3M™ Dynamar™ RA 5300 Rubber Process Additive for FKM Compounds

Executive Summary

Based on experimental results described in this paper, the use of 3M™ Dynamar™ RA 5300 as a process aid in fluoroelastomer compounds offers both processing and performance improvements over many commercial products typically used in the industry. Sharper edges and smoother surfaces were achieved in Garvey Die extrusions, along with improved mold release and reduced fouling in injection molding, without sacrificing compression set and flexibility.

Objectives

The chemical structure of fluoroelastomers (FKM) allows them to be used in environments where harsh chemicals and extreme temperatures are present. The carbon – fluorine bond allows the polymer to be resistant to hydrocarbon fluids and is thermally stable at temperatures up to and above 200°C (392°F). Compounds based on fluorocarbon elastomers typically are not heavily filled due to the resistance of their structure to most plasticizers and their high uncured hardness as compared to other elastomers.

Processing FKM compounds can be troublesome due to the high polymer content. This can result in dry, rough extrudates and problems with flow, as well as sticking during compression and injection molding processes. As result, most FKM compounds utilize some form of hydrocarbon-based processing aid, such as Carnauba Wax. In this case, the chemical resistance of FKM results in an incompatibility with the additive that pushes it towards the surface of the compound. There it forms a film at the compound/metal interface, reducing friction and allowing the compound to be processed smoothly with limited sticking.

During the curing process, the incompatibility of the processing aid allows it to volatilize, or evaporate, from the compound. This can affect the curing and physical properties of the compound. Physical properties, such as tensile strength, elongation, modulus, and compression set can all be impacted by the processing aid.

The unique chemistry of 3M™ Dynamar™ RA 5300 could be an option to replace the conventional materials if it performs at a higher level with less sacrifice to the desirable properties of an FKM compound. The objective of this paper is to evaluate the performance of RA 5300 as a potential replacement option for conventional materials in FKM compounds.

Equipment / Experiment Set-up

The elastomer base selected was a 40 Mooney Viscosity, 66 weight % fluorine copolymer of hexafluoropropylene and vinylidene fluoride with a Bisphenol AF cure system incorporated – sold by 3M under the product name Dyneon FE 5640. In this work, we used the industry standard compound for technical data sheets and product comparison. It includes 100 parts per hundred rubber (PHR) of the elastomer base, 30 PHR of N990 carbon black, 6 PHR of calcium hydroxide, and 3 PHR of magnesium oxide. The carbon black is a reinforcing filler, while the calcium hydroxide and magnesium oxide are functional components of the cure system.

To compare properties, this compound was produced with four different variations: A control with no processing additive incorporated, and three compounds varying the processing additive incorporated at 1 PHR. The three additives used were Carnauba Wax, Struktol® WS-280, and the new Dynamar RA 5300.

Carnauba Wax is produced from the leaves of palm trees and has been widely used as a processing aid in FKM compounds, particularly for extrusion applications. WS-280 is a condensation product of special fatty acids and silicones on an inorganic carrier, with the active ingredients making up about 75% of the product. It is also widely used for FKM compounding to improve flow and mold release properties of such compounds.

Table 1 shows the compound design for the four compounds used for the evaluation.

TABLE 1
Compounds for Evaluation

Compound	1	2	3	4
3M™ Dyneon™ FE 5640	100	100	100	100
N990	30	30	30	30
Calcium Hydroxide HP XL	6	6	6	6
Elastomag® 170	3	3	3	3
3M™ Dynamar™ RA 5300		1		
Carnauba Wax			1	
Struktol® WS-280				1
Total PHR	**139**	**140**	**140**	**140**

As an initial evaluation, the following properties were tested: flow, cure, physical strength, compression set and heat resistance. Table 2 shows the test methods used for each property.

