Keltan ACE™ High-VNB Products for Peroxide Cure Applications

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VKRT meeting, February 12, 2009

DSM Elastomers' Innovation Pillars

- Three technology platforms for innovation
  - Keltan ACE™ Technology
  - Reactive Extrusion Technology
  - Product and Application Development Technology

- DSM Elastomers investments in support of innovation programs
  - Organizational alignment in support of innovation programs (2006)
  - Increase in manpower for new product and application development (2006)
  - New Keltan product introductions (2006-2008)
  - New reactive extrusion plant in Triunfo, Brazil (January 2008)
  - Start up of Keltan ACE™ Technology in Geleen, The Netherlands (November 2008)

Keltan ACE™ Technology

- Base catalyst technology licensed from Nova Chemicals.
- DSM developed a catalyst family for the production of Keltan and holds strong patent positions.
- Green technology. No catalyst waste and reduced energy consumption.
- New catalyst system creates the opportunity to develop high value products that are not attainable with state-of-the-art Ziegler-Natta or classical metallocene chemistry.
- **First products to be launched with new advanced catalyst technology are high-VNB products, dedicated to peroxide curing of EPDM. First new product is Keltan DE 8270C.**
- The trade name for new advanced catalyst technology by DSM is…

…Keltan ACE™

High VNB Products Enabled by Keltan ACE™ Technology

Clearly, EPDM containing VNB shows outstanding peroxide cross-Linking efficiency, but … commercial production of VNB-EPDM's with classical catalysts is restricted; the incorporation of high VNB levels results in excessive reactor fouling due to the formation of highly branched products.

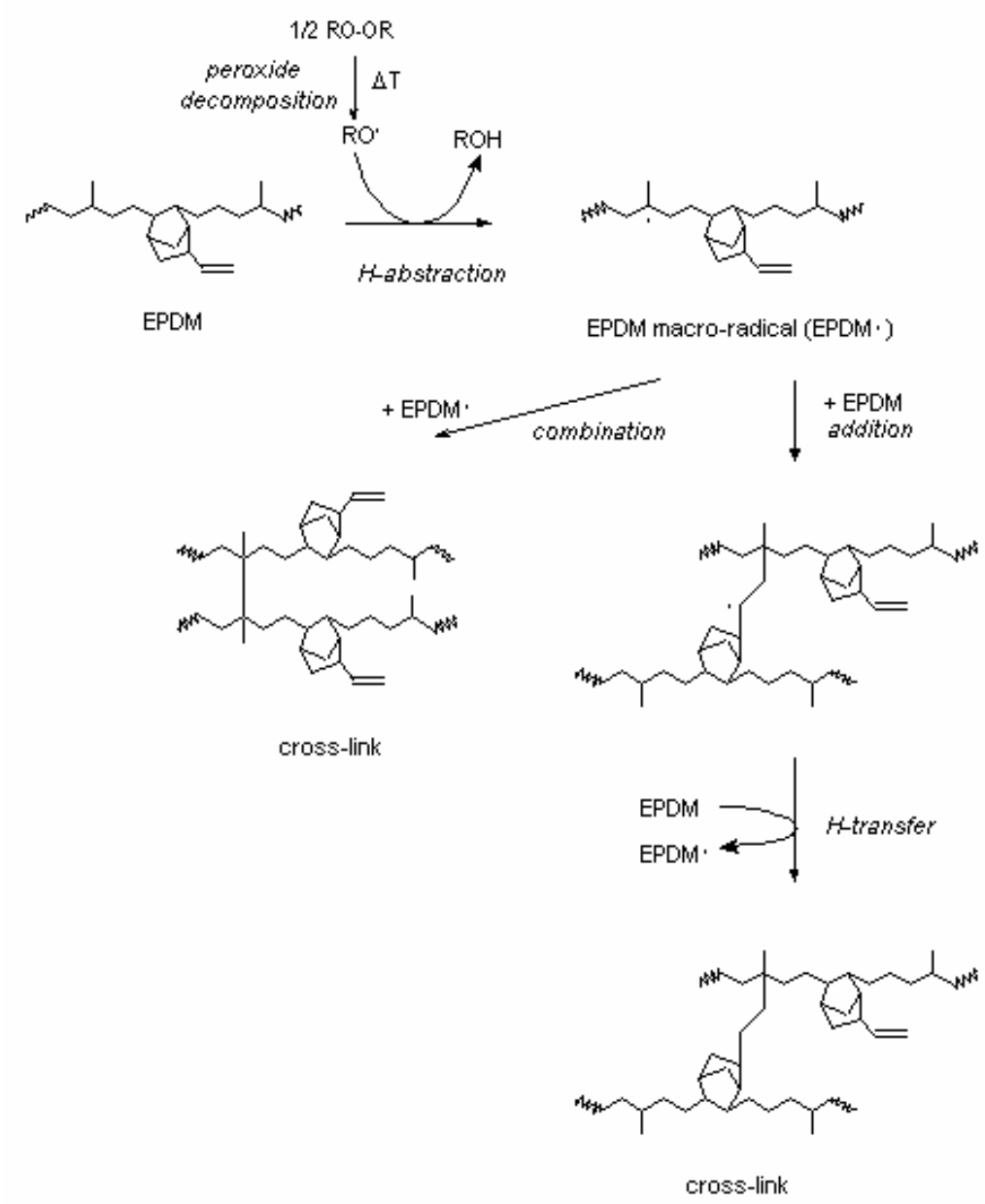
The patent protected Keltan **ACE™** technology enables the production of a unique class of EPDM products with a high VNB content. High VNB products are the first Keltan products to be launched using Keltan **ACE™** technology. First new high-VNB product is Keltan DE 8270C. Please, keep in mind…

