

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

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

Industrial Solutions  
The Hallstar Company  
5851 West 73<sup>rd</sup> Street,  
Bedford Park, IL 60638

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## ABSTRACT

Ethylene acrylic elastomers have traditionally been used in applications requiring high level of performance under extreme temperature conditions. They are typically used in a wide variety of automotive applications, such as turbo chargers, oil cooler hoses, seals and gaskets. Recent advancements in ethylene acrylic elastomers by DuPont™ have pushed this performance to higher temperatures and longer periods of time through their Vamac™ VMX 5000 series of polymers. Low temperature improvements, however, are traditionally achieved through the addition of high performance ester plasticizers. While many of these plasticizers have been used in Vamac™ compounds to great effect in the past, the need for performance at higher temperatures necessitates the development of new materials to improve on permanence and volatility. This paper provides information on newly developed plasticizers intended to improve high temperature resistance without sacrificing low temperature performance. Test data include heat aging for varying durations at high temperatures as well as comparative changes in physical and low temperature properties before and after aging. The information provided indicates that the permanence of the plasticizer is key to maintaining compound performance after extended exposure to high temperatures.

## INTRODUCTION

Acrylic elastomers are used in applications requiring continuous service up to 175 °C and intermittent exposure to extremely high temperatures of up to 200 °C.<sup>1</sup> These elastomers are considered lower cost alternatives to other high-temperature elastomers, such as fluoroelastomers (FKM) and fluoro-silicones (FVMQ). Furthermore, they exhibit improved high-temperature resistance over more expensive alternatives, such as HNBR and ECO elastomers. There are two well-known groups of acrylic elastomers: 1) **A**crylic **C**o-**M**onomer (**ACM**) and 2) **A**crylic-**E**thylene **M**onomer (**AEM**) elastomers.<sup>2</sup> Both have saturated aliphatic backbones synthesized via free-radical copolymerization processes. While ACM elastomers are “all-acrylic” copolymers, the AEM elastomers also contain ethylene monomer in their structure. Examples of common acrylic monomers are shown in Scheme 1.

The choice of monomers is critical for optimal properties of the elastomer. In some instances, additional specialty comonomers (e.g. chlorovinyl ether, vinyl chloroacetate, allyl glycidyl ether, glycidyl methacrylate or other carboxy- or epoxy-functional comonomers) are used to deliberately create cure sites along the polymer backbone. It is important to point out that due to the high acrylic monomer content, both types of acrylic elastomers are fairly polar. Thus, the use of higher polarity ester plasticizers is critical to assure optimal compatibility and compound performance. Because of high temperature post-cure required by most acrylic elastomers and the higher maximum temperature of the application, only a few plasticizers show a reasonable degree of utility.<sup>3</sup> Building on this fact, our goal is to present new generation of high-performance ester modifiers and help expand modifier options for the acrylic elastomer market.

Until several years ago, standard AEM elastomer compounds relied solely on fillers like carbon black or silica to provide strength and stiffness to the finished compounded articles.<sup>4</sup> However, it was found that these fillers accelerate oxidative degradation, thus significantly reducing thermal stability of filled AEM compounds. To address these issues, DuPont™ developed new melt-blending technology which allowed reinforcement of AEM elastomers with a dispersion of grafted PA6 droplets.<sup>5</sup> This technology was patented in 2015<sup>6</sup> and DuPont™ launched VMX 5000 Series of AEM pre-compounds on the market. These novel elastomers are blended with amine curatives for efficient cure. Crosslinking these blends produces strong, heat-resistant vulcanizates with good heat-aging and compression set properties. Enhanced performance of these novel cured articles was attributed to extensive AEM-PA6 grafting, absence of filler-filler contacts, and beneficial modification of the oxidation profile under diffusion limited conditions. These novel pre-compounds are being marketed for variety of high-temperature applications including turbochargers, oil cooler hoses, seals and gaskets.<sup>7</sup>

In this study, we evaluated several novel ester plasticizers in the new VMX 5000 series blend compounds consisting specifically of VMX 5015 and VMX-3040 (aka Vamac™ Ultra IP). This new blend of elastomers aims to push the maximum performance temperature of the compounds higher. Standard polymeric esters are well known for their permanence in these elastomers, but are insufficient at improving low temperature performance. The esters tested in this study are lower molecular weight esters that have high heat resistance, but provide much needed low temperature flexibility, both before and after high heat-aging.

