorch at 121 °C, T5 (minutes)	6.8	8.1	5.7
Rheometer at 160 °C, T90 (minutes)	8.7	15.2	4.7

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Physical properties (Cure: 160 °C/90 minutes)			
Hardness (Shore A)	73	71	75
Modulus at 100% elongation (MPa)	4.2	3.6	5.0
Tensile strength (MPa)	16.3	16.2	17.3
Elongation at break (%)	380	475	355
Heat ageing at 100 °C/72 h			
Hardness (Shore A)	80	78	82
Tensile strength retention (%)	85	68	57
Compression set			
100 °C/22 h (%)	31	50	55
Recipe: Medium acrylonitrile NBR 100; N-550 40; N-770 40; plasticiser di(2-ethylhexyl)phthalate (DOP) 15; zinc oxide 5; stearic acid 1; TMQ 1; 6PPD 2			

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Cure Systems for Polychloroprene

- CR can be vulcanised in the presence of zinc oxide alone, but magnesium oxide is necessary to confer scorch resistance.
- Along with the metal oxides, TMTD, DOTG and sulfur are used. This is a good method to obtain high resilience and dimensional stability.

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Table 21 Vulcanisation systems for CR (phr)

Curatives/Stock	1	2	3
Zinc oxide	5	5	5
Magnesium oxide	4	0	4
Calcium stearate	0	5.5	0
Stearic acid	0	0	1
TMTM	0	0	1
DOTG	0	0	1
ETU	0.5	0.5	0
Sulfur	0	0	1

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Cure Systems for Butyl and Halobutyl Rubber

- The low degree of unsaturation requires the use of ultra accelerators, such as thiuram or dithiocarbamate. Phenolic resins, bisazoformates , and quinone derivatives can also be employed.

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Table 22 Model formulation of butyl rubber (inner tubes)

Ingredients/stock	**01**
IIR Polysar 301	100
N-660	70
Zinc oxide	5
Stearic acid	1
Paraffinic Oil Sunpar 2280	28
Perkacit MBTS	0.5
Perkacit TMTD	1.0
Sulfur	2.0

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- Sulfur crosslinks have limited stability at elevated temperatures and can rearrange to form new crosslinks.
- Resin cure systems provide C-C crosslinks and heat stability.

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Halobutyl Rubber

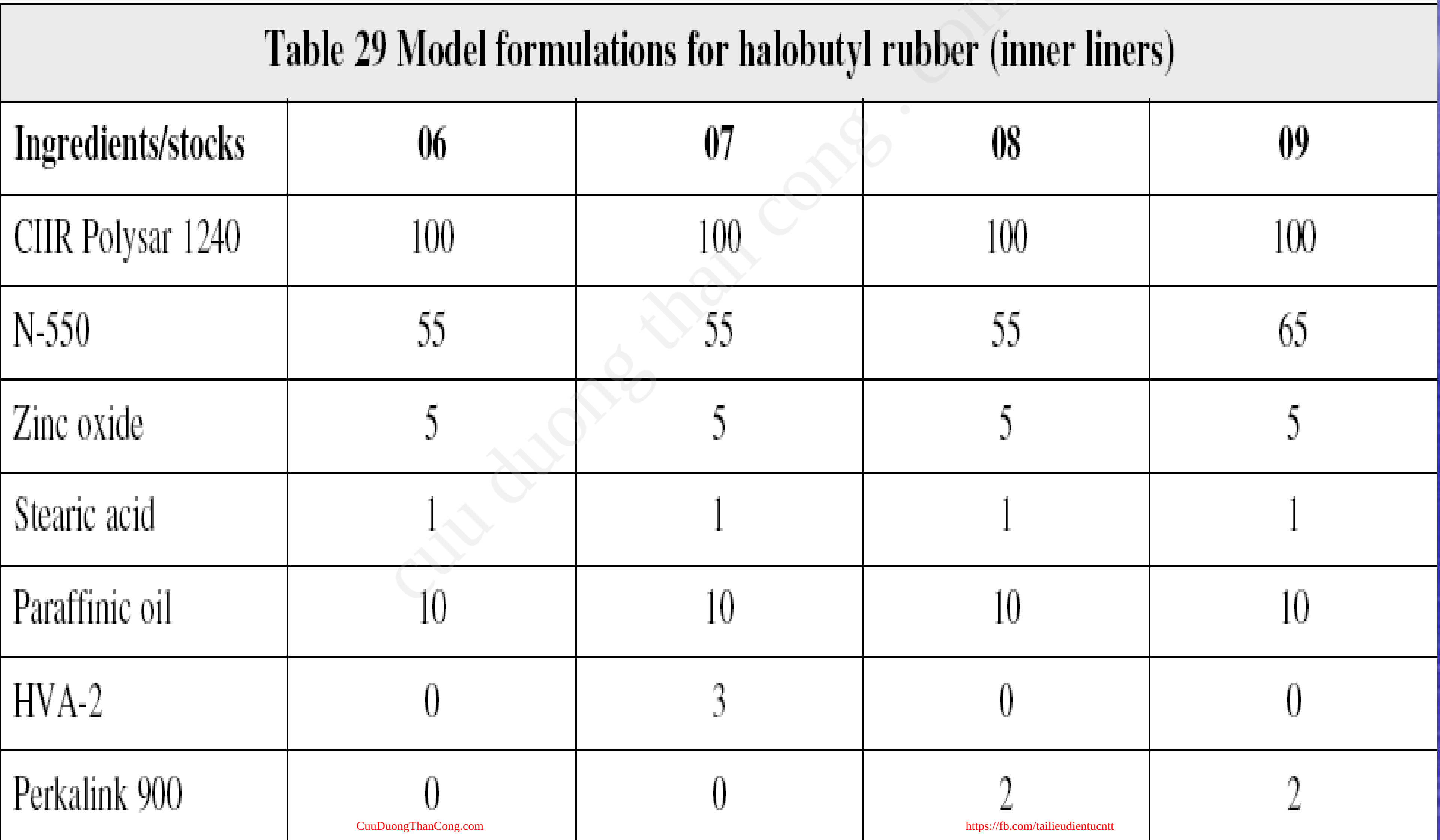

Table 29 Model formulations for halobutyl rubber (inner liners)

Ingredients/stocks	06	07	08	09
CIIR Polysar 1240	100	100	100	100
N-550	55	55	55	65
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Paraffinic oil	10	10	10	10
HVA-2	0	3	0	0
Perkalink 900	0	0	2	2

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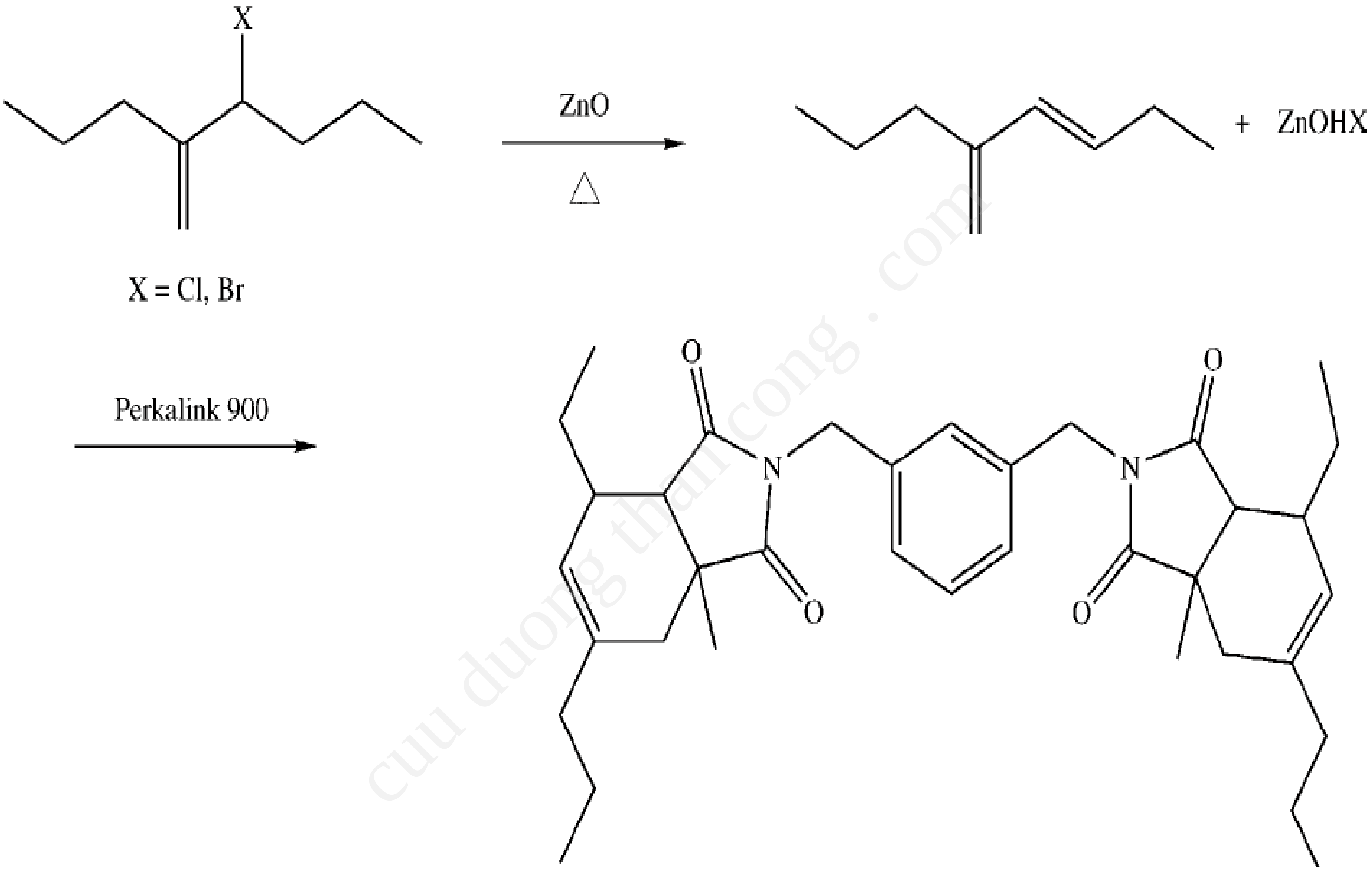

Figure 9

Reaction of Perkalink 900 with XIIR in the presence of zinc oxide

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Peroxide Cure Systems

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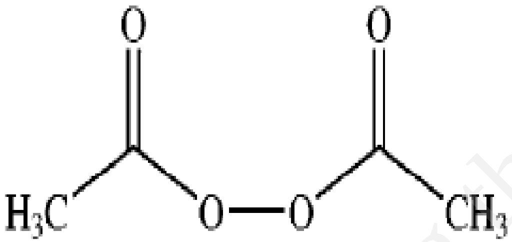
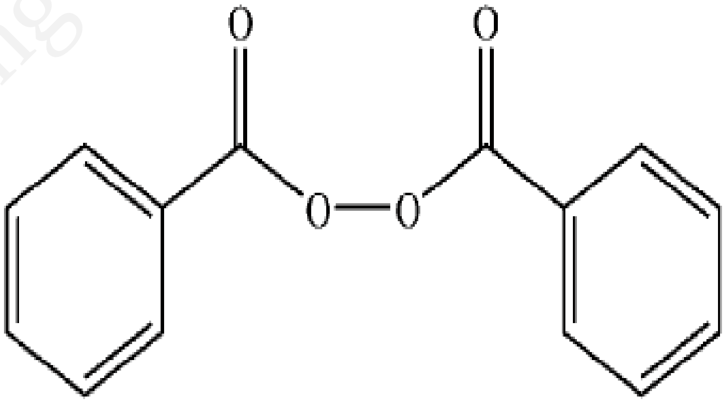
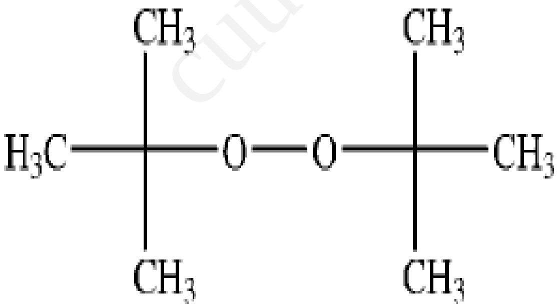
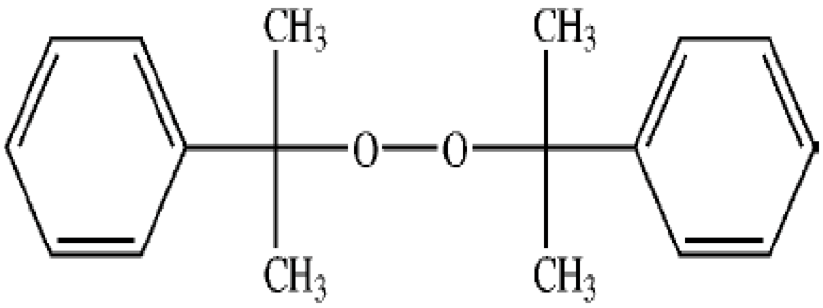
	Aliphatic	Aromatic
Peroxides with carboxyl groups	 Diacyl peroxide	 Dibenzoyl peroxide
Peroxides without carboxyl groups	 Di-t-butyl peroxide	 Dicumyl peroxide