Keltan ACE™ ≠ high VNB Keltan products

Peroxide vulcanization of EPDM

- Total market for EP(D)M is ~1100 ktpa
- Main chain is fully saturated
  - → EP(D)M has excellent heat, ozone and UV resistance
  - → good outdoor performance
- Incorporation of non-conjugated diene is essential for sulfur vulcanization and boosts efficiency of peroxide curing.
- About 12-15% of all EP(D)M is cross-linked with peroxides to ensure
  - → excellent performance at high temperatures
  - → low compression set values
  - → excellent electrical properties
- Typical peroxide cure applications include:
  - → window gaskets (DIN 7863)
  - → automotive (coolant) hoses
  - → heat resistant (automotive) belts
  - → cable insulation
  - → muffler mounts
  - → potable water seals
  - → class A automotive sponge sealing systems

Mechanism of EPDM Peroxide Curing

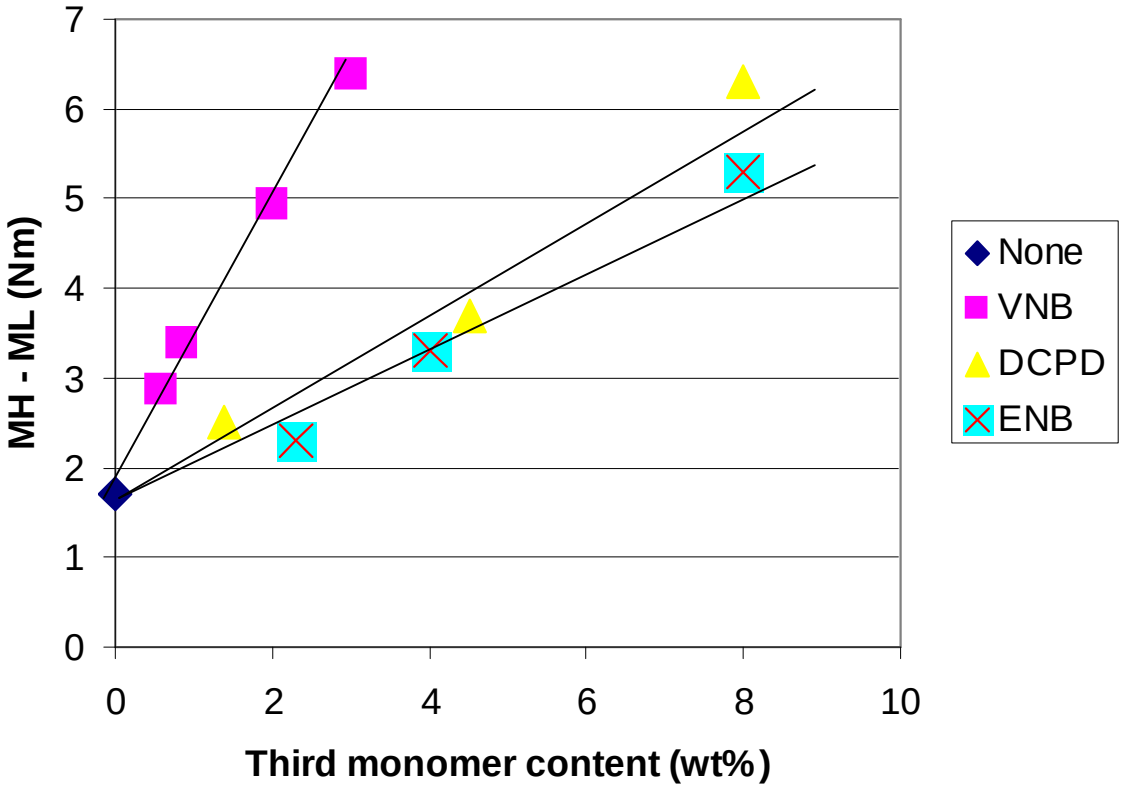


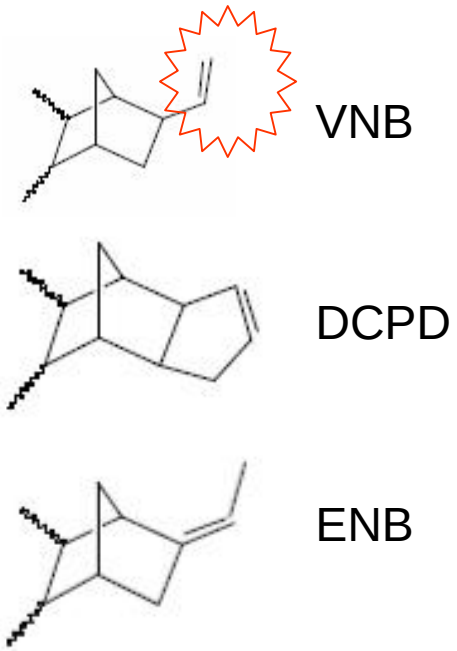
Peroxide decomposition governs kinetics of peroxide (PO) curing.

With EPM, network is formed by combination of macro radicals (EPM•).

With EPDM, cross-links are formed also by addition to double bond.

