Consumer Actives

Polymer Performance Solutions

Industrial Specialities

Thomas Swan

Performance Chemicals · Responsible Chemistry

Mix time and energy savings, and green compound stability with Pepton® DBD-based chemical peptisers

DKT Show – 03 July 2024

Gabriele Benzi

Commercial Manager

Performance Chemicals

Thomas Swan Overview

Thomas Swan
Chemical manufacturing since 1926

98 Years

4th Generation Family Owned Company Est. 1926

£45m Turnover

Offices and warehousing in the UK, USA and China

150 Employees

GOLD 2023 ecovadis Sustainability Rating

Ecovadis Gold Certification

ISO

ISO:9001
ISO: 14001
ISO: 45001

Thomas Swan Carbon Net Zero

36% Reduction in Scope 1 emissions since 2019
Carbon Net Zero by 2030

30.1% energy from non fossil fuels in past year

Introduction - Mastication

"...NR is usually masticated for viscosity reduction through breakdown of the long molecular chains to facilitate subsequent processing steps (e.g., extrusion and calendaring) and improve rheological properties..."

- Airboss via RubberWorld March 2022

Mastication may be required when other process aids have a negative impact on product performance attributes

Introduction - free radical formation during mastication

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Confirmatory Evidence for the Proposed Theory of Milling

Electrical Effects. The importance of the electrical effects in the breakdown of rubber during milling as postulated above is supported by some rather interesting observations on the accompanying luminescence effects. When rubber is milled on a 4 × 4 inch mill with cold rolls, no electrical discharge takes place underneath the bite, as might be expected, but there is a more or less even glow over the surface of the rubber for about 1 or 2 cm. where the rubber enters the bank, and occasionally tiny sparks can be seen jumping from the blanket to the bank. In fact, most of the frying and crackling noise that is heard on a small mill, which is often attributed to the bursting of small air bubbles, is due to these sparks. This effect can be observed with gas-black mixtures as well as with pure gum stocks and with dead-milled, as well as slightly milled rubber, providing the rolls are cold. However, if the rolls are heated, this effect disappears, but it reappears on cooling the rolls. This shows a striking correlation with the smaller yield of peroxide which was observed on hot-milling, and with the fact that the rate of breakdown of rubber is greater when the rolls are cool than when they are hot.

Industrial and Engineering Chemistry, Vol 24, No 2, p 144, Feb 1, 1932

1932…

- Cold roll rubber milling
  - Emits a glow over the rubber surface
  - Generates peroxides
  - → ***Evidence of free radical generation***
  - Faster viscosity reduction

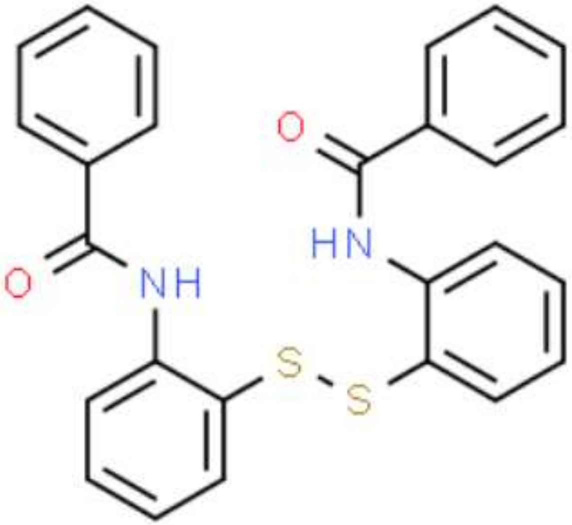
Introduction - what is a chemical peptiser?

The Science of Rubber Compounding

9.6.3 Chemical Peptizers

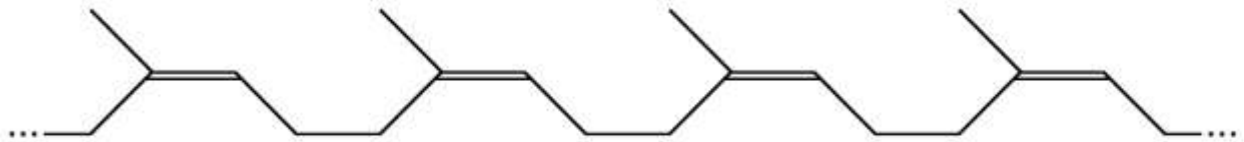
Peptizers serve as either oxidation catalysts or radical acceptors, which essentially remove free radicals formed during the initial mixing of the elastomer. This prevents polymer recombination, allowing a consequent drop in polymer molecular weight, and thus the reduction in compound viscosity. This polymer softening then

B. Rodgers, W. Waddell, *The Science and Technology of Rubber (4th Ed), 2013*



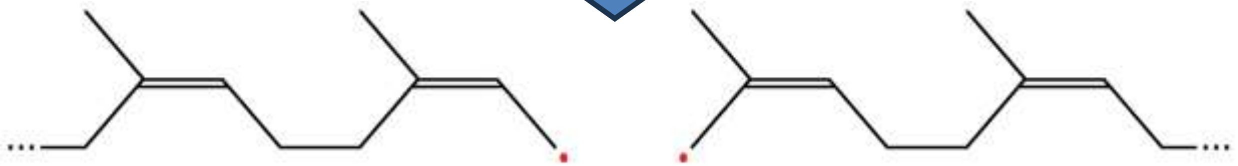
2,2'-Dibenzamido Diphenyl Disulphide (DBD)

Mastication and Pepton mechanism



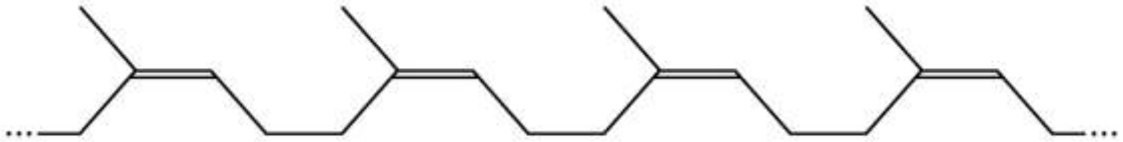
Cis-polyisoprene (NR)

Mastication
shear + heat
+ oxidization



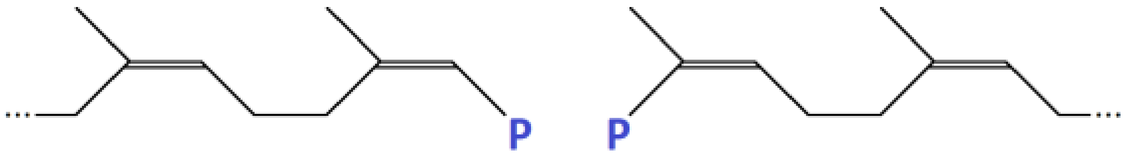
Free-radical ends

3 general outcomes



Re-combination → ***100% waste of energy***

Free-radical reaction with other polymer chains
Partial waste of energy & negative side products such as gel



The outcome we want…
Free-radical radical ends captured by radical acceptor preventing recombination and side reactions
Optimal utilization of energy

Introduction – General conception

"Green compounds green stored with peptiser will turn to bubble gum"

