

超高分子量EPDM的技术特点和典型应用

官同华| 阿朗新科高性能弹性体
第七届无锡橡胶技术论坛| 无锡, 2018



目录

Content

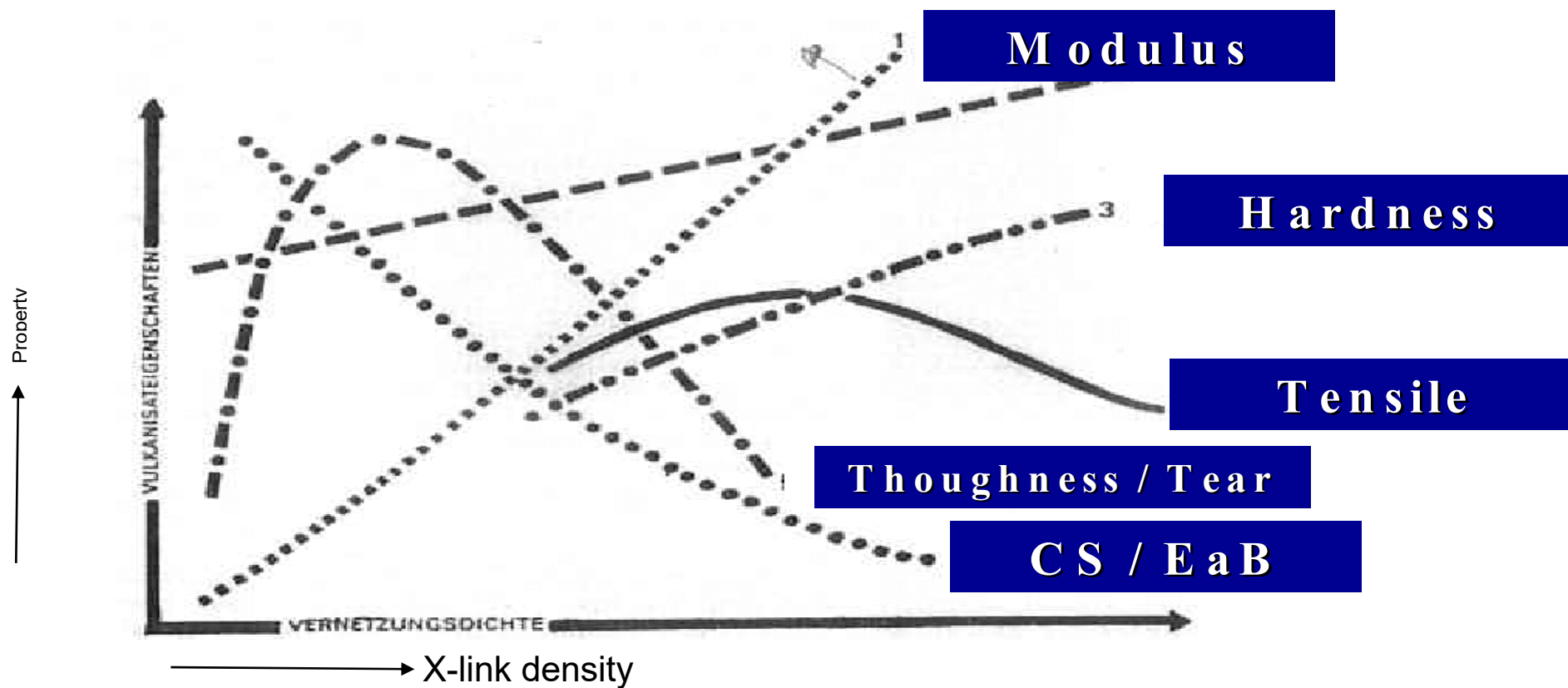
- ❑ 配方设计的限制因素
- ❑ 要求矛盾性能的几个典型应用
- ❑ 超高分子量**K13561C**的特点和应用举例
- ❑ 结语

配方设计的限制因素

- 矛盾的性能此消彼长
 - EPDM乙烯含量：拉伸/撕裂强度-低温性能（低温压缩变形+室温回弹）
 - 门尼粘度：强度/压变-工艺性能
 - 填料种类和数量：拉伸和撕裂强度-压缩变形/回弹
 - 硫化体系/交联密度：定伸-扯断伸长率，拉伸/（热）撕裂-压缩变形，压缩变形-耐磨（模具污染）
- 矛盾的性能要求限制了配方的工艺表现
 - 拉伸/撕裂+压缩变形+耐热→混炼胶门尼→挤出工艺、焦烧
 - 拉伸+压缩变形+耐热+耐油→热撕裂
- 如何整体提升相互矛盾的性能及工艺要求???