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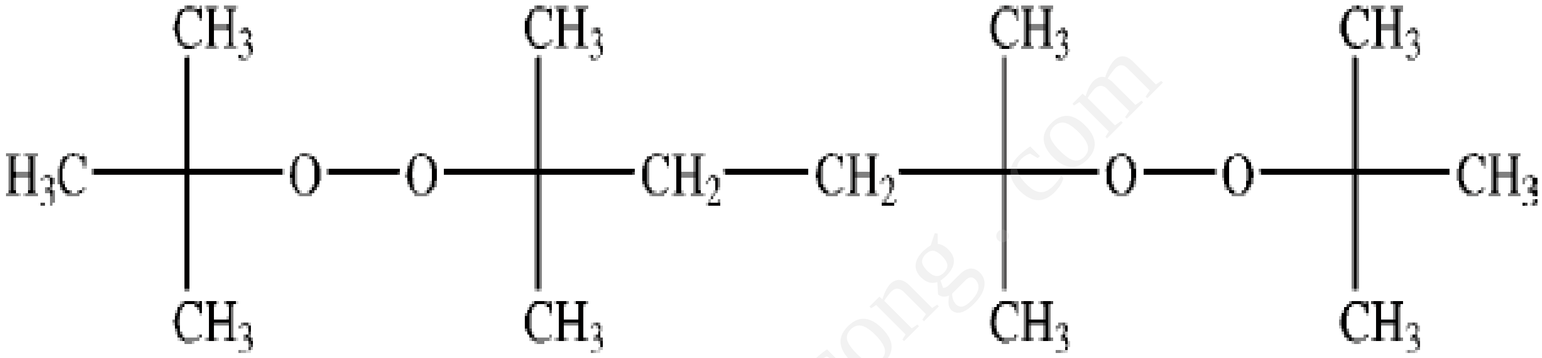
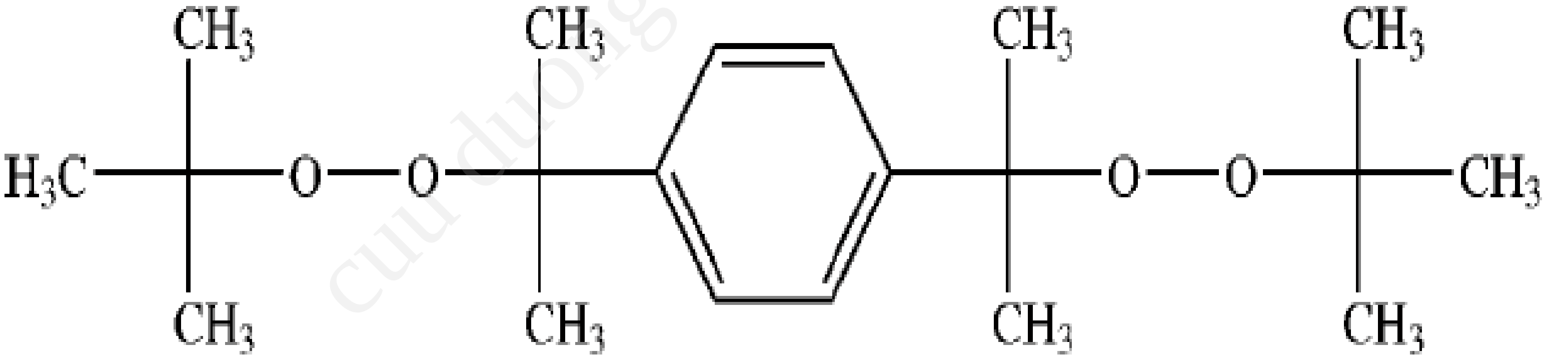


2,5-Bis(tert-butylperoxy)-2,5 dimethyl hexane



1,4-Bis(tert-butylperoxy isopropyl) benzene

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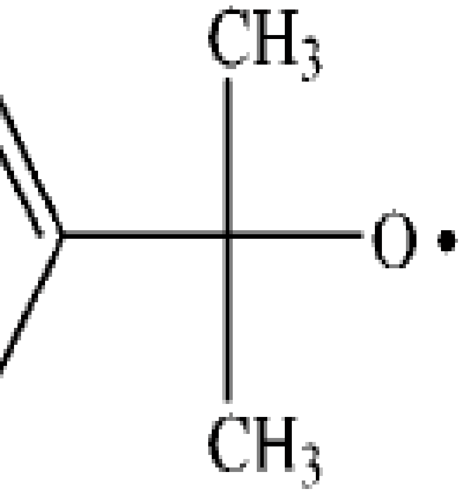
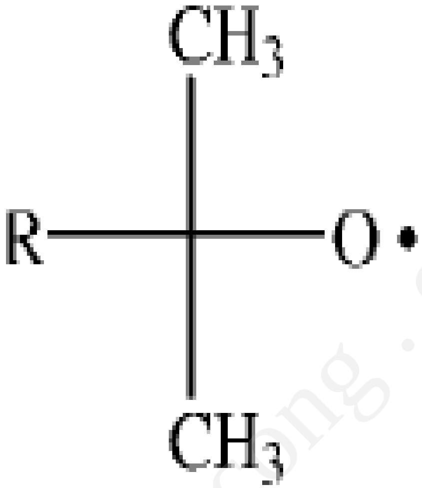
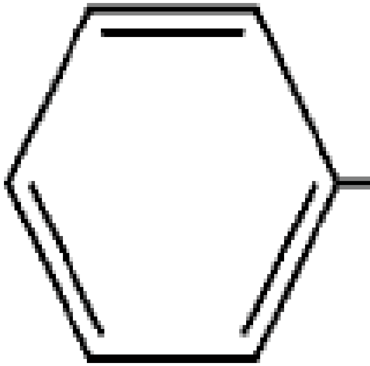


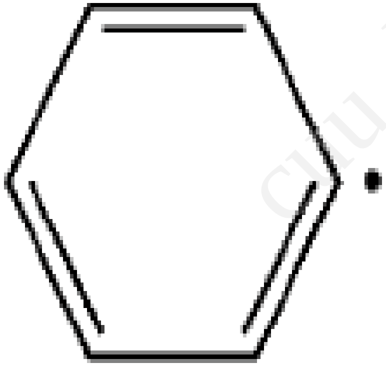
loxy radical



Alkyloxy radical



Acyloxy ra



Phenyl radical

$CH_3 \bullet$

Methyl radical

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Peroxide Vulcanisation of EPDM

- Peroxide vulcanisation of EPDM is growing in popularity because of enhanced ageing resistance.
- A comparison of sulfur and peroxide cure systems for EPDM is shown in **Table 32** .

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Table 32 Comparison of properties of sulfur and peroxide cured EPDM (403)

ients	Sulfur cure	Di-Cup cure	Vul-Cup cure
rdel 1040	100	100	100
F black	50	50	50
c oxide	5	5	5
aric acid	1	0	0
fur	1.5	0	0
TM	1.5	0	0
T	0.5	0	0
Cup 40KE*	0	6.6	0
-Cup 40KE*	0	0	4.1
eRite Resin D	0.5	0.5	0.5

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Cure temperature (°C)	160	171	177
Cure time (minutes)	20	20	20
Physical properties			
Modulus at 100% elongation (MPa)	2.2	1.8	1.9
Modulus at 200% elongation (MPa)	6.1	4.9	5.3
Tensile strength (MPa)	17.9	17.2	16.7
Elongation at break (%)	400	375	375
Hardness (Shore A)	68	62	60
Aged properties (70 h/150 °C)			
Modulus at 100% elongation (MPa)	5.4	1.7	2.1
Modulus at 200% elongation (MPa)	12.8	4.7	5.2
Tensile strength (MPa)	15.0	17.4	16.7
Elongation at break (%)	220	400	350
Hardness (Shore A)	78	58	60
Compression set (%)			
(70 h/150 °C)	77	21	19

* Di-Cup 40KE = dicumyl peroxide, Vul-Cup 40KE = (phenylene diisopropylidene) bis (tert-butyl peroxide)

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- Apart from peroxide type and the amount of peroxide incorporated in compounds, the efficiency of crosslinking depends on coagents.

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- The commercially important ones are:
  - Maleimide type: *N,N* -phenyl maleimide
  - Allylic type: triallyl cyanurate (TAC)
    triallyl isocyanurate (TAIC)
  - Methacrylate type: zinc dimethacrylate
  - Acrylate type: ethylene glycol diacrylate
    zinc diacrylate
  - Polymeric coagents: liquid 1,2-polybutadiene resin

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Sulfur Free Curing Systems

Some special vulcanising agents can cure diene rubbers such as NR, SBR and BR.

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Phenolic Curatives, Benzoquinone Derivatives and Bismaleimides

- Diene rubbers can be vulcanised by the action of phenolic compounds like phenol-formaldehyde resin (5-10 phr). Resin cured NR offers good set properties and low hysteresis.

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- Resin curing of SBR and BR imparts excellent cut growth and abrasion resistance.
- Resin cured nitrile rubber shows high fatigue life and high relaxation.
- Resin-cured butyl rubber shows outstanding ozone and age resistance.

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A high diene rubber can also be vulcanised by the action of a dinitrosobenzene, made *in situ* by the oxidation of a quinonedioxime

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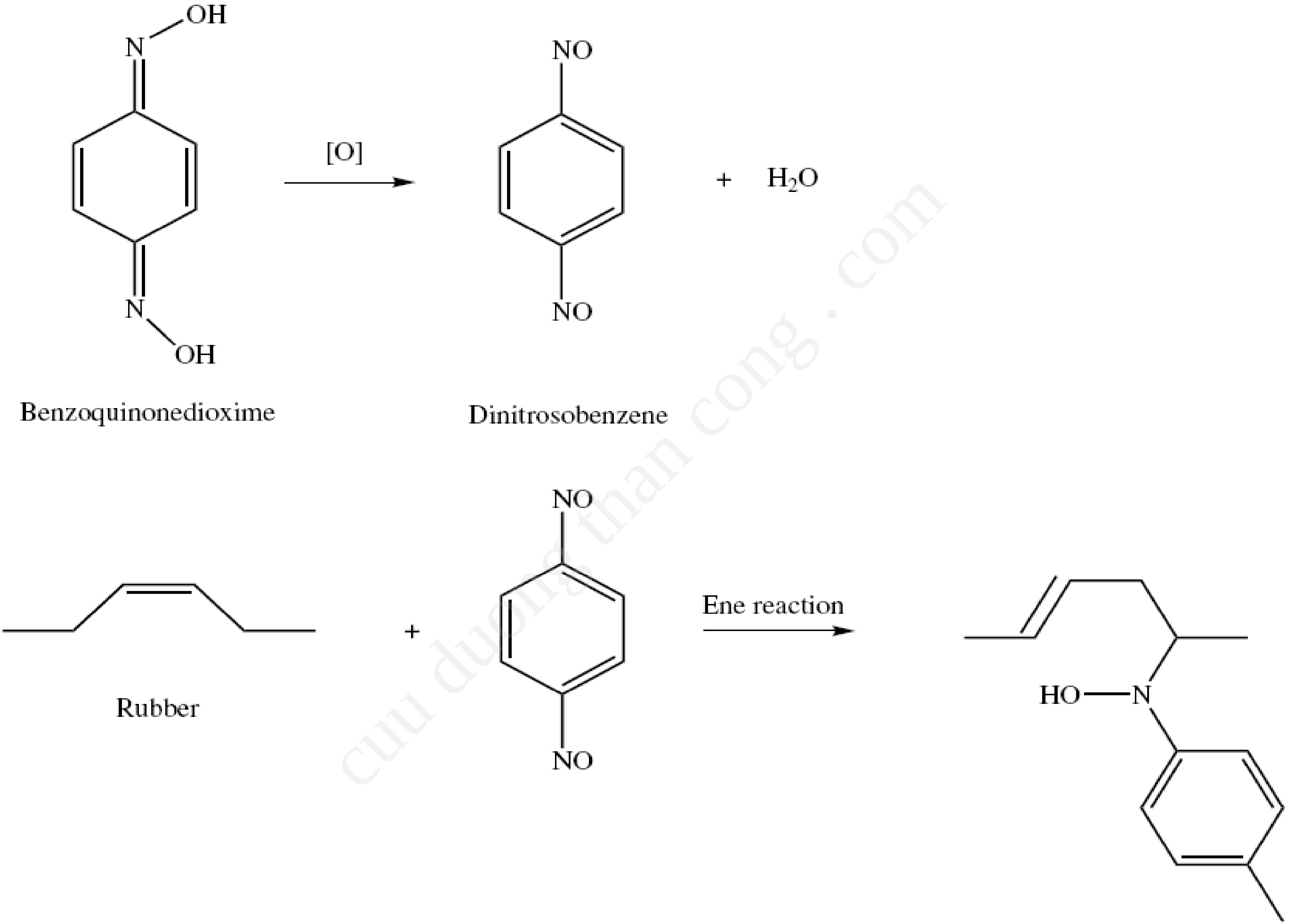

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Figure 13

Vulcanisation by benzoquinonedioxime

Vulcanisation by Triazine Accelerators

- The triazine accelerators are more effective than the thiazole accelerators and produce highly reversion resistant vulcanisates.

