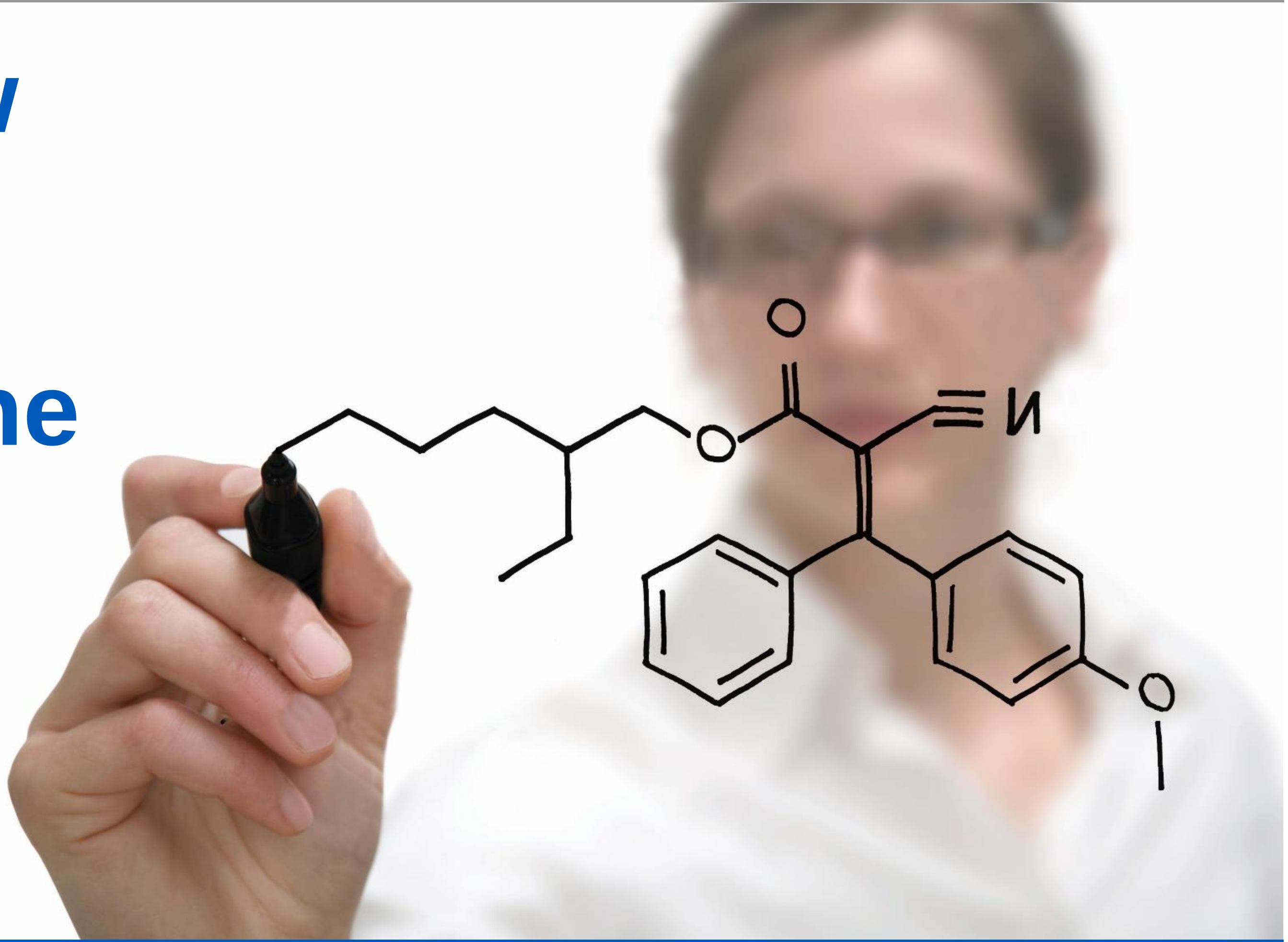
Development of New Generation of Ester Plasticizers for High Temperature Ethylene Acrylic Elastomers



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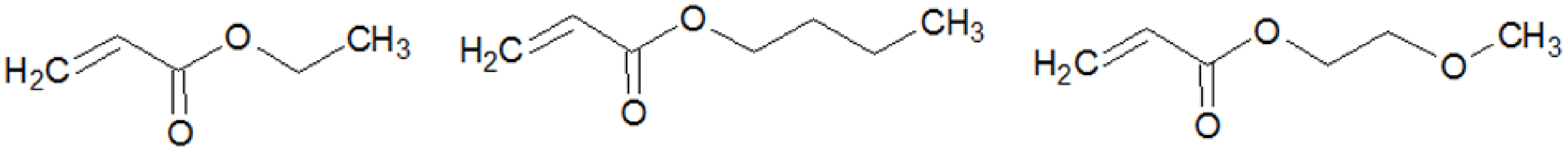
Agenda

- Background on EAM elastomers
- Plasticizer for high-temperature AEM applications
- Goal of the project
- Overview of the experimental plan
- Results and discussion
- Conclusions
- Acknowledgements

Background on AEM Elastomers

- AEM are used in applications requiring continual service up to 175°C and intermittent exposure to extremely high temperatures of up to 200 °C
- Lower cost alternatives to FKM and FVQM
- Exhibit improved high temperature resistance over HNBR and ECO
- There are two well known types:
  - ACM (**A**crylic **C**o-**M**onomer)
  - AEM (**A**crylic-**E**thylene **M**onomer)