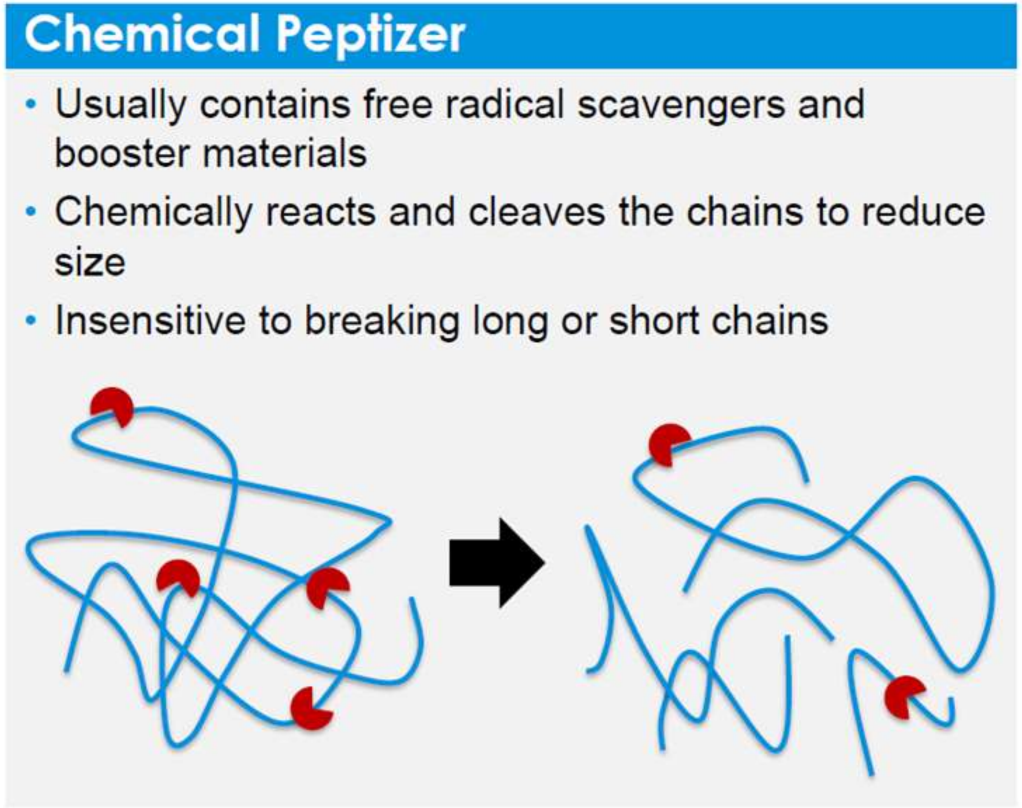
We will show evidence to the contrary

"Mastication has to be done without other masterbatch ingredients because the peptiser will react with them"

Maybe true but we saw no impact

"You can reduce viscosity with better mixing…you don't need peptiser"

True but Pepton products save time



Rauschmann & Reddy, Tire Technology Expo 2019

Presentation objectives

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Chemical manufacturing since 1926

Pepton mechanism and supporting data

- GPC data on molecular weight impact

Pepton reduced viscosity in less time than control formulas

- Pepton continued to work in the presence of other ingredients

Show the impact on elastomer molecular weight

- MW reduced faster when Pepton was present
- Observed benefit of formulated products versus pure DBD

Pepton has no measurable impact on cured physical properties

- Highlighted in various parts of the presentation

Show the stability of uncured compounds stored for 60 days

Experimental formula and mix methods

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Stage	Ingredient	PHR	ACE LABORATORIES *1.57L Reliable BR, 40HP **Tangential*** *Aug 2021*	***Smithers*** *1L Kneader SK1, 25HP **Intermeshing*** *Jan 2023*
Mastication	Ace #3 RSS Smithers #1 RSS	100	75RPM, **30 seconds** ***Continue to master*** *Actual temps 89-96°C*	Pre-heat 93°C, 75RPM, **drop ~30 seconds** ***Stop to collect GPC sample*** *Actual drop temps 94-99°C*
	Peptizer	**Varies**		
Master	N330	80	75RPM, sweep 82°C, **drop 160°C** *Actual mix times varied 150-210 seconds*	Pre-heat 93°C, 50RPM, **drop ~300 seconds** *Actual drop temps varied 142-160°C*
	Process oil	30		
	6PPD	2		
	ZnO	5		
	Stearic acid	1		
	Ultra Blend 4000	5		
Final	Rubbermakers sulfur	2	45RPM **Drop at 100°C** *Actual mix times 162-252 seconds*	Pre-heat 49°C, 45RPM, **drop ~300 seconds** *Actual drop temps 81-91°C*
	TBBS	0.75		

Peptisers evaluated

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Formulated?	Peptizer	DBD (%)	Other content	Physical form	ACE DBD (PHR)	Smithers DBD (PHR)
Unformulated	Pepton 22	100%	-	Powder	0.25, 0.50*	0.25
	Pepton 22 + carrier	50%	Carrier (added separately)	Powder	0.25, 0.50*	0.25
Formulated	Pepton 44	50%	Carrier, activator	Powder	0.25, 0.50*	0.25
	Pepton 62	40%	Carrier, activator, dispersant	Oiled powder	-	0.25
	Pepton 82	25%	Carrier, activator, dispersant	Oiled powder	-	0.25
	Pepton 66	40%	Carrier, activator, dispersant	Pellets	-	0.25