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Urethane Crosslinkers

- Natural rubber can be crosslinked by a blocked diphenyl methane diisocyanate to produce urethane crosslinks.
- The crosslinking agent dissociates into two quinonedioxime molecules and one diphenyl methane diisocyanate.
- The quinone reacts with the rubber via a nitroso group and forms crosslinks via a diisocyanate group.

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Other Crosslinking Agents

- There exist a considerable number of compounds containing labile chlorine which bring about sulfurless vulcanisation at levels of approximately 3 phr.
- Basic chemicals such as lead oxides and amines are needed.

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New Developments

- Maintaining properties and performance throughout a rubber product’s service life is directly related to maintaining the integrity of the vulcanisate structure under both thermal and thermal oxidative conditions.

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- Two additives have allowed compounders to forget this compromise, namely hexamethylene-1,6-bisthiosulfate (HTS), a post vulcanisation stabiliser and 1,3-bis(citraconimidomethyl) benzene (BCI-MX, Perkalink 900)

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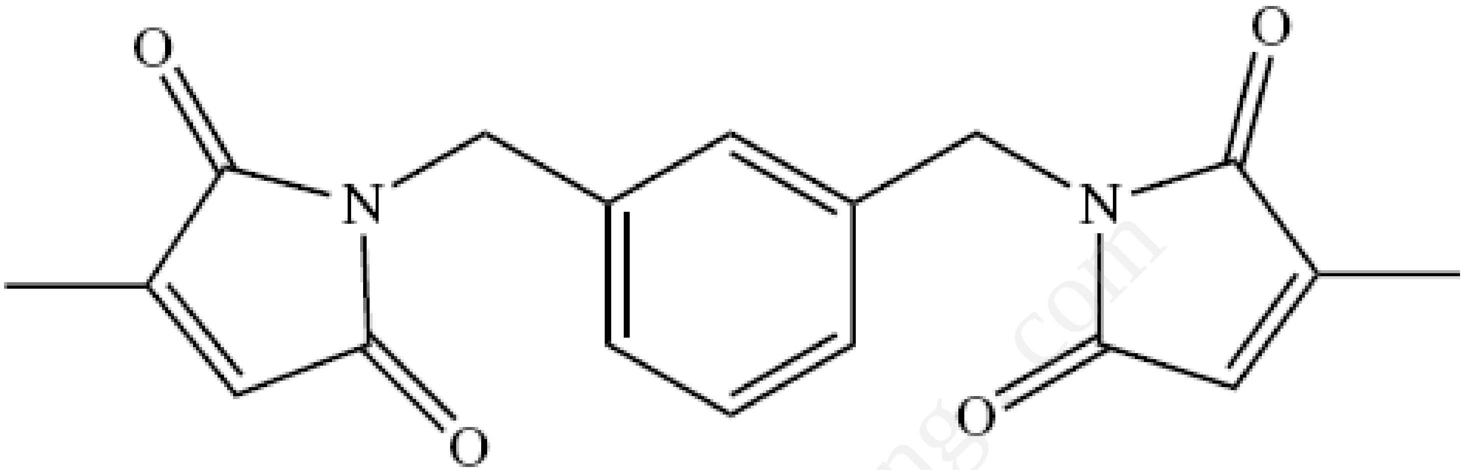

BCI-MX

HTS

Figure 14

Structures of HTS and BCI-MX

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Some Practical Examples with Varying Cure Systems

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Tyres

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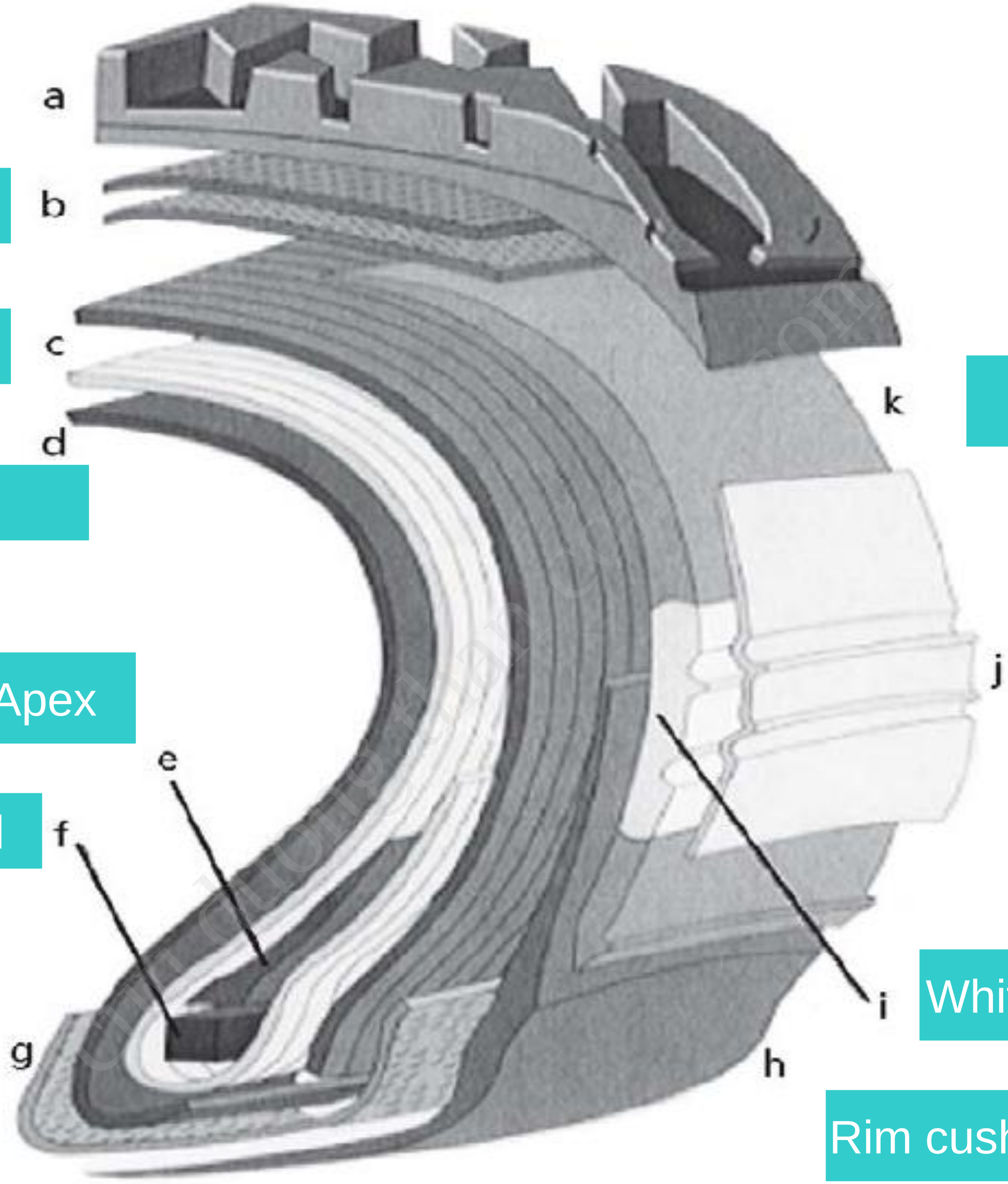

Tread

Steel belts

Carcass plies

Inner liner

Apex

Bead

Chafer

Black sidewall

Veneer coverstrip

White sidewall

Rim cushion

Figure 11.1 Typical radial passenger tyre construction with a) tread, b) steel belts, c) carcass plies, d) inner liner, e) apex, f) bead, g) chafer, h) rim cushion, i) white sidewall, j) veneer coverstrip and k) black sidewall

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Tread

- Trying to balance the three main apparently conflicting needs of wear, wet grip and rolling resistance
- The cure system should be CV/SEV. Accelerators used are sulfenamide class (TBBS, CBS, MBS).
- For improving heat resistance, the use of Perkalink 900 is recommended

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Table 35 Radial truck tread formulation

Ingredients	phr
NR	100
N-234	55
Zinc oxide	5
Stearic acid	2
Aromatic oil	8
6PPD	2
TMQ	1.5
TBBS	1.5
PVI	0.1
Sulfur	1.5

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RADIAL TRUCK TREAD FORMULATION

Ingredients	phr
NR	100
ZnO	5
Stearic acid	2
TBBS	1.5
Sulfur	1.5
N-234	55
Aromatic oil	8
6 PPD	2
TMQ	1.5
PVI	0.1

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Perkalink 900

- Perkalink 900 is an antireversion agent which provides long term heat stability in sulfur vulcanized compounds by substituting stable, flexible carbon-carbon crosslinks for the sulfur crosslinks that are destroyed by reversion in the mold or during product service life.

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Table 36 Bias truck tread (Lug) formulation

Ingredients	phr
NR, RSS	100
Renocit 11	0.1
N-330	50
Aromatic oil	8
Zinc oxide	5
Stearic acid	2
TMQ	1
6PPD	2
MBS	0.6
PVI	0.2
Sulfur	2.3
Perkalink 900	0.5

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Table 37 Conventional passenger tread formulation

Ingredients	phr
SBR 1712	82.5
BR CB 29	55
N-220	70
Zinc oxide	3
Stearic acid	2
6PPD	1
TMQ	2
Microcrystalline wax	3
TBBS	1
Sulfur	2

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- Silica as a reinforcing filler is being used more extensively in the tyre industry to provide improved tear resistance and decreased rolling resistance.
- In order to maximise these benefits the silane coupling agent bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) is often employed.

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- A passenger tread containing silica needs a cure system based on sulfenamide/sulfur (SEV/CV system) and guanidine activators (DPG).

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Table 38 Green tyre formulation – passenger tread

Ingredients	phr
SBR Cariflex S1215	75
BR Buna CB 10	25
Silica, Perkacil KS 408	80
Zinc oxide	3
Stearic acid	2
Aromatic oil	34
Coupling agent, TESPT	6.4
Santoflex 6PPD	2
Wax PEG 4000	3
Perkacit TBBS	1
Perkacit DPG	2
Sulfur	2

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Aircraft tread requires a high modulus, better abrasion resistance and low heat generation.

The above requirements could be satisfied by using a CV/SEV cure system with DCBS as accelerator and insoluble sulfur (IS) as crosslinker.

For achieving high modulus, HMT and a resorcinol system is used.

In order to reduce the heat generation, the use of Perkalink 900 has been suggested.

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Table 40 Aircraft tyre tread formulation

Ingredients	phr
NR	100
N-330	50
Zinc oxide	5
Stearic acid	2
6PPD	1.1
TMQ	1.0
Resorcinol	1.5
MC Wax	1.0
Aromatic oil	3.0
Hexamethylene tetramine (HMT) Cohedur H 30	0.8
DCBS	1.1
PVI	0.2
IS OT 20	2.2

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Tread Base or Sub Tread

- A natural rubber rich undertread layer can enhance the adhesion between belt or cap-ply and tread.
- The cure system needs better flexibility and low heat generation. Typically the cure system will be based on CV/SEV.

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Table 41 Tyre tread base formulation

Ingredients	phr
NR	100
N-550	45
Zinc oxide	5
Stearic acid	2
Aromatic oil	10
6PPD	2.5
Microcrystalline wax	2
CBS	0.9
PVI	0.1
Sulfur	1.5
Perkalink 900	0.5

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Belts

- In radial tyres, sets of belts or breakers made from brass coated steel cords are layed at alternate bias angles.
- to provide a trellising effect, to stiffen the area under the tread and also to prevent growth under inflation or high speed rotation.
- These belts provide a rigid support to the tread offering a more controlled contact with the road.

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- The design of the belt package should give a smooth ride with minimum energy loss, but with sufficient stiffness to prevent undue movement within the contact area causing irregular or rapid tyre wear.
- The cure package is composed of a slow accelerator (DCBS, or TBSI) with a high level of sulfur for improving the bond strength between the rubber and brass layer.

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- Addition of Duralink HTS (hexamethylene-1,6- bis(thiosulfate), disodium salt dihydrate) improves adhesion characteristics under ageing environments.

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Table 42 Typical formulation for tyre belts

Ingredients	phr
NR	100
N-326	45
Silica	15
Zinc oxide	8
Stearic acid	1.2
Tackifier SP 1068	2
Cobalt salt (NAPCO 105)	0.75
Resorcinol	2
Hexamethoxymethylmelamine (HMMM)	3
TMQ	1
6PPD	1
DCBS	1
PVI	0.1
OT 20	5
Duralink HTS	1.5

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Sidewall

- Sidewall compounds cover the thinnest part of the tyre where most flexing occurs as the tyre deflects.
- They therefore need to have a high degree of flex resistance and good dynamic properties, as well as excellent age resistance.

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- Sidewall compounds contain additional ingredients to prevent oxidative or ozone attack since this part of the tyre will be particularly exposed to the sun and the elements.
- The cure system should be CV or between CV/SEV.

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Table 43 Sidewall

Ingredients	phr
NR	50
BR	50
N-550	50
Naphthenic oil	6
Zinc oxide	4
Stearic acid	1
TMQ	1.5
6PPD	2.5
Microcrystalline wax	2.0
CBS	1.0
Sulfur	1.2

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Carcass

- The cure system of choice for a carcass compound is based on a scorch resistant cure package.
- thermally stable, insoluble sulfur and bloom resistant adhesion additives are required.