Ethyl Acrylate   n-Butyl Acrylate   2-Methoxyethyl Acrylate

Background on AEM Elastomers

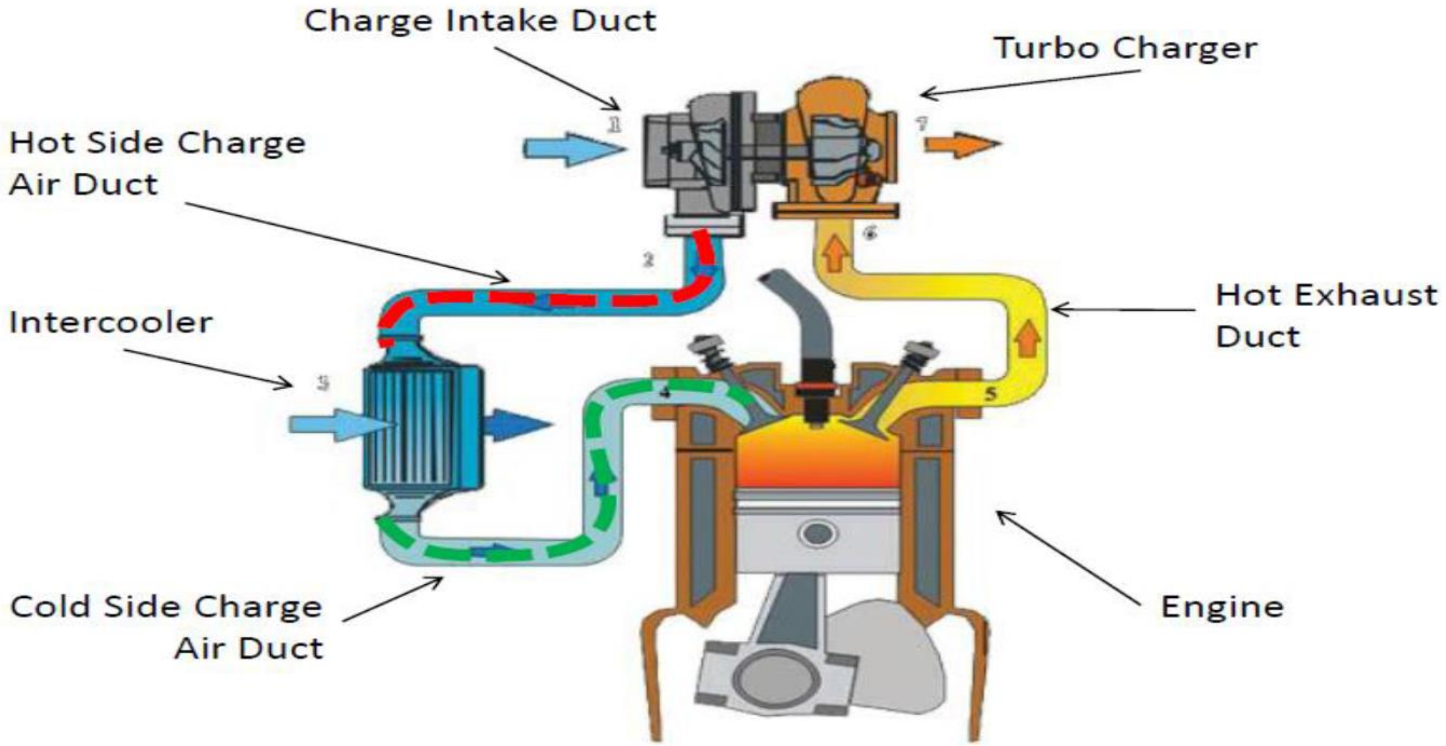
- Conventional CB and Silica fillers provide stiffness in AEM compounds but
  - Accelerate oxidative degradation
  - Reduce thermal stability
- DuPont™ developed novel melt-blending technology which allowed reinforcement of AEM with a dispersion of grafted PA6 droplets
- DuPont™ VMX 5000 elastomers are based on amine cure system
- Result is a strong, heat-resistant elastomer compound with good heat-aging and compression set properties
- Enhanced performance is due to
  - Extensive AEM-PA6 grafting
  - Absence of filler-filler contacts
  - Beneficial modification of oxidation profile under diffusion-limited conditions

Plasticizer for high-temperature AEM applications

- Highly polar AEM elastomers require higher-polarity ester plasticizers to assure optimal compatibility
- Due to the high post-cure and application temperature requirements few plasticizer have found utility in demanding AEM applications
- Polar monomeric plasticizer have good low temperature properties but suffer from higher weight losses during high temperature aging
- Polar high MW plasticizer have good permanence but lack optimal low temperature flexibility

Goal of the Project

- To develop new generation of high-performance ester modifiers and help expand modifier options for the acrylic elastomer market.



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Experimental Plan – Part I

Material	Wt (phr)	% in the formula
Vamac™ Ultra IP [a]	45	28.64%
Vamac™ VMX 5015 [a]	100	63.65%
N550 Carbon Black [b]	2	1.27%
ADPA Anti-oxidant [c]	1.4	0.89%
Vanfre VAM [d]	0.5	0.32%
Stearic Acid	0.5	0.32%
Plasticizer	5	3.18%
DIAK™-1 [d]	0.7	0.45%
Vulcofac ACT 55 [e]	2	1.27%
Total	**157.1**	**100%**

[a] *Provided by DuPont Performance Elastomers*
[b] *Provided by Sid Richardson*
[c] *N-Phenyl-p-Phenyldiamine (CAS#101-54-2) purchased from Sigma-Aldrich*
[d] *Vanderbilt Chemicals LLC*
[e] *Provided by Safic-Alcan*

SAMPLES USED IN THIS STUDY

TegMeR® 812	- lower MW polyether ester
RX-14434	- higher MW polyether ester
RX-14562	- aliphatic polyester
RX-14565	- aromatic polyether ester

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Testing

Mooney Viscometer	ASTM D1646-94, viscTECH+, large rotor, 1 minute Preheat
Oscillating Disc Rheometer	ASTM D2084-93, RheoTECH Rheometer, round die, 3° Arc, 30 sec preheat. MH at central point of torque rise, rate – one lb., 2.5 cm / 5 min
Original Properties	
Tensile, Elongation, Modulus	ASTM D412-92, Method A, Die C, Crosshead speed 51.0 cm/min
Hardness	ASTM D2240-91, 1s reading
Specific Gravity	ASTM D792-91
Low Temperature	
Gehman	ASTM D1053
T_g by DSC	Perkin Elmer Diamond DSC Temperature ramp of -100 to 70 °C at 20 °C/min
Air Oven Aging	ASTM D573-81
Compression Set	ASTM D395, Test Method B