超高门尼+可控长链支化

交联密度-性能



几个典型的应用 相互矛盾的性能要求（物性+工艺要求）

- 污水处理曝气膜（管）
- 洗衣机门封
- 汽车线束
- 汽车减振
- 汽车散热器胶管

污水处理曝气膜（管）的技术要求

CJ/T 264-2007

Item	Spec.	Method
Hardness, Shore A	60+/-3	GB/T 531
Tensile strength, Mpa	>=14	GB/T 528
EAB, %	>=500	GB/T 528
Tear strength, KN/m	19	GB/T 529
Rebound resillience, %	>=40	GB/T 1681
Compression set, 23°CX70h, %	<=15	GB/T 1683
Hot air aging (70°CX70h)		GB/T 3512
Tensile strength change, %	<3	
EAB change, %	<25	
Water resistance, 23°CX168h		GB/T 1690
Weight increase, %	<1.5	
Volume increase, %	<3	
Acid resistance coefficient (28% H ₂ SO ₄ X24h), %	1	
Alkali resistance coefficient (38% NaOHX24h), %	0.9	
Resistance to 1# oil, 23°C, weight increase, %	1.8	



变形和撕裂是目前市场上的产品经常见到的问题

配方原则

- 牌号选择:

- > 中高门尼，中低乙烯（低温弹性+扯断变形）(K8550C, K6950C, K9950C)
- > 并用少量高乙烯牌号（抗撕裂性能）(K8570C, K6470C)
- > **K13561C**：一个曝气膜的理想牌号(不推荐于曝气管)

- 填料:

- > 200~250Phr, N550（或并用少量N774）

- 硫化体系:

- > 传统硫磺硫化体系
- > 半有效硫化体系（压缩变形+耐热）

实验配方和性能

Compound	1	2	3	4	5
K8570C	100.0			50.0	100.0
K8550C		100.0			
K9650Q			100.0	50.0	
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic	1.0	1.0	1.0	1.0	1.0
PEG4000	3.0	3.0	3.0	3.0	3.0
N550	80.0	80.0	80.0	80.0	80.0
Sunpar 2280	55.0	55.0	55.0	55.0	55.0
CBS	1.0	1.0	1.0	1.0	
MBT	1.0	1.0	1.0	1.0	
TMTD	0.5	0.5	0.5	0.5	
S	1.25	1.25	1.25	1.25	0.5
DCP					3.0
SUM PHR	247.75	247.75	247.75	247.75	247.5
Moving Die Rheometer (ISO 6502)					
170°C , 0.5° ARC	1	2	3	4	5
S'Max - S'Min, dNm	16.5	15.0	16.0	16.3	14.2
Tc - 90, min	6.51	5.74	3.69	4.58	9.37
Ts - 2, min	0.88	0.92	0.74	0.79	0.82

Unaged Properties

Tensile Strength (ASTM D412 Die C) Machine: Zwick 010					
SHORE-A: 3 "	63	57	60	59	62
25% MODULUS , MPa	1.0	0.8	0.9	0.9	1.0
50% MODULUS , MPa	1.5	1.2	1.3	1.4	1.4
TENSILE, MPa	21.1	14.8	14.1	17.9	20.3
ELONGATION, %	549	481	488	518	476
Permanent Set, %	21.2	8.4	10.9	11.3	6.6
Tear Resistance (ASTM D624 Die C)					
Tear Strength, KN/m	38.7	28.1	28.1	32.7	37.3
Rebound resilience-ISO 4662/DIN 53512					
At 23 °C, %	63.8	58.0	62.3	63.7	62.5
Tension Set Test , (ASTM D412) : 100% extension for 10 min, 10 min relaxation					
Tension set, %	2.2	0.5	0.5	0.7	2.4
Stress Relaxation , (Internal method) Machine: Instron 3365					
Test condition: 23°C×17hrs	1	2	3	4	5
Stress Relaxation (R _t) at 20%, %	51	25	22	30	55
Stress Relaxation (R _t) at 50%, %	36	21	19	25	41
Compression Set: 25% -Compression ISO 815 Type B Small Button					
Aged (0°C x 72hrs)	76	14	12	48	78
Aged (23°C x 70hrs)	27	5	5	11	28
Aged (70°C x 24hrs)	11	9	8	9	9

实验配方和性能

Compound	1	2	3	4	5
K8570C	100.0			50.0	100.0
K8550C		100.0			
K9650Q			100.0	50.0	
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic	1.0	1.0	1.0	1.0	1.0
PEG4000	3.0	3.0	3.0	3.0	3.0
N550	80.0	80.0	80.0	80.0	80.0
Sunpar 2280	55.0	55.0	55.0	55.0	55.0
CBS	1.0	1.0	1.0	1.0	
MBT	1.0	1.0	1.0	1.0	
TMTD	0.5	0.5	0.5	0.5	
S	1.25	1.25	1.25	1.25	0.5
DCP					3.0
SUM PHR	247.75	247.75	247.75	247.75	247.5

Ageing properties

Ageing in: 28% H2SO4 (ASTM D471) Machine: Zwick 010

Condition: 23°C x 24hrs	1	2	3	4	5
CHANGE SHORE-A: 1"	1	-1	-2	2	1
CHANGE Tear Strength, %	3	4	8	3	6
CHANGE 25% MODULUS %	10.0	0.0	0.0	0.0	10.0
CHANGE 50% MODULUS %	6.7	8.3	0.0	0.0	7.1
CHANGE TENSILE: %	7.6	2.7	3.5	2.8	2.5
CHANGE ELONGATION: %	4.2	1.2	1.8	2.1	-5.0
CHANGE VOLUME: %	0.2	-0.2	-0.4	0.2	-0.2
CHANGE MASS: %	0.2	0.3	0.1	0.3	-0.1

Ageing in: 38% NaOH (ASTM D471) Machine: Zwick 010

Condition: 23°C x 24hrs	1	2	3	4	5
CHANGE SHORE-A: 1"	0	0	0	2	0
CHANGE Tear Strength, %	4	6	-5	2	4
CHANGE 25% MODULUS %	0.0	0.0	0.0	0.0	0.0
CHANGE 50% MODULUS %	0.0	0.0	7.7	0.0	0.0
CHANGE TENSILE: %	1.4	-2.0	2.8	1.7	0.5
CHANGE ELONGATION: %	0.0	-3.7	-1.6	5.0	-3.8
CHANGE VOLUME: %	0.2	0.0	-0.1	0.2	0.1
CHANGE MASS: %	0.0	-0.1	0.0	0.0	-0.1

