DEVELOPMENT OF NEXT-GENERATION ESTER PLASTICIZERS FOR HIGH TEMPERATURE ETHYLENE ACRYLIC ELASTOMERS

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Presented at the Fall 192nd Technical
Meeting of Rubber Division, ACS
Cleveland, OH
October 10-12, 2017

ISSN: 1547-1977

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 transmission oil cooler hoses, turbocharger hoses and seals and gaskets for automatic transmissions and engines. 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

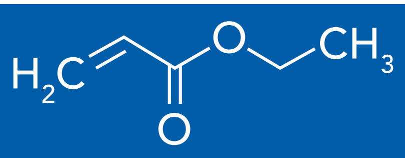
Acrylic elastomers are used in applications requiring continuous service up to 175 °C and intermittent exposure to extremely high temperatures of up to 200 °C.[1] These elastomers are considered lower cost alternatives to other high-temperature elastomers, such as fluoroelastomers (FKM) and fluoro-silicones (FVMQ). Furthermore, they exhibit improved high-temperature resistance over more expensive alternatives, such as HNBR and ECO elastomers. There are several well-known groups of acrylic elastomers:

1. Acrylic Co-Monomer (ACM)[2],
2. Acrylic-Ethylene Monomer (AEM),[3]
3. Ethylene-Vinyl Acetate-Acrylic- Monomer (ER) elastomers.[4,5]

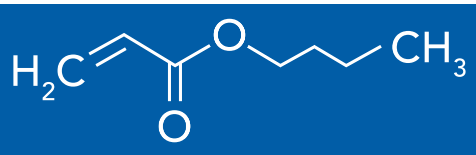
All have saturated aliphatic backbones synthesized via free-radical copolymerization processes. While ACM elastomers are "all-acrylic" copolymers, AEM elastomers contain ethylene comonomer, while ER elastomers contain both ethylene and vinyl acetate comonomers in their structure.

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. Examples of typical acrylic monomers and comonomers are shown in **Scheme 1.** It is important to point out that due to the high acrylic monomer content, both types of acrylic elastomers are quite 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.[6] 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.

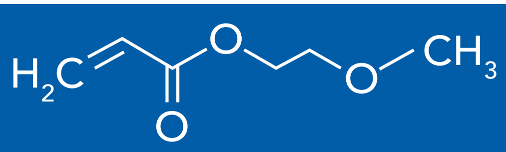
Scheme 1



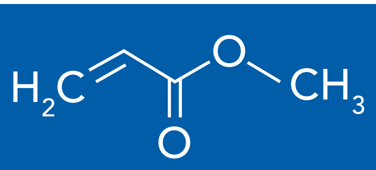
Ethyl Acrylate



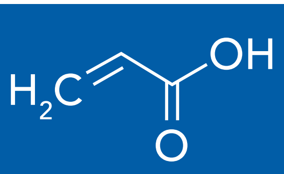
n-Butyl Acrylate



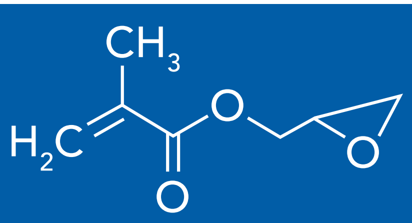
2-Methoxydethyl Acrylate



Methyl Acrylate



Acrylic Acid



Glycidyl Methacrylate

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.[7] 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.[8] This technology was patented in 2015[9] 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 turbocharger hoses, oil cooler hoses, seals and gaskets.[10]

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. Historically, plasticizers such as TP-759 and TegMeR® 812 are commonly recommended as they show excellent low temperature performance, but as they are monomeric esters, they lack permanence at extreme high temperatures.[11] 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 polymeric esters that have high heat resistance, but provide much needed low temperature flexibility, both before and after high heat-aging.

EXPERIMENTAL

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

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%**

In the first part of this study, 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 - medium MW 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.

Part II.
Based on results from the first part of the study, the formulation was adjusted to allow for a larger quantity of plasticizer while maintaining Shore A hardness by changing the polymer ratio. The larger quantity of plasticizer helps to emphasize and differentiate performance between different plasticizer compounds. Therefore, for the second part of our study the following formulation was adopted:

Material	Wt (phr)	% 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%**

Results from the first part of the study led to the following new plasticizers being tested in this formulation, against a control compound without plasticizer:

- 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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[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

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.

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
Tg 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

RESULTS

Part I.
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.

