HALLSTAR

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

Erica Anderson*, Sean Neuenfeldt, Dejan Andjelkovic, Stephen O'Rourke, Urvil Shah

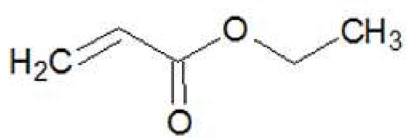
HALLSTAR

# Agenda

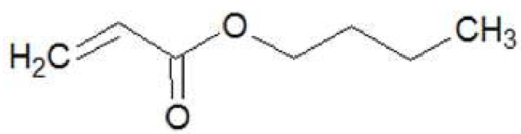
- Background on AEM elastomers
- Plasticizers for high-temperature AEM applications
- Goal of the project
- Overview of the experimental plan
- Results and discussion
- Conclusions
- Acknowledgements

# Background on AEM Elastomers

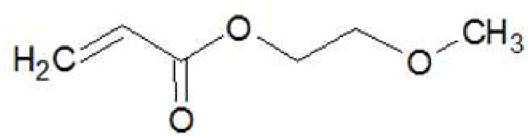
- AEM elastomers are used in applications requiring continual service up to 175°C and intermittent exposure to extremely high temperatures of up to 200 °C
- Lower cost alternatives to FKM and FVQM
- Exhibit improved high temperature resistance over HNBR and ECO
- There are two well known types:
  - ACM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

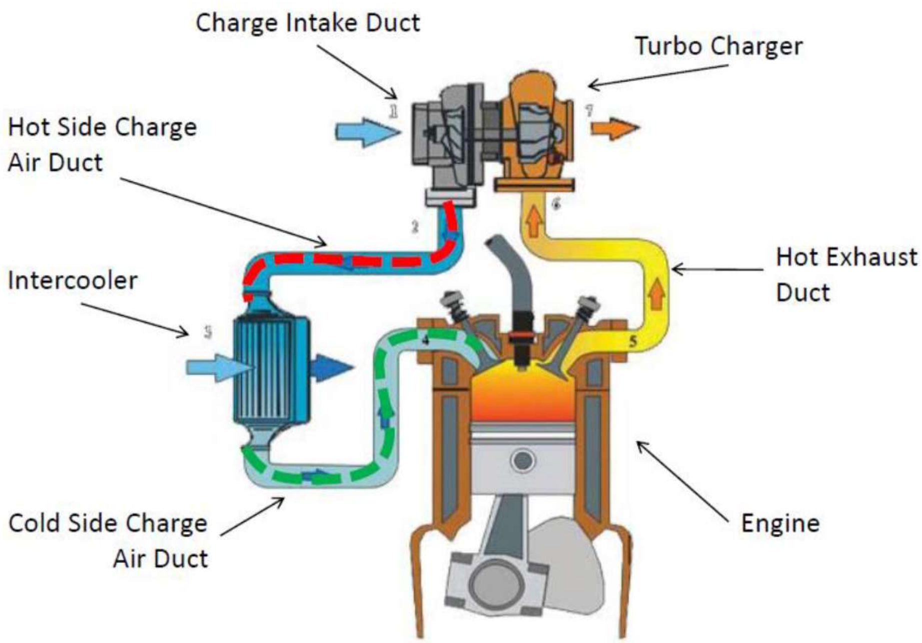
HALLSTAR

# Plasticizers 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




HALLSTAR

# Experimental Plan

| Material | Wt (g) | % 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 polyester |

HALLSTAR

# 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., 2.5cm/5min

## Original Properties
- Tensile, Elongation, Modulus – ASTM D412-92, Method A, Die C, Crosshead speed 5130 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

