Evaluation of Fully Renewable Polymeric Plasticizers in PVC Compound Formulations

Hallstar Industrial Solutions Company

Commercial Development Group

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Project Goals

- The goal of the project was to synthesize a selection of 100% renewable polyester plasticizers and then conduct side-by-side comparative evaluations of said plasticizers in the standard PVC compound formulations against selected control plasticizers

- Another goal of the project was to showcase an example of a calculation of the overall performance ratings of all plasticizers used in the study based on the priorities assigned to the key performance criteria

Data Review and Discussion

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Formulations and Tests

Ingredients	Parts
S-PVC (K 68-70)	100.0
Ca/Zn Stabilizer	2.0
ESO	5.0
Plasticizer	67.0

Test	Conditions
Originals (basic tensile properties)	Room temperature Instron testing
Air Aging	70 hours @ 136°C
DI Water Aging	24 hours @ 90°C followed by dry-out (DO) for 24 hours @ 60°C
Cottonseed Oil Aging	24 hours @ 60°C
Tg by DSC250	Original and after air ageing
IRM 902 Oil Ageing	96h @ 100°C

NOTE: *All compounds were milled on a Reliable two-roll mill at 365°F (180°C) set temperature for about 5-10 min followed by compression molding of 6 x 6 x 0.075 inch plaques at 340°F (171°C) for 10 min*

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Renewable Polyester QC Properties

	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Form @ 25°C	Semi-Solid	Semi-Solid	Liquid	Solid	Liquid	Liquid	Liquid
Melting Point Range (°C)	5 to 30	5 to 30	NA	50 to 60	NA	NA	NA
AV	2.1	0.5	0.1	0.2	0.4	~ 1.0	~ 1.0
Viscosity (cP)	172 @ 40°C	264 @ 40°C	3610 @ 25°C	N/A	3032 @ 25°C	~ 3500 @ 25°C	~ 3900 @ 25°C
Molecular Weight	Medium	Medium	Medium	High	Medium	Medium	Medium
Specific Gravity	0.996 @ 40°C	1.047 @ 40°C	1.07 @ 25°C	N/A	1.093 @ 25°C	1.085	1.09
Refractive Index	1.462	1.46	1.471	N/A	1.463	1.467	1.458
Biobased content (%)	100	100	100	100	100	0	0

NOTE: *All RX polyesters were synthesized using a range of commercially available plant-derived renewable raw materials*

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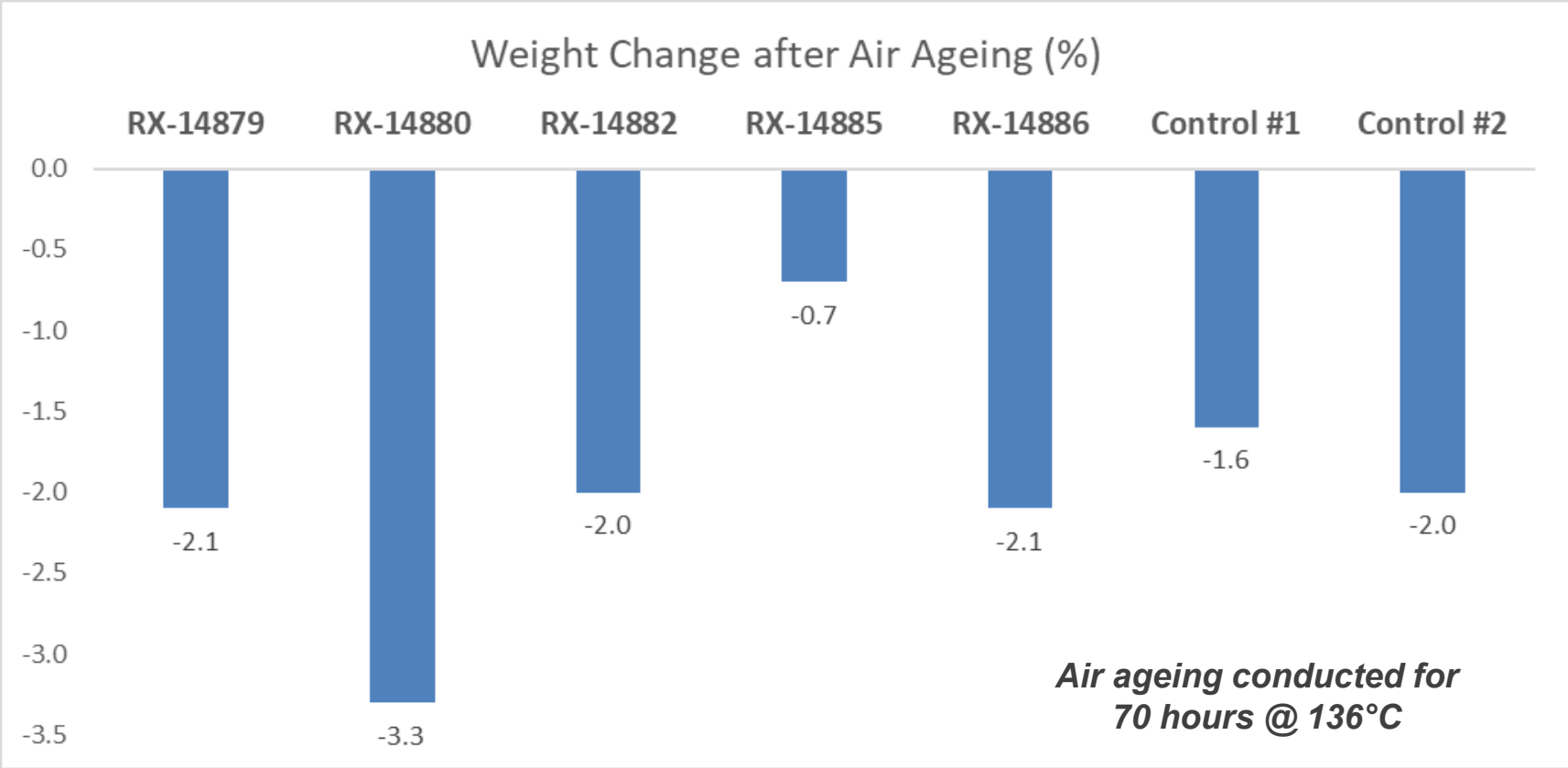
Weight Change After Air Ageing