*0.50PHR DBD is higher than recommended level

To simplify the presentation, we will focus on **Pepton 22** and **Pepton 44**

ACE study - mix profile, time savings and viscosity impact

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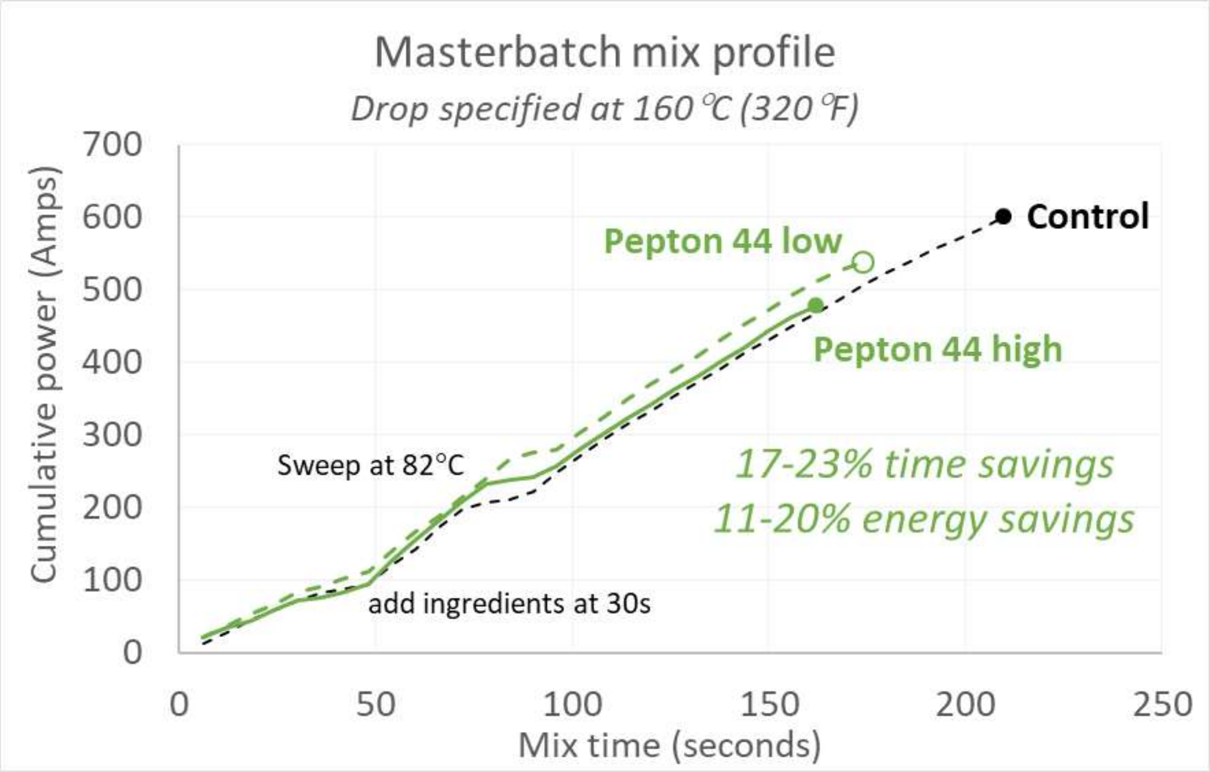
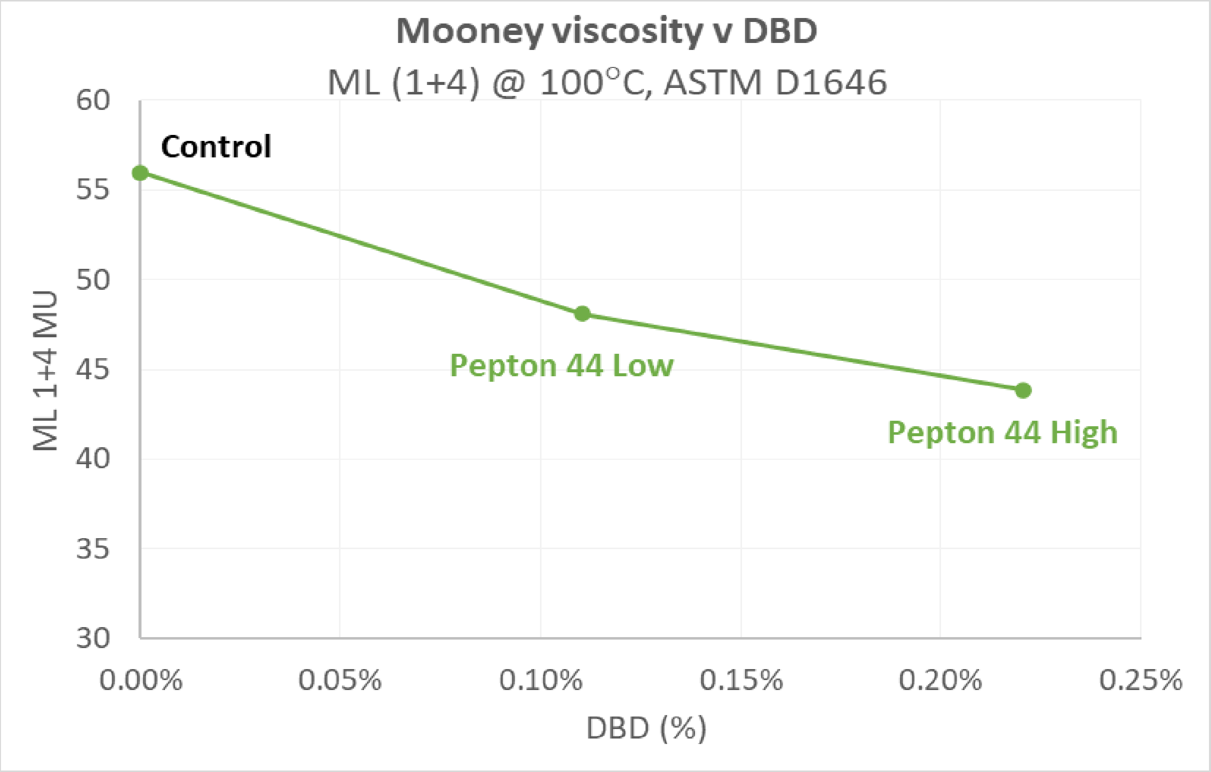
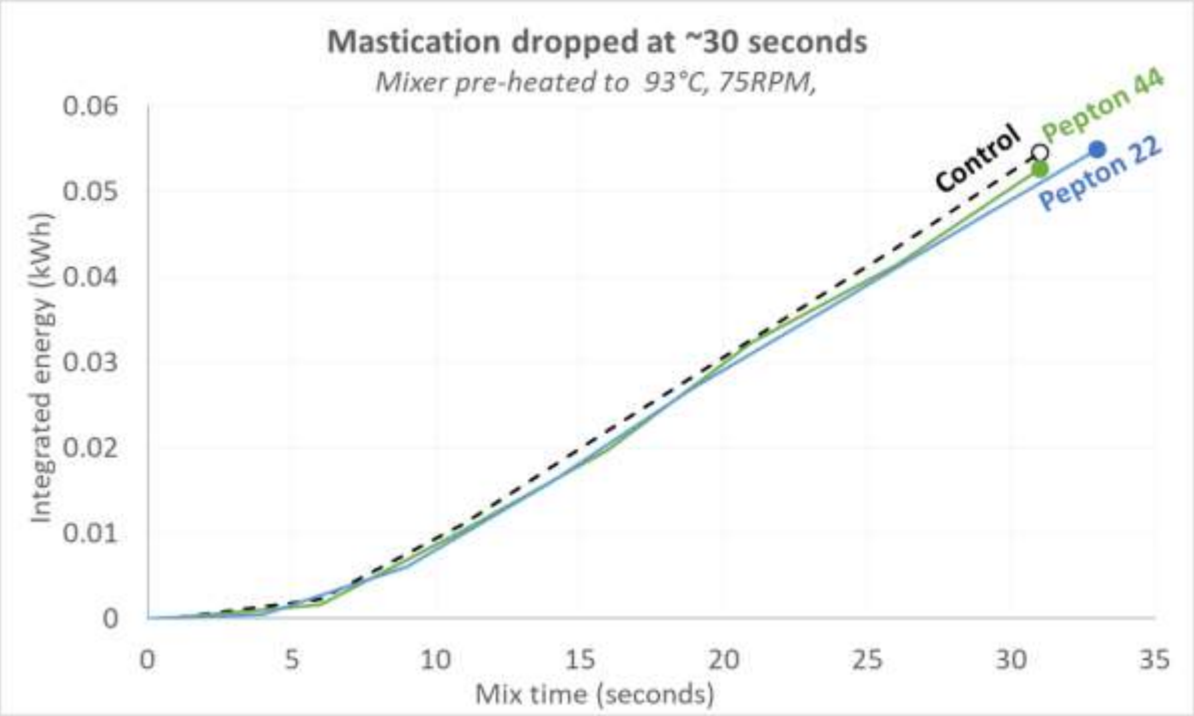
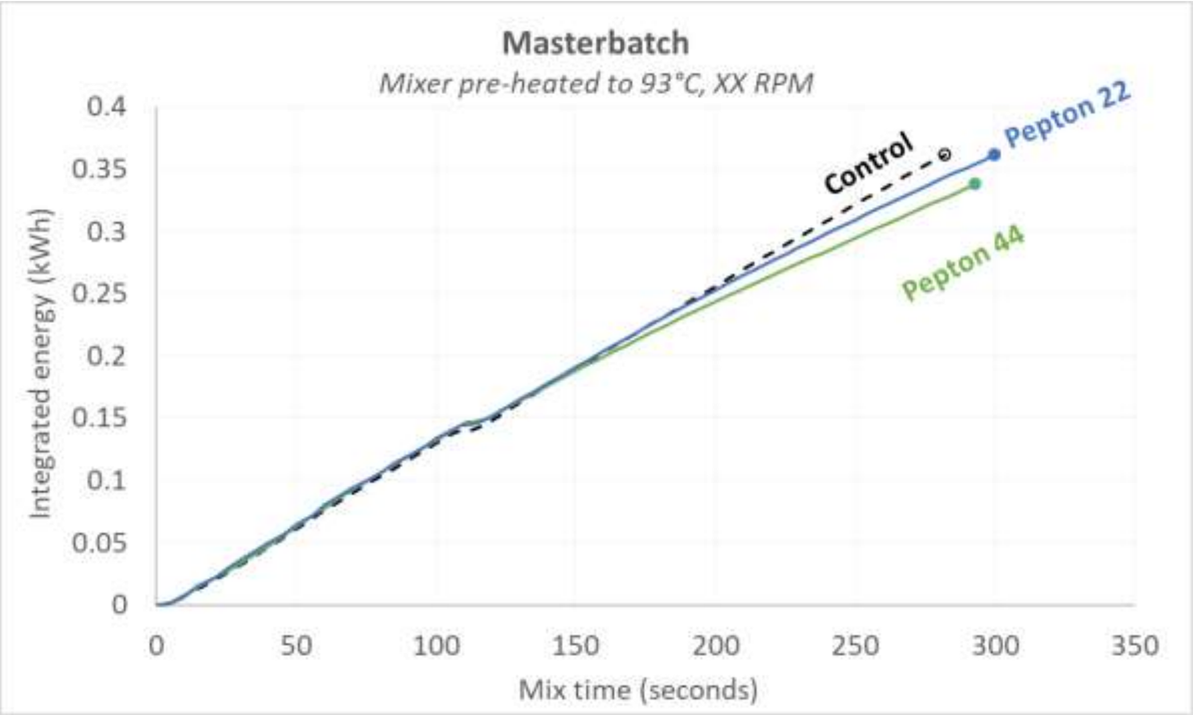