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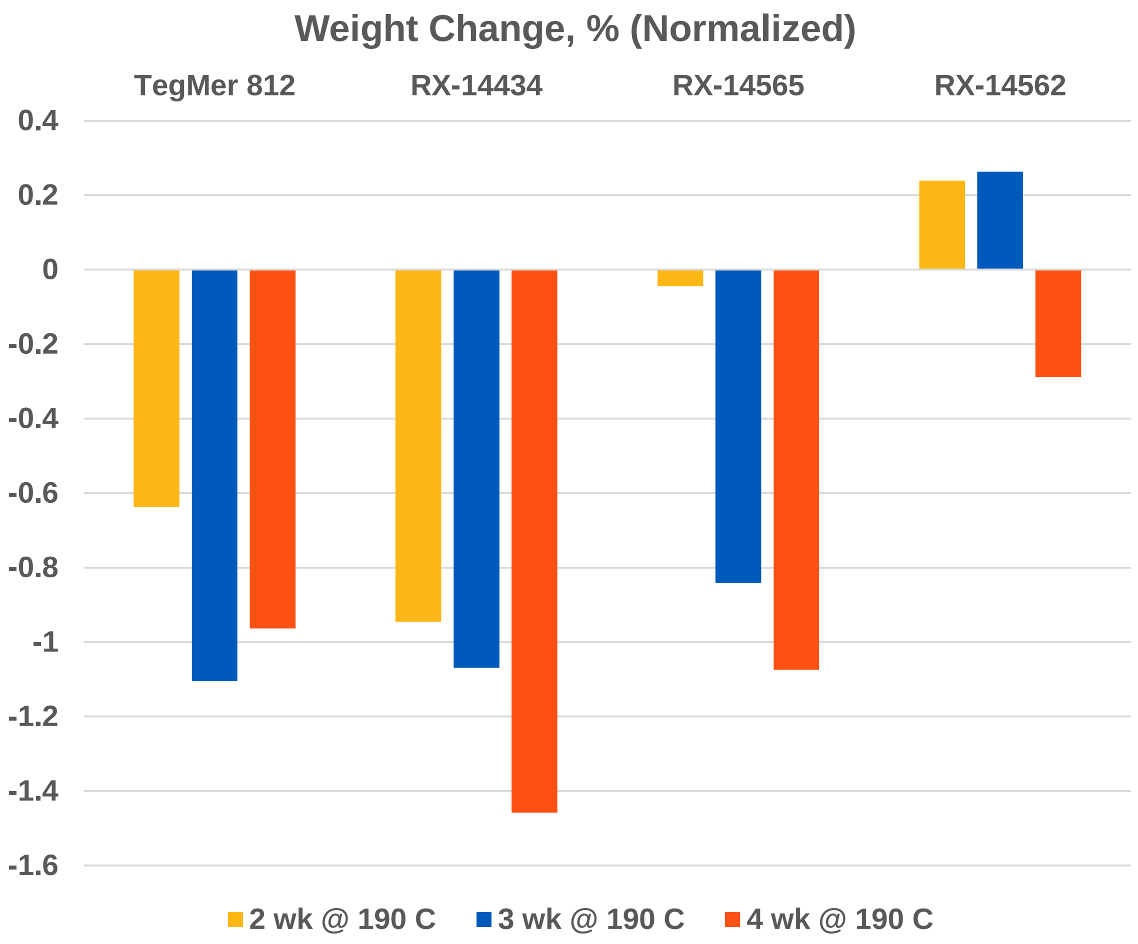
Original Properties – Part I

	TegMeR 812	RX-14434	RX-14565	RX-14562	No plasticizer
Stress @ 100% Elongation, MPa	2.1	2.0	2.4	2.2	3.0
Stress @ 200% Elongation, MPa	5.6	6.2	7.1	6.6	9.1
Stress @ 300% Elongation, MPa	10.3	11.9	12.6	12.1	15.1
Tensile Ultimate, MPa	13.8	15.6	14.6	14.6	16.2
Elongation @ Break, %	382	367	348	359	318
Hardness Duro A, pts.	60	60	63	58	65
Specific Gravity	1.078	1.078	1.078	1.078	1.079

Heat Aging – Weight Change, Part I



- Neat AEM polymer exhibited some weight loss so all of the data were normalized.
- Normalized data helped elucidate performance differentiation between the 4 samples used in this study

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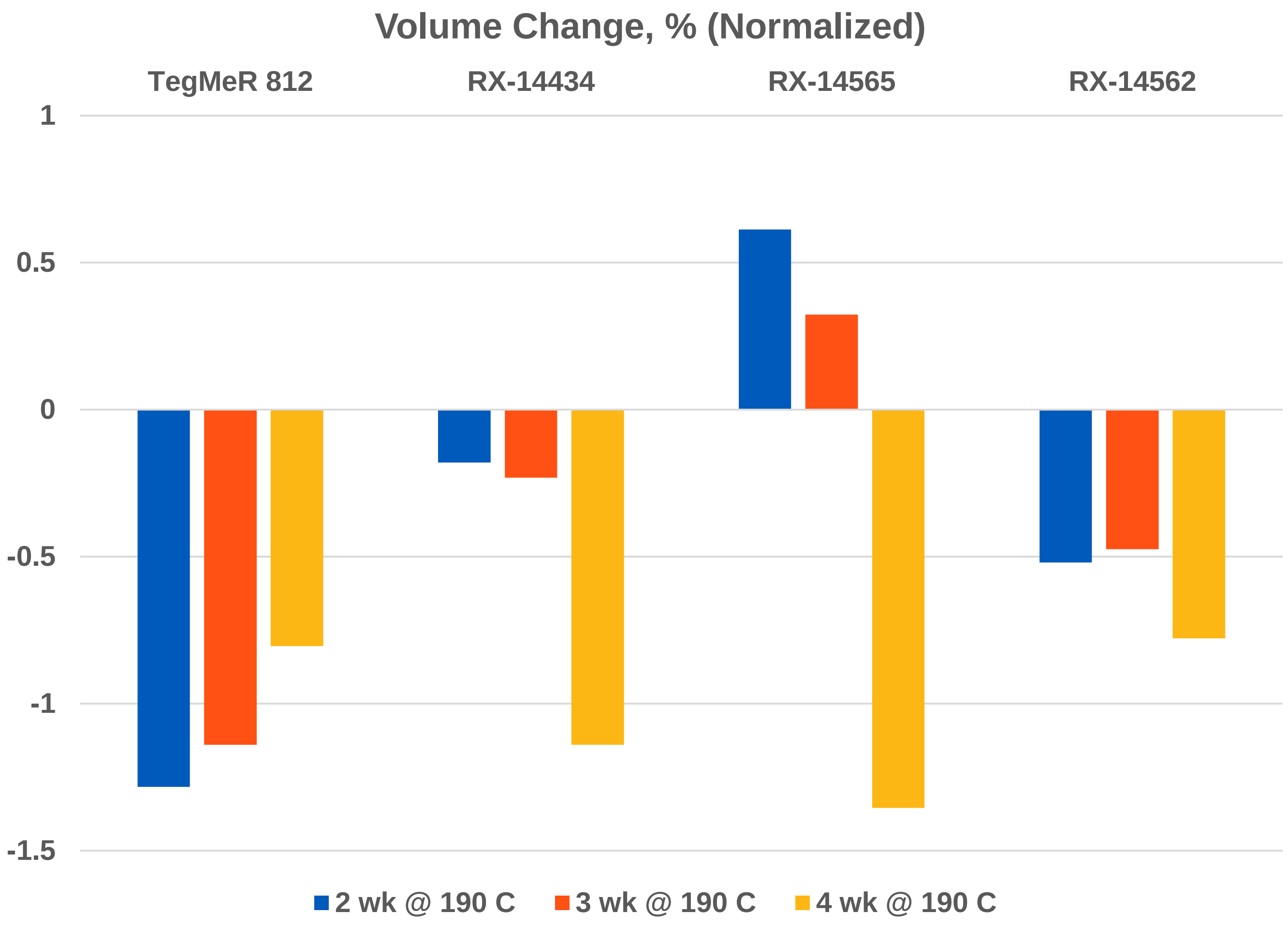
Heat Aging – Volume Change, Part I