## EXPERIMENTAL

The following formulation was provided by DuPont™ as a general-purpose low-durometer Vamac™ VMX 5000 series acrylic compound:

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

<sup>a</sup> Provided by DuPont Performance Elastomers

<sup>b</sup> Provided by Sid Richardson

<sup>c</sup> N-Phenyl-p-Phenyldiamine (CAS#101-54-2) purchased from Sigma-Aldrich

<sup>d</sup> Vanderbilt Chemicals LLC

<sup>e</sup> Provided by Safic-Alcan

Four plasticizers were evaluated along with a control compound without plasticizer:

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

TegMeR® 812 and RX-14434 have similar structures, though RX-14434 has higher molecular weight. The expectation is that RX-14434 would exhibit improved permanence during heat aging. RX-14562 is a medium molecular weight aliphatic polyester, while RX-14565 is a lower molecular weight aromatic polyether ester. Since filled acrylic elastomers cannot trade off on mechanical properties too much, many Vamac™ formulations use low loadings of plasticizers and other additives. Therefore, 5 phr loading of plasticizer was initially selected to best represent typical industrial formulations.

## TEST METHODS

The compounds for performance testing were mixed in a BR Banbury internal mixer following standard mixing procedures. Curatives were withheld from the Banbury charge and added on a two-roll, 611 x 1311 laboratory mill during finishing operations. Test specimens for compound performance properties were molded at 180 °C for 10 minutes at 5.75 MPa on the sheet surface. Sheet specimens were then post-cured in a hot air oven for 4 hours at 175 °C. Specimens for original properties, low temperature testing, and air oven aging were die-cut from molded sheets.

<b>Mooney Viscometer</b>	ASTM D1646-94, viscTECH+, large rotor, 1 minute Preheat
<b>Oscillating Disc Rheometer</b>	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
<b>Original Properties</b>	
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
<b>Low Temperature</b>	
Gehman	ASTM D1053
T <sub>g</sub> by DSC	Perkin Elmer Diamond DSC Temperature ramp of -100 to 70 °C at 20 °C/min
<b>Air Oven Aging</b>	ASTM D573-81
<b>Compression Set</b>	ASTM D395, Test Method B

## RESULTS

All materials were aged in hot air ovens at 190 °C for 2 weeks, 3 weeks, and 4 weeks. Due to the weight and volume loss we noticed in the control compound without the plasticizer, we normalized the losses in the other compounds to show losses from plasticizer alone. These results are shown in Figures 1 and 2. Assumption was that normalization would also help us present performance differentiation between the selected plasticizers in this study more easily.

Although the greatest losses in both weight and volume appear to be present in the compounds containing TegMeR® 812 and RX-14434, it should be noted that these losses are still small (e.g. less than 1.5%). In fact, the plasticizer accounts for approximately 3.2% of the compound by weight and none of the compounds lose as much as half this plasticizer amount even after full 4 weeks of aging at 190 °C. 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.

Several physical properties were also tested before and after heat aging, including tensile properties and durometer hardness. Table I compares changes in these physical properties after heat aging. On average, all compounds showed similar changes in physical properties to the compound containing TegMeR® 812, with the RX-14562 showing a slight improvement in maintaining original physical properties.