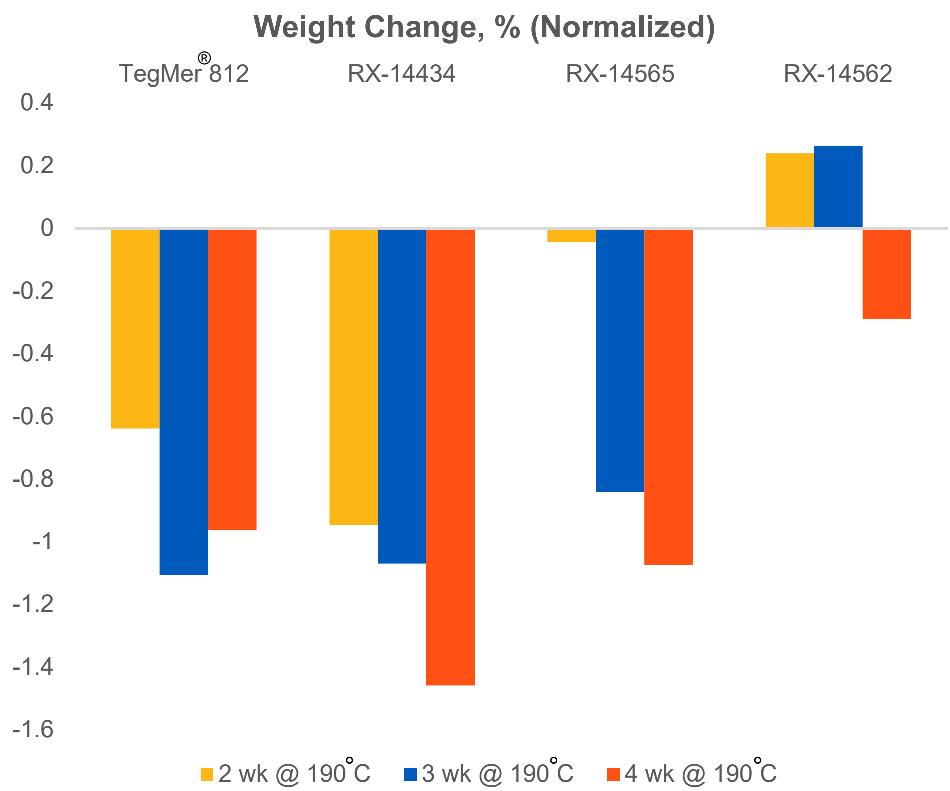
## Air Oven Aging
ASTM D573-81

## Compression Set
ASTM D395, Test Method B

# Original Properties – Round 2

| | 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 |

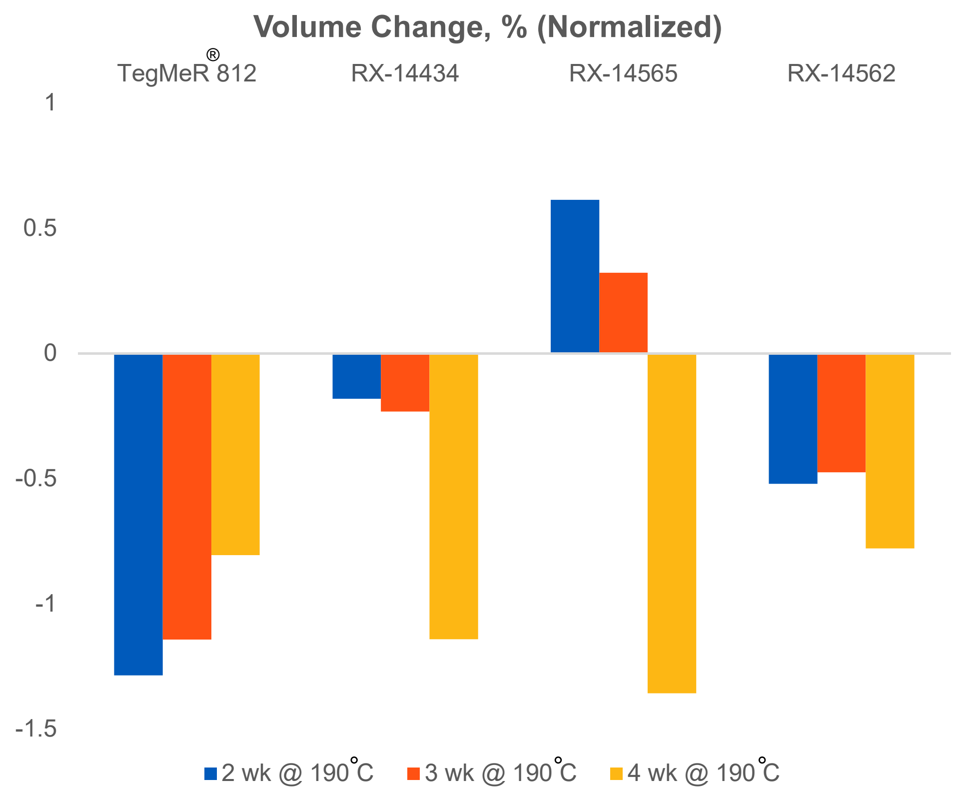