- The compounds showing a weight or volume “gain” are at low enough levels as to be considered equivalent with the control compound, effectively losing no weight or volume due to plasticizer loss

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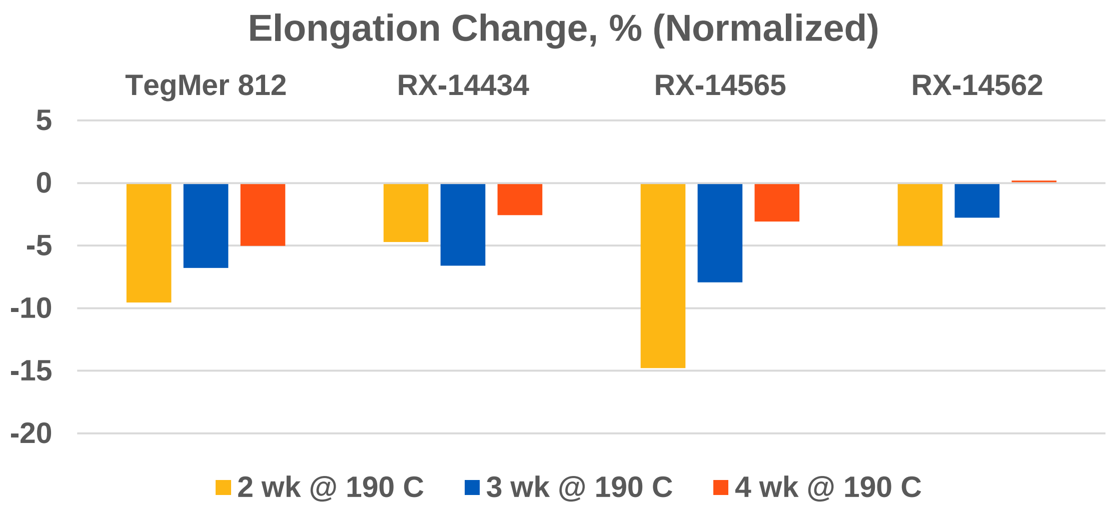
Heat Aging – Changes in Elongation, Part I

Recipe Variable	TegMeR® 812	RX-14434	RX-14565	RX-14562	Control
Elongation at Break					
Original, %	382.4	366.9	347.7	358.9	318.3
Air Oven, 2 wk @ 190 °C, % change	-45.5	-40.7	-50.8	-41.0	-36.0
Air Oven, 3 wk @ 190 °C, % change	-58.6	-58.4	-59.7	-54.6	-51.8
Air Oven, 4 wk @ 190 °C, % change	-68.9	-66.5	-67.0	-63.7	-63.9



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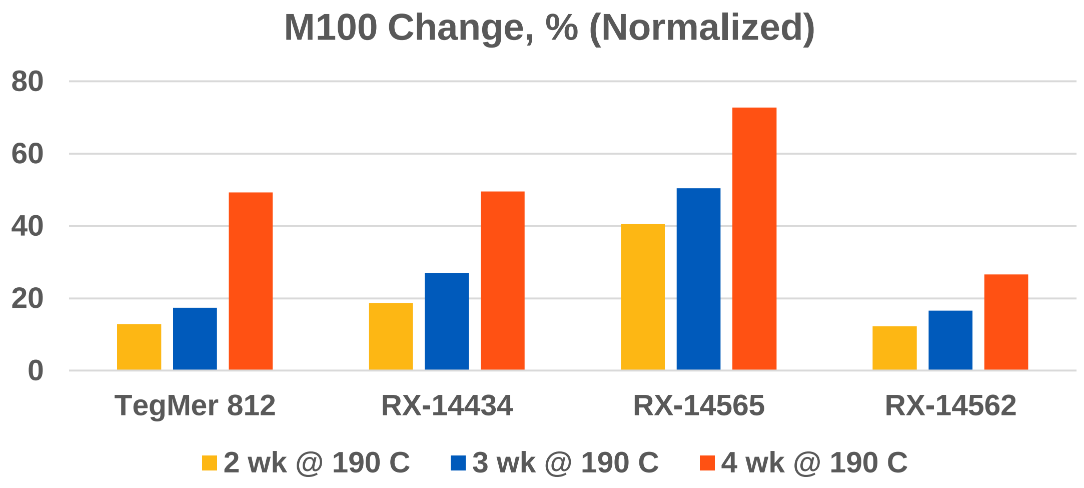
Heat Aging – Changes in Tensile Properties, Part I

Recipe Variable	TegMeR® 812	RX-14434	RX-14565	RX-14562	Control
Tensile Ultimate					
Original, psi	2004	2256	2123	2122	2347
Air Oven, 2 wk @ 190 °C, % change	-45.4	-44.7	-46.1	-46.1	-41.6
Air Oven, 3 wk @ 190 °C, % change	-56.7	-64.5	-52.5	-55.5	-59.0
Air Oven, 4 wk @ 190 °C, % change	-64.4	-66.9	-58.8	-61.3	-73.7

Plot Area



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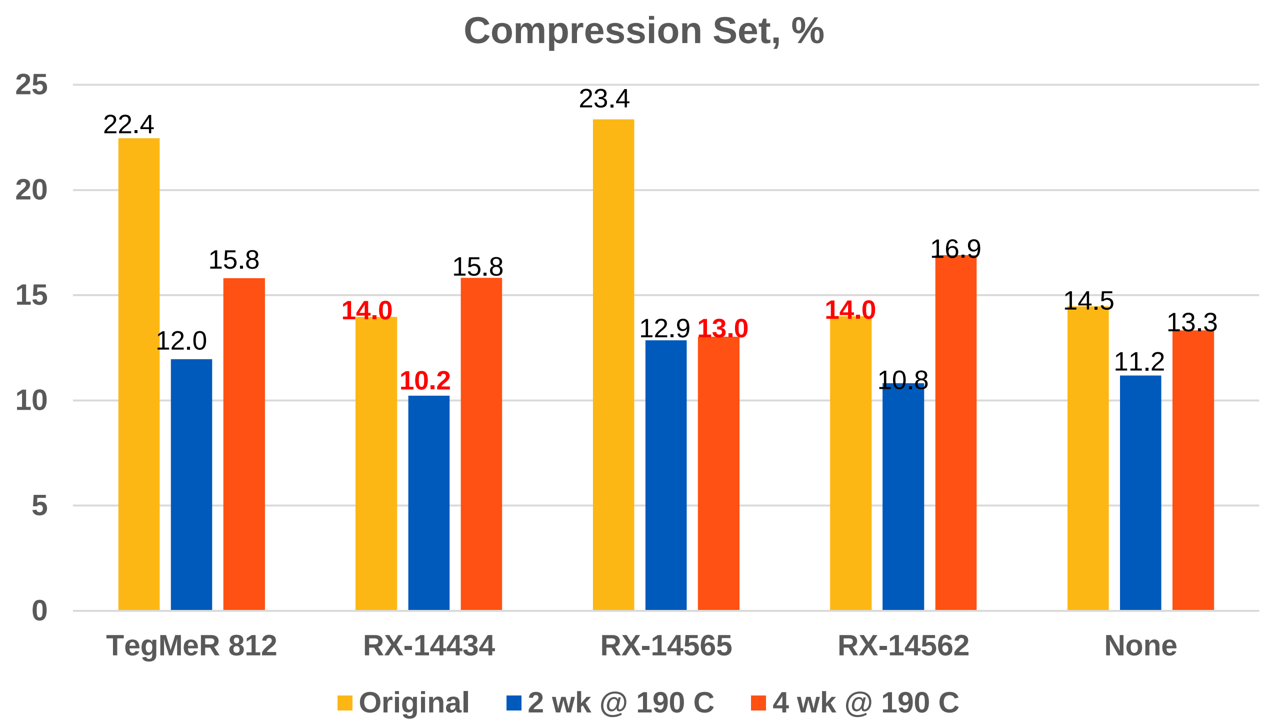
Heat Aging – Compression Set, Part I