Since great number of applications for acrylic elastomers are in the automotive industry, compression set is considered a vital property. It is known that under the compressive stress over time rubber materials lose their ability to return to its original dimensions. Such loss of resiliency (rebound) reduces the ability of seals and gaskets to perform over long period. The resulting permanent set in these parts can cause leaks and catastrophic failures. Therefore, low compression set values are essential to maintain effective sealing.<sup>8,9</sup> In our study, compression set was tested on all compounds in their original state as well as after air-aging for 2 weeks and 4 weeks at 190 °C. Compression set was measured after 70 hours at 150 °C under constant deflection per ASTM D395 Method B. Samples were allowed half an hour at room temperature after deformation was released before the measurement was taken. Figure 3 shows comparative values. In all compounds, an improvement in compression set was observed after 2 weeks of air-aging with a subsequent loss after 4 weeks. This is believed to be due to further post-curing of the material during the first week of aging. Additional assumption is that polymer degradation accelerated during the final weeks of aging, thus reducing the crosslink density and reversing the trend for compression set performance.

Furthermore, the higher molecular weight plasticizers, i.e. RX-14434 and RX-14562, offer the best original compression set as well as excellent maintenance of this compression set after 2 weeks of aging. This is comparable to or better than the control material with no plasticizer. Conversely, RX-14565 sample exhibited the best compression set properties after full 4 weeks of aging, despite its initially high values.

Finally, low temperature properties were measured in two ways: glass transition by DSC and torsion stiffness by the Gehman method. Figure 4 shows the glass transition of all materials in their original state and after extensive hot-air aging. As expected, all four esters show improvement over the control compound with no plasticizer, especially after aging. This shows that all plasticizers remain in the compound after aging in sufficient quantity to render it flexible and operational at lower temperatures. TegMeR® 812 and RX-14434 exhibit lower glass transitions before aging, but show greater change in  $T_g$  after aging. This indicates a loss in performance due to the volatility and/or degradability of these esters at extremely high temperatures when compared to the higher molecular weight polymeric ester RX-14562.

Figure 5 shows the comparison of  $T_{10}$ , as measured by the Gehman method, both before and after extensive heat-aging.  $T_{10}$  is defined as a temperature for which the relative modulus of the compound is 10.

The relative modulus at any temperature is defined as the ratio of the modulus at that temperature to the modulus at 23 °C.<sup>10</sup> As expected, all esters showed an improvement in torsional stiffness over the control compound, with the higher molecular weight monomeric material RX-14434 showing the best overall initial and aged values, indicating excellent balance of permanence in the compound and maintenance of low temperature flexibility after aging.

## SUMMARY

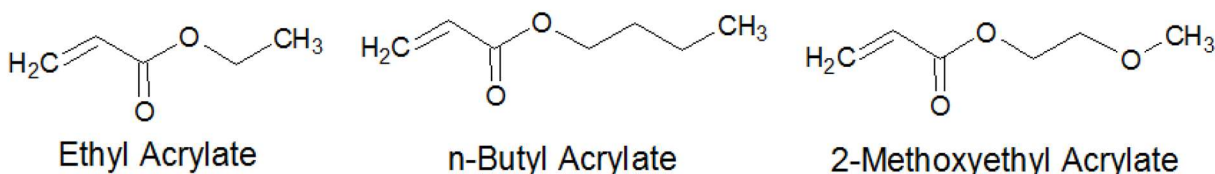
In summary, compound made from RX-14562 offers several advantages over other ester plasticizers in high temperature AEM elastomers. These include significantly lower weight and volume change and better balance of retention of physical and low temperature performance after extreme high heat aging. This compound also offers excellent compression set both before and after extreme heat aging. Future work will focus on further improvements of high-temperature polymeric plasticizers to optimize the balance between low temperature performance and retention of performance after extreme high heat aging.