Peroxide Curing Efficiency: Effect of 3rd monomers





- **Peroxide cross-linking efficiency of VNB is ~4 x ENB efficiency.**
- **Efficiency governed by steric environment of pendant unsaturation.**
- **Terminal unsaturation is ideal.**

Unique Benefits of High-VNB Products - 1

- Increased peroxide curing efficiency. Up to 70% of peroxide reduction can be achieved.
  - Direct savings on peroxide cost
  - Limited or no bloom from peroxide decomposition products
  - Reduced smell of peroxide decomposition products
  - Reduced fogging
  - Reduced shrinkage
  - Less residual peroxide after curing → improved high temperature set properties
  - Less residual peroxide after curing → improved ageing characteristics
  - Improved electrical properties
  - Improved Mooney scorch characteristics (one step mixing, extrusion output)
  - Less stickiness after peroxide curing
- Instead of reducing peroxide, one can also choose to:
  - Increase total compound loading (typically 15-20% increase of total phr)
  - Improve overall balance of cured properties, *e.g.* improved oil tolerance, improved compression set, improved snappiness.

Unique Benefits of High-VNB Products - 2

- Low residual unsaturation
  - Peroxide curing ‘consumes’ the vast majority of VNB unsaturation in contrast with peroxide cures of ENB or DCPD containing EPDM grades
    - Lower residual unsaturation offers a 5-10°C improvement of heat resistance!
  - The low level of VNB unsaturation prevents black scorch

- Hyper-branched structures
  - A small fraction of hyper-branched polymer chains contributes to:
    - Enhanced shear-thinning behaviour
    - Excellent bale integrity
    - Improved compound integrity

Performance Benefits in Various Applications

	coolant hoses	V belts	brake parts	turbo charger hoses	air intake hoses	sponge sealing systems	airco hoses	anode caps	wipers	cable insulation	window gaskets	potable water seals	conveyor belts	O-rings	roller covers	plat heat exchanger gaskets	TPV
Peroxide reduction																	
> cost reduction	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
> no blooming	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
> odor/taste improvement												■					■
> reduced fogging			■			■											■
> reduced shrinkage			■											■		■	
> improved electrical properties								■		■							
> less down shearing (TPV)																	■
Increased crosslink density																	
> reduced (oil) swell	■	■	■	■	■		■						■		■		
> increased filler loading	■	■		■	■	■	■		■		■	■	■		■		
> improved chloramine resistance												■					
Reduced residual peroxide																	
> improved high T ageing performance	■	■	■	■	■		■						■	■		■	
> improved high T compression set	■	■	■	■	■		■							■		■	
Unique branch structures																	
> enhanced Mooney scorch times	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	
> high collapse resistance	■	■		■	■	■	■		■		■		■				■
> excellent high-shear properties						■			■	■	■						■
Low residual unsaturation																	
> improved ageing performance	■	■	■	■	■		■						■	■		■	
> improved high T compression set	■	■	■	■	■		■							■		■	
VNB cure site																	
> enhanced hydrosilylation curing																	■
> enhanced ene grafting/curing																	■
> absence of black scorch	■					■			■		■						

Keltan DE 8270C Specifications

Properties	Units	
Mooney Viscosity ML (1+4) 125ºC	MU	80 ± 5
Volatile	wt%	≤ 0.5
Ethylene Content	wt%	50.0± 2.1
VNB Content	wt%	3.0 ± 0.5
Molecular Weight Distribution*	-	Medium

- General Sales Specification apply
- Product Data Sheet and Safety Data Sheet will be made available
- Standard packaging; coding on bale, box and labels

Keltan ACE run in November 2008

- Proven capability for production of high-VNB products
- Produced 200 mT in-spec Keltan DE8270C in short test run
- Internal evaluation in progress and supports all prior findings

Peroxide Reduction
Cost reduction

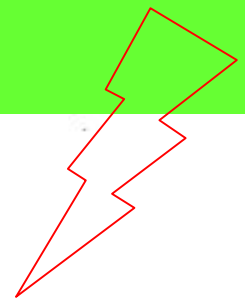
- Based on lab studies peroxide savings can amount from 15 up to 70%, whilst maintaining the same state of cure.
  - Very high ENB grades (about 10%) → 10-15%
  - High ENB grades (about 8%) → 15-20%
  - Normal ENB grades (about 4%) → 30-40%
  - DCPD grades (4-5%) → 40-50%
  - Low ENB grades (2%) → 50-60%
  - Copolymers → 60-70%

- Co-agents levels can be downward corrected proportionally

Peroxide Reduction
No blooming

- Perkadox 14/40 most popular cross-linking peroxide
- Bis(hydroxy-isopropyl)-benzene blooms from cured products, forming needle-like crystals.
- Blooming can be prevented if less than 4.5 phr is added to a typical EPDM formulation