# Heat Aging – Weight Change




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

HALLSTAR

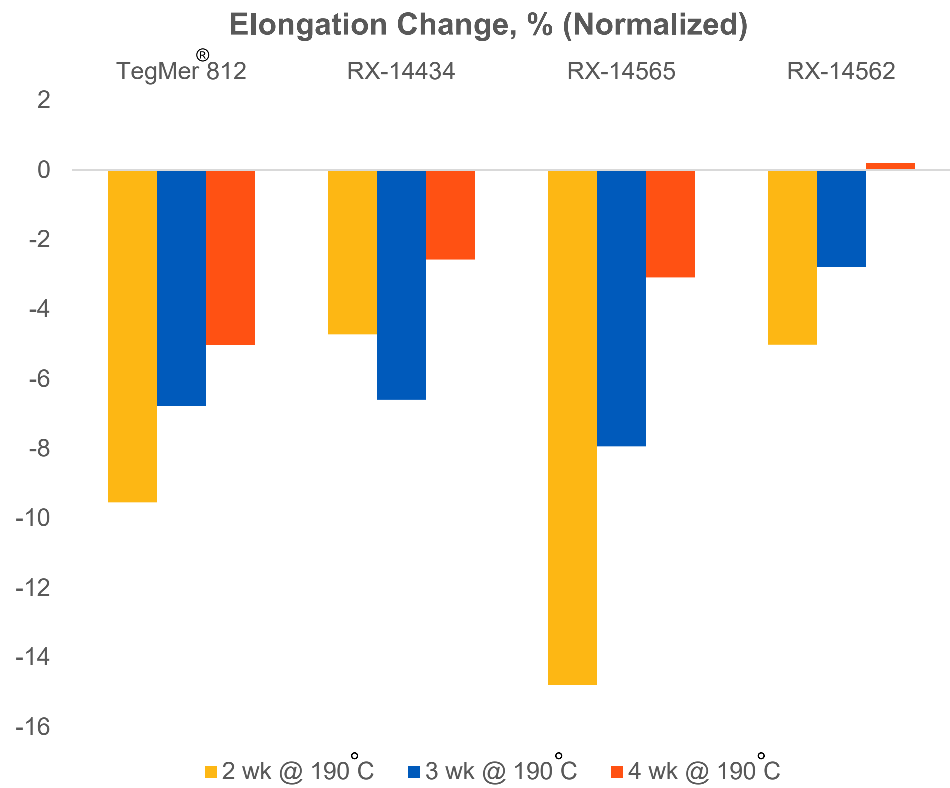
# Heat Aging – Volume Change




- The compounds showing 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

HALLSTAR

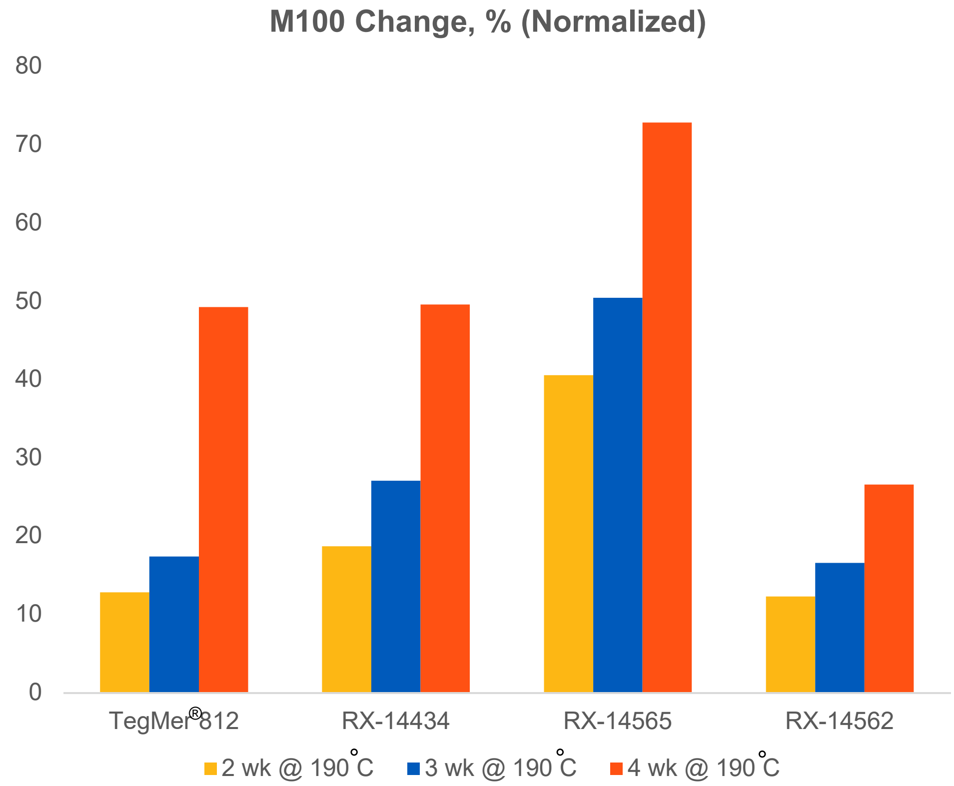