TABLE 2
Test Methods for Initial Evaluation

Test	Method
Moving Die Rheometer	ASTM D6204
Mooney Viscosity	ASTM D1646
Hardness	ASTM D2204
Tensile Strength	ASTM D412
Elongation at Break	ASTM D412
100% Secant Modulus	ASTM D412
Heat Resistance	ASTM D571
Compression Set	ASTM D395 Method B

Capillary Rheometry was used to compare the flow properties of each compound over a range of shear rates. The equipment used was a Rosand Capillary Rheometer and the test conditions are listed in Table 3:

TABLE 3
Capillary Rheometer Test Set Up

Parameter	Condition
Die L/D	16/1 mm, 90° Entrance
Temperatures	100 and 150°C
Shear Rates (/s)	100, 145, 214, 310, 450, 660, 960, 1400, 2150, 3000
Measurements	Shear Stress (kPa) Shear Viscosity (Pa.s) Pressure (psi)

Processability of the four compounds was also evaluated using a Haake drive unit with an extruder barrel equipped with a Garvey Die. The test conditions are listed in Table 4.

TABLE 4
Garvey Die Extrusion Set Up

Parameter	Condition
Die	Garvey
Zone 1 Temperature, °C	90
Zone 2 Temperature, °C	90
Zone 4 Temperature, °C	90
RPM	25
Measurements	Screw Torque, ASTM D2230, Rating A

Injection Molding Evaluation – Set Up

To further compare processing characteristics of the compound variations, an injection molding trial was performed to evaluate flow, mold release, and fouling. The polymer used in the initial evaluations is not ideal for injection molding due to the mid-range Mooney viscosity of the polymer. For this purpose, an equivalent grade polymer was used having a lower Mooney viscosity more intended for injection molding applications – 3M™ Dyneon™ FE-5620. All other compounding ingredients were kept the same, as seen in Table 5.

TABLE 5
Injection Molding Compounds

Compound	1	2	3	4
3M™ Dyneon™ FE 5620	100	100	100	100
N990	30	30	30	30
Calcium Hydroxide HP XL	6	6	6	6
Elastomag® 170	3	3	3	3
3M™ Dynamar™ RA 5300		1		
Carnauba Wax			1	
Struktol® WS-280				1
Total PHR	**139**	**140**	**140**	**140**

The compounds were processed with a Rutil TechnoMini injection press, holding the same processing parameters for each compound as they were molded into two spiral cavity molds having different groove designs to accent flow and release. Two experiments were performed, varying the platen temperatures. Standard press settings are outlined in Table 6.

TABLE 6
Injection Press Parameters

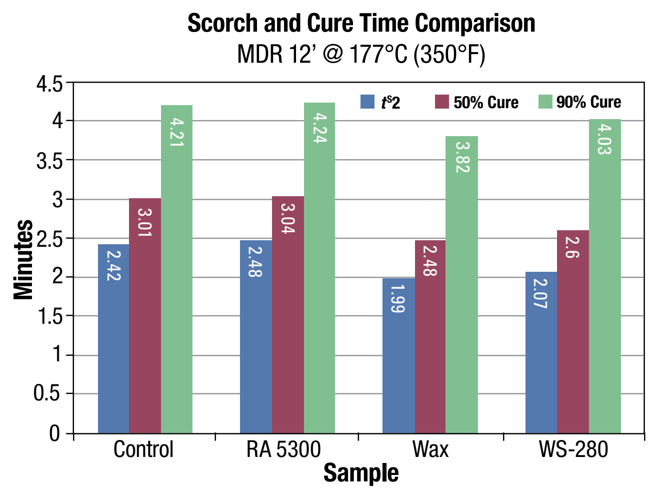
Parameter	1	2
Clamping pressure, bar	130	130
Shot size, mm	20	12
Cure time, seconds	300	300
Platen Temperatures, °C	166	204
Thermolator temperature, °C	90	90

The top mold platen was flat, with a small nozzle opening for injection, and the bottom platen had either a half-round groove to evaluate flow or a deeper submerged half round that increased the rubber to metal contact, giving a comparison for mold release.

Experiments & Results

The Moving Die Rheometer (MDR) results are reported in Figure 1. The results show that Carnauba Wax and Struktol® WS-280 have a larger influence on cure rate and cure level when compared to the RA 5300. No significant difference was observed between the control compound without process aid and the compound containing 1 PHR of RA 5300 while both compounds using 1 PHR Carnauba Wax or Struktol WS-280 had shorter t_s2 scorch times, as well as 50 and 90% cure times. The compounds containing Carnauba Wax and Struktol WS-280 also had slightly higher maximum torque values (MH), reflecting a higher modulus than the control compound and the compound containing 1 PHR RA 5300.