洗衣机门封 (Washing Machine Gasket, Bull eye)

➤ 关键性能 Key Performance

- 耐洗涤剂
- 无颜色污染
- 热撕裂强度高
- 弹性、压缩变形
- 高温段时间硫化 (200度100秒)

➤ 配方设计 Compound Design

- **K4869C** (K4551A), **K5467C**
K5469 (K5531A, Buna EP T 5459 CL)
K13561C
- 有效硫化体系



橡胶线束 (Grommet of wire harness)

➤ 关键性能 Key Performance

- 低硬度: **50 (40~60) Shore A**
- 拉伸强度: **> 15MPa**
- 扯断伸长率: **> 800%**
- 撕裂强度
- 回弹性

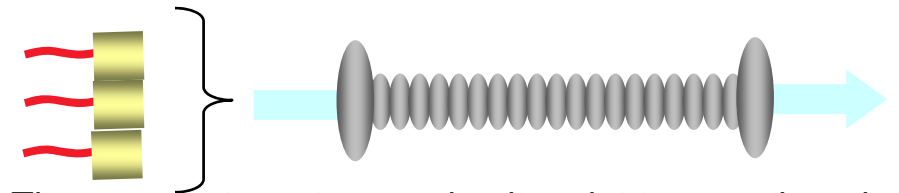
➤ 配方设计 Compound Design

- **K4869C** (K4551A), **K5467C**
K5469 (K5531A, Buna EP T 5459 CL)
K9565Q, **K13561C**
- 总份数: **330 Phr**
- 半有效硫化体系

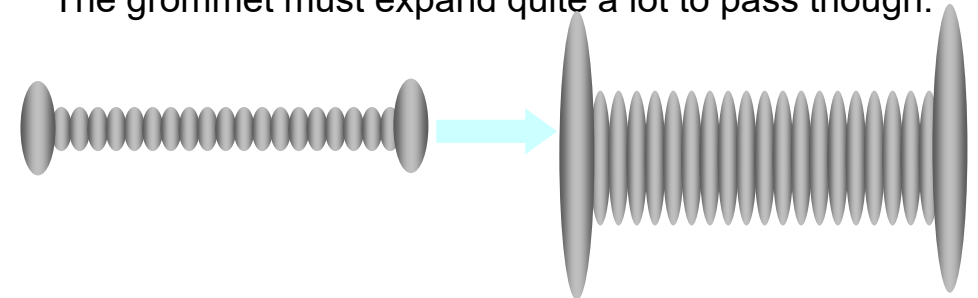
Wire harness is made by cable wire and connector.



The connector of wire harness is thick. Several connectors should pass through grommet at the same time.



The grommet must expand quite a lot to pass through.



减震橡胶件 (Anti vibration part: Engine mount)

➤ 关键性能 Key Performance

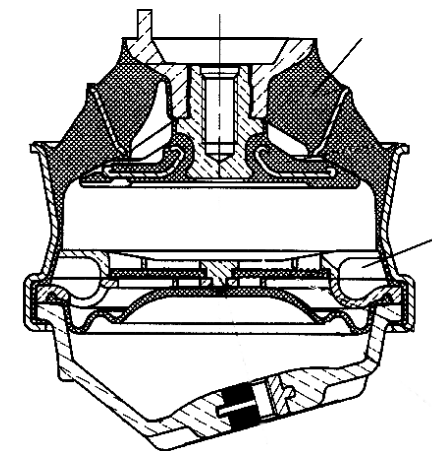
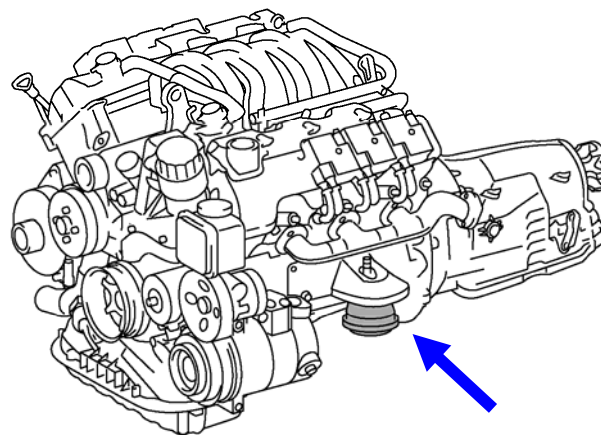
- 动态性能 (Kd/Ks)
- 耐高温
- 蠕变性能
- 裂口增长 + 撕裂强度

➤ 配方设计 Compound Design

- **K4869C** (K4551A, K509X100), **K5467C**, **K5469** (K5531A, Buna EP T 5459 CL), **K9565Q**, **K6471** (K6531A, K708X15)