70 hrs at 150°C, under constant deformation

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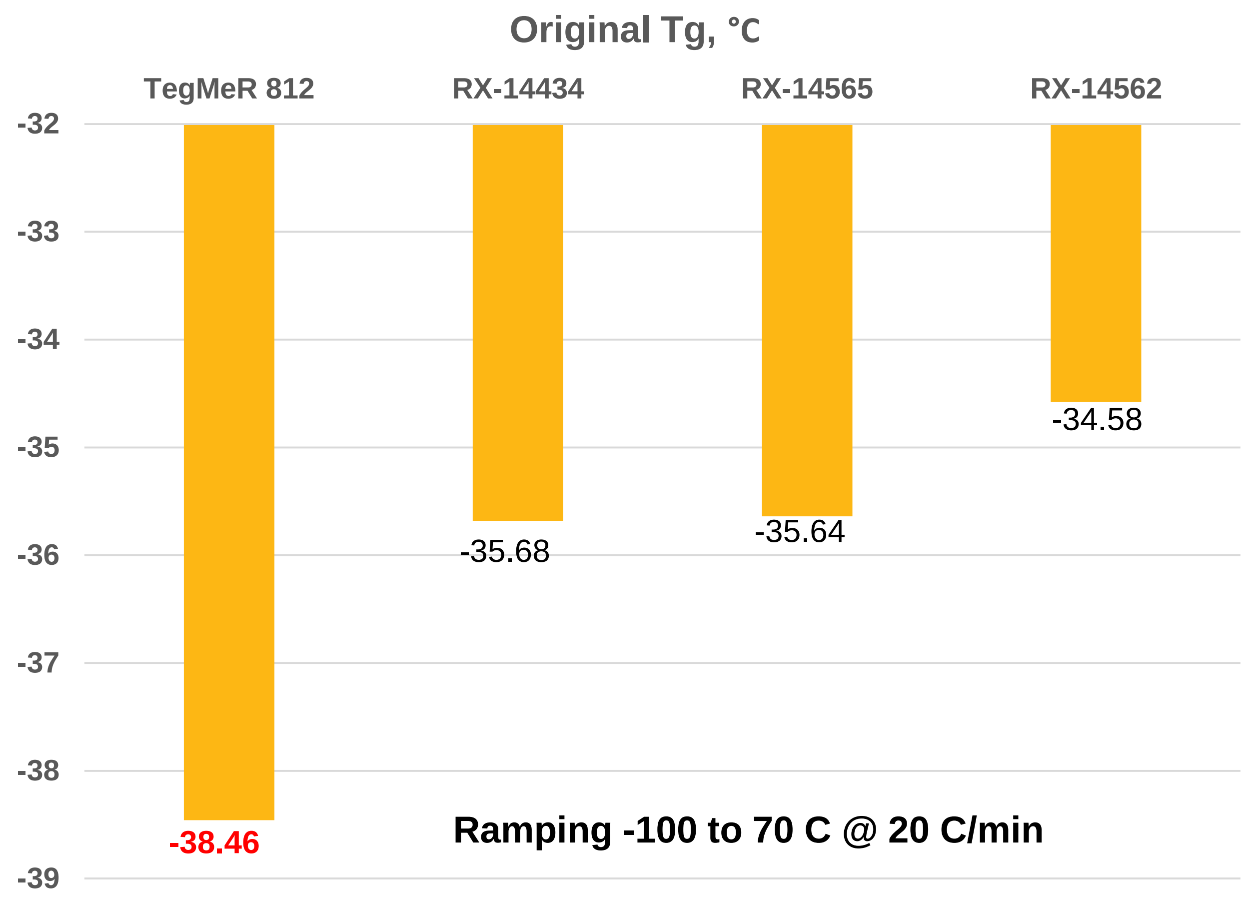
Original Tg, Part I



- As expected, TegMeR 812 is most efficient at lowering Tg compared to experimental polymeric materials
- All provide good starting Tg