FIGURE 1
MDR Cure and Scorch Comparison



The Mooney Viscosity results are consistent with the MDR data, showing faster scorch time for the Carnauba Wax, being the only material to induce a $t^{S}3$ result. They show Carnauba Wax to have slightly more effect on viscosity with a slightly lower Initial (IV) and Minimum (MV) results (see Table 7). RA 5300 resulted in a slightly lower minimum value, but no significant difference for the initial measurement.

TABLE 7
Maximum Torque and Mooney Viscosity Test Results

Moving Die Rheometer 12' @ 177°C	1	2	3	4
Maximum Torque, in-lbs	23.52	22.91	24.15	26.29
Mooney Viscosity, MS 1+60 @ 121°C	**1**	**2**	**3**	**4**
Initial Viscosity (IV), MU	76.9	77.2	65.1	75.8
Minimum Viscosity (MV), MU	38.1	36.5	37.6	39.2
Time to 3 point rise ($t^{S}3$), minutes	—	—	37.02	—

The addition of RA 5300 produced some slight differences in mechanical properties when compared to the control, as shown in Table 8. Hardness, tensile strength, and modulus values were slightly decreased, with no significant change in elongation at break. The Carnauba Wax increased the tensile strength and the modulus, while decreasing the elongation at break, reflecting a higher level of cure which is consistent with its MDR results.

TABLE 8
Physical Property Comparison

Press Cure 10' @ 177°C (350°F); Post Cure 16hr @ 232°C (450°F)	1	2	3	4
Tensile Strength (psi)	2331	2090	2614	2170
Elongation at Break (%)	200	206	177	185
100% Modulus (psi)	978	901	1152	1022
Hardness (Shore A)	76	74	77	76

The compression set results reported in Figure 2 show that the higher cure level for the Carnauba Wax and Struktol® WS-280 does not correspond to an increased cross link density as one would expect. The control and RA 5300 compounds exhibited virtually identical compression set, while the Carnauba Wax and Struktol WS-280 resulted in noticeably higher compression set.

FIGURE 2
Chart of Compression Set Results

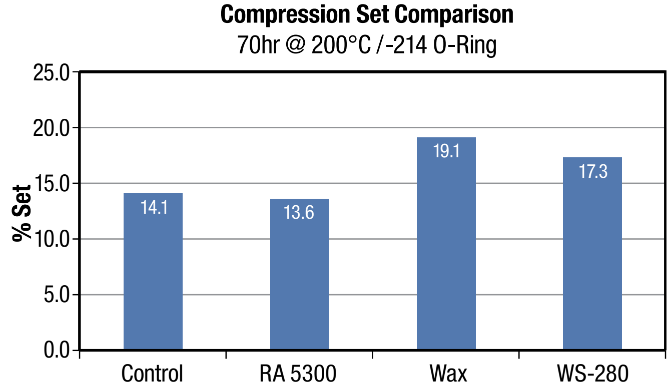
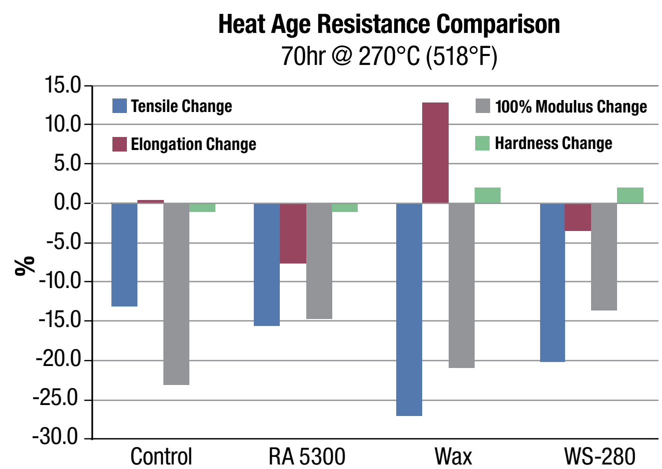


Figure 3 shows the change in mechanical properties after heat aging for 70hr at 270°C (518°F). The compound containing Carnauba Wax showed higher tensile strength loss and elongation increase after heat aging as compared to the other compounds. The RA 5300 containing compound had relatively low losses in all categories when compared to the control.