K13561C

- 硫化体系:
 - 有效硫化体系
 - 过氧化物
- 总份数: **300 Phr**



散热器胶管 TL52361

性能要求

- 耐热: 125°C~150°C
- 电化学腐蚀: ECD
- 一定的耐油性能
- 工艺要求: 穿芯棒、抗塌陷



Pilot Recipe VW TL 52361

EPDM KELTAN 8550C	70.0
EPDM KELTAN 6471	35.0
MgO-80 (R. G3)	4.0
Carbon black N-550	30.0
Carbon black Dur O	40.0
Al-silicate S. N85	25.0
PEG (B. PEG3400)	4.0
Par.oil BP T1993	37.00
TMQ (A. Resin D)	1.0
NDBC (P. NDBC)	2.0
Perkadox 14-40 MB	3.0
DHBP-40 (T. 101)	5.00
TMPT	2.0
Total phr lab	258.0

Hardness	[° Shore A]	64
After Hot air, 94.0hrs / 160° C		
Hardness	[° Shore A]	70
Oil 22.0hrs / 100° C		
Hardness	[° Shore A]	51
Mass change oil 22 hour 100° C		
Mass change	[%]	57
Tensile strength	[MPa]	11
M 100	[MPa]	3.3
Elongation	[%]	327
After Hot air, 94.0hrs / 160° C		
Tensile strength	[MPa]	12.2
M 100	[MPa]	4.3
Elongation	[%]	332
Compression set (VW) 22 hour/160°C		
Set 5 sec.	[%]	35
Set 60 min.	[%]	28

- 牌号: K8550C/K6470C, K8550C/K5467C, **K13561C**

K13561C

生胶的性能测试 - 产品指标

	单位/ unit	Keltan® 13561C DE	测试标准 Test method
门尼粘度ML (1+8)150° C Mooney Viscosity	MU	88	ISO 289 Milled samples
乙烯含量 Ethylene Content	wt %	56 *)	ASTM D 3900A
第三单体种类及含量 Termonomer Type & Content	wt %	ENB 5.5	ASTM D 6047
充油份数 Oil content	Phr (wt %)	15 (13)	ISO 1407
分子量分布 Molecular weight distribution		CLCB	ARLANXEO

*) The C2 content is based on ACE catalysis

- Product ML(1+4)125° C: 130 MU
- Polymer ML(1+4)125° C: 151 MU (Note: calculated value without oil)

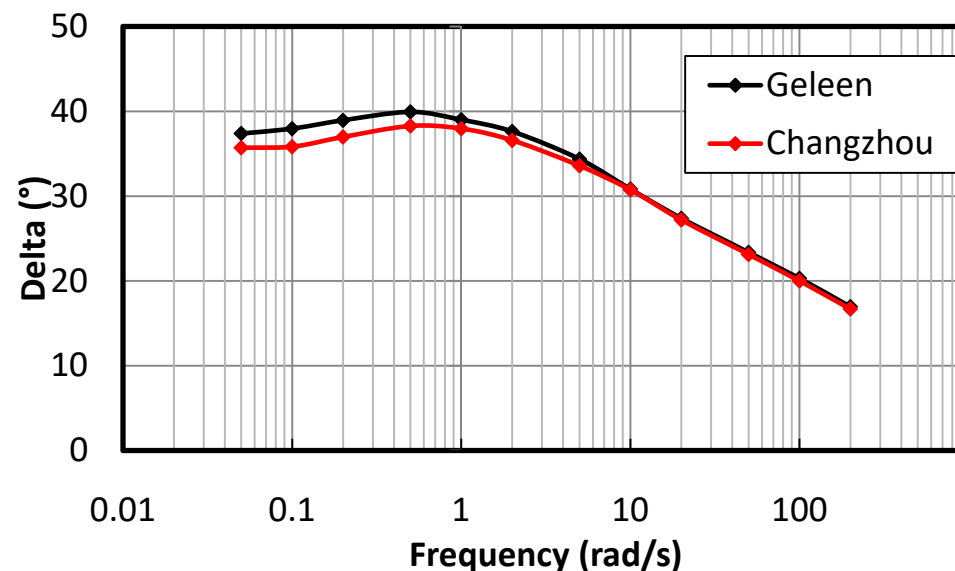
ACE技术与可控长链支化(CLCB)相结合

■ 采用可控长链支化(CLCB)专利技术的高性能EPDM High-Performance EPDM based on proprietary CLCB Technology

- 混炼速度快，分散性能好
- 挤出速度快，抗塌陷性能好
- 硫化速度快，压缩永久变形好

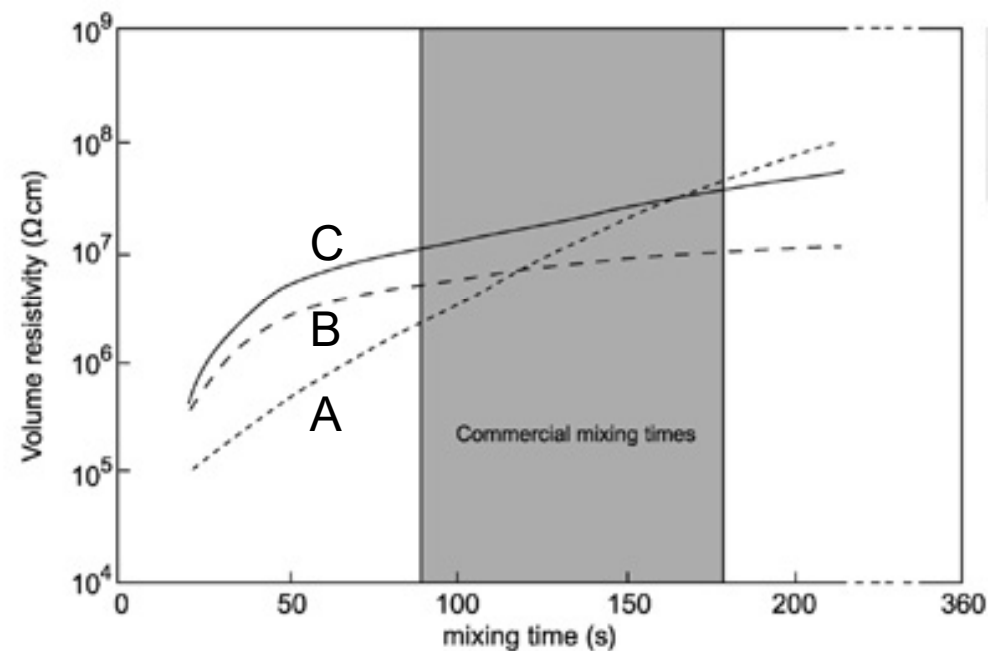
■ ACE可生产带支链的EPDM – 独到之处 ACE can produce branched EPDM - Unique feature