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- the cure system suitable for this application is based on a slow accelerator such as DCBS with a high amount of insoluble sulfur (generally 4-5 phr).

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Table 44 Truck radial carcass formulation

Ingredients	phr
NR SMR L	100
N-339	55
Aromatic oil	3.0
Zinc oxide	8.0
Stearic acid	0.5
TMQ	1.0
6PPD	2.0
Wingstay L	1.0
NAPCO105 (10%Co)	0.63
D-HTS	1.5
DCBS	1.1
Insoluble sulfur OT 20	5.0

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Table 45 Passenger tyre carcass formulation

Ingredients	phr
NR	60
BR	20
SBR	27.5
N-660	40
Zinc oxide	3
Stearic acid	2.0
Processing oil	13
TMQ	0.5
Octylated diphenylamine	1
Resin	1.0
MBTS	0.1
TBBS	0.7
IS OT 20	2.8
PVI	0.1

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Bead

- require high modulus and good adhesion to steel wires.
- High modulus is achieved by using resorcinol/HMMM or phenol formaldehyde resins.
- The cure system is based on sulfenamide with a high amount of insoluble sulfur.

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Table 46 Tyre bead formulation

Ingredients	phr
NR	100
N-330	65
Zinc oxide	10
Stearic acid	2
Aromatic oil	8
TMQ	1
Resorcinol	3.5
HMMM (0.65%)	3
PVI	0.1
CBS	1.0
IS OT 20	6.5

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Apex

- The apex components provide the gradual shape and stiffness reduction from the rigid bead coil to the flexible mid-sidewall of the tyre.
- These components need to be very hard to provide good vehicle handling and to reduce the risk of flexural fatigue at component endings.

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Table 47 Tyre apex formulation

Ingredients	phr
NR	100
N-351	55
Zinc oxide	10
Stearic acid	2
SP 6700 Resin	2
Phenol formaldehyde resin	10
Bonding agent	2
6PPD	2
TMQ	1
TBBS	0.6
TBzTD	0.2
PVI	0.2
IS OT 20	5.0

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Cap-Ply

- act as a barrier layer between the tread and the casing to restrict migration of chemicals from the tread into the belt.
- requires high modulus and good adhesion behaviour.
- The cure system used to achieve the target properties is based on a combination of CBS and DCBS with a high amount of insoluble sulfur.
- A resorcinol/HMMM system is used to obtain the required high modulus.

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Table 48 Passenger tyre cap-ply formulation

Ingredients	phr
NR	80
BR	20
Mineral oil	7
N-326	55
Silica	7.5
Mixture of N,N´-diaryl-p-phenylenediamines (DTPD)	1
TMQ	1
Resorcinol	1.25
HMMM	1.5
CBS	0.4
DCBS	1.0
ZnO	8
Zinc stearate	1.0
IS OT 20	4.5

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Inner Liner

- Zinc oxide with MBTS and a small amount of sulfur is used to crosslink halobutyl rubber.

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Table 49 Inner liner formulation

Ingredients	phr
Chlorobutyl 1065	100
N-660	60
Naphthenic oil	8
Stearic acid	2
Phenolic resin tackifier	4
Homogenisers	7
Magnesium oxide	0.15
Zinc oxide	3
Sulfur	0.5
MBTS	1.5

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Industrial Rubber Products

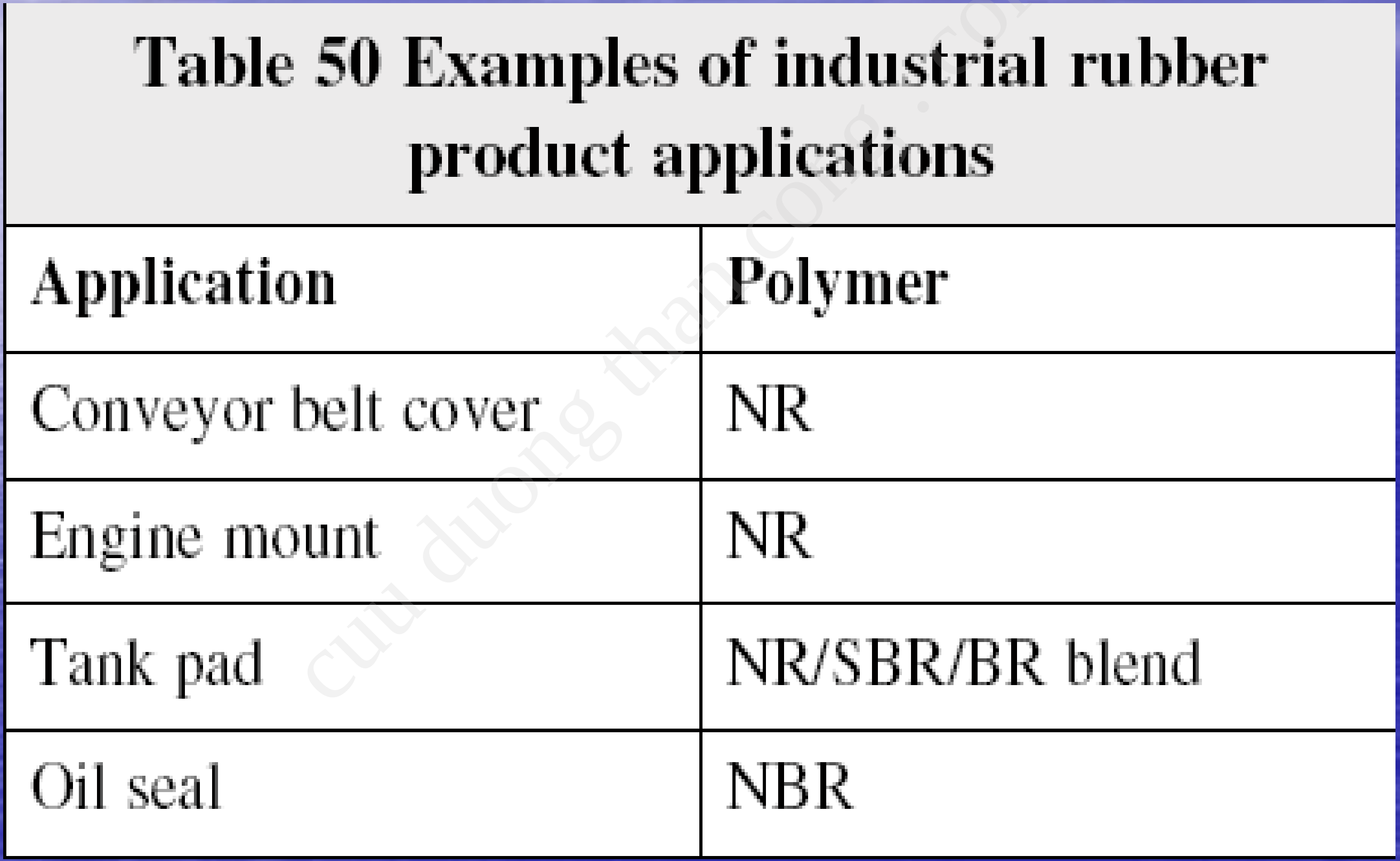

Table 50 Examples of industrial rubber product applications

Application	Polymer
Conveyor belt cover	NR
Engine mount	NR
Tank pad	NR/SBR/BR blend
Oil seal	NBR

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Conveyor Belt Cover - NR

- flex resistance, abrasion resistance and low heat build up.
- In order to achieve better flex resistance, a conventional cure package is recommended (however, such a system suffers from the adverse effects of heat generation).
- In a recent study, the addition of Perkalink 900 was recommended

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Table 51 Conveyor belt cover formulations

Ingredients	Control	+ Perkalink 900
NR	100	100
N330	45	45
Aromatic oil	4	4
ZnO	5	5
Stearic acid	2	2
6PPD	1	1
CBS	0.5	0.5
Sulfur	2.5	2.5
Perkalink 900	-	1

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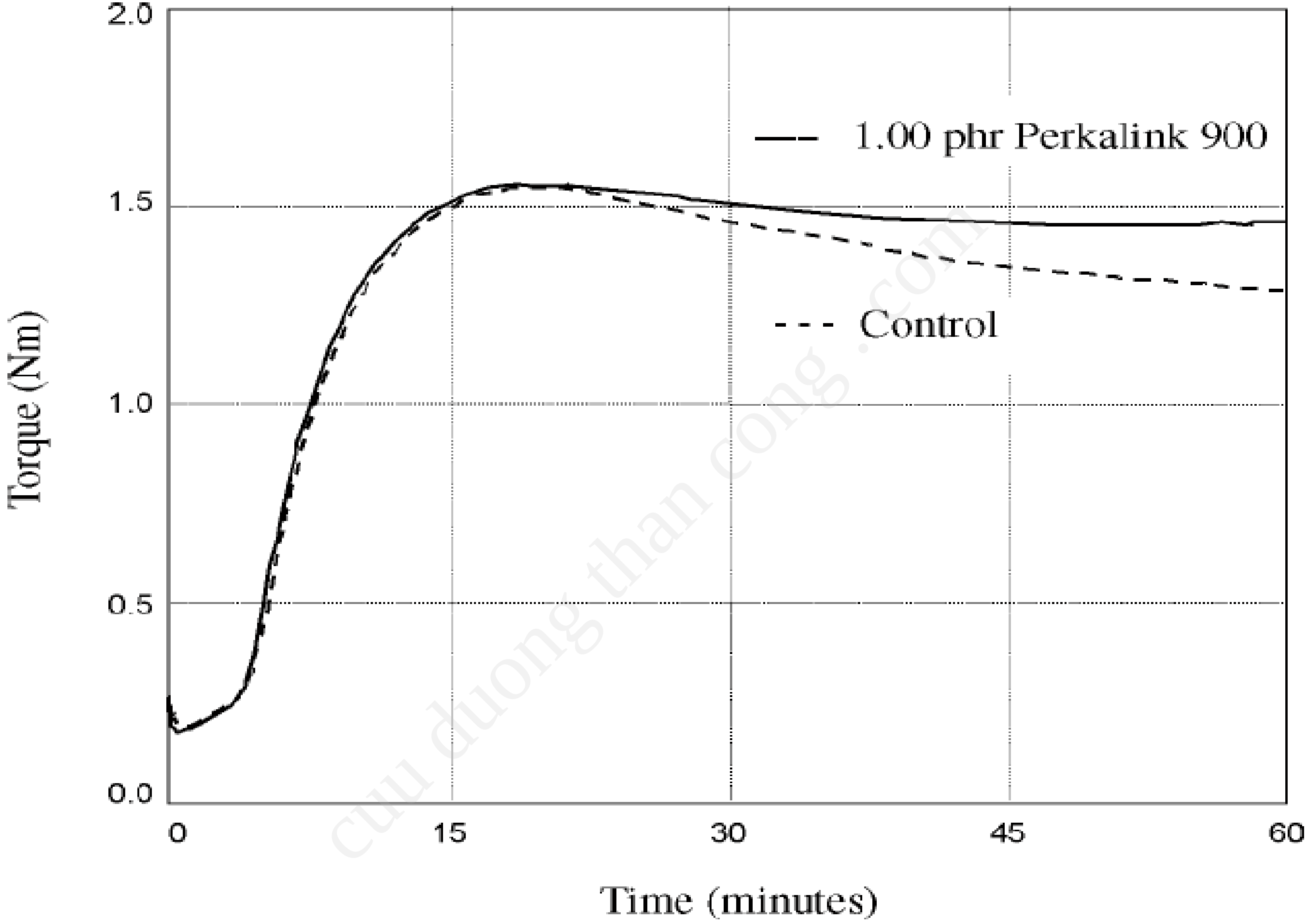

Figure 15

Cure characteristics of conveyor belt cover formulations at 150 °C

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- The antireversion agent has no effect on scorch resistance and time to optimum cure.
- The compound containing the antireversion agent maintains a torque level close to the maximum.
- The antireversion effect is also evident in the stability of vulcanisate properties following overcure or air ageing at 100 C.