Pepton achieved lower viscosities with less mix time and energy

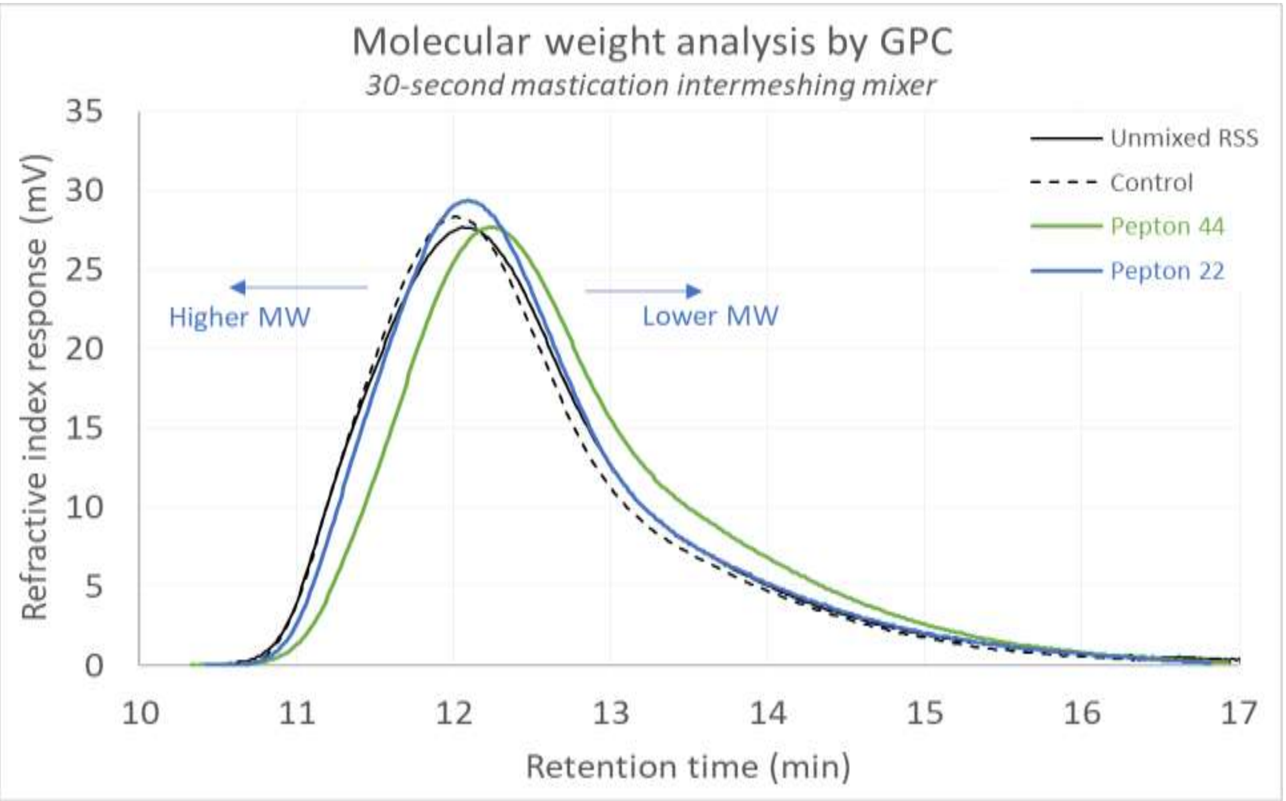
Smithers study - mix profile





- The Smithers mixes were longer (not dropped at a specific temperature)
- Intent – longer mix time to see differences in various versions of Pepton

Effect on molecular weight



Control compound

- Minimal impact on molecular weight

Pepton 22 (100% DBD)

- Less Mw impact within 30 seconds

Pepton 44 (formulated)

- Measurable Mw reduction
- Mechanism → carrier ingredients cause faster dispersion

- Pure mastication → polymer and peptizer only in 30-second intermesh lab mix
- *GPC analysis cannot be performed when carbon black is present*