- KELITAN的ZN和ACE催化剂均可采用CLCB技术生产长支链的EPDM
- 采用ACE催化剂的产品的分子量分布从窄分布到中等分布
- 市场上其他的茂金属催化剂生产的产品无法支化，只能得到窄分布的牌号



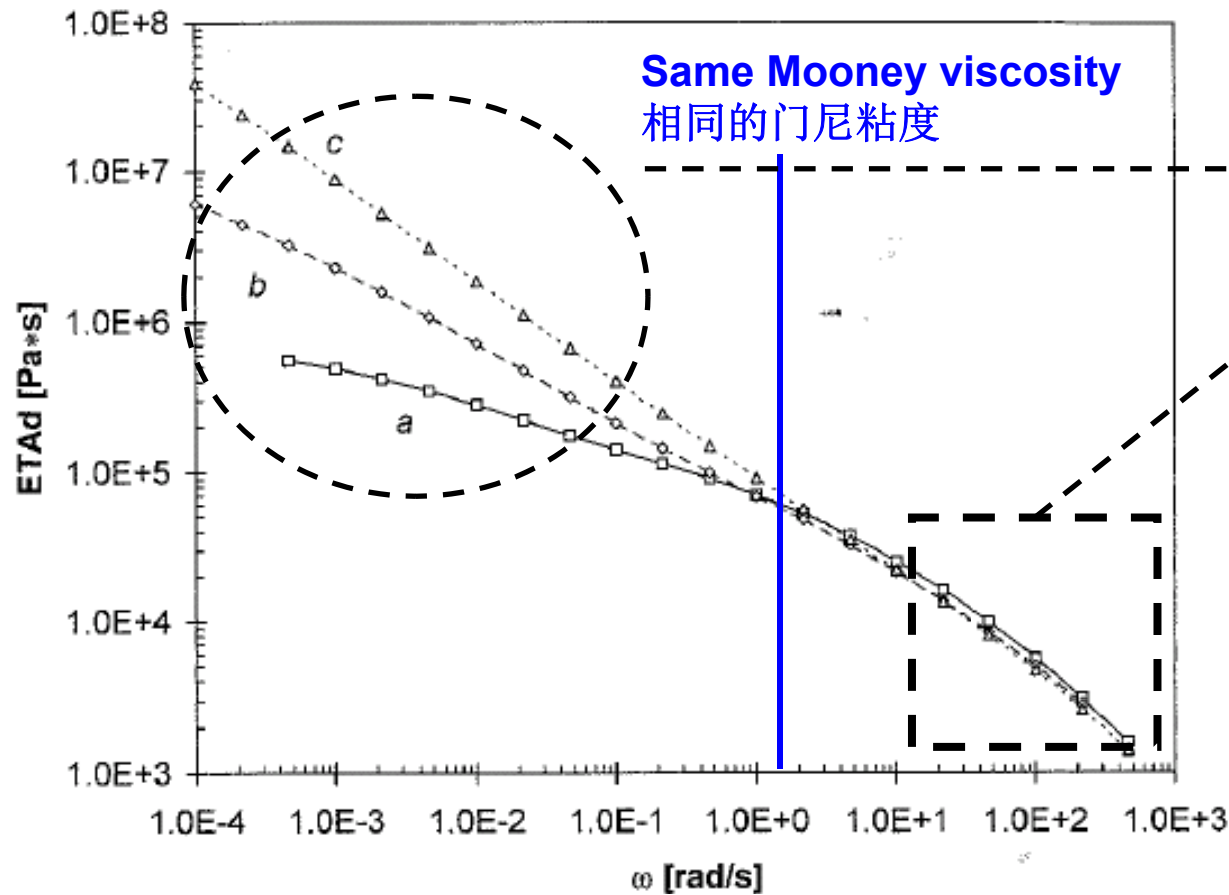
可控长链支化(CLCB)的优点：混炼性能得到提高

- 随着炭黑分散程度高，胶料的体积电阻增加
Volume resistivity increases with CB dispersion.
- CLCB同时具有：
 - 炭黑混入速度快(窄分布的优点)
Fast CB incorporation (Narrow MWD)
 - 分散程度高(支化度高的优点)
High dispersion degree (High branching level)



EPDM A: 宽分布 (Broad MWD)
EPDM B: 窄分布 (Narrow MWD)
EPDM C: CLCB (K8550C)