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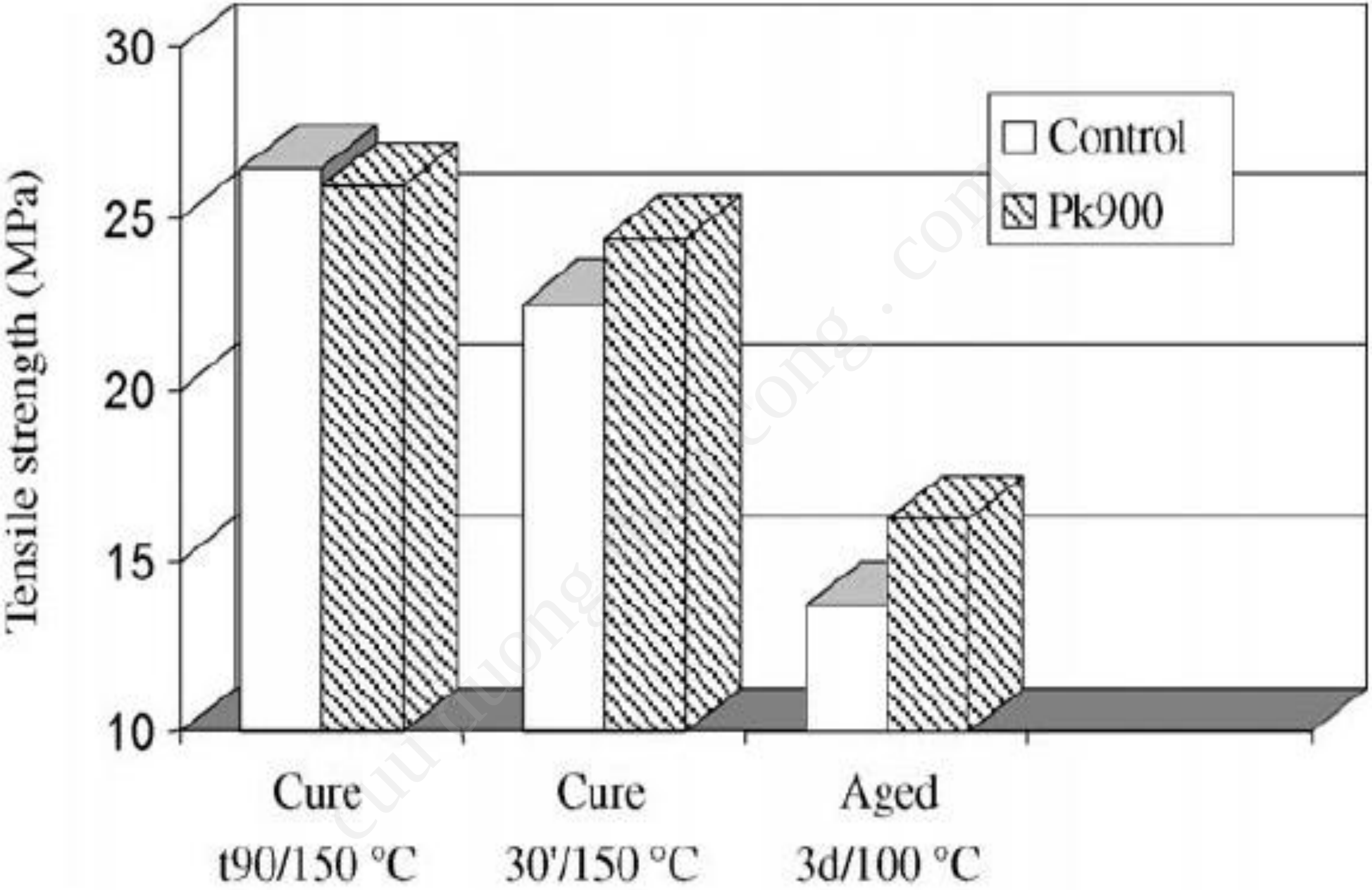

Figure 16

Tensile strength of conveyor belt cover formulations

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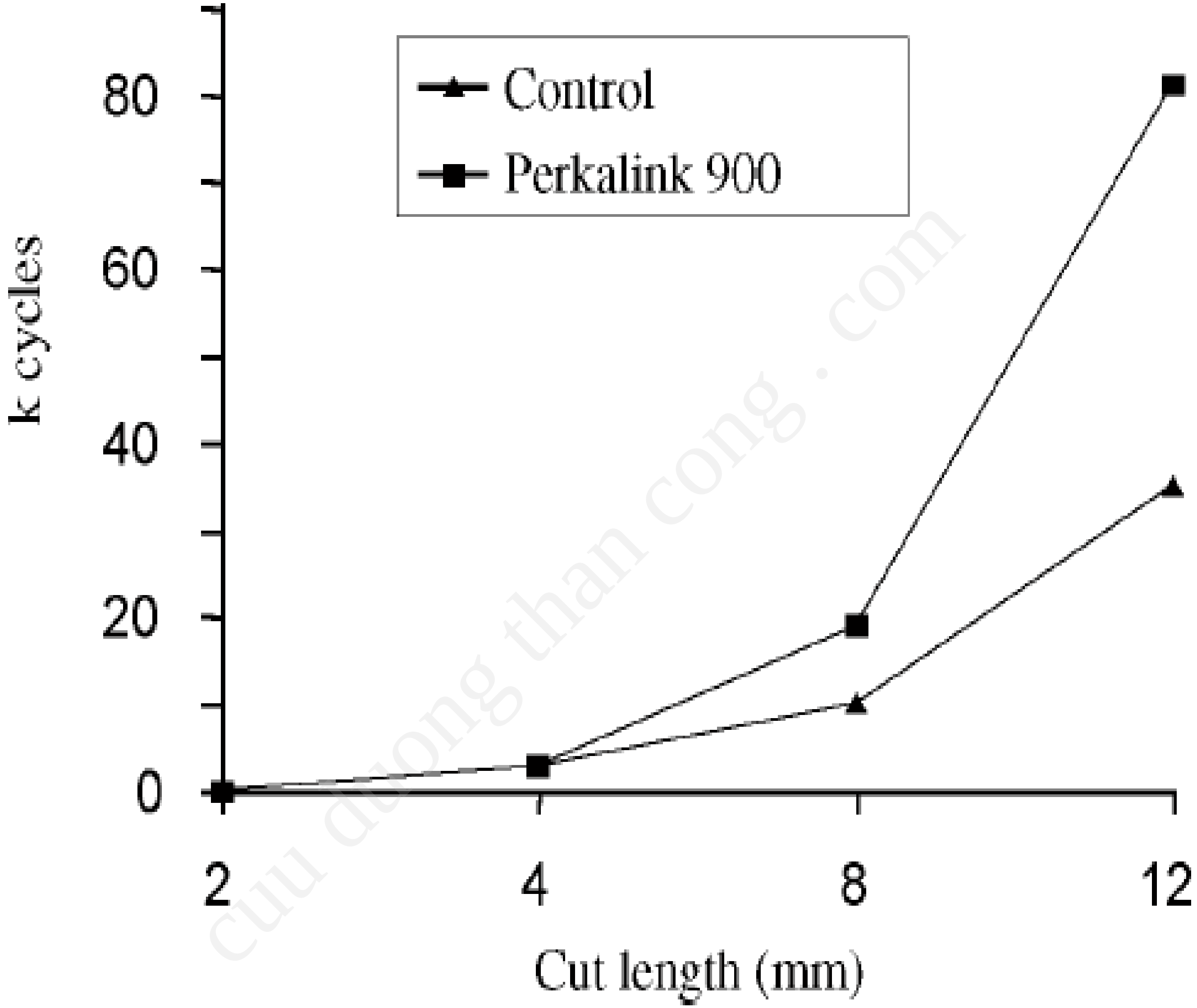

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Figure 17

De Mattia flex/cut growth of conveyor belt cover formulation (cure 30′/150 °C)

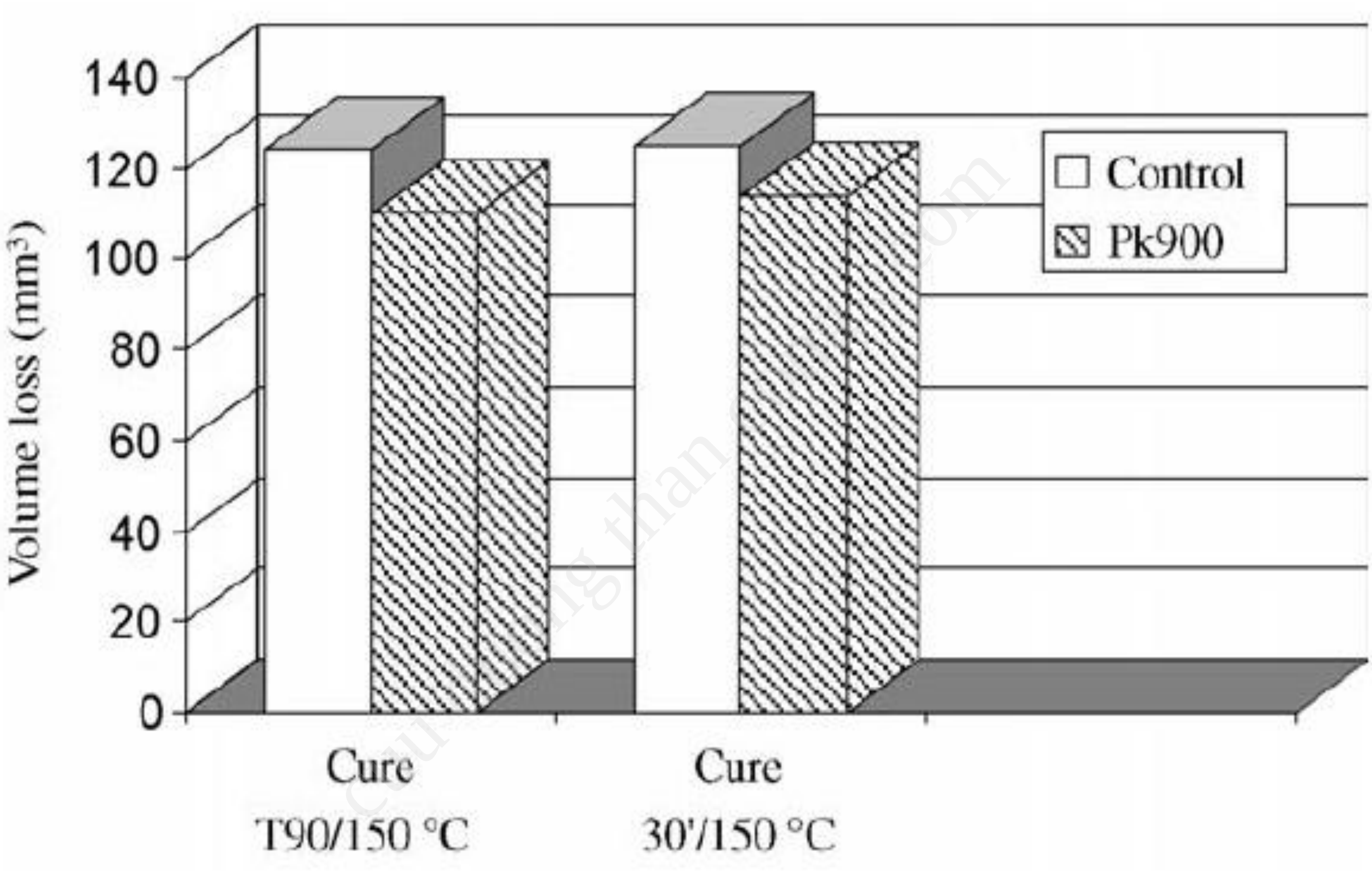

Figure 18

Abrasion loss (DIN) of conveyor belt cover formulations

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Engine Mount - NR

- The essential performance properties for an engine mount are low heat build up and low dynamic compression set.
- a cure system comprising of sulfenamide
- (moderate loading, 1.2-1.7 phr) with sulfur (2-2.5 phr) is recommended.
- A small amount of ultra accelerator might be necessary to generate a crosslink network capable of improving dynamic compression set as well as heat build up.

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- In spite of this modified cure system (CBS/TMTD/S), the properties are still not optimum, particularly with regard to heat build up.
- The addition of an antireversion agent might provide advantage and with this in mind the effect of Perkalink 900 has been studied.