Figure 1
Weight Change, % (Normalized); Part I

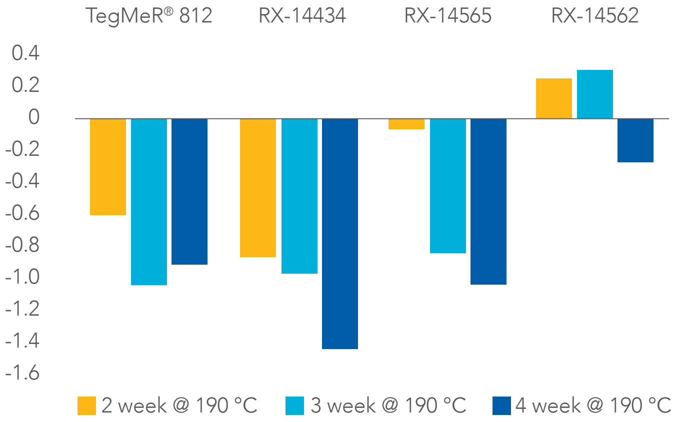
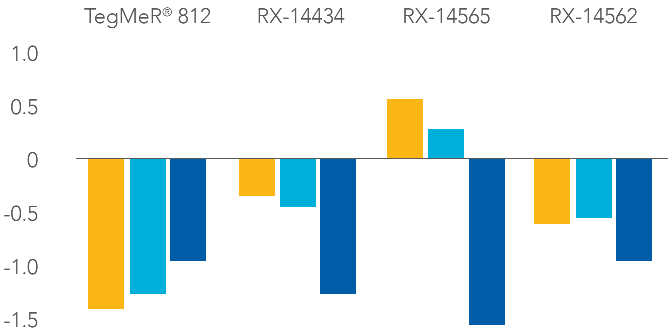


Figure 2
Volume Change, % (Normalized); Part I



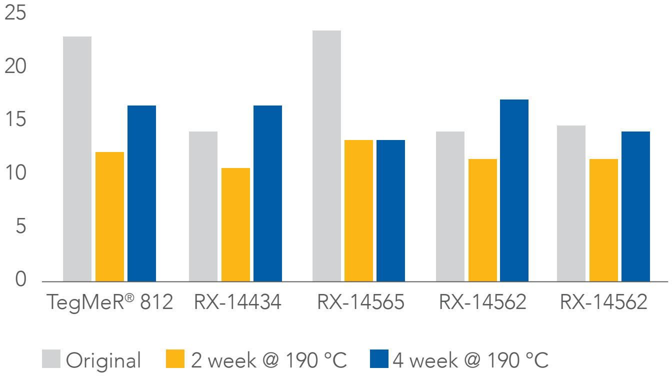
Several physical properties were also tested before and after heat aging, including tensile properties and durometer hardness. **Table 1** compares changes in these physical properties after heat aging. On average, all compounds showed similar changes in physical properties to the compound containing TegMeR® 812, with the RX-14562 showing a slight improvement in maintaining original physical properties.

Table 1
Physical Properties, Before and After Heat Aging; 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
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
Hardness Duro A					
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

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.[12,13]
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.

Figure 3
Compression set, %; Part I



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 Tg 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 T10, as measured by the Gehman method, both before and after extensive heat-aging. T10 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.14 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.