FIGURE 3
Chart of Property Losses After Heat Aging



The apparent shear stress, as measured at 100°C by Capillary Rheometry, was plotted vs. shear rate, as reported on Figure 4. Under those conditions, the RA 5300 was comparable to the Carnauba Wax, showing improved flow properties at lower shear rates. At shear rates below 500/s, the RA 5300 and Carnauba Wax compounds produce a much lower stress, indicating lower apparent viscosities than the control and the compound containing Struktol WS-280. At rates of approximately 1000/s, all of the compounds have similar flow properties.

A similar chart for the measurement at 150°C is shown on Figure 5. In this case, the RA 5300 containing compound exhibits better flow properties at shear rates below 500/s, but at and above 500/s, the Carnauba Wax containing compound results in a considerably lower stress.

FIGURE 4
Capillary Rheometry Test at 100°C

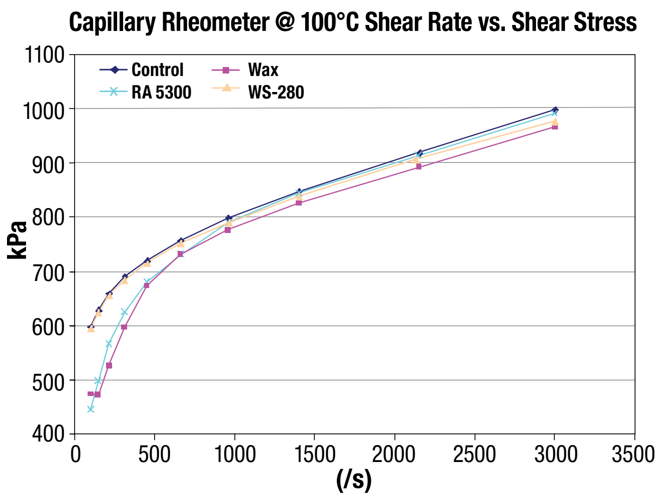
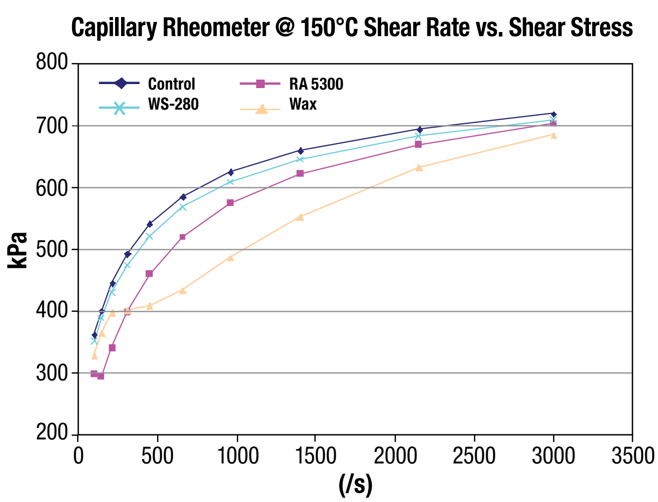


FIGURE 5
Capillary Rheometry Test at 150°C



Extrusion with a Garvey die shows the advantage for using RA 5300 in comparison to Carnauba Wax, Struktol® WS-280, or the control. Extrudate samples of each material are shown in Picture 1 and the ASTM D2230 ratings are listed in Table 9. The sample containing RA 5300 produced better surface finish and better defined lines and edges as compared to any of the other samples. The sample containing Carnauba Wax offered some improvement over the control, but had a rougher surface and edges than the sample containing RA 5300.