Smithers study - viscosity and time savings

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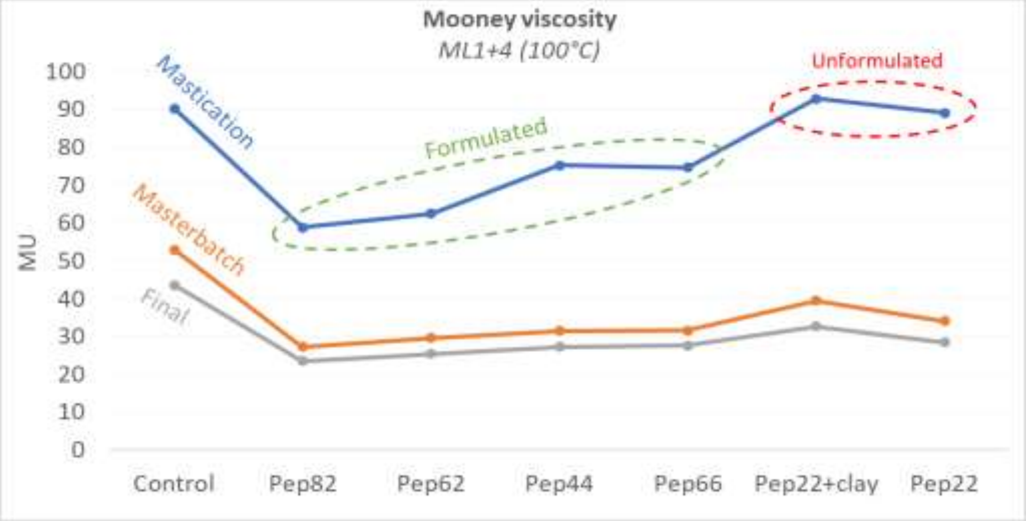
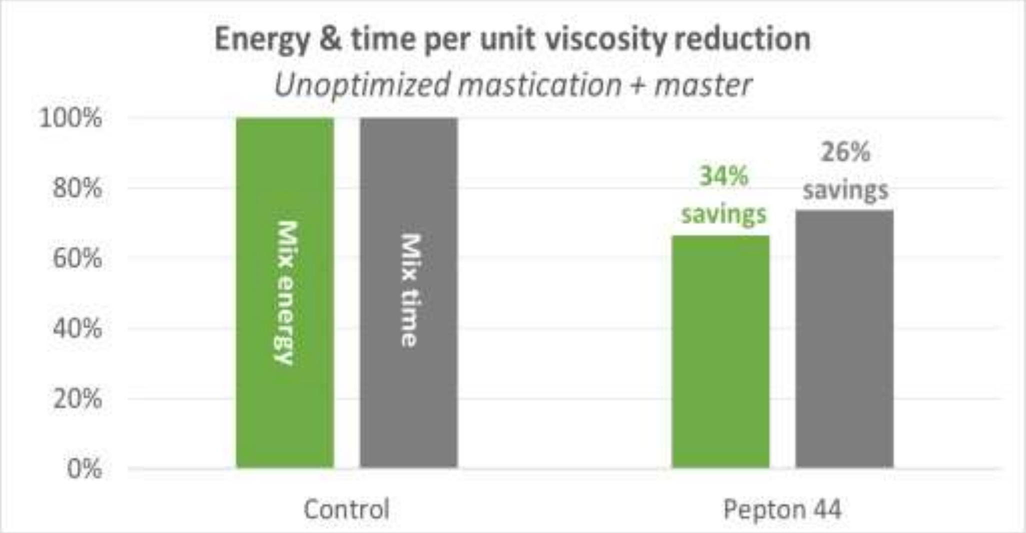




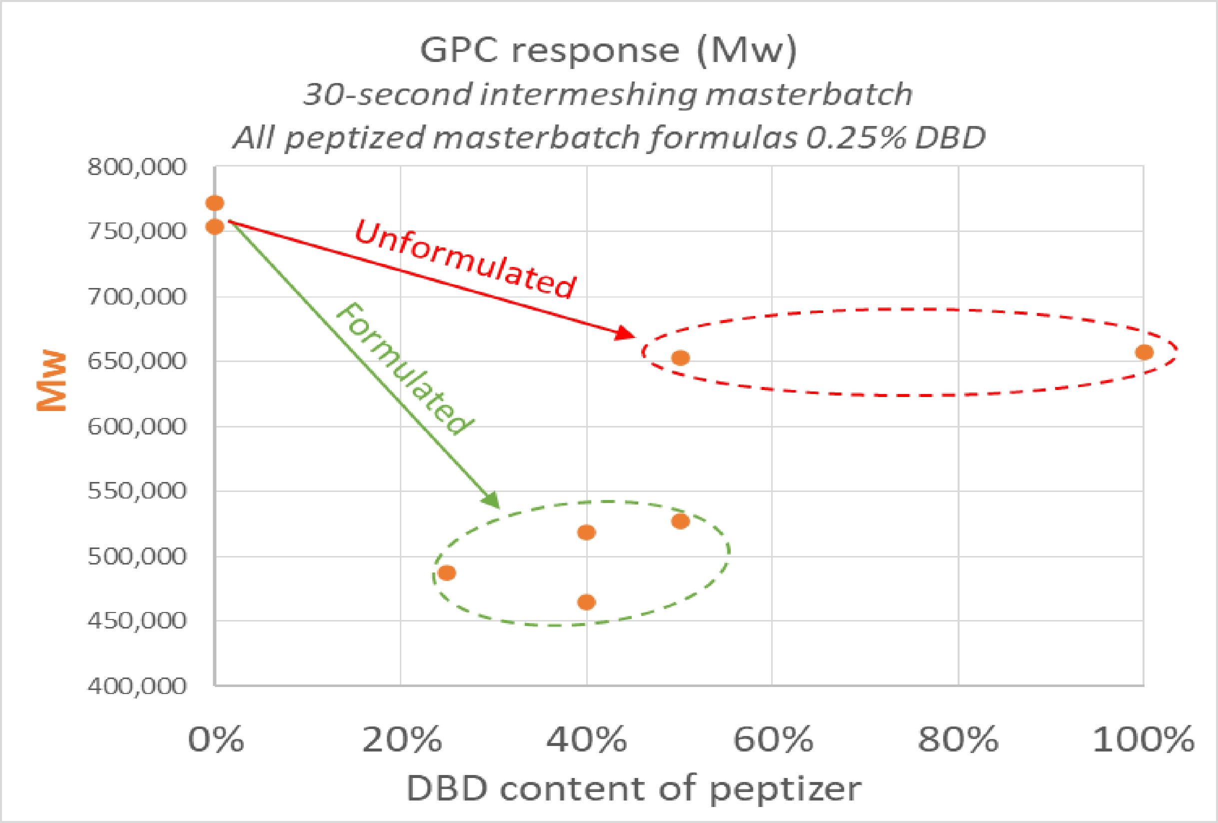
<u>Observation</u>

- Formulated Pepton products seem to reduce viscosity earlier, likely due to faster dispersion
- Unformulated versions continue to work in the masterbatch *in the presence of other ingredients*