Figure 4

Glass Transition Temperature (Tg, °C); Part I

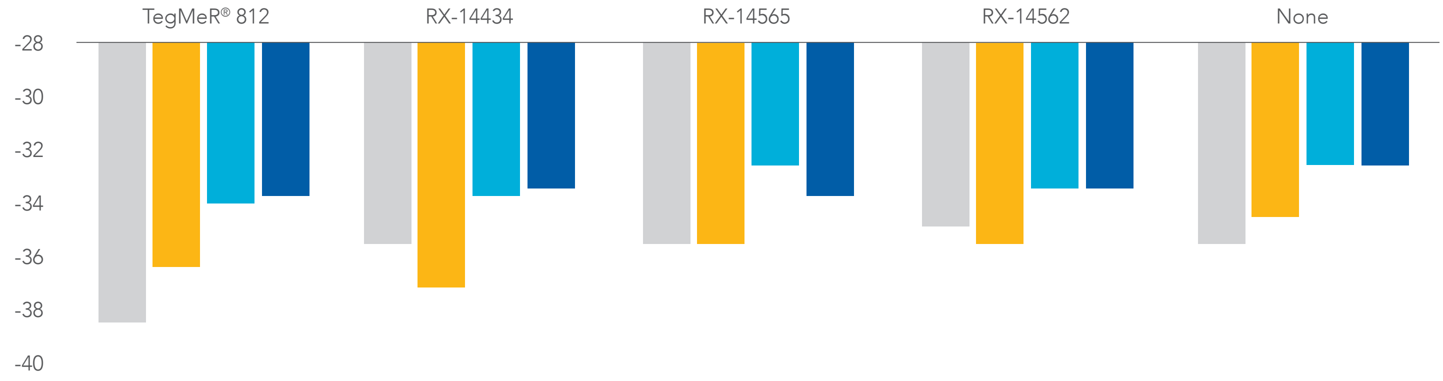
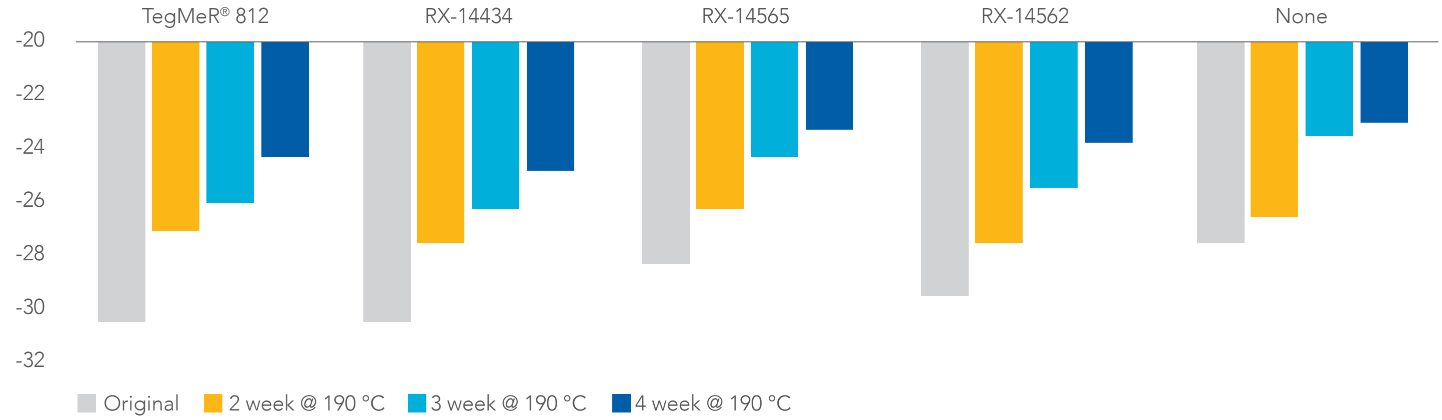


Figure 5

T_{10} values from the Gehman testing, °C; Part I



Part II.
Again, all materials were aged in hot air ovens at 190 °C for 2 weeks, 3 weeks, and 4 weeks. We once again normalized the volume and weight losses in these compounds to show losses from plasticizer alone. These results are shown in **Figures 6 and 7.**

The same physical properties were tested again on this round of compounds both before and after heat aging. **Table 2** compares changes in the se physical properties. On average, all compounds showed similar or slightly greater changes to the compound containing RX-14562, with the closest being RX-14600.