可控长链支化(CLCB)对工艺性能的影响

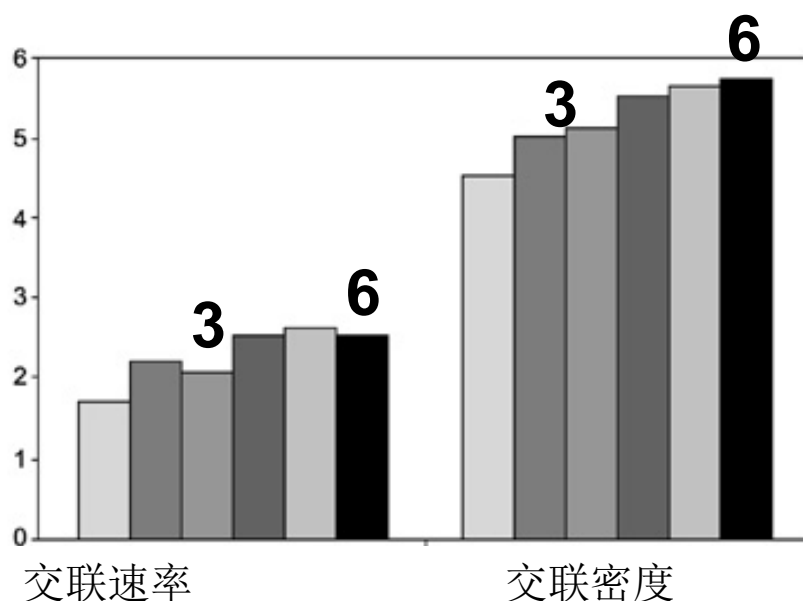


- EPDM a → c: 支化程度提高
Polymers a → c: branching degree ↑
- 支化度高: $\eta_0 \uparrow$, 抗塌陷性能↑
Branching ↑: $\eta_0 \uparrow$, collapse resistance ↑
- 支化度高: $\eta \downarrow$, 粘度↓
Branching ↑: $\eta \downarrow$, viscosity ↓
- 混炼(Mixing): $100-300 \text{ s}^{-1}$
- 挤出(Extrusion): 1000 s^{-1}
- 注塑(Injection Molding): 10000 s^{-1}

可控长链支化(CLCB)的特点: 交联密度高, 压缩永久变形好

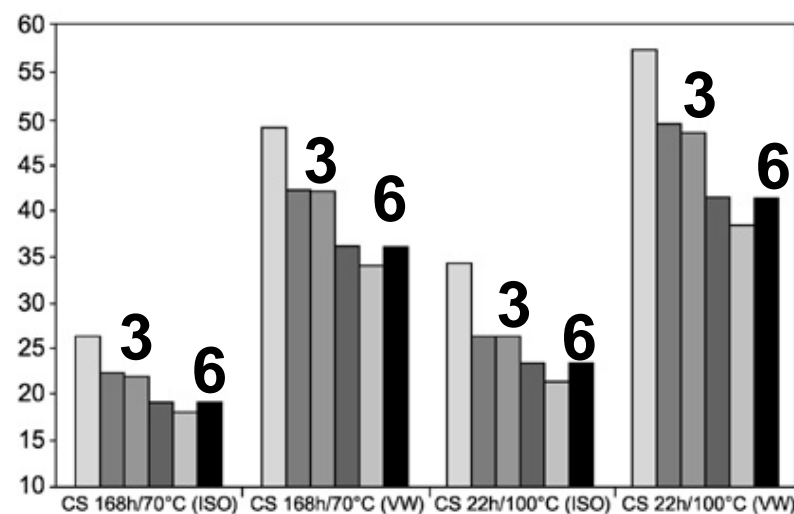
硫化特性 (Cure)

- 传统EPDM: 交联速率与分子量分布及ENB含量有关
- CLCB EPDM: 交联速率比传统EPDM快(相同ENB含量)



压缩永久变形 (Compression set)

- 传统EPDM: 压变随着ENB的增加降低很少, 这是由于ENB的反应性逐次递减。
- CLCB EPDM: 尽管ENB含量较低, 由于窄分子量分布及可控长链支化, 使得硫化效率提高, 压变更好。