Decomposition products of Perkadox 14/40



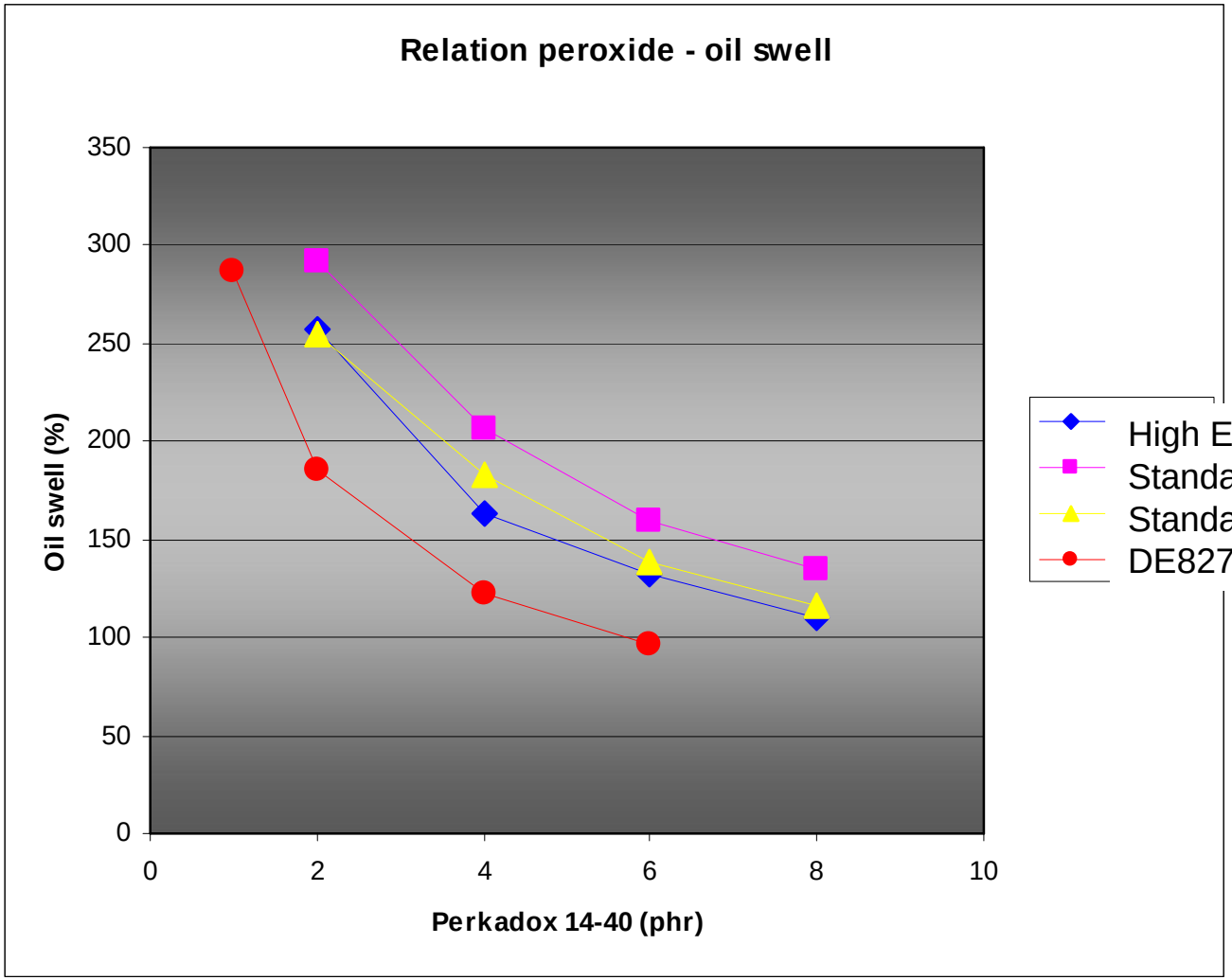
Tert. butanol		1.56
Acetone		0.44
Methane		1.35
Bis (hydroxy isopropyl) benzene		0.22
Acetyl-hydroxy isopropyl benzene		0.52
Di acetyl benzene		0.15
Water	about	0.02
Isobutene	"	0.01
Substituted α-methyl styrenes	"	0.01

Peroxide Reduction

Low odor, taste, fogging, shrinkage, conductivity

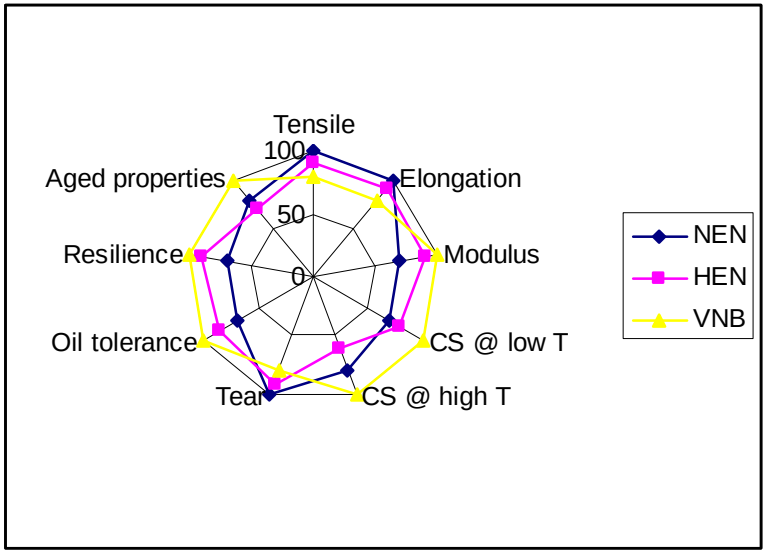
- Odour and taste characteristics of VNB similar to ENB (isomeric compounds).
- Low third monomer content → low residual diene.
- Less volatiles and extractables from peroxide decomposition products.
- Polar peroxide decomposition products reduce dielectric strength.
- Post-curing processes aimed for reducing peroxide decomposition products from cured products can be made more cost-effective.