## ACKNOWLEDGEMENTS

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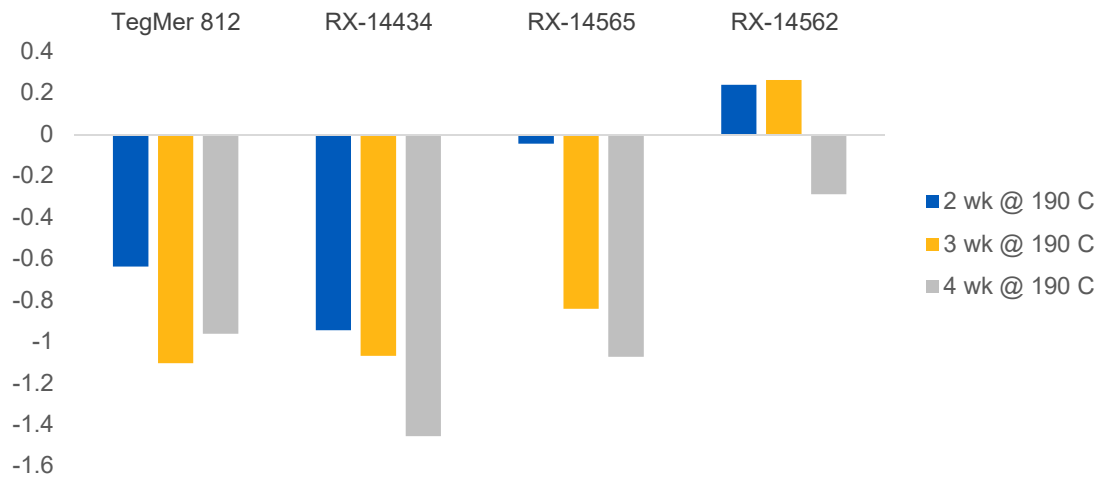
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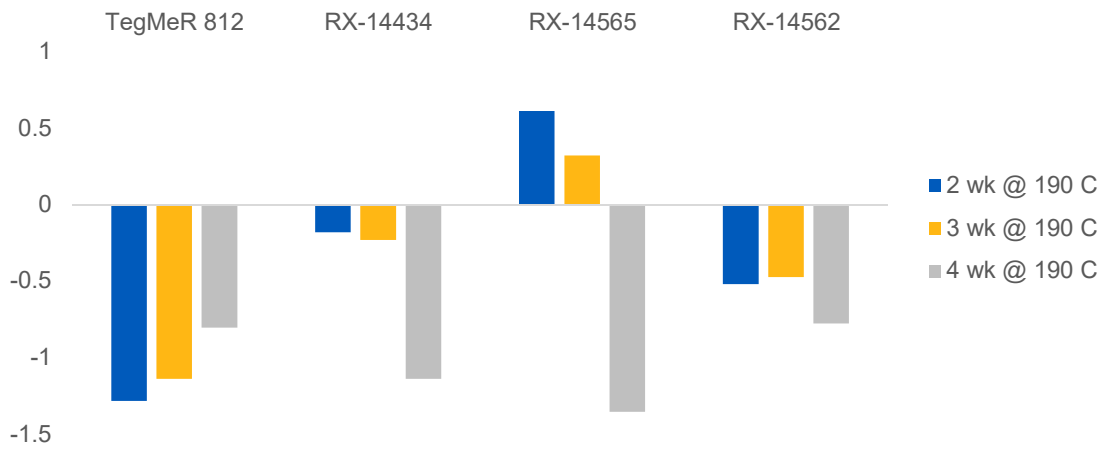