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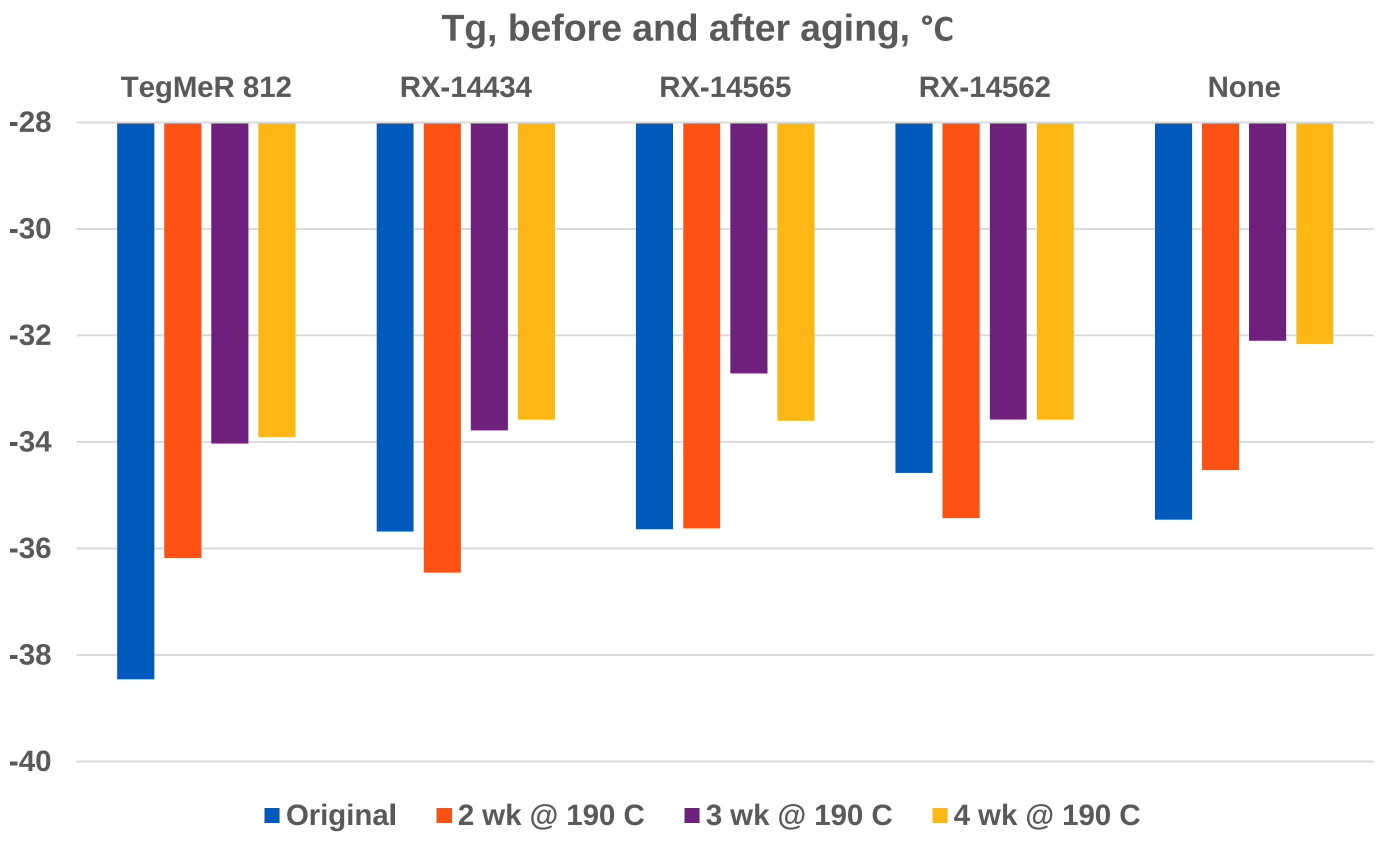
Heat Aging – Effect on Low Temperature, Part I



- TegMeR 812, while starting with the lowest Tg, loses the most performance after aging
- RX-14562 retains the best performance after aging

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Experimental Plan – Part II

Material	Wt (g)	% in the formula
Vamac™ Ultra IP [a]	36.2	21.38%
Vamac™ VMX 5015 [a]	116	68.51%
N550 Carbon Black [b]	2	1.18%
ADPA Anti-oxidant [c]	1.4	0.83%
Vanfre VAM [d]	0.5	0.30%
Stearic Acid	0.5	0.30%
Plasticizer	10	5.91%
DIAK™-1 [d]	0.7	0.41%
Vulcofac ACT 55 [e]	2	1.18%
Total	**169.3**	**100%**

[a] *Provided by DuPont Performance Elastomers*
[b] *Provided by Sid Richardson*
[c] *N-Phenyl-p-Phenyldiamine (CAS#101-54-2) purchased from Sigma-Aldrich*
[d] *Vanderbilt Chemicals LLC*
[e] *Provided by Safic-Alcan*

- Based on results from Part I, the formula was adjusted to increase plasticizer level
- RX-14562, as the best performing material in Part I, is used as a control

SAMPLES USED IN THIS STUDY

RX-14562	- medium MW aliphatic polyester
RX-14600	- lower MW aliphatic polyester
RX-14601	- higher MW polar aliphatic polyester
RX-14602	- low MW polar aliphatic polyester
RX-14603	- medium MW polar aliphatic polyester

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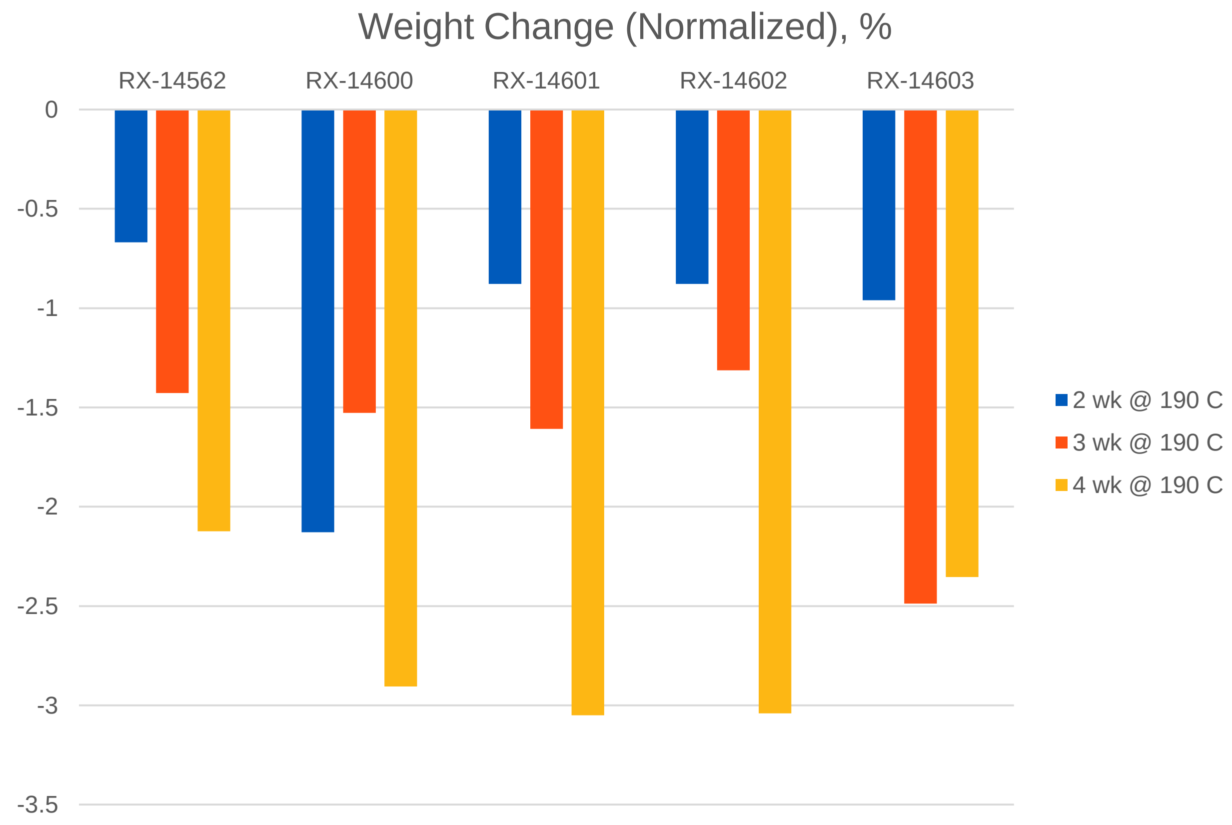
Original Properties – Part II