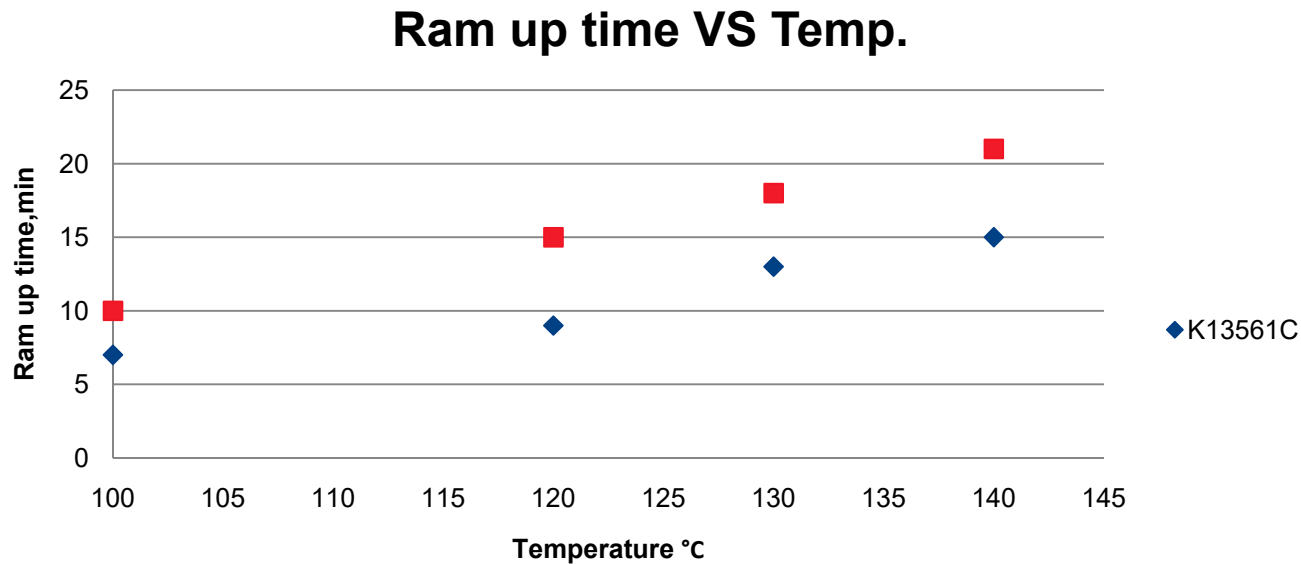
EPDM 3: K4802; EPDM 6: K8550C

K13561C应用：低硬度制品-线束 配方和性能

	1	2	3
13561C	115		
A		85	
B			88.8
C		48	48
ZnO	5	5	5
SA	1	1	1
TMQ	1	1	1
MB	1		
N550	50	62	65
RP-16(Close to Clay)	30		
CaCO3	30	35	35
Silica	10	10	10
PEG4000	2	2	
WB42	1.5	1.5	3
internal release agent			3
Coumarone			5
500号# paraffin oil	105	105	100
Si-69	2	2	2
S-80	0.6	1.2	1
TMTD	0.5	0.5	0.4
M	1	0.8	0.8
ZDEC	1	1	0.8
ZDBC	1	1	0.8
DPTT	0.5	0.5	0.4
Total Phr	368.1	362.5	371
含胶率	27%	28%	27%

	1	2	3	要求
ML,120°C (1+4)	26.4	20.3	19.2	
T10,min	0.73	0.75	0.82	
T90,min	3.87	3.67	4.08	
Hardness, ISO7619, HA	41	40	39	40±5
Tensile, Mpa,	13.1	10.8	10.4	≥10
Elongation @ break,%,	778	700	788	≥400
Tear	22.1	20.1	19.5	≥20
C.S. 25% 100°C×22h	28	31	29	≤35
Hot Air 100°C×72h				
Hardness Change,°	+5	+7	+4	0~+10
Tensile, Change%	-6	-16	-20	< - 25
Elongation @ break Change,%	-20	-22	-24	< - 25

K13561C应用：低硬度制品-线束 炼胶效率



- 达到同样的排胶温度，K13561C 需要更短的炼胶时间（少 5min）

K13561C应用 - 密封条

配方和性能

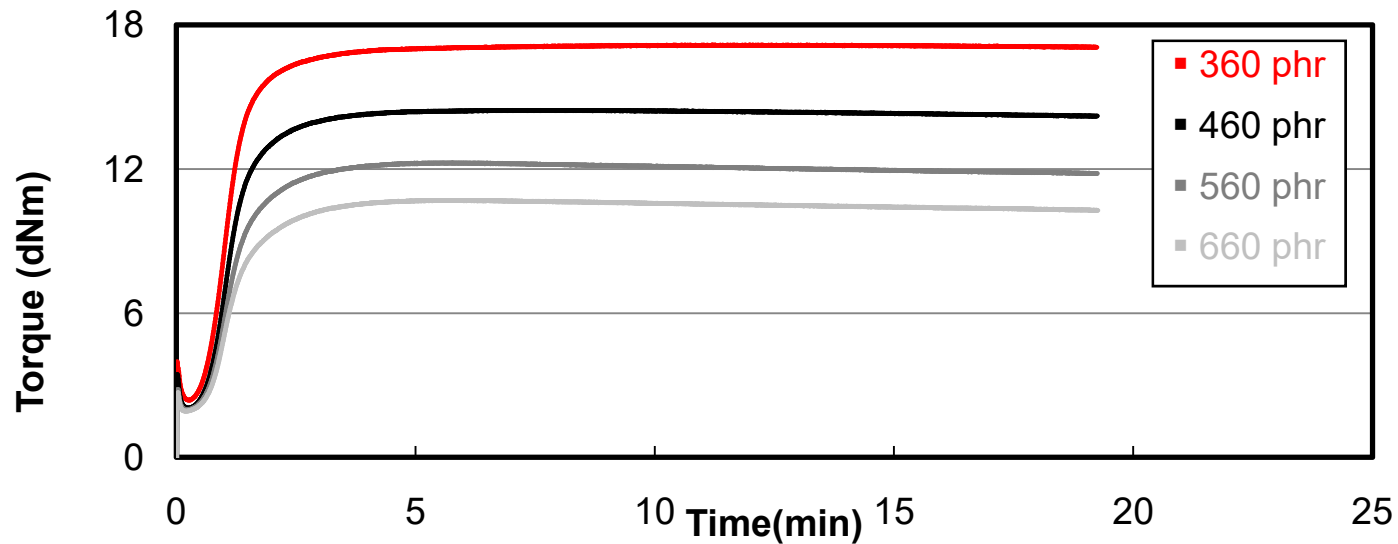
Formulation	1	2	3	4
K13561C DE	115	115	115	115
ZnO-active	6	6	6	6
Stearic acid	2	2	2	2
PEG	4	4	4	4
Carbon black N-550	125	175	225	275
CaCO3	40	50	60	70
Sunpar2280	55	95	135	175
Vulkalent E/C	0.30	0.30	0.30	0.30
Curing package	14.15	14.15	14.15	14.15
Total PHR	361	461	561	661