# Heat Aging – Changes in Elongation




| 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 |

HALLSTAR

# Heat Aging – Changes in Tensile Properties

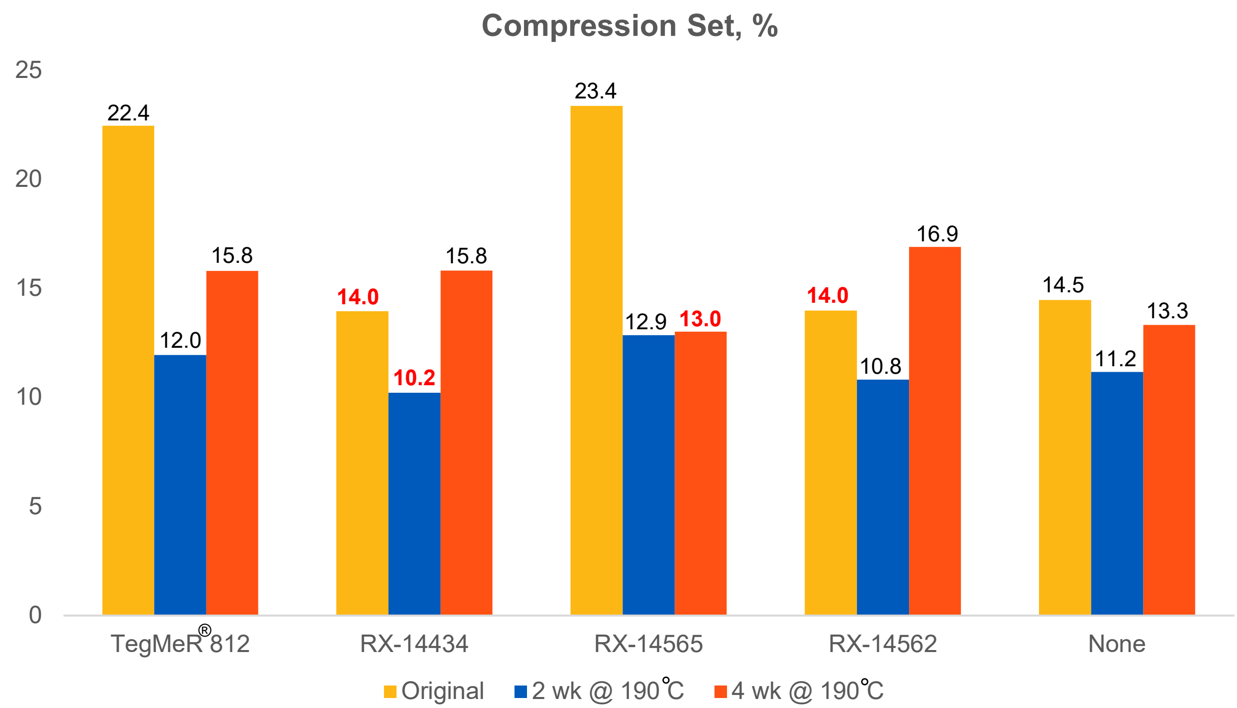



| Recipe Variable | TegMeR® 812 | RX-14434 | RX-14565 | RX-14562 | Control |
|---|---|---|---|---|---|
| **Tensile Ultimate** | | | | | |
| Original, psi | 2004 | 2256 | 2123 | 2122 | 2347 |
| Air Oven, 2 wk @ 190 °C, % change | -45.4 | -44.7 | -46.1 | -46.1 | -41.6 |
| Air Oven, 3 wk @ 190 °C, % change | -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