Increased Cross-link Density
Reduced (oil) swell



Increased Cross-link Density
Increased filler loading

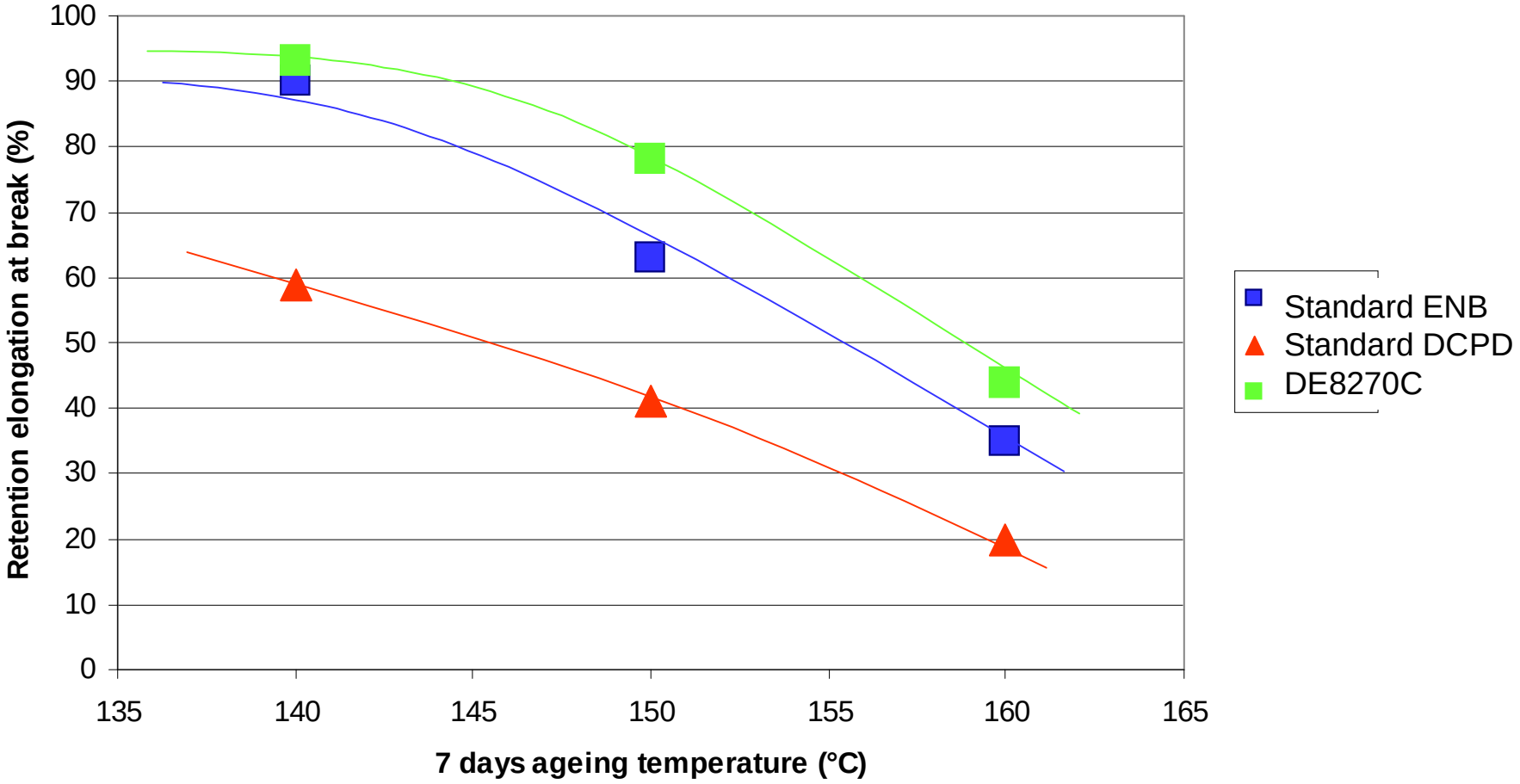
- *'If vulcanisate properties are expressed in a spider web diagram, connecting data points for the various properties with a piece of string, the data points for high VNB products can be connected with a larger piece of string.'*



- Use of high VNB typically allows about 15%-20% increase of compound loading, depending on the constraints in the actual compound formulation.