**Scheme 1.** Example acrylic monomers for acrylic elastomers





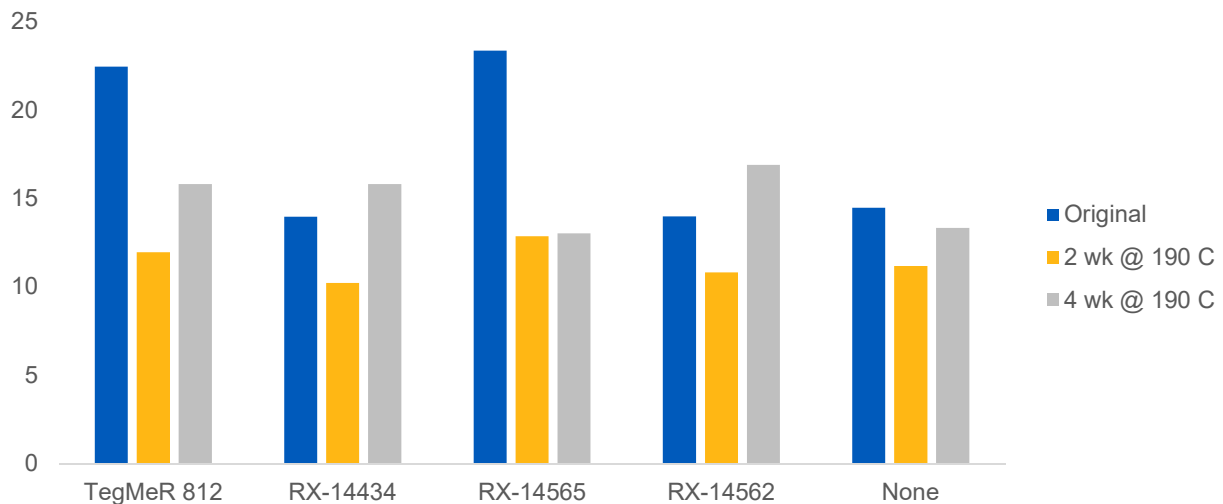
**Figure 1. Weight Change, % (Normalized)**



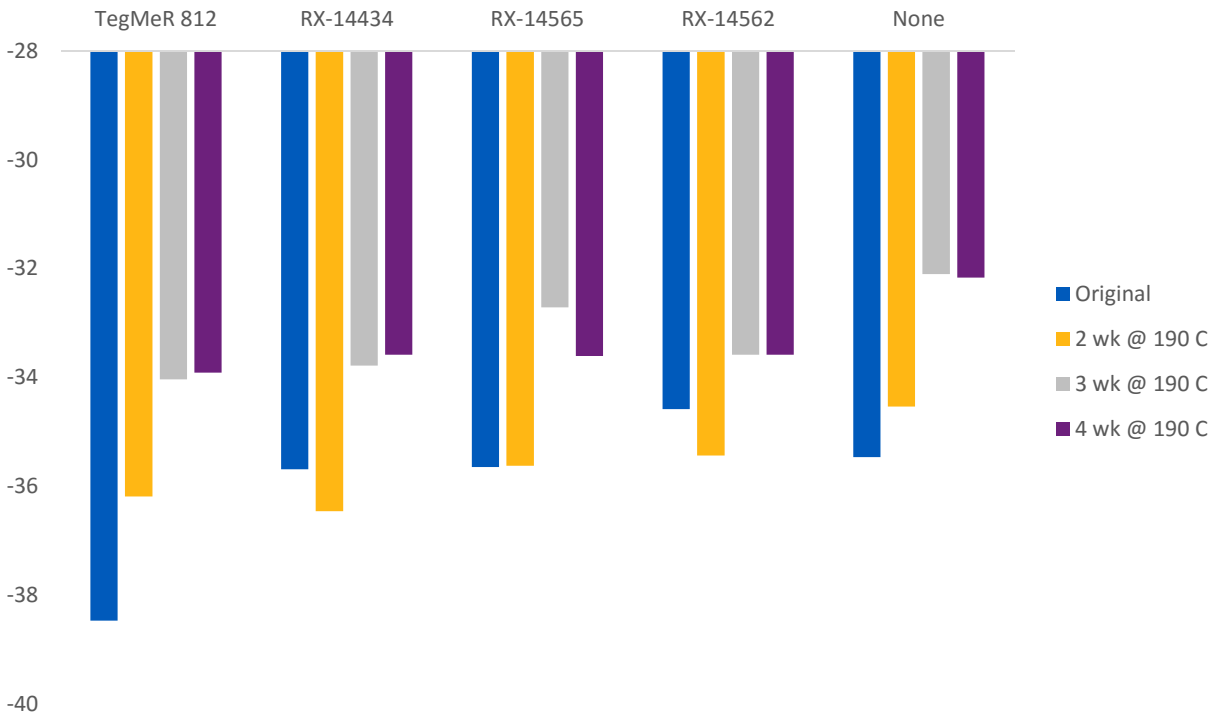
**Figure 2. Volume Change, % (Normalized)**