	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603	No Plasticizer
Stress @ 100% Elongation, MPa	2.6	2.7	3.1	2.8	2.7	4.4
Stress @ 200% Elongation, MPa	7.6	7.5	8.5	7.8	7.5	12.4
Stress @ 300% Elongation, MPa	12.8	13.2	---	13.2	12.5	---
Tensile Ultimate, MPa	13.0	14.2	13.3	13.9	13.1	16.9
Elongation @ Break, %	305	320	293	316	308	275
Hardness Duro A, pts.	59	58	59	59	57	64
Specific Gravity	1.081	1.082	1.086	1.086	1.085	1.084

Heat Aging – Weight Change, Part II



- Neat AEM polymer exhibited some weight loss so all of the data were normalized.
- Normalized data helped elucidate performance differentiation between the 5 samples used in this study

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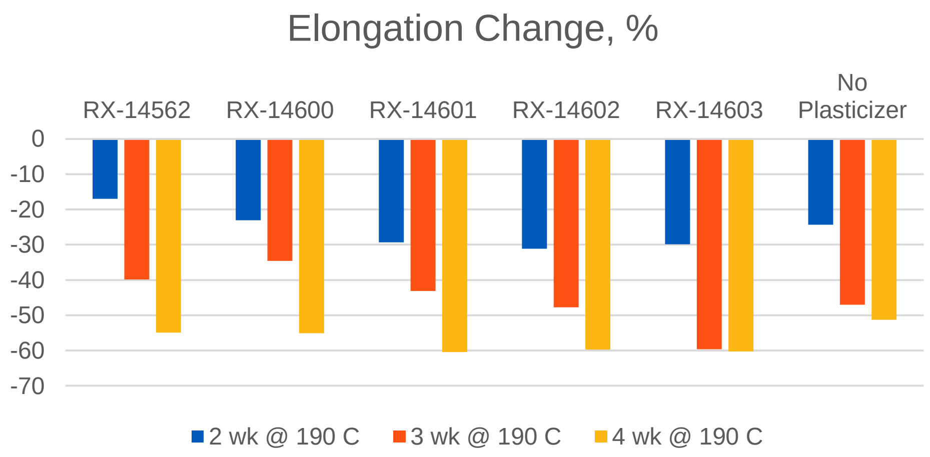
Heat Aging – Changes in Elongation, Part II

Recipe Variable	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603	Control
Elongation at Break						
Original, %	305.3	319.5	293.0	316.3	308.1	275.0
Air Oven, 2 wk @ 190 °C, % change	-17.0	-23.1	-29.4	-31.2	-29.9	-24.3
Air Oven, 3 wk @ 190 °C, % change	-39.9	-34.6	-43.1	-47.8	-59.6	-47.0
Air Oven, 4 wk @ 190 °C, % change	-54.9	-55.1	-60.4	-59.7	-60.3	-51.3



- All plasticizers show good behavior with elongation loss compared to non-plasticized control
- RX-14562 and RX-14600 show best retention of elongation after aging

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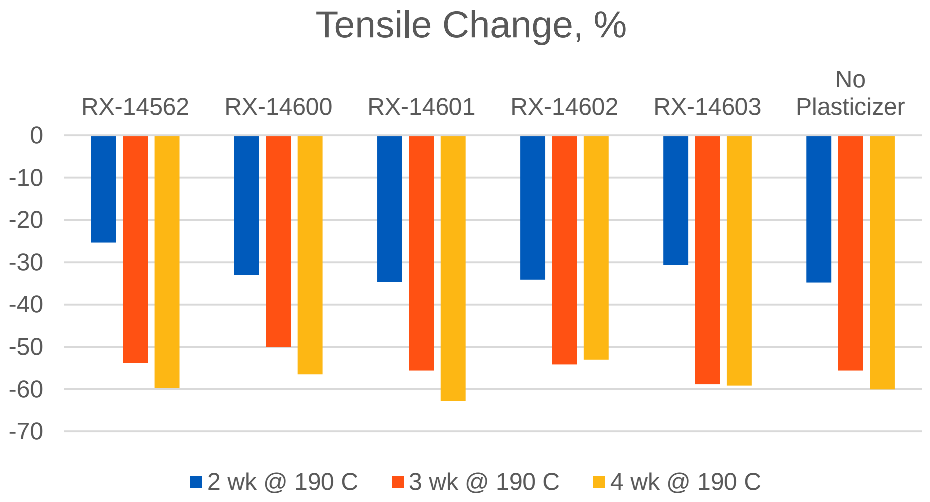
Heat Aging – Changes in Tensile Properties, Part II

Recipe Variable	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603	Control
Tensile Ultimate						
Original, psi	1892	2065	1930	2009	1896	2453
Air Oven, 2 wk @ 190 °C, % change	-25.3	-33.0	-34.7	-34.1	-30.7	-34.8
Air Oven, 3 wk @ 190 °C, % change	-53.8	-50.0	-55.6	-54.2	-58.9	-55.6
Air Oven, 4 wk @ 190 °C, % change	-59.8	-56.5	-62.8	-53.0	-59.2	-60.1



- All plasticizers show good behavior with tensile strength loss compared to non-plasticized control
- RX-14562, RX-14600, and RX-14602 show best retention of tensile strength after aging