Reduced Residual Peroxide

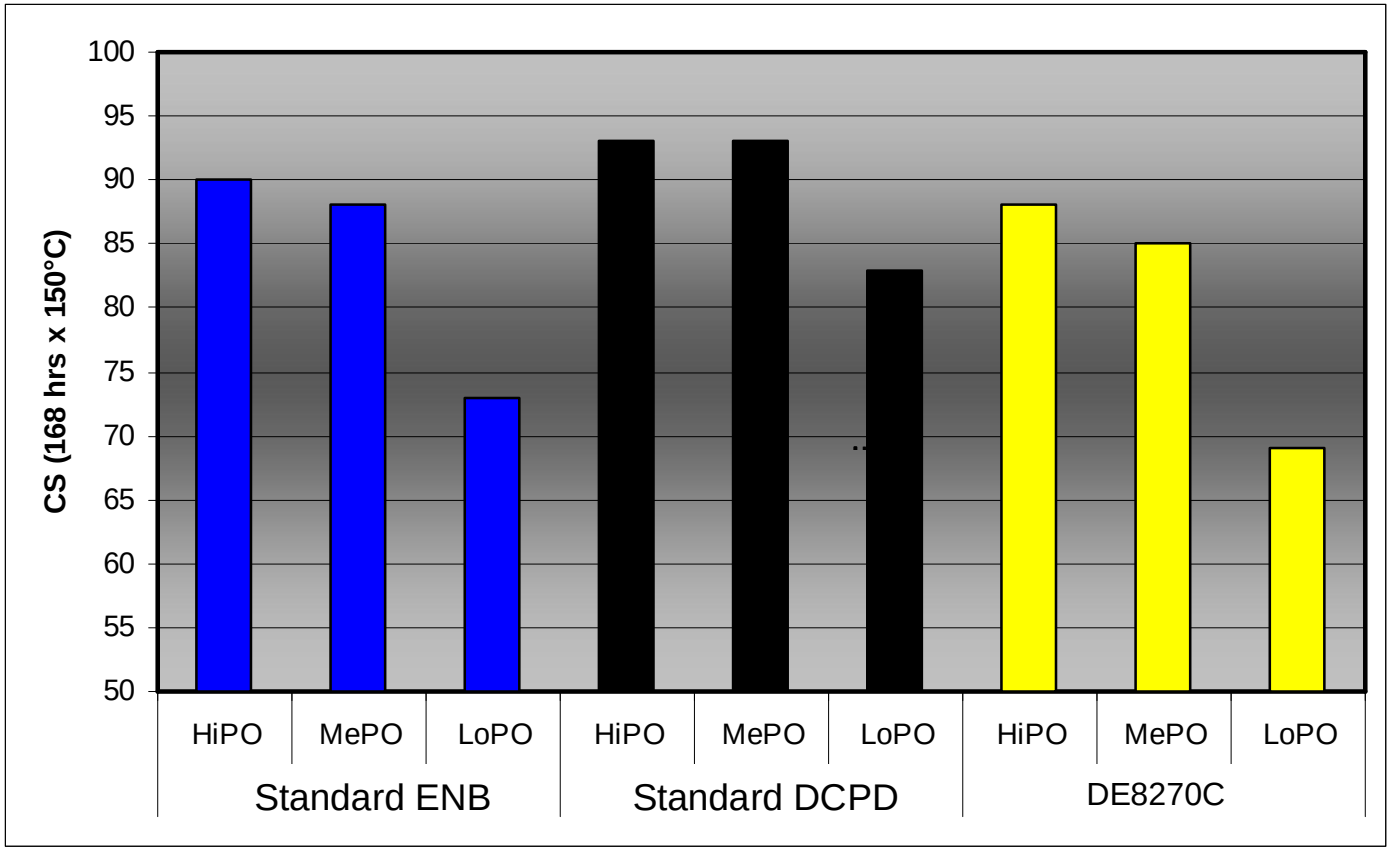
Improved high temperature ageing



Reduced Residual Peroxide

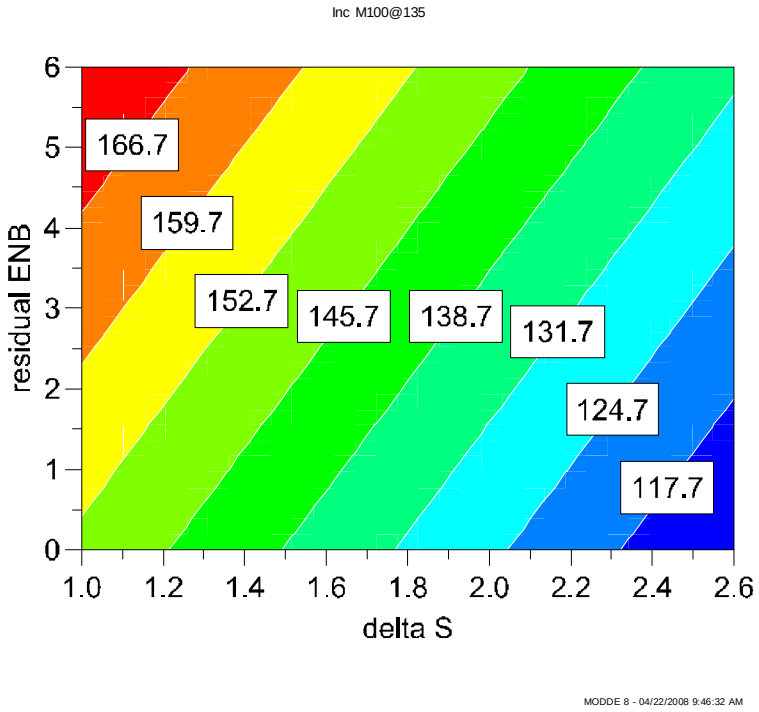
Improved high temperature compression set

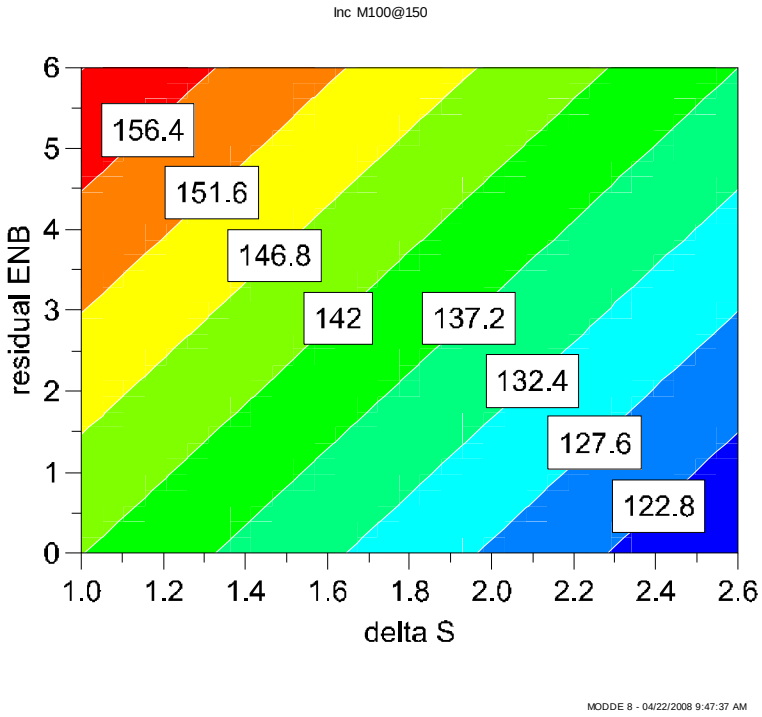
- All compounds cured to same crosslink density.
- Lower residual peroxide in high-VNB explains better high temperature compression set performance.