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Table 52 Engine mount formulations

Ingredients	Control	Perkalink 900
NR	100	100
N-660	42	42
Zinc oxide	5	5
Stearic acid	2	2
Oil	9	9
MC wax	2	2
6PPD	2	2
TMQ	2	2
Resin	2	2
Santocure CBS	2.5	2.5
Perkacit TMTD	0.2	0.2
Sulfur	2.25	2.25
Perkalink 900	–	0.75

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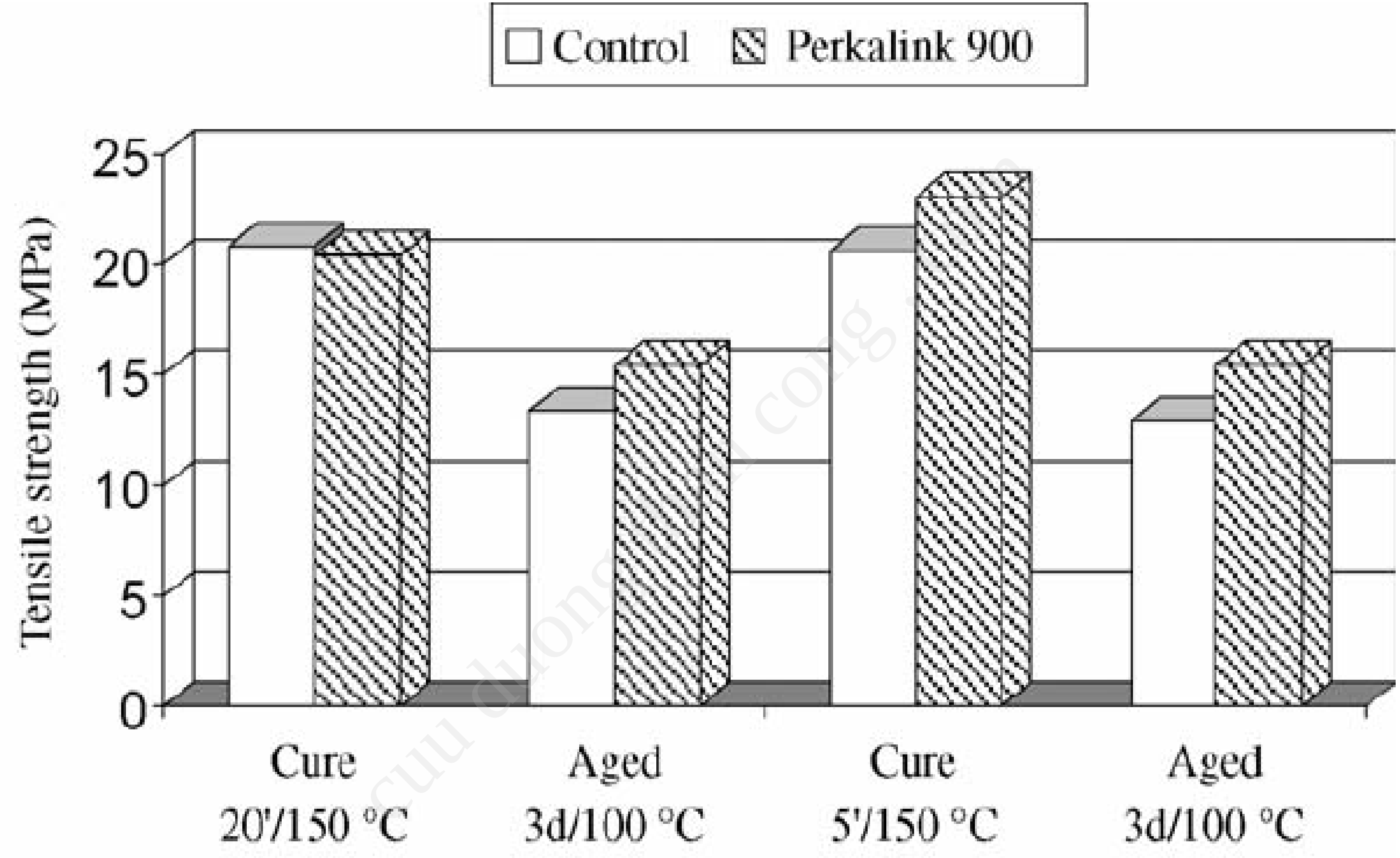

Figure 20

Tensile strength tests on engine mount compounds

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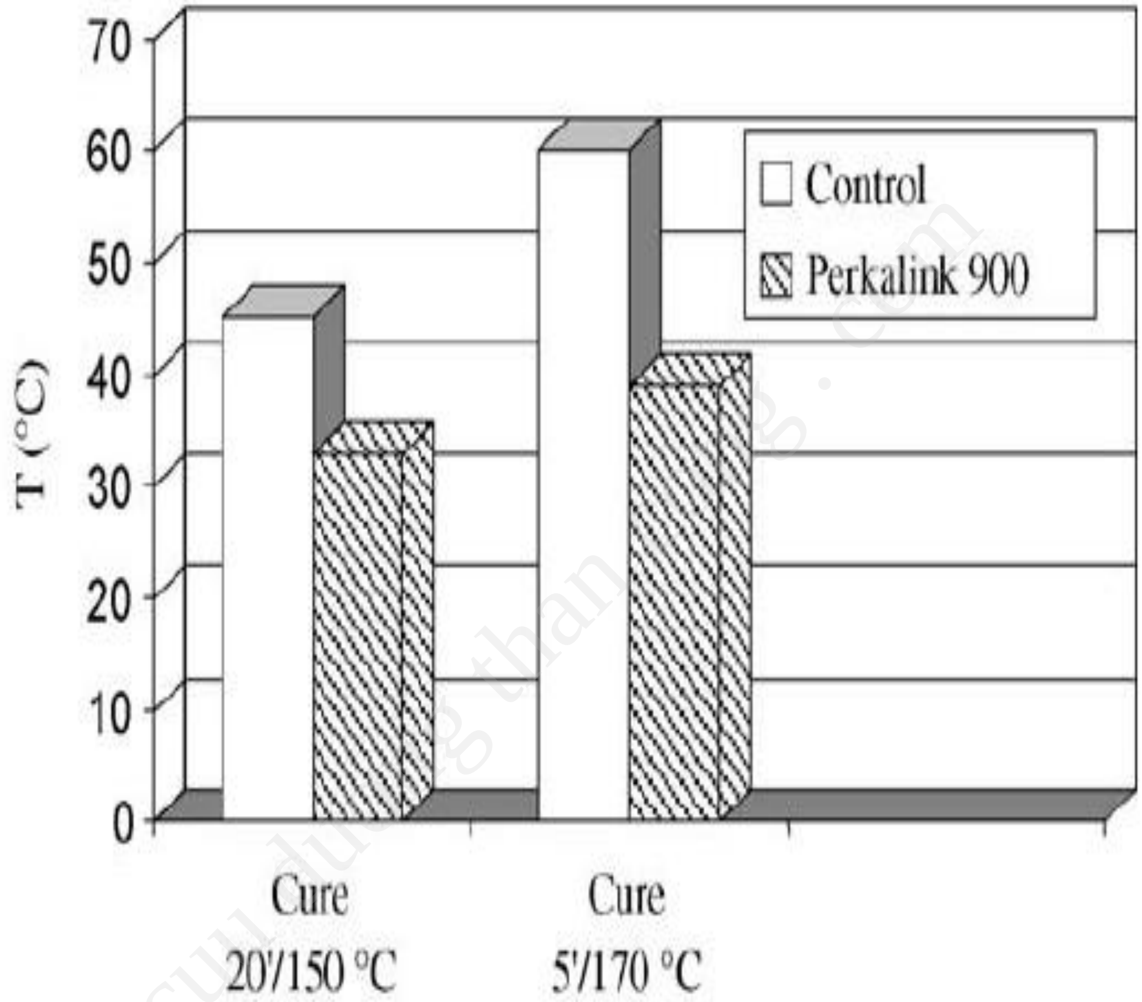

Figure 21

Goodrich Flexometer heat build up at 100 °C after 30 minutes – tests on engine mount compounds (Load 108 N, Stroke 4.45 mm, Frequency 30 Hz)

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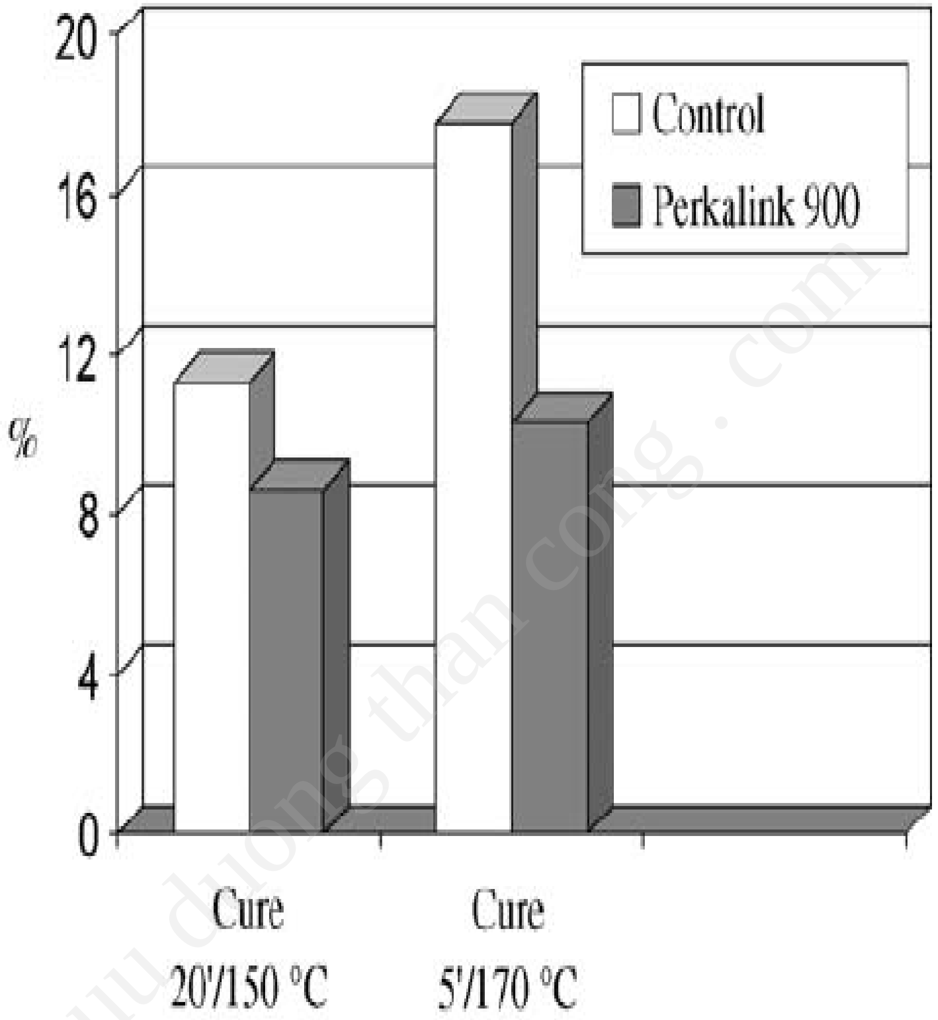

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Figure 22

Goodrich Flexometer Dynamic Permanent Set at 100 °C after 30 minutes – tests on engine mount compounds (Load 108 N, Stroke 4.45 mm, Frequency 30 Hz)

Tank Pad – NR/SBR/BR Blend

- The required properties for a tank pad are heat stability, low heat generation, improved flex and good compression set.
- This can be achieved by selecting a cure package between SEV and towards an EV cure.A combination of a sulfenamide with a thiazole is suitable.
- Generally the sulfenamide level should be low and the thiazole accelerator should be high.

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- The sulfur loading is generally high to address the improved flex requirements.
- Because of high sulfur loadings, the system suffers from the adverse effects of heat and reversion resistance.
- Perkalink 900 is active in compounds based on blends of NR with the synthetic elastomers SBR and BR.

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Table 54 Tank pad formulations

Ingredients	1	2	3
NR	60	60	60
SBR 1500	20	20	20
BR Buna CB10	20	20	20
N-220	70	70	70
Zinc oxide	4	4	4
Stearic acid	2	2	2
Oil	40	40	40
Santoflex 6PPD	1	1	1
MC wax	3	3	3
Santocure TBBS	1	1	1
Perkacit MBTS	2	2	2
Santogard PVI	0.15	0.15	0.15
Sulfur	2	2	2
Perkalink 900	-	0.5	0.75

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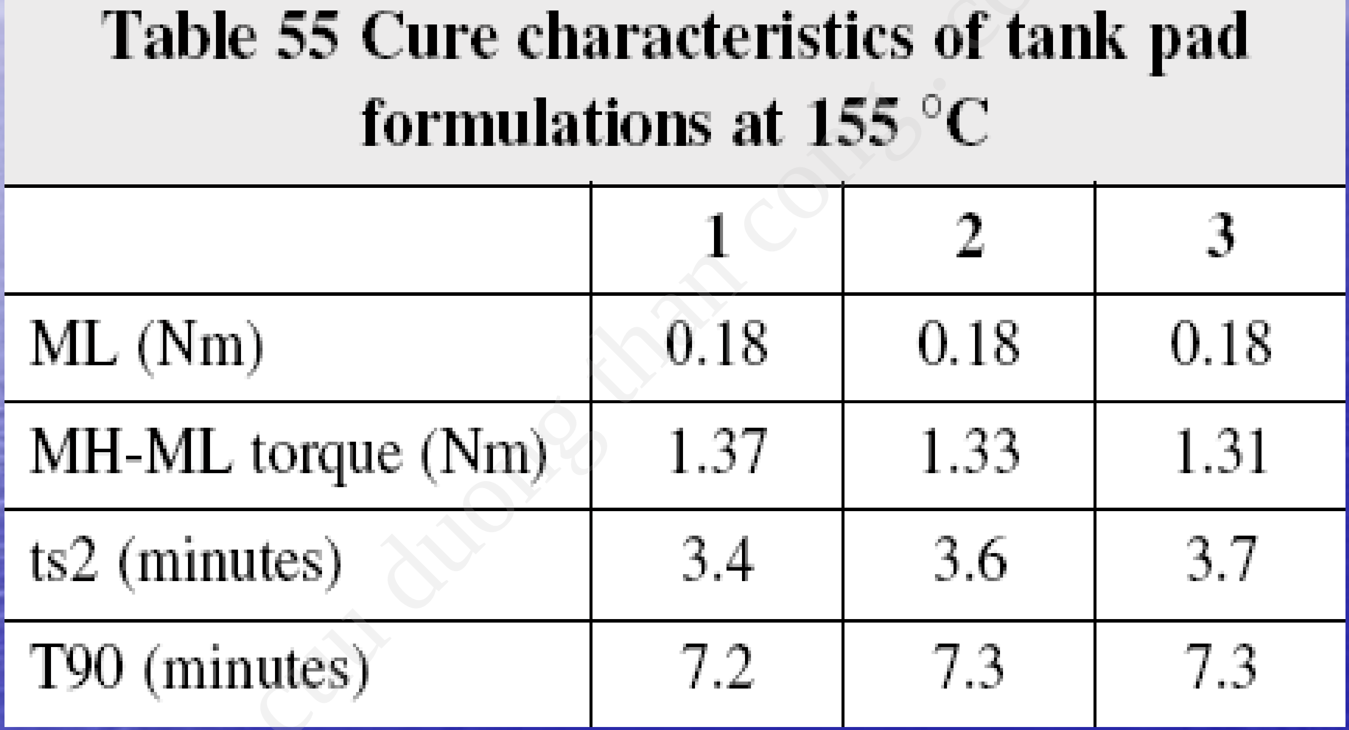