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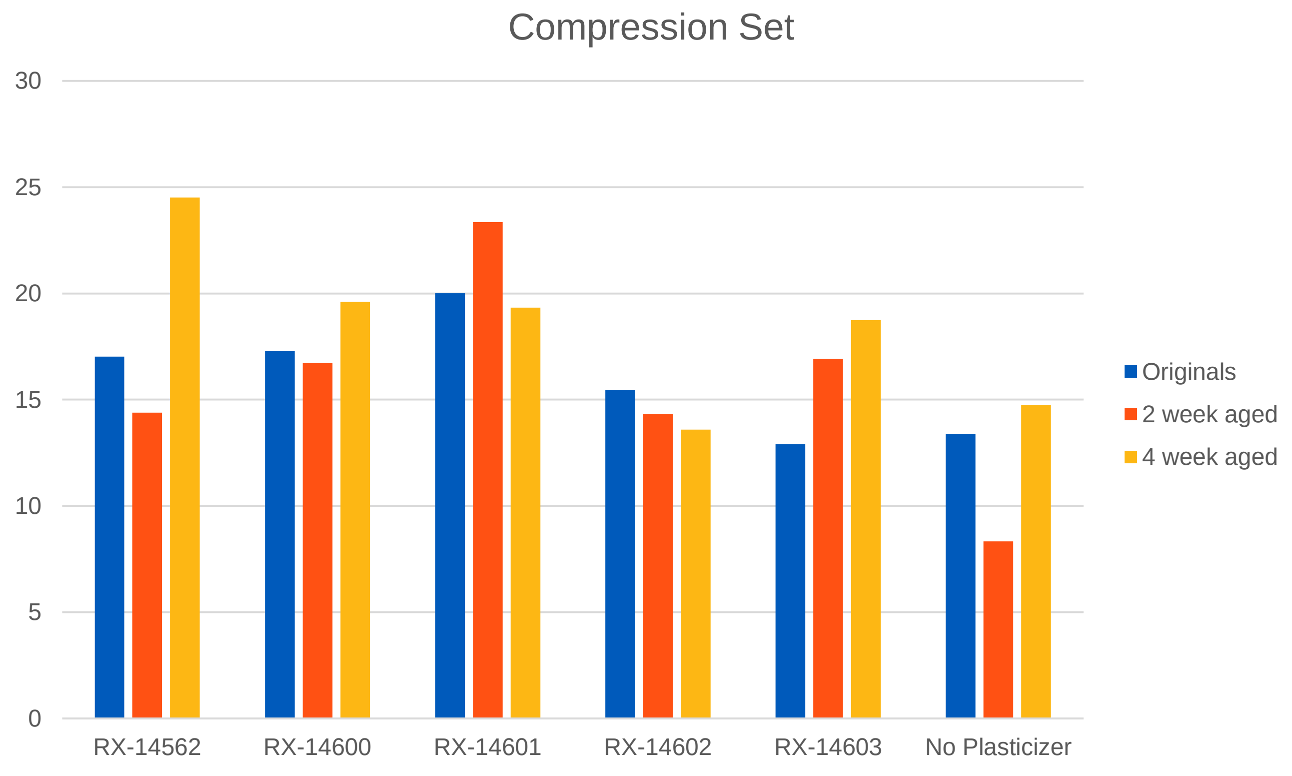
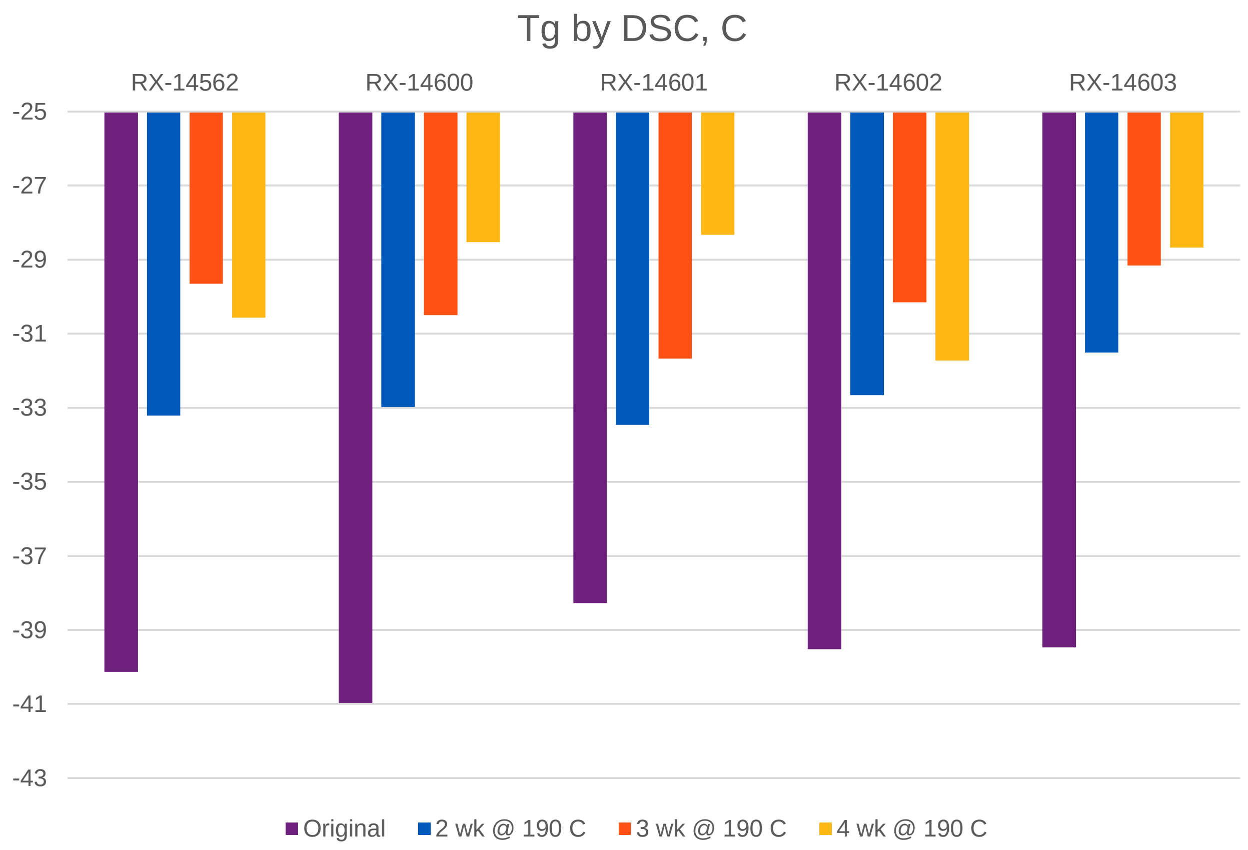
Heat Aging – Compression Set, Part II



70 hrs at 150°C, under constant deformation

- Decrease in compression set after aging in most cases likely due to increased cross-linking during aging
- Increase in set after aging likely due to degradation
- RX-14602 overall best initial compression set and retention after aging

Heat Aging – Effect on Low Temperature, Part II



- All plasticizers have excellent initial low temperature properties
- RX-14562 and RX-14602 offer best retention of low temperature properties after heat aging

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Conclusions

	TegMeR 812	RX-14434	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603
Initial low temp	Excellent	Good	Good	Good	Good	Good	Good
Tg loss after aging	Fair	Good	Excellent	Fair	Good	Good	Fair
Weight loss after aging	Fair	Fair	Excellent	Fair	Good	Good	Good
Modulus loss after aging	Fair	Fair	Good	Excellent	Excellent	Good	Good
Elongation loss after aging	Good	Excellent	Excellent	Good	Good	Good	Good
Initial compression set	Fair	Good	Good	Good	Fair	Excellent	Excellent
Compression set after aging	Good	Good	Fair	Good	Fair	Excellent	Fair

First Choice   Second Choice

- Plasticizers tested here offer better performance than others in different aspects
- Overall, RX-14562, RX-14600, and RX-14601 offer best maintenance of properties after extreme heat aging
- Adjusting molecular weight and chemistries of polymeric materials can optimize properties according to application requirements

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