Figure 6
Weight Change, % (Normalized); Part II

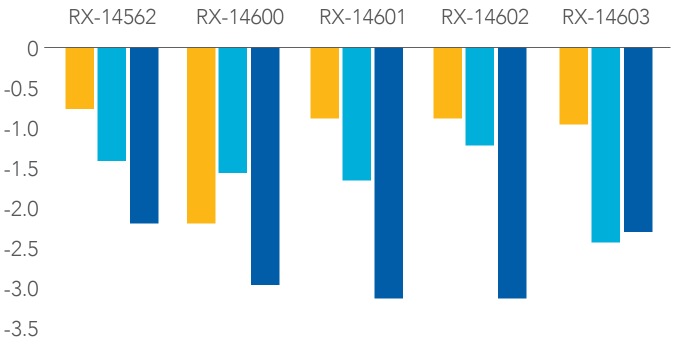


Figure 7
Volume Change, % (Normalized); Part II

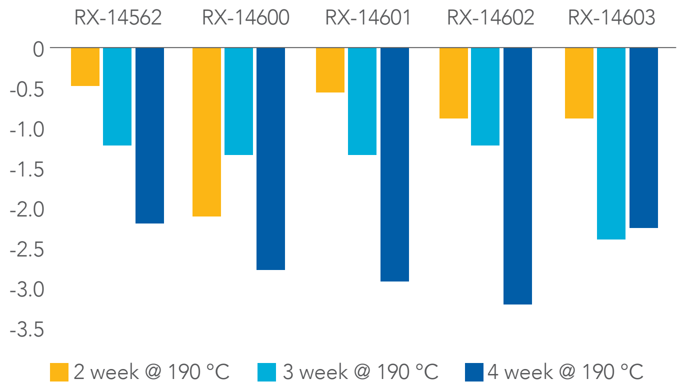


Table 2
Physical Properties, Before and After Heat Aging; Part II

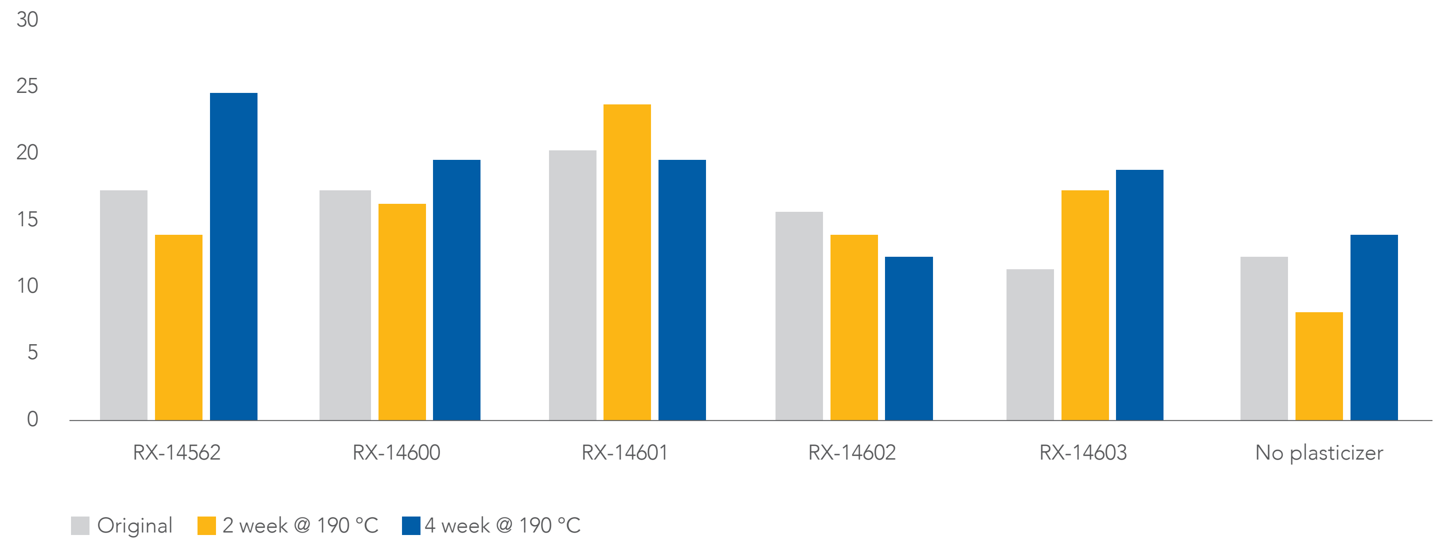
Recipe Variable	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603	Control
Elongation at Break						
Original, %	305.3	319.5	293.0	316.3	308.1	275.0
Air Oven, 2 wk @ 190 °C, % change	-17.0	-23.1	-29.4	-31.2	-29.9	-24.3
Air Oven, 3 wk @ 190 °C, % change	-39.9	-34.6	-43.1	-47.8	-59.6	-47.0
Air Oven, 4 wk @ 190 °C, % change	-54.9	-55.1	-60.4	-59.7	-60.3	-51.3
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
Hardness Duro A						
Original, pts	59	58	59	59	57	64
Air Oven, 2 wk @ 190 °C, pts change	-3	-4	-4	-4	-2	-2
Air Oven, 3 wk @ 190 °C, pts change	-3	-3	-3	-3	-1	-5
Air Oven, 4 wk @ 190 °C, pts change	-4	-4	-3	-3	-2	-7