Table 55 Cure characteristics of tank pad formulations at 155 °C

	1	2	3
ML (Nm)	0.18	0.18	0.18
MH-ML torque (Nm)	1.37	1.33	1.31
ts2 (minutes)	3.4	3.6	3.7
T90 (minutes)	7.2	7.3	7.3

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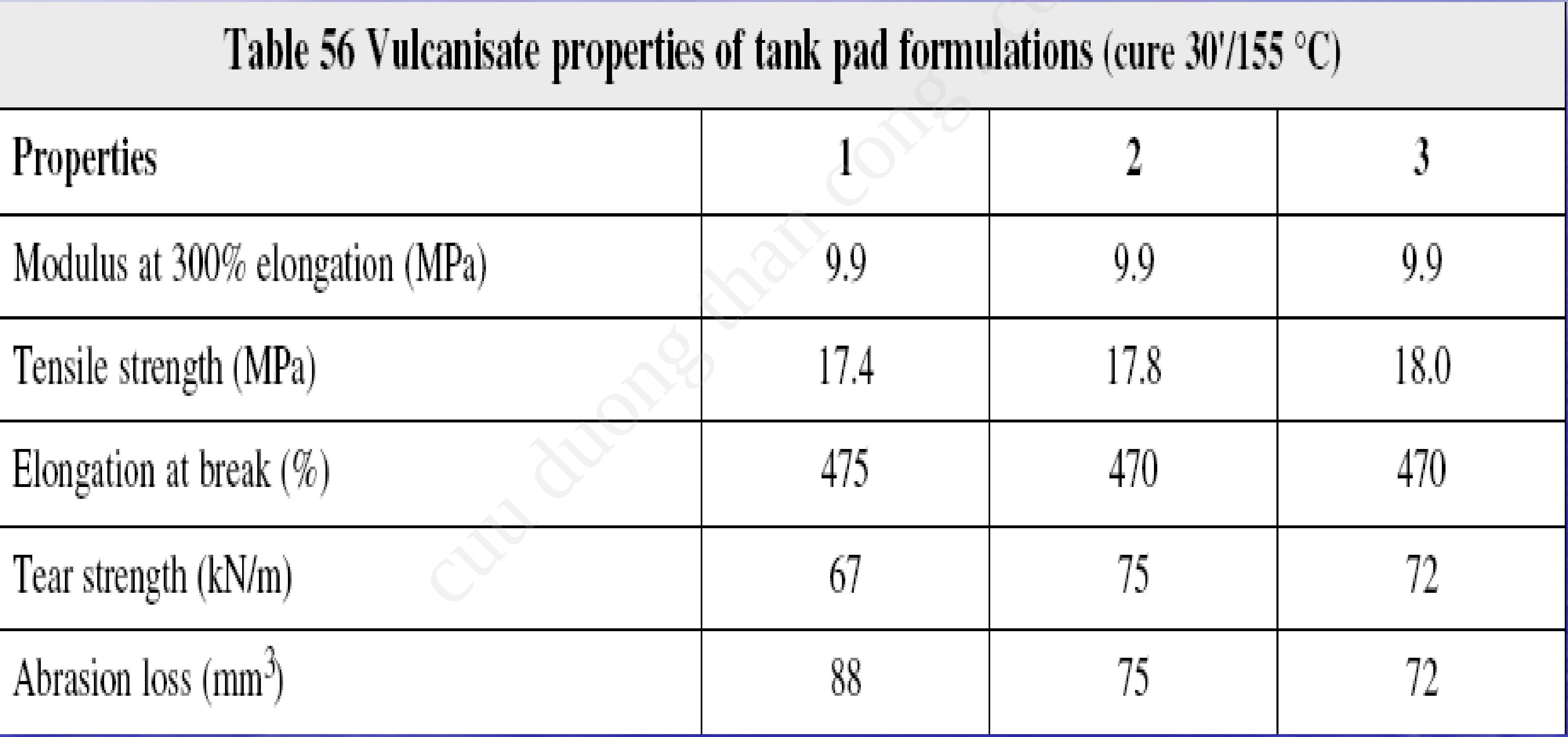

Table 56 Vulcanisate properties of tank pad formulations (cure 30'/155 °C)

Properties	1	2	3
Modulus at 300% elongation (MPa)	9.9	9.9	9.9
Tensile strength (MPa)	17.4	17.8	18.0
Elongation at break (%)	475	470	470
Tear strength (kN/m)	67	75	72
Abrasion loss (mm^3)	88	75	72

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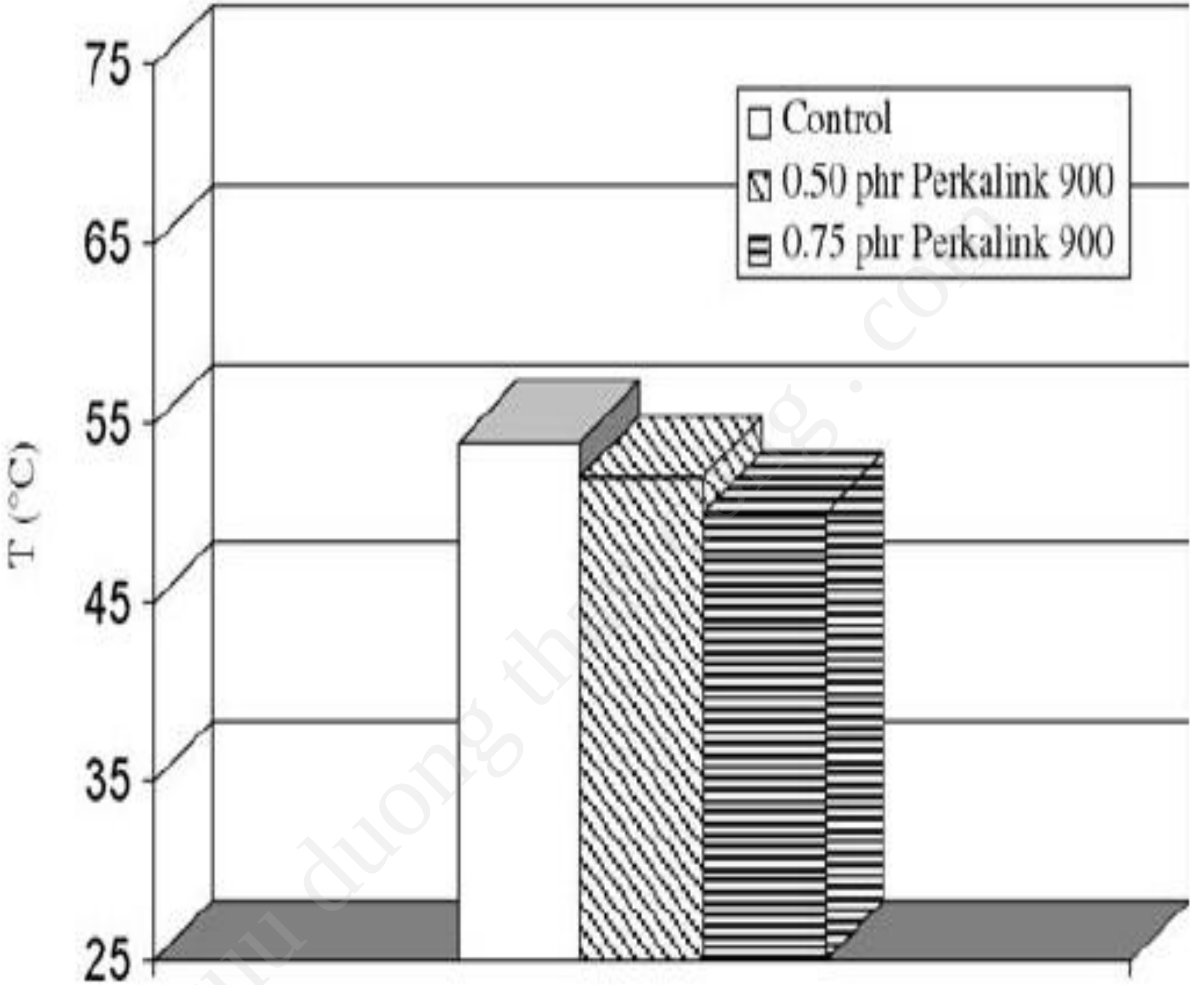

Figure 23

Goodrich Flexometer heat build up at 100 °C after 60 minutes – tests on tank pad formulations
(Load 108 N, Stroke 4.45 mm, Frequency 30 Hz)

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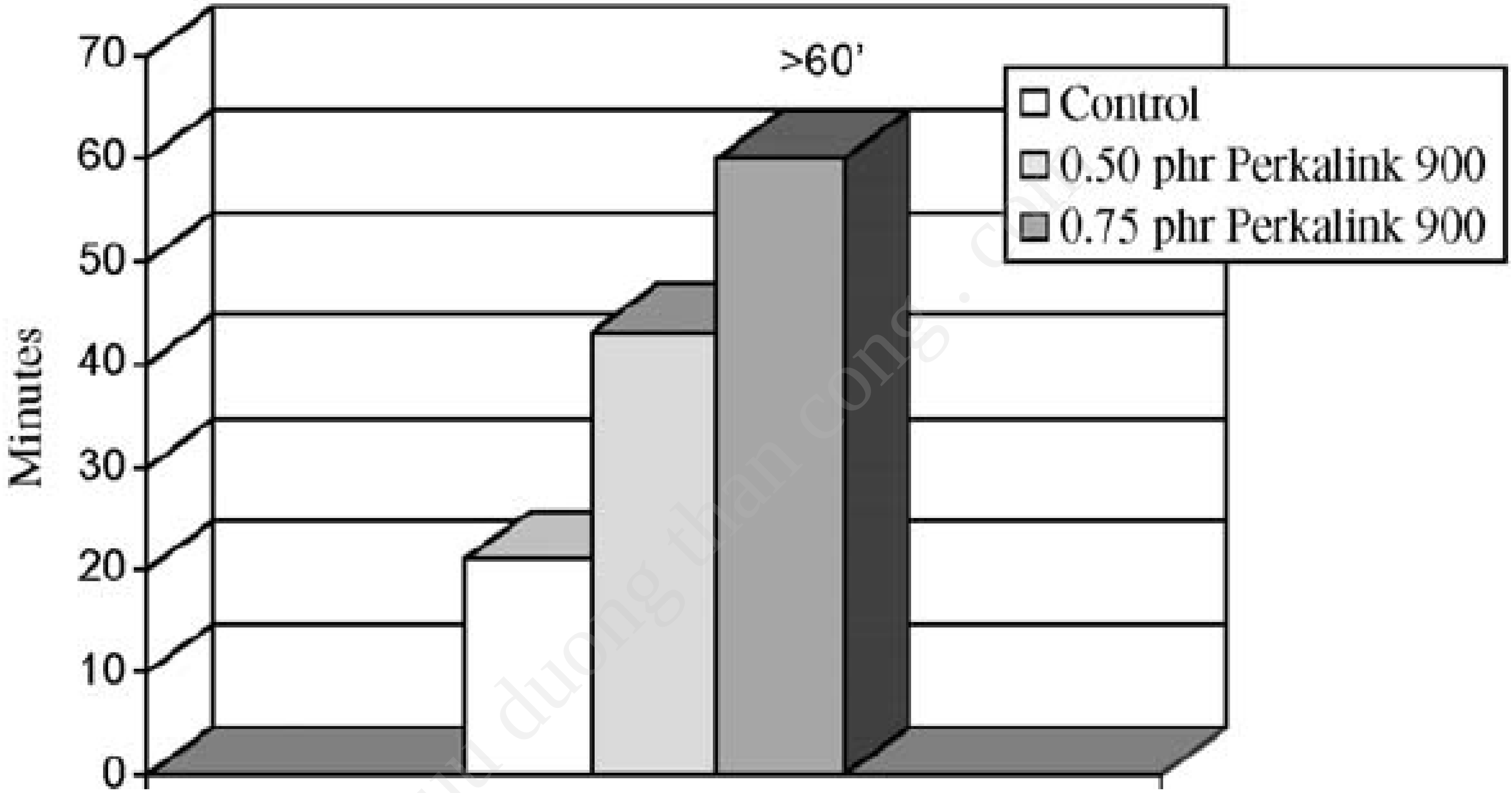

Figure 24

Goodrich Flexometer blow-out at 100 °C – tests on tank pad formulations
(Load 216 N, Stroke 4.45 mm, Frequency 30 Hz, test time 60')

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Oil Seal - NBR

- The general requirement for oil seal applications is oil resistance, low compression set, high elongation and good heat stability.
- In order to achieve this, a cure system comprising of MBTS/TMTD and sulfur is preferred.
- TMTD is used in a small amount so that elongation is not negatively affected.