PICTURE 1
Garvey Die Extrudate Samples

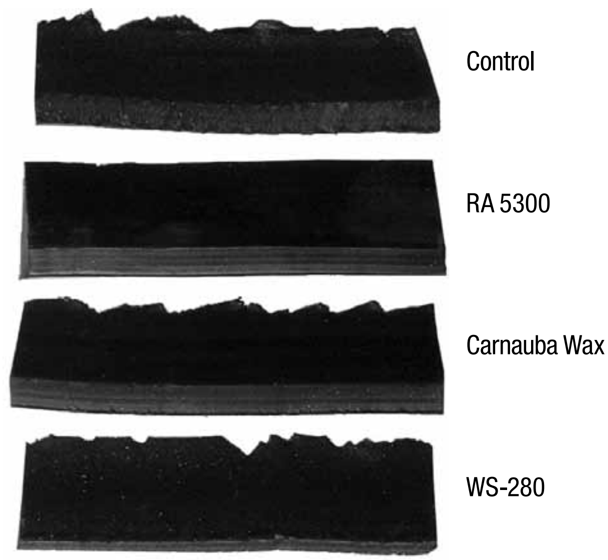


TABLE 9
Garvey Die Extrudate Ratings per ASTM D2230, Rating System A

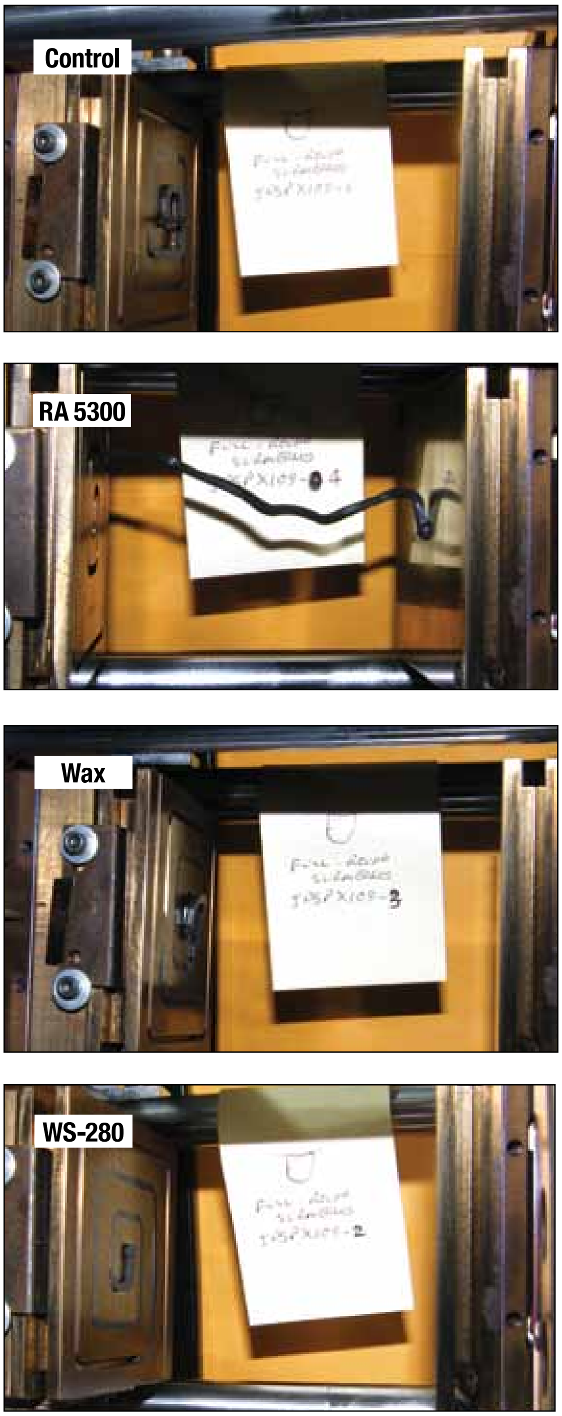
	Control	RA 5300	Wax	WS-280
Swelling and Porosity	2	3	2	2
30° Edge – sharpness and continuity	1	4	3	1
Surface smoothness	2	4	2	2
Corner – sharpness and continuity	1	3	2	1
Average	**1.5**	**3.5**	**2.3**	**1.5**

Scoring range is from 1 (poor) to 4 (excellent)

Flow comparisons from the injection molding experiments produced insignificant results. That was not the case for the release and mold fouling evaluation, however. Samples molded in the half round spiral tool all released from the groove easily and allowed for relatively simple part removal. The deeper, more submerged sample was not as forgiving.