Low Residual Unsaturation

Improved high temperature ageing

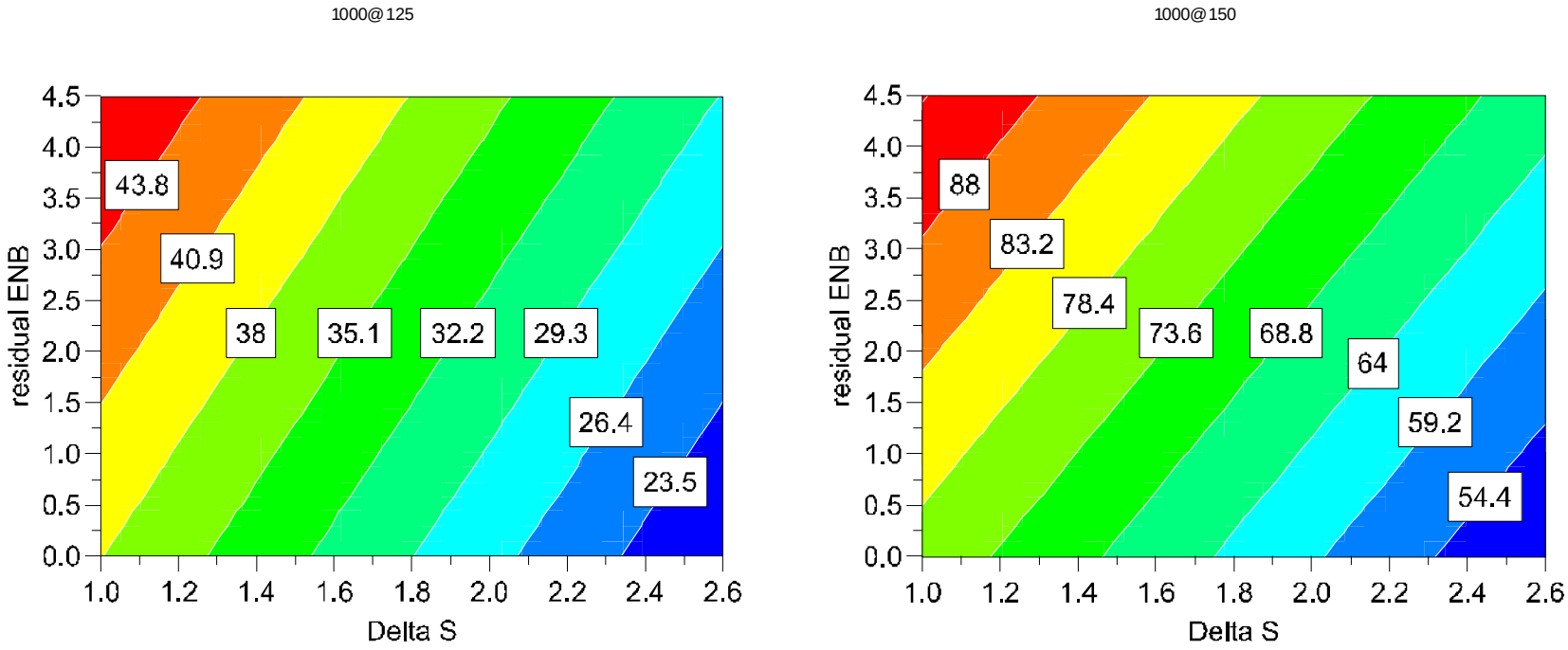




- Ageing performance improves with increase of cross-link density and minimized residual (ENB or DCPD) unsaturation.
- Both aspects can be combined with Keltan DE 8270C.

Low Residual Unsaturation

Improved high temperature compression set

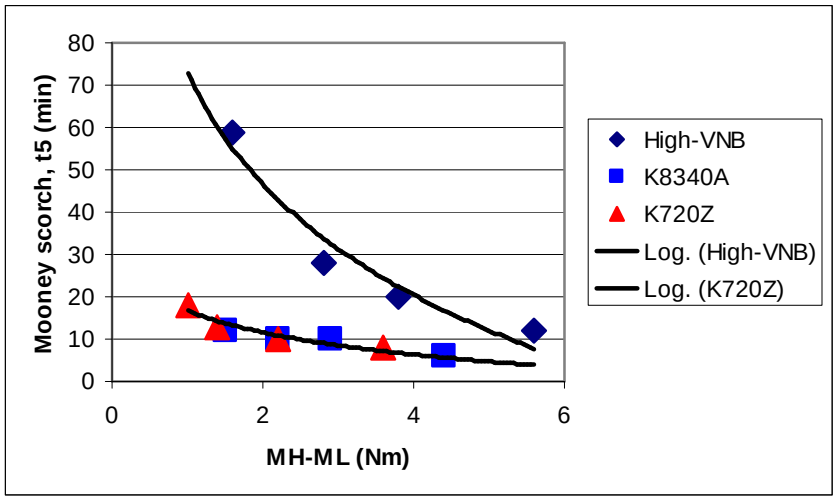


- Low compression set calls for high cross-link density
- High temperature performance calls for low residual unsaturation
- Keltan DE8270C can combine high crosslink density with low residual unsaturation.