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- In order to keep high elongation, the amount of sulfur should not be too low.
- Compression can be negatively affected if the sulfur loading is too high.
- The heat stability can be improved by incorporating antireversion agent Perkalink 900.

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Table 57 NBR based oil seal formulations

Ingredients	Control	+Perkalink 900
NBR	100	100
N-550	60	60
ZnO	5	5
Stearic acid	1	1
DOP	15	15
TMQ	2	2
MBTS	1	1
TMTD	0.1	0.1
Sulfur	1.5	1.5
Perkalink 900	-	0.75

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Table 58 Cure characteristics at 170 °C of NBR oil seal formulations

	Control	**+ Perkalink 900**
M_H-M_L torque (Nm)	1.36	1.39
ts2 (minutes)	0.9	0.9
T90 (minutes)	1.9	2.1

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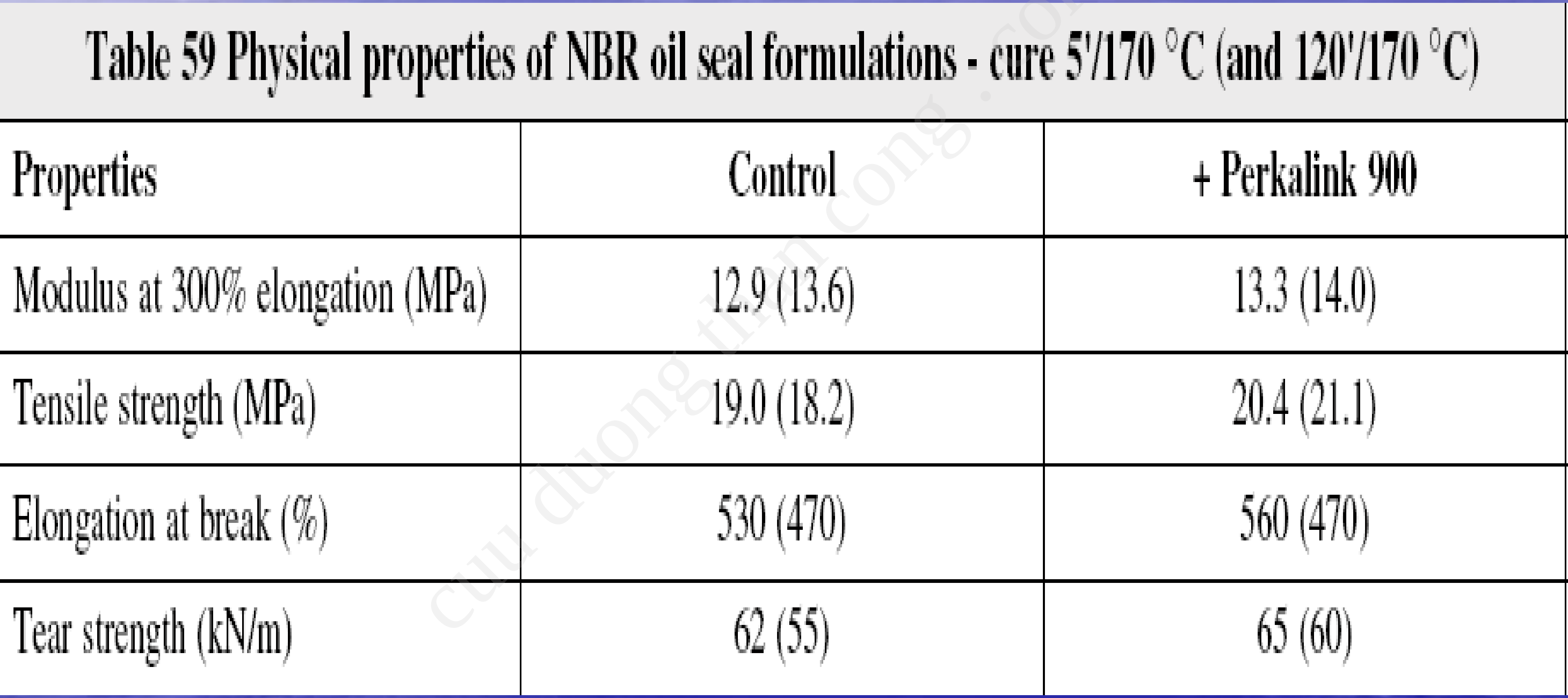

Table 59 Physical properties of NBR oil seal formulations - cure 5'/170 °C (and 120'/170 °C)

Properties	Control	+ Perkalink 900
Modulus at 300% elongation (MPa)	12.9 (13.6)	13.3 (14.0)
Tensile strength (MPa)	19.0 (18.2)	20.4 (21.1)
Elongation at break (%)	530 (470)	560 (470)
Tear strength (kN/m)	62 (55)	65 (60)

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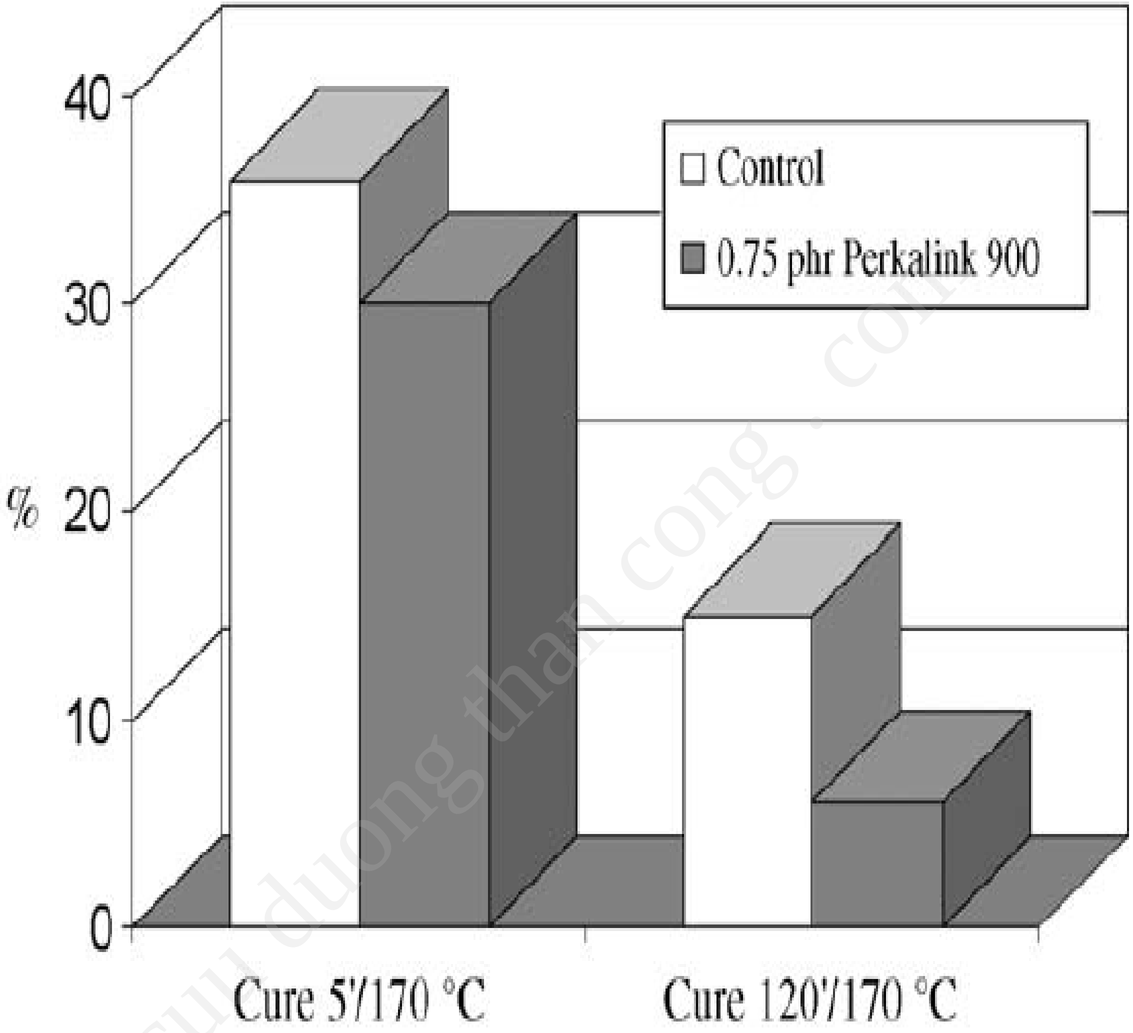

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Figure 25

Goodrich Flexometer Dynamic Permanent Set at 100 °C after 120 minutes – tests on NBR oil seal formulations (Load 108 N, Stroke 4.45 mm, Frequency 30 Hz)

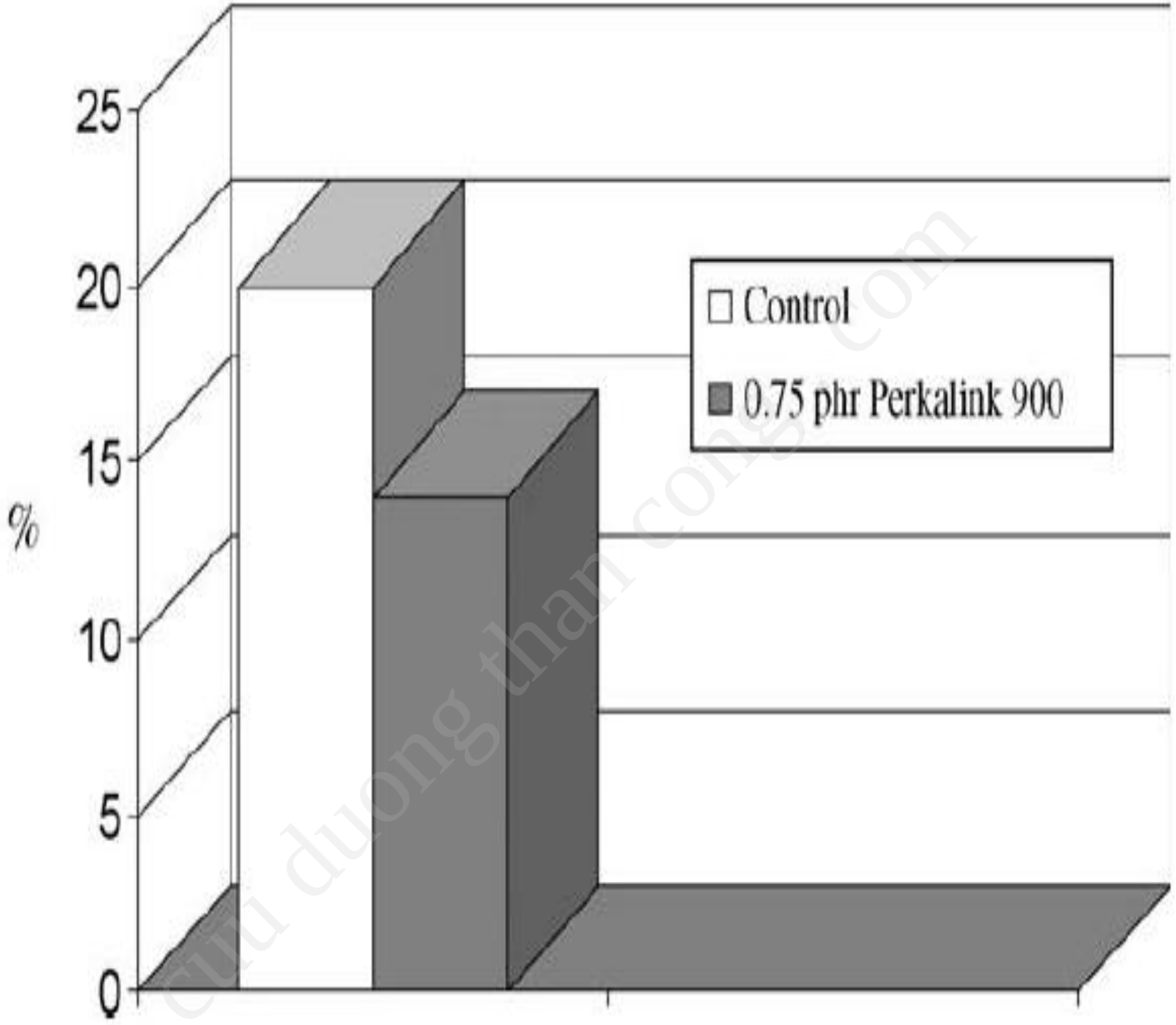

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Figure 26

Swelling in ASTM oil #3, 168 hours at 150 °C (cure 5'/170 °C) – tests on NBR oil seal formulations

Concluding Remarks

- Cure systems play an important role in achieving the performance requirements of rubber articles.
- Antireversion chemicals constitute a class of such materials, and can improve service performance.

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- Cure systems, however, paint only part of the picture with regard to the manufacture of rubber articles.
- polymers and fillers are equally important in meeting performance requirements.
- In addition, compound mixing and processing play a critical role in achieving the final vulcanisate properties.

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