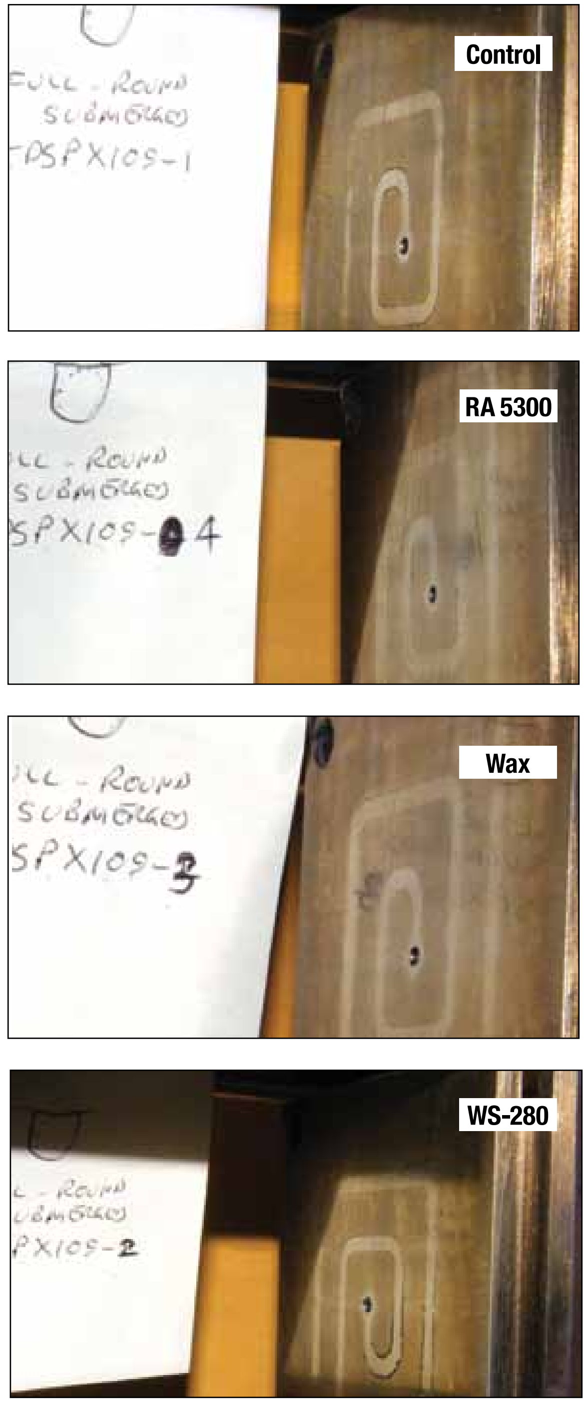
All of the samples, except those produced using the RA 5300, stuck in the grooves, pulling the part away from the nozzle tip and having to be pried out of the mold with a wooden tool. Parts molded using the RA 5300 released totally from the groove, allowing the operator to pull the parts out normally, without the use of any tooling. Picture 2 reflects these results.

PICTURE 2
Mold Release Evaluation



Analysis of the flat, top platen after molding showed the wax and RA 5300 to be better for mold fouling than the control and the WS-280 (see Picture 3).

PICTURE 3
Mold Fouling Analysis



The Effect of RA 5300 concentration on Properties

Using RA 5300, compounds were mixed and tested with increasing levels of RA 5300 up to 1 part per hundred rubber to evaluate the effect of the loading level on properties. The compound composition, MDR, and mechanical property data are reported in Table 10. The only noticeable difference in the MDR and mechanical test results is the slightly lower tensile strength for the 1 PHR loading compared to the lower concentrations.

TABLE 10

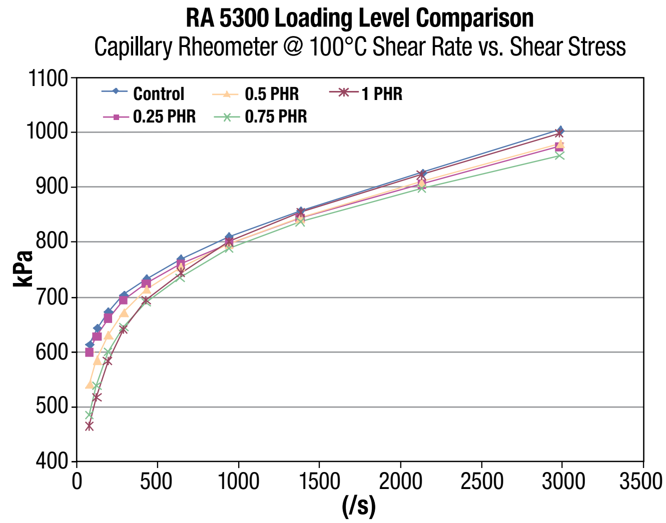
MDR and Physical Properties at Varying Levels of RA 5300