<u>Time and energy savings</u>

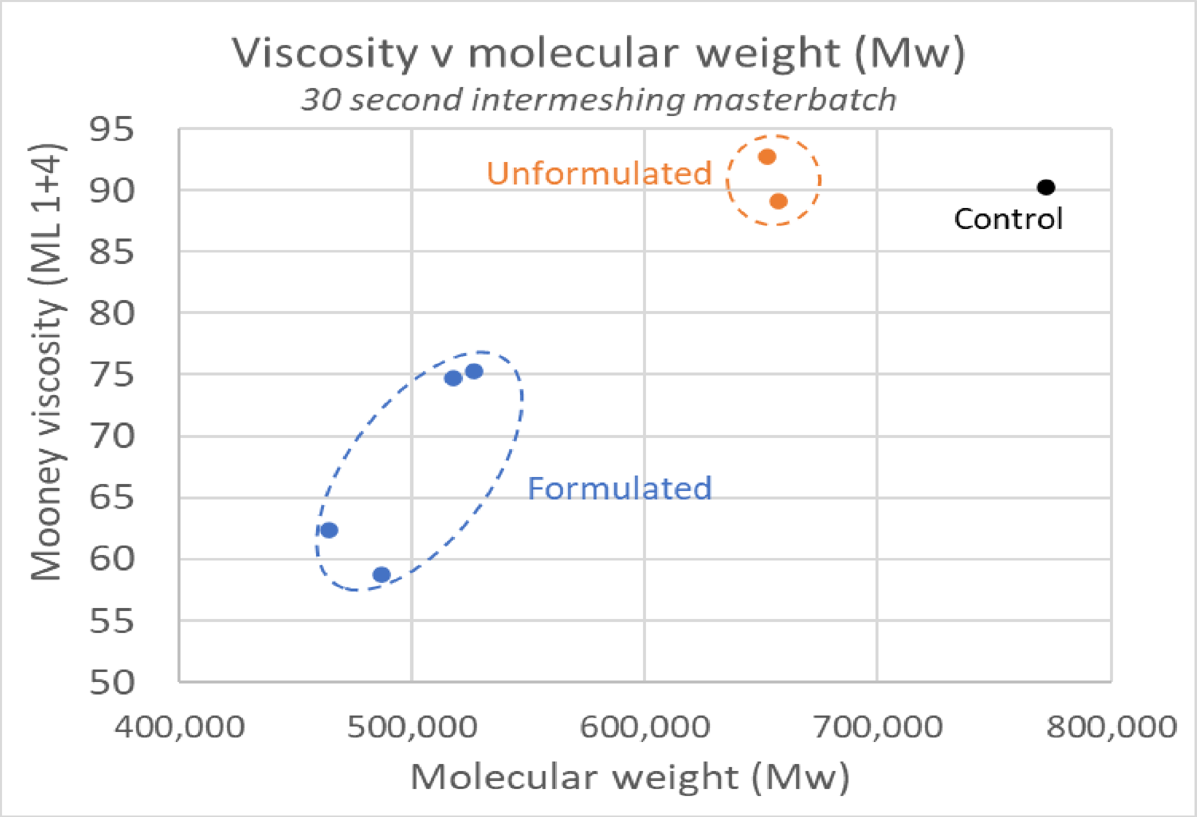
- *Pepton saves measurable time and energy per unit viscosity reduction*
- *Customers who have optimized their mix process report over 40% mix time savings*

Molecular weight impact on viscosity



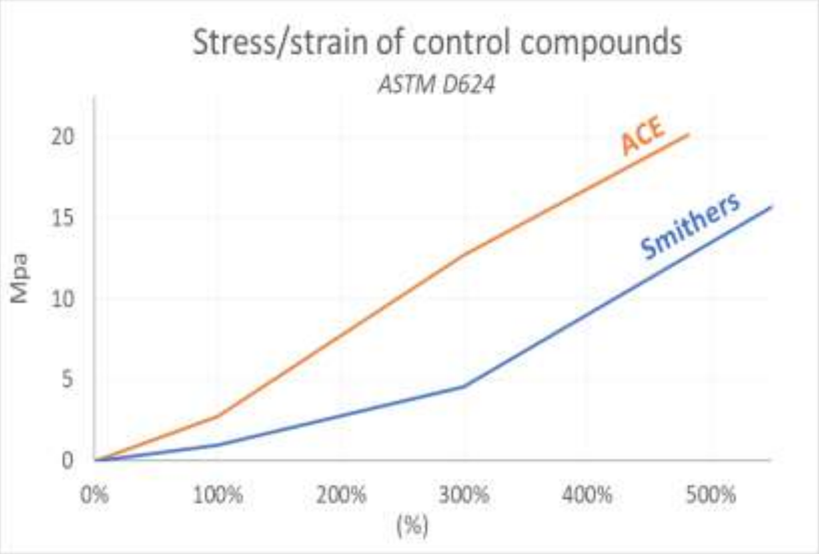
- All Pepton versions showed measurable reduction in Mw after 30-second mastication
- Formulated Pepton versions show higher Mw impact than unformulated (DBD)

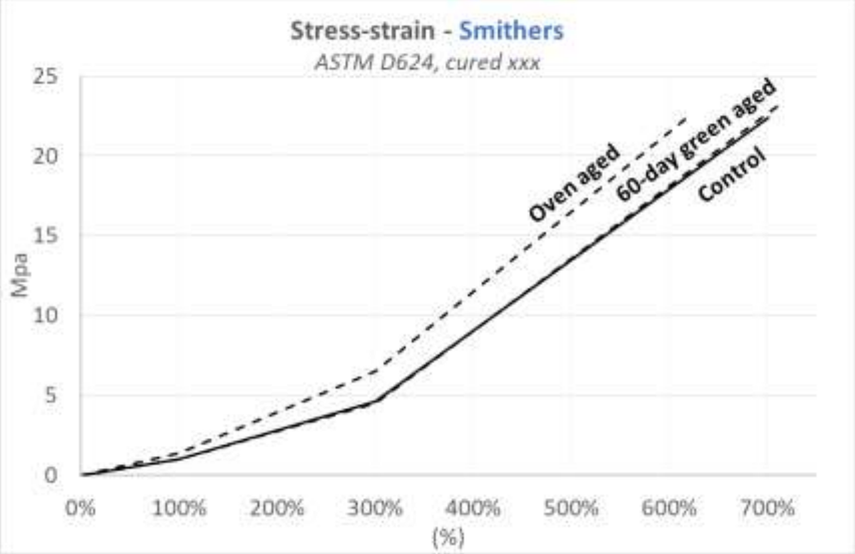
Molecular weight impact on viscosity

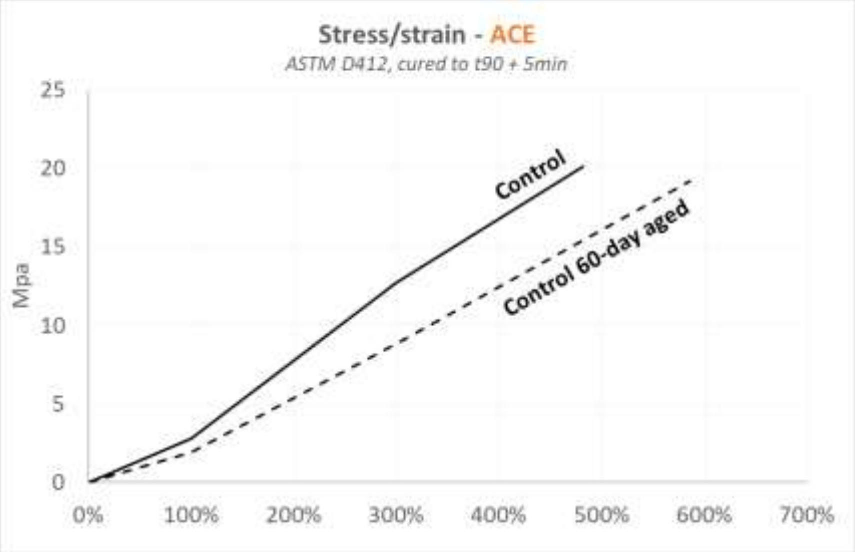


- Correlation between Mw and mastication stage viscosity
- Formulated Pepton versions show higher Mw impact than unformulated (DBD)