As the RX-14562 showed the most promising results in Part I of this study, this material was used as a control for comparison. As can be seen in Figures 6 and 7, the new materials offered similar or slightly higher weight and volume losses when compared to RX-14562, but all compounds continued to show half or less of the plasticizer present in the material after 4 weeks of aging at 190 °C, with a maximum of about 3% weight loss due to plasticizer out of the possible 5.9% present by weight. All materials in this part of the study were intended to improve on low temperature performance from the previous part, so a slight loss in high temperature performance is to be expected. Again, as in Part I, several other physical properties were tested and compared before and after heat aging and can be seen in Table II. These losses were again very similar with little variation between plasticizer choice, with the RX-14600 and RX-14601 showing a slight improvement overall in maintaining original physical properties.

The compression set testing from Part I was repeated for Part II, testing on original compound and after aging 2 weeks and 4 weeks at 190 °C. **Figure 8** shows these comparative values. Results in Part II were more variable than in Part I without a constant trend between compounds. Some compounds, like those using RX-14601 and RX-14602, reduced compression set overall after aging, likely due to increased cross-linking during aging and better retention and incorporation of plasticizers. Others, like those using RX-14600 and RX-14603, increased compression set after long-term aging due to plasticizer loss and degradation. Overall, RX-14602 resulted in the best overall compression set properties with a low starting value and slight decrease after extensive heat aging.

Figure 8

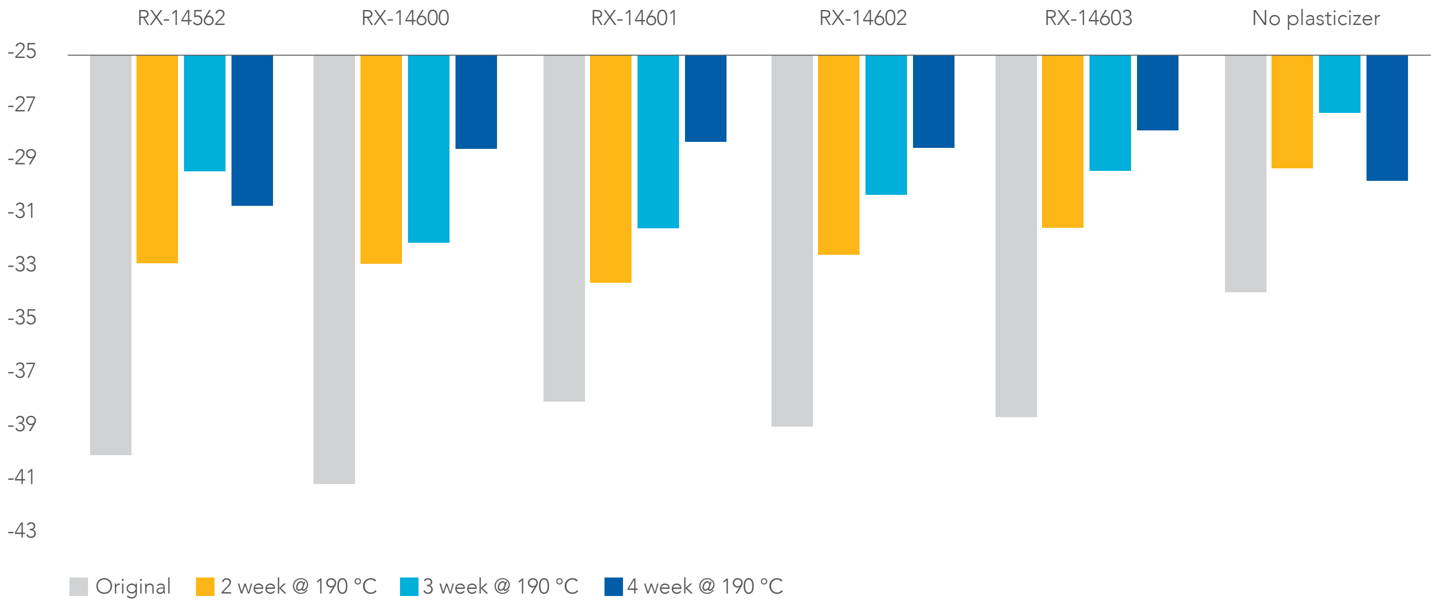
Compression Set, %; Part II



Finally, low temperature properties were compared using glass transition temperature measured by DSC. **Figure 9** shows the glass transition temperatures of all compounds tested in Part II before and after heat aging. All plasticizers show a significant improvement over the compound with no plasticizer, as can be expected. Most low temperature performance is lost after the first 3 weeks of heat aging with very little change between 3 and 4 weeks. Overall, RX-14601 and RX-14602 offered the best retention of low temperature performance after extreme heat aging.