Ingredient	1	2	3	4	5
3M™ Dyneon™ FE 5640	100	100	100	100	100
3M™ Dyneon™ RA 5300	-	0.25	0.50	0.75	1
N990	30	30	30	30	30
Calcium Hydroxide HP XL	6	6	6	6	6
Elastomag® 170	3	3	3	3	3
Total	**139**	**139.25**	**139.50**	**139.75**	**140**
MDR (177°C for 12 min)					
MH (in-lb)	23.52	23.93	23.93	23.55	22.91
ML (in-lb)	1.35	1.37	1.35	1.38	1.35
t_s2 (min)	2.42	2.13	2.16	2.16	2.48
T ' 50 (min)	3.01	2.64	2.68	2.67	3.04
T ' 90 (min)	4.21	4.08	4.13	4.11	4.24
Press Cure 10' @ 177°C (350°F); Post Cure 16hr @ 232°C (450°F)					
Tensile Strength (psi)	2331	2344	2412	2355	2090
Elongation at Break (%)	200	202	209	216	206
100% Secant Modulus (psi)	978	940	983	884	901
Hardness (Shore A)	76	74	75	73	74

Further comparison was done by Capillary Rheometry, as seen in Figure 6. Improved flow was obtained with increasing concentration and lower shear rates. The increased concentrations had little effect on flow at higher shear rates. At all rates, the compound with 0.75 PHR loading was just as effective as the 1PHR loading, and the compound with 0.5 PHR was only slightly lower.

FIGURE 6

Capillary Rheometer Chart for RA 5300 at Different Loadings



Discussion

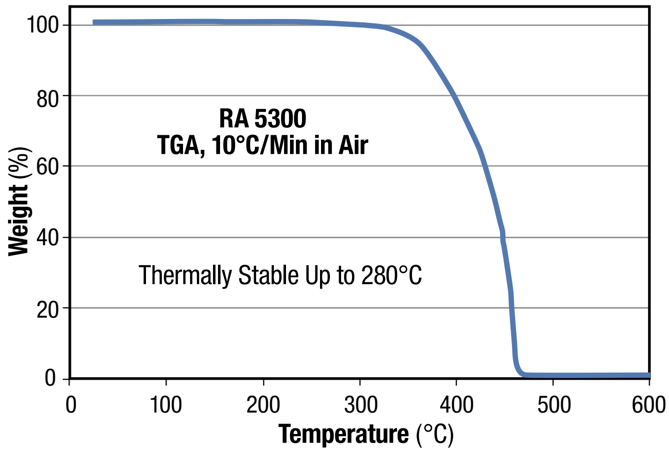
The testing performed demonstrated the inherent properties of the RA 5300 with a positive impact on flow and release, in particular at lower shear rates. At loadings as low as 0.5 PHR, improved flow properties can be seen.

Although hydrocarbon process aids exhibited similar improvement in flow and fouling in some cases, the improved MDR, compression set, and mold release results obtained with the RA 5300 might be explained by a compatibility of the RA 5300 with the fluoroelastomer that is not present with the other processing aids. The thermal stability of the RA 5300 could also be impacting these results. Figure 7 shows charted results achieved when tested by a Thermogravimetric Analyzer (TGA). The RA 5300 does not begin to degrade until 280°C, reflecting excellent thermal stability.

Analytical tests with an X-ray photoelectron spectrometer (XPS) on the control compound (no processing additive) processed through an extruder following extrusion of the compound containing RA 5300, clearly show amounts of the RA 5300 material on the surface. This may show an affinity of the RA 5300 material to the extruder barrel, screw, and die surface. This is likely to be the reason for the improved Garvey Die extrusions.

Immersion tests were performed on these same compounds to compare compatibility in a variety of different fluids. The results produced no noticeable differences and the data are available upon request.

FIGURE 7
TGA Degradation Testing



Conclusions & Recommendations

Based on the results of the experiments used for this report, the use 3M™ Dynamar™ RA 5300 as a process aid in fluoroelastomer compounds could offer both processing and performance improvements over many commercial products typically used in the industry. Sharper edges and smoother surfaces were achieved in Garvey Die extrusions, along with improved mold release and fouling in injection molding, without sacrificing compression set and flexibility. Incremental processing improvements can be achieved with increased loadings of the RA 5300, with 0.5 and 1.0 PHR being the optimal loading range.

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