Unique Branch Structures

Enhanced Mooney scorch times

EPDM	Keltan 8270C	4 wt% ENB-EPDM
Peroxide dosing (phr)	6	9
Mooney scorch data at 135°C		
T2 (min.)	3.6 (+20%)	3.0
T5 (min.)	4.1 (+21%)	3.4
T35 (min.)	7.2 (+31%)	5.5
Rheometer data at 180°C		
Ts2 (min.)	0.3	0.3
t90 (min.)	3.3	3.3
Cross-link density (MH-ML)	1.3	1.2

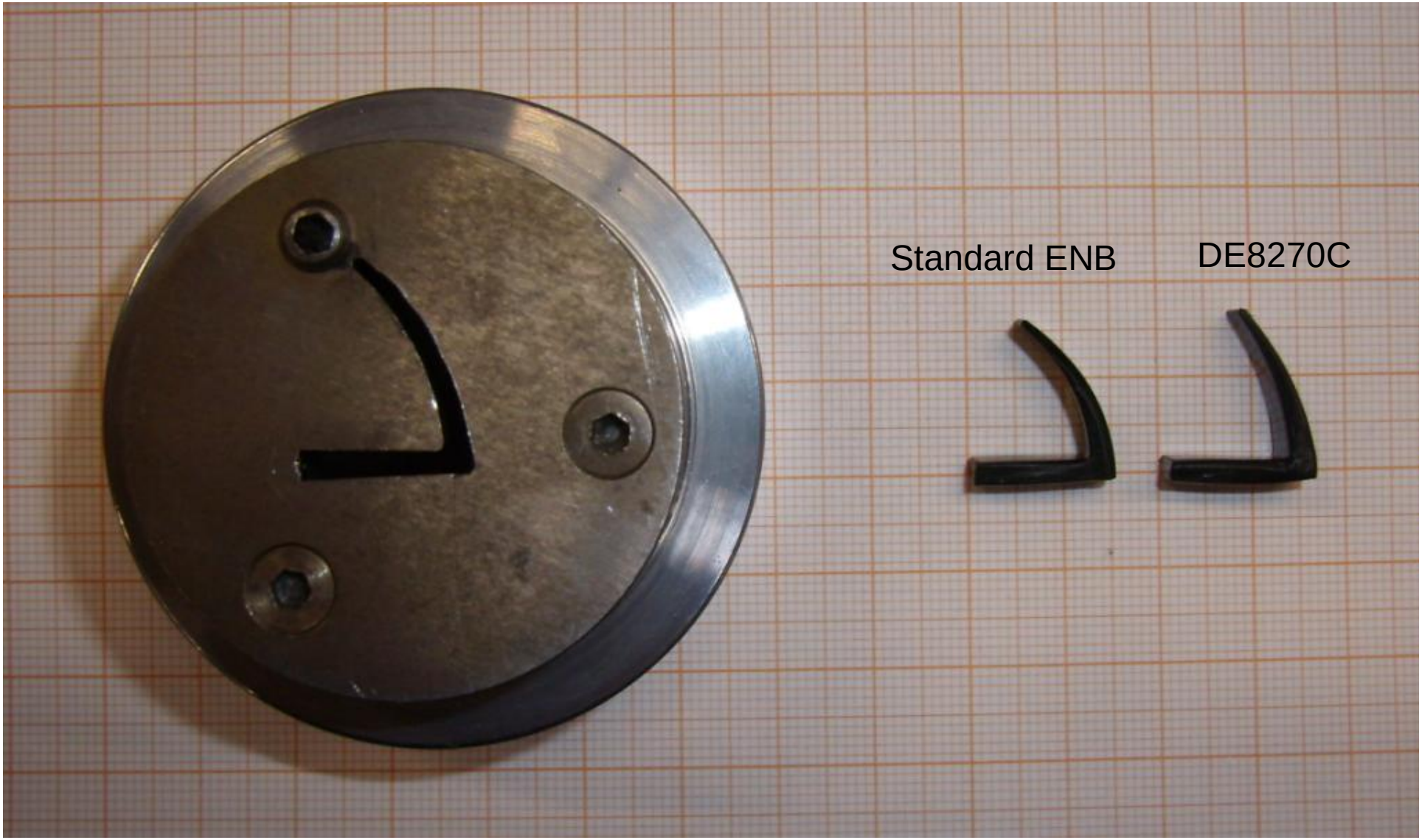


- Significant increase of Mooney scorch times, whilst…
- … maintaining similar cure times.
- → one step mixing
- → prolonged compound storage
- → increased extrusion temperatures/output

Unique Branch Structures
High collapse resistance - 1

- Standard solid extrusion application
- Collapse die
- Temperature settings and rpm systematically changed
- Responses:
  - Extrudate exit temperature (IR)
  - Head pressure
  - Power consumption
  - Die swell
  - Extruder output
  - **Collapse resistance**

INGREDIENT	PHR
Polymer	100
Stearic acid	0.5
PEG	2
CaO-80	6
N550 carbon black	130
Whiting	60
Tudalen B-8014	70
Perkadox 14-40	6


Standard ENB
DE8270C

Summary and Conclusions

- Successful Keltan ACE™ run in November 2008
- Internal evaluation in progress
- Preparing for commercial launch of first high-VNB product, Keltan DE8270C
- Keltan DE8270C has unique performance benefits in terms of:
  - Extremely efficient peroxide curing
  - Improved balance of aged and unaged material properties
  - Improved processability

Contact us…

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