Stress strain results







Very different mix conditions yielded very different stress-strain curves

<u>60-day RT green aging</u>

- ACE showed lower-than-original S/S properties after uncured compound sat for 61 days at RT
- Smithers sample was unaffected

<u>2-day 100°C oven aging</u>

- Not done at ACE
- Smithers sample showed expected increase in modulus

Aged stress strain

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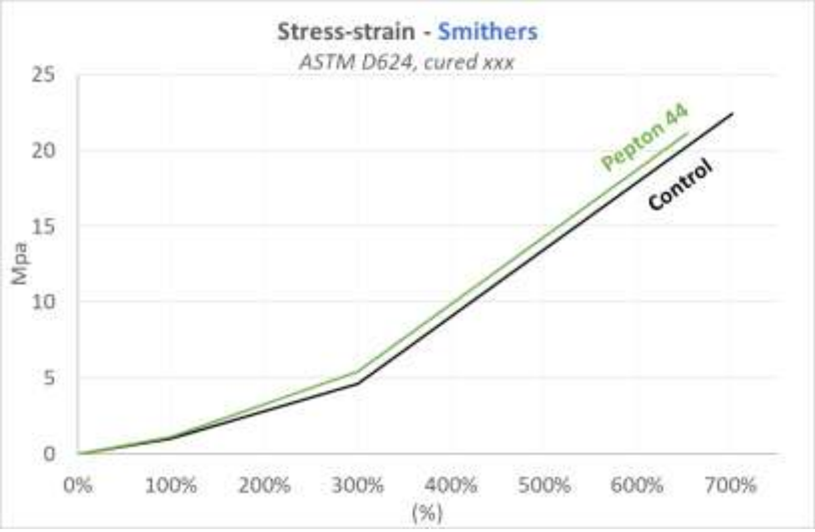
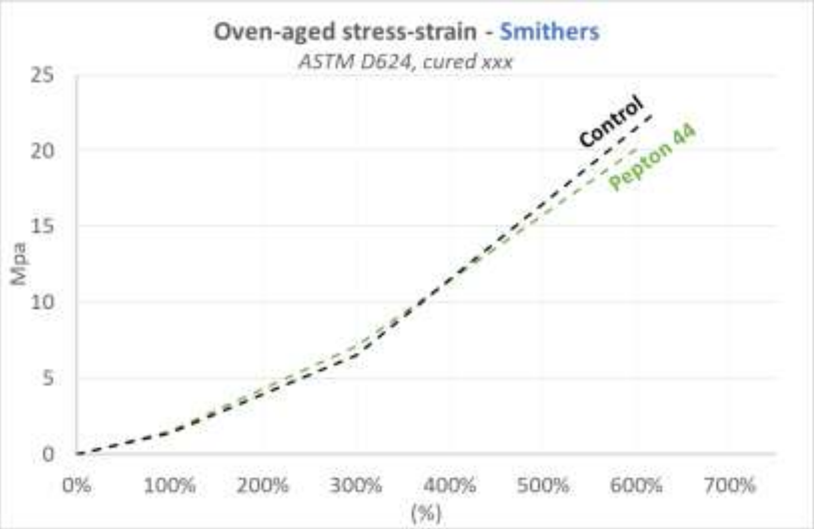
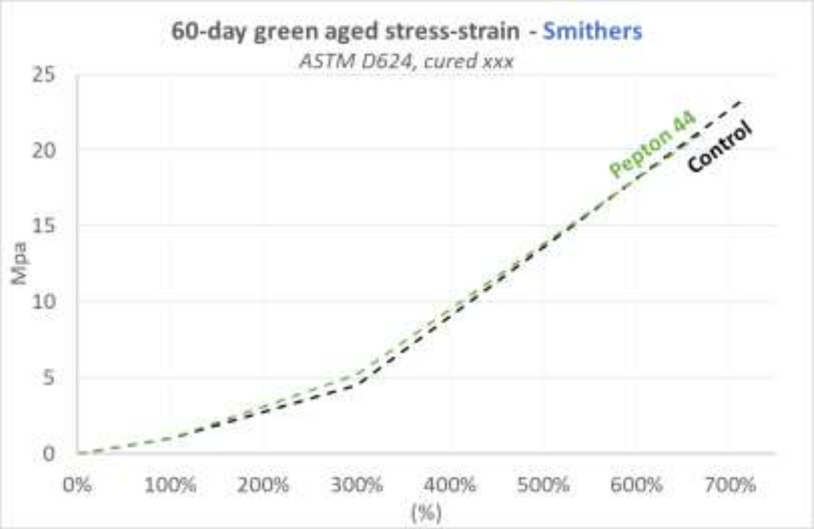
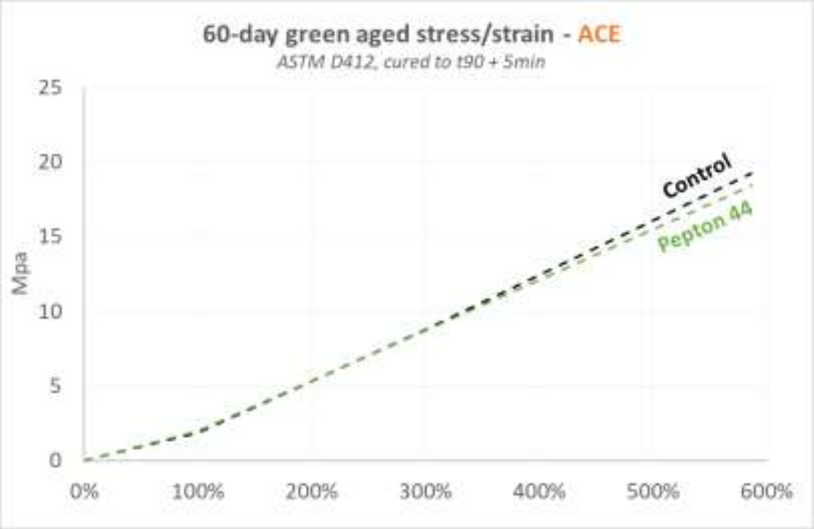