Recipe Variable	TegMeR® 812	RX- 14434	RX- 14565	RX- 14562	Control
<b>Elongation at Break</b>					
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
<b>Tensile Ultimate</b>					
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
<b>Hardness Duro A</b>					
Original, pts	60	60	63	58	65
Air Oven, 2 wk @ 190 °C, pts change	-6	-7	-6	-1	-7
Air Oven, 3 wk @ 190 °C, pts change	-5	-5	-5	-4	-7
Air Oven, 4 wk @ 190 °C, pts change	-6	-6	-4	-2	-8

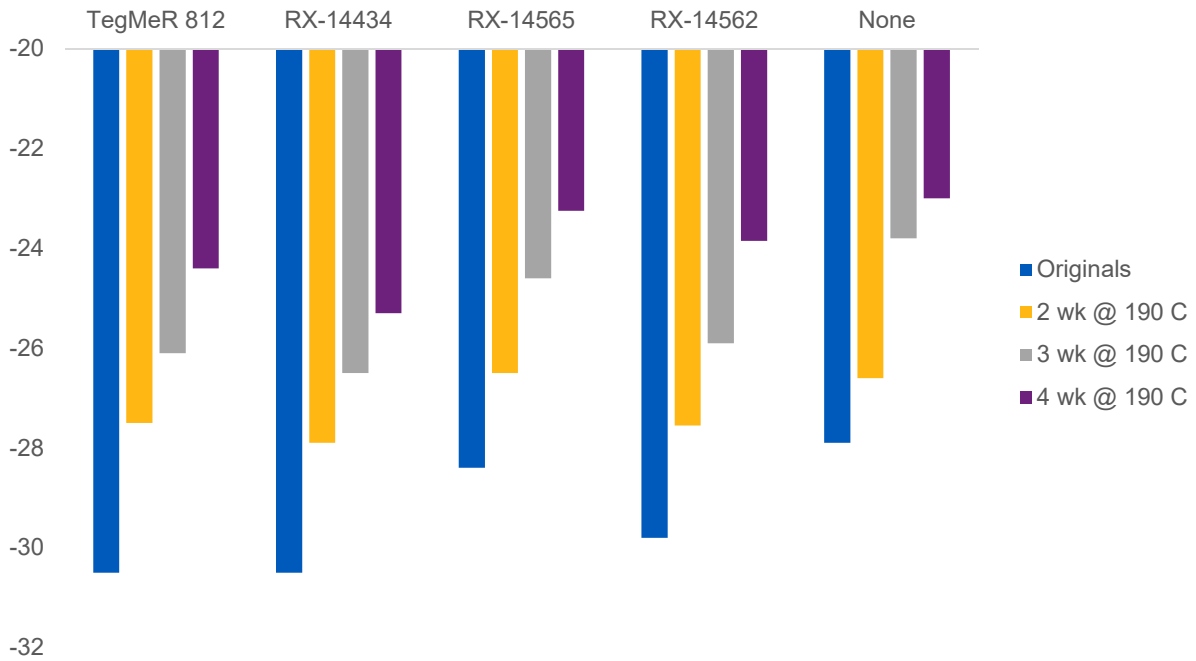
**Table I.** Physical Properties, Before and After Heat Aging



**Figure 3.** Compression set, %



**Figure 4.** Glass Transition Temperature (T<sub>g</sub>, °C)



**Figure 5.** T<sub>10</sub> values from the Gehman testing, °C