Figure 9

Tg by DSC, °C; Part II



SUMMARY

In summary, the work performed here shows that some plasticizers offer better performance than others in different aspects. Overall, RX-14562, RX-14600, and RX-14601 offer the best maintenance of properties after extreme heat aging. However, by adjusting molecular weight and chemistries of polymeric materials, high and low temperature performance can easily be optimized according to the requirements of the application. To help visualize these optimizations, **Table 3** shows recommendations for each product tested here in relation to different test parameters. This table indicates which product should be selected based on key performance requirements and can help guide a custom optimized product if none presented are exactly as needed. As some of the products were tested in different formulations (Part I and II of the study), comparing quantitative values for these properties is counterproductive. Because RX-14562 was used in both parts of the study, though, it can be used as a means of comparison to bridge this gap in data. Table 3 summarizes this comparison using general descriptions and highlighting the best products for performance in a variety of scenarios.

Table 3

Product Recommendations, by Performance Requirement

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

🟦 First choice 🟧 Second choice

Table 4

Physical Properties and MW Ranges of Neat Plasticizers

	RX-14562	RX-14600	RX-14601	RX-14602	RX-14603
State	Soft solid	Liquid	Liquid	Liquid	Soft solid
Acid Value	1.32	0.6	9.01	4.64	5.00
Moisture Content (%)	0.074	0.150	0.147	0.155	0.09
Refractive Index at 25 °C	1.462	1.500	1.465	1.461	1.500
Specific Gravity	1.047	1.00	1.104	1.072	1.100
Viscosity at 25 °C, cps	N/A	172	966	296	N/A
Melt point, °C	42.8	N/A	N/A	N/A	30.0

For polyether esters - lower MW is roughly about 1000-1100 g/mol and the higher MW range is about 1400-1600 g/mol; For aliphatic polyesters - lower MW is roughly about 1500 g/mol and the medium MW range is about 2100 g/mol; For polar aliphatic polyesters - lower MW is roughly about 1400 g/mol, medium MW is about 1700 g/mol and the higher MW range is 1800-2000 g/mol.

ACKNOWLEDGEMENTS

Hallstar Industrial Solutions 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.

REFERENCES

(1) "HyTemp Technical Manual," Zeon Chemicals L.P. (2011)

(2) "HyTemp ACM Technical Guide," Zeon Chemicals L.P. (2015)

(3) Edward McBride, Serge Bouvier and Klaus Kammerer "AEM Compounds: Recent Developments in Fluid Aging," Rubber World, 2018, 258(1), 34-45

(4) Toshiaki Miyauchi, "Recent Advancement in Denka ER for Automotive Applications," a presentation at the Hose Manufacturing Conference, October 25, 2017, Akron, OH

(5) Acrylic elastomer abbreviations used per ASTM 1418 and ISO/DIN 1629

(6) O'Rourke, S.E., Laboratory Report, "Plasticizers for Acrylic Elastomers," The Hallstar Company (2007)

(7) DuPont™ VAMAC® Ethylene Acrylic Elastomer – VMX5000 Series Pre-Compound – On-line TDS, VME-A11215-00-A1016 by E. I. du Pont de Nemours and Company

(8) Oriani, S. R. "Reinforcement of ethylene-acrylic elastomer with a dispersion of grafted PA6 droplets," J. Appl. Polym. Sci. 2016, 133, 43995

(9) Steven R Oriani, "Heat-stabilized acrylate elastomer composition and process for its production," US Patent 8,940,824 dated Jan. 27, 2015.

(10) DuPont™ Vamac® Ethylene Acrylic Elastomer – Thrive in a harsh world - On-line Vamac™ Brochure, VME_A10650_00_B0715 by E. I. du Pont de Nemours and Company

(11) O'Rourke, S.E., "Plasticizers for DuPont/Dow Elastomers," The Hallstar Company (1997)

(12) ASTM Standard D395-16e1, "Standard Test Method for Rubber Property – Compression Set," Annu. Book ASTM Stand. 09.01 (2016)

(13) Elastomer Engineering Guide, online guide by James Walker Sealing Products and Services Ltd

(14) Elastomer Market Terminology, online document available on hallstar.com

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