Curing package	
CaO-80	6
MBTS-80	1.30
ZBEC-70	2
ZDBP-50	2
DPG-80	0.50
TBBS	0.50
S-80	0.85
DTDC-80	1
Total PHR	14.15



K13561C应用 - 密封条

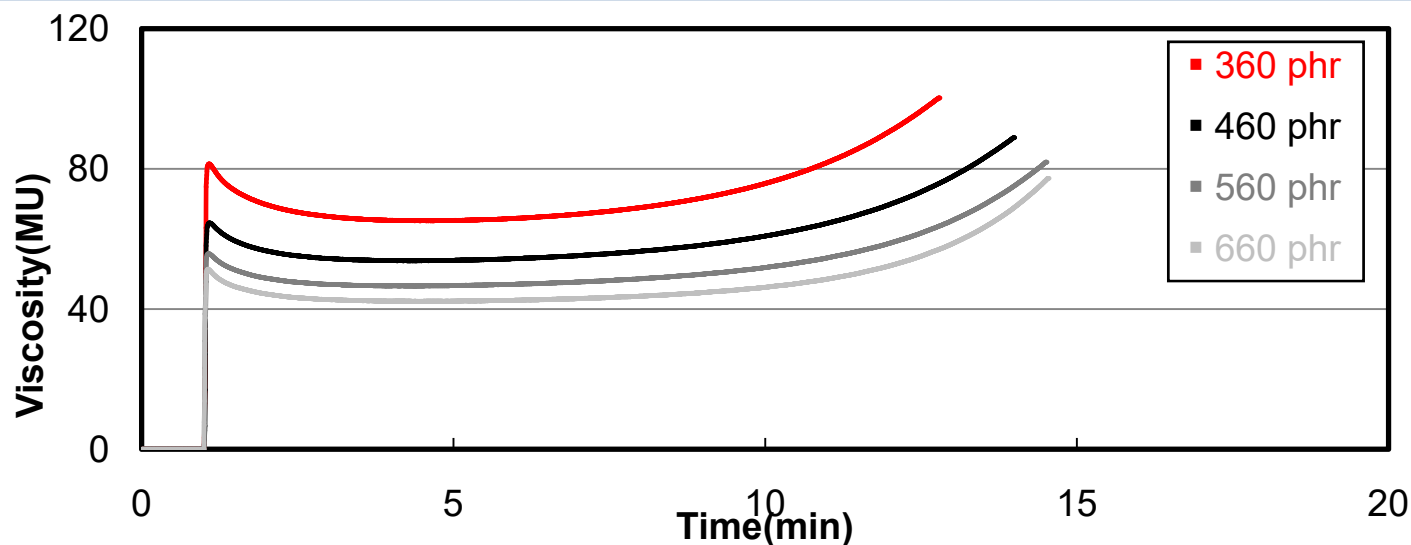
配方和性能



	360phr	460phr	560phr	660phr
ML1+4, MU @100C	85	71	62	55
MDR, 180°C×20min ,0.5° ARC				
MH-ML,dNm	14.8	12.4	10.3	8.8
MH,dNm	17.2	14.4	12.3	10.7
Tc - 90, min	1.9	2.1	2.3	2.4
Ts - 2, min	0.70	0.77	0.83	0.87

K13561C应用 - 密封条

配方和性能



Mooney Scorch @ 125°C	360phr	460phr	560phr	660phr
Min. Viscosity	65	54	47	42
t2, min	7.1	7.5	7.9	8.6
t5, min	8.5	9.2	9.9	10.5
t35, min	12.8	14	14.5	14.5
t35 – t5, min	4.3	4.8	4.6	4.1

K13561C应用 - 密封条

配方和性能

Vulcanizate Properties	硫化胶性能	单位/ unit	360phr	460phr	560phr	660phr
Hardness	硬度	Shore-A:3''	64	64	64	62
Tensile Strength	拉伸强度	MPa	13.2	10.4	7.8	6.2
Modulus 100%	100%定伸应力	MPa	3.1	3.0	2.9	2.6
Modulus 300%	300%定伸应力	MPa	9.9	8.2	6.9	5.9
Elongation at Break	扯断伸长率	%	385	394	340	334
Tear Strength Delft	撕裂强度 (Delft)	N	38.4	37.0	32.4	27.3

小结

- 基于常规牌号的配方设计，平衡相互矛盾的苛刻性能及工艺要求充满挑战；
- 常规高门尼牌号能满足相互矛盾的苛刻性能，但工艺性能难以兼顾
- **K13561C**，可控长链支化的超高门尼牌号，
 - 整体提升配方的综合性能（拉伸/撕裂/扯断-压缩变形/弹性）
 - 兼顾优越的工艺性能（混炼/挤出/硫化效率）
- **K13561C**，进一步拓宽了单个EPDM牌号的应用范围：
 - 挤出：密封条、胶管
 - 模压：洗衣机门封、减震、线束、波纹管(35~60ShoreA)
- **K13561C**，更低的系统成本
 - 更高的填充
 - 替代充油胶

ARLANXEO

Performance Elastomers