Pepton showed no negative effect on any aged or original S/S properties



Viscoelastic Properties

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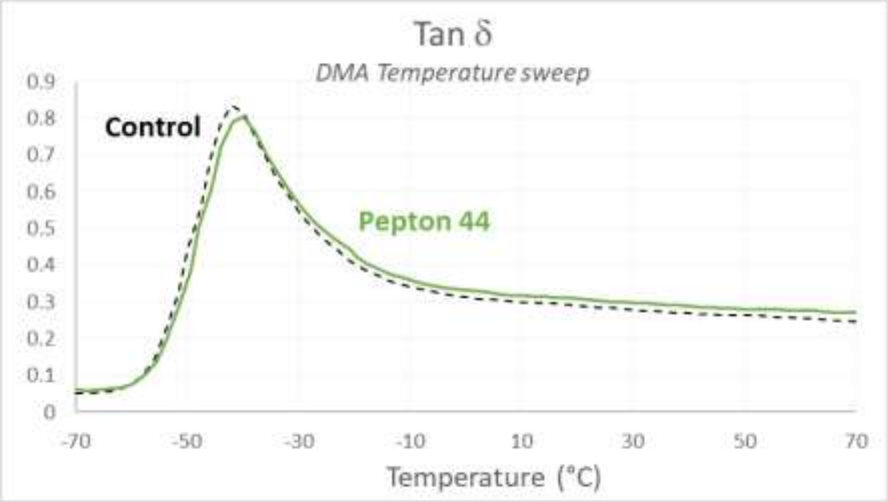
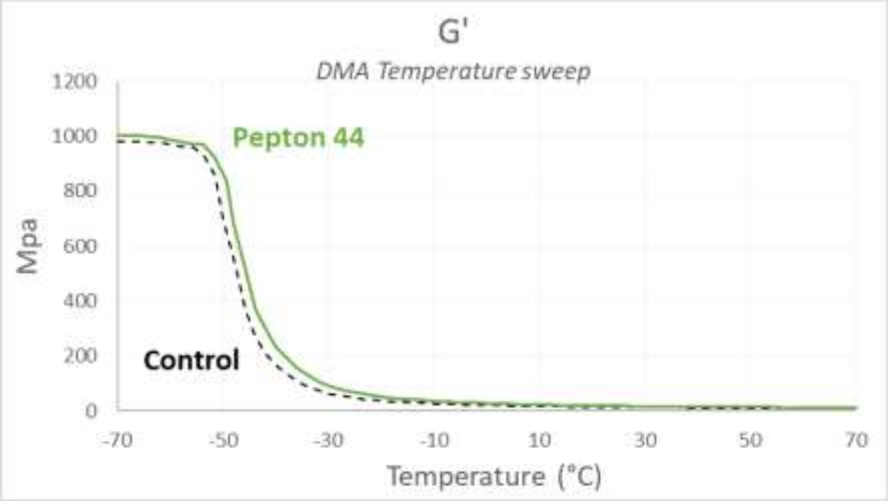
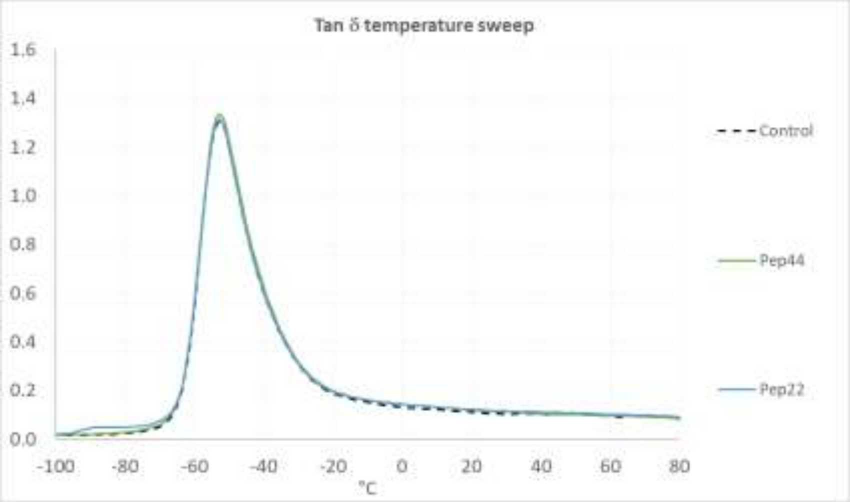
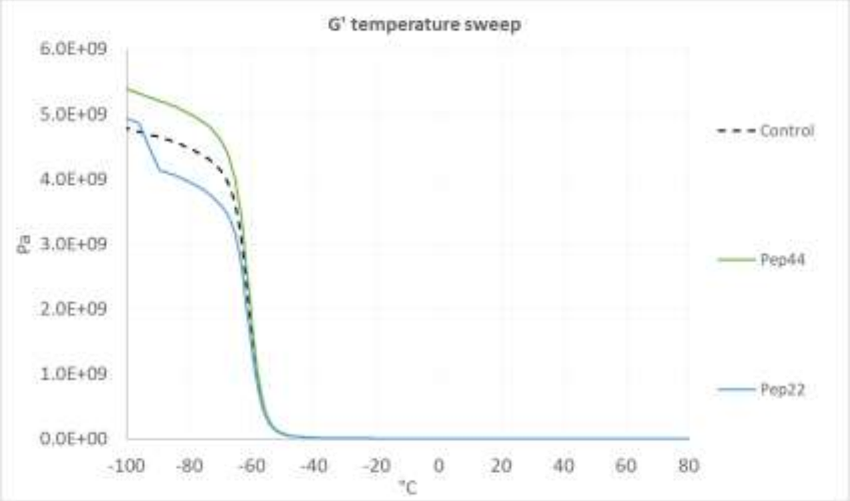




Pepton showed insignificant effect on tire performance parameters

DMA Tire Performance Predictors
G', Storage Modulus at -20°C (Pa) Winter Traction (lower better)
Tan Delta at -10°C Ice Traction (higher better)
Tan Delta at 0°C Wet Traction (higher better)
Tan Delta at 30°C Rolling Resistance (lower better)
G', Storage Modulus at 30°C (Pa) Dry Handling (higher better)
J", Loss Compliance at 30°C (1/Pa) Dry Traction (higher better)
Tan Delta at 60°C Rolling Resistance (lower better)
G', Storage Modulus at 60°C (Pa) Dry Handling (higher better)





Conclusions

- **Pepton mechanism involves capturing of free radicals resulting from mixing shear**
  - *Molecular weight reduction was observed*
  - *Viscosity reduction was faster than unpeptised control formulae*

- **Significant mix time reductions are possible versus simple mastication**
  - *Formulated Pepton products worked faster than pure DBD*

- **Pepton continued to be effective in the presence of other formula ingredients**
  - *You should confirm for yourself*

- **Pepton showed no impact on compounds stored at room temperature for up to 60 days**

- **Pepton showed no impact on static or dynamic physical properties**

Thank You

Thomas Swan

Chemical manufacturing since 1926

Headquarters & Manufacturing Site

Consett, UK

Offices & Warehousing

New Jersey / Akron , US

Offices & Warehousing

Shanghai, China

Appendix

Smithers test methods

Test	Method	Cure conditions	Test and age conditions	Details
Mooney viscosity	ASTM D1646	-	ML 1+4 at 100°C	
Mooney Scorch	ASTM D1646	-	30 Min @ 125°C	
MDR	ASTM D5289	-	30 Min @ 145°C	
Stress/strain and aged S/S	ASTM D412	145°C Tc90+5 min	48 hours at 100°C	Average of 5 samples
60-day uncured aged stress/strain	ASTM D412	145°C Tc90+5 min	60 days at RT	Average of 5 samples
Tear & aged tear	ASTM D624	145°C Tc90+5 min	48 hours at 100°C	Average of 3 samples
DMA Temperature sweep			1 Hz, 0.25% strain, -100-80°C	

Ace test methods

Test	Method	Cure conditions	Test and age conditions	Details
Mooney viscosity	ASTM D1646	-	ML 1+4 at 100°C	
Mooney Scorch	ASTM D1646	-	30 Min @ 125°C	
MDR	ASTM D5289	-	30 Min @ 145°C	
Stress/strain	ASTM D412	145°C Tc90+5 min	-	Average of 5 samples
60-day uncured aged stress/strain	ASTM D412	145°C Tc90+5 min	60 days at RT	Average of 5 samples
Tear	ASTM D624	145°C Tc90+5 min	-	Average of 5 samples
DMA Temperature sweep			10 Hz, 0.50% strain, -70-70°C	