HALLSTAR

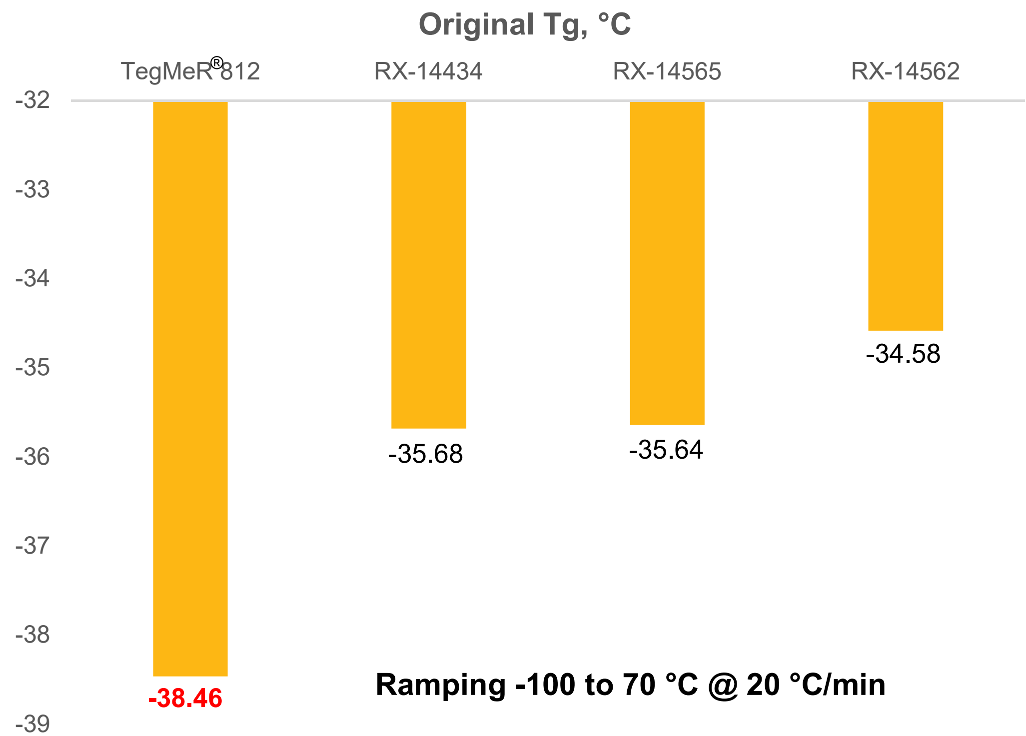
# Heat Aging – Compression Set




**70 hrs at 150°C, under constant deformation**

HALLSTAR

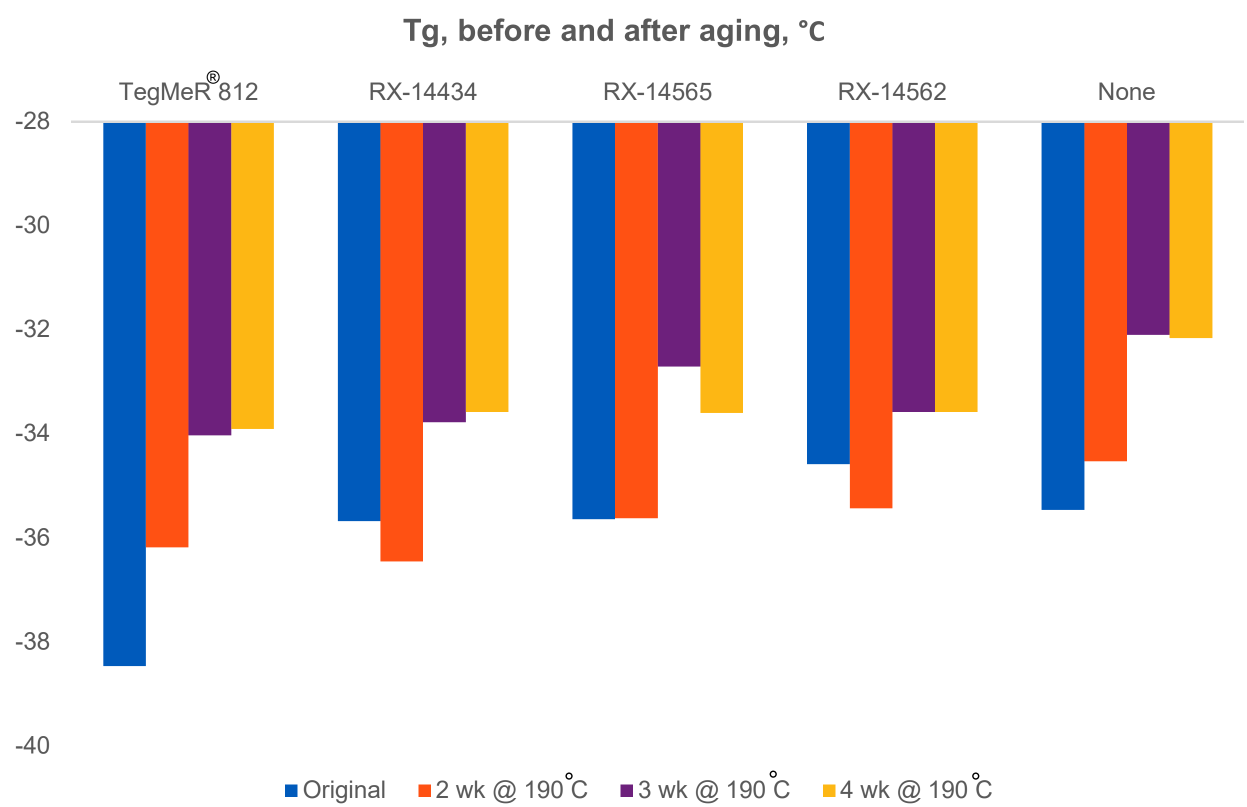
# Original Tg




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

HALLSTAR

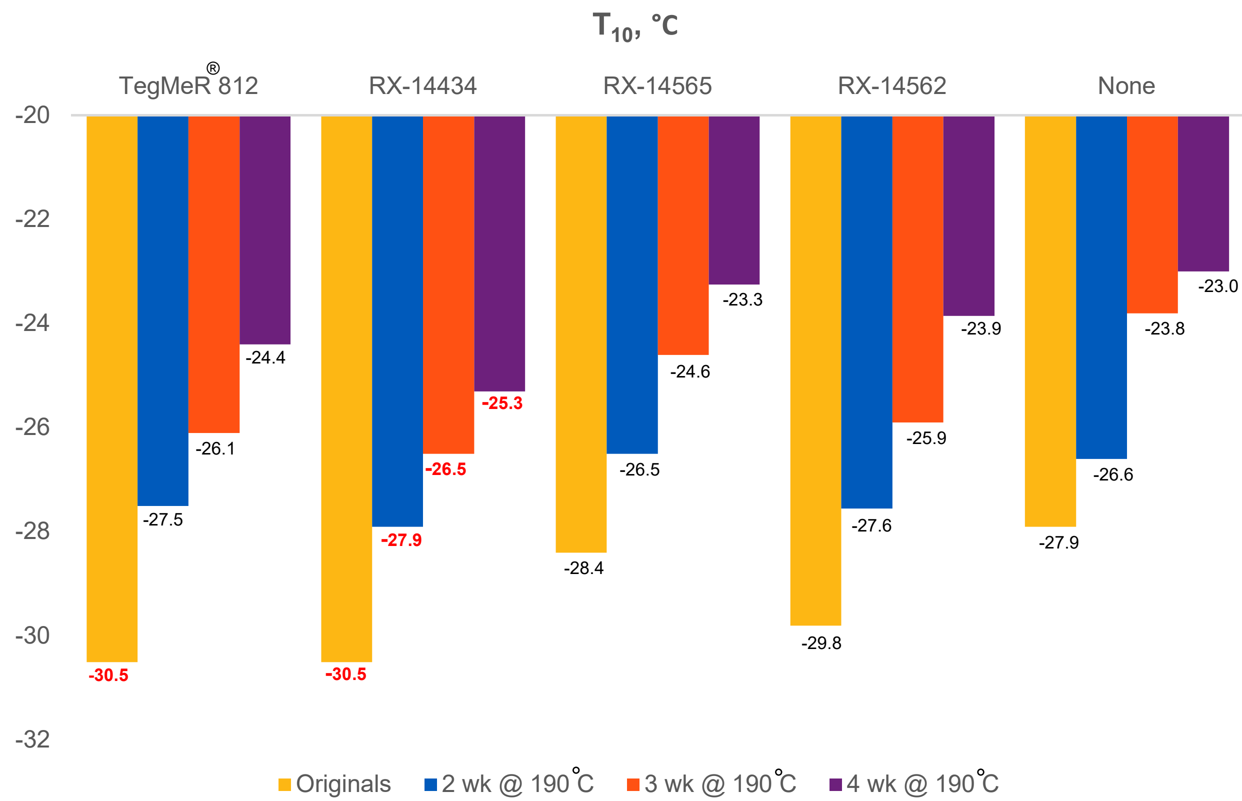
# Heat Aging – Effect on Low Temperature




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

HALLSTAR

# Low Temperature – Gehman Data




- All plasticizers improve low temperature performance versus control
- TegMeR® 812 continues to offer best original properties, but loses more performance after aging than RX-14434 and RX-14562

HALLSTAR

# Conclusions

- Significant improvement in permanence after heat aging was achieved by increasing molecular weight of plasticizer
- RX-14562 shows the best retention of physical and low temperature properties after heat aging

# Acknowledgements

- Hallstar Industrial Solution team would like to express our appreciation to Steven Oriani, Edward McBride and Mark Stewart of DuPont Performance Polymers group for providing elastomer samples and their guidance and support on this project

HALLSTAR

HALLSTAR