- Renewable polyester plasticizer RX-14885 exhibited the lowest weight change after air ageing, significantly better than that of both Controls
- RX-14880 polyester plasticizer exhibited the highest weight loss

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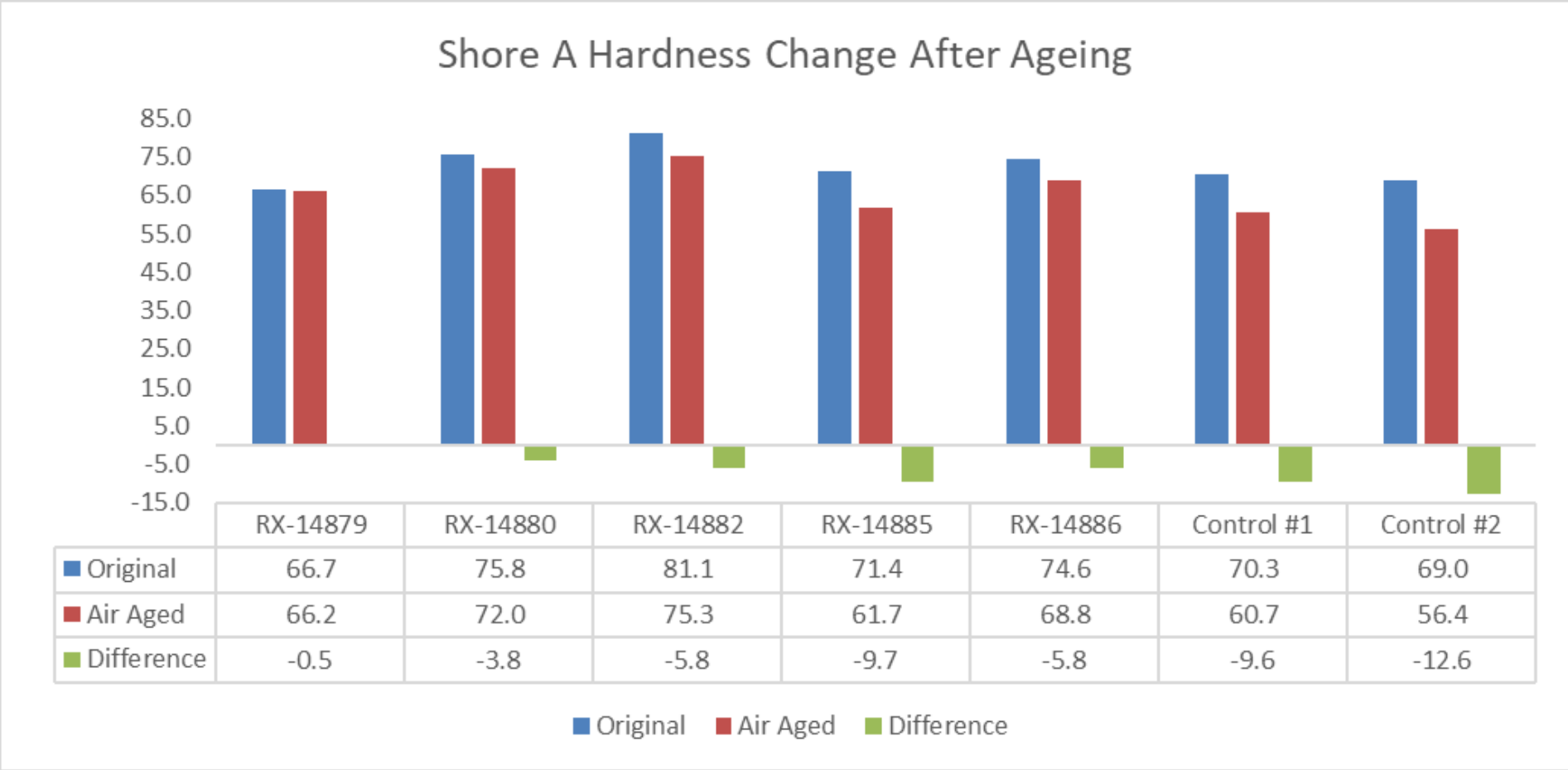
Hardness Change After Air Ageing for Incumbents



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Original	66.7	75.8	81.1	71.4	74.6	70.3	69.0
Air Aged	66.2	72.0	75.3	61.7	68.8	60.7	56.4
Difference	-0.5	-3.8	-5.8	-9.7	-5.8	-9.6	-12.6

- Renewable polyester plasticizers RX-14879 and RX-14880 exhibited the lowest change in PVC compound hardness after air ageing
- RX-14879 also exhibited the lowest original hardness while RX-14882 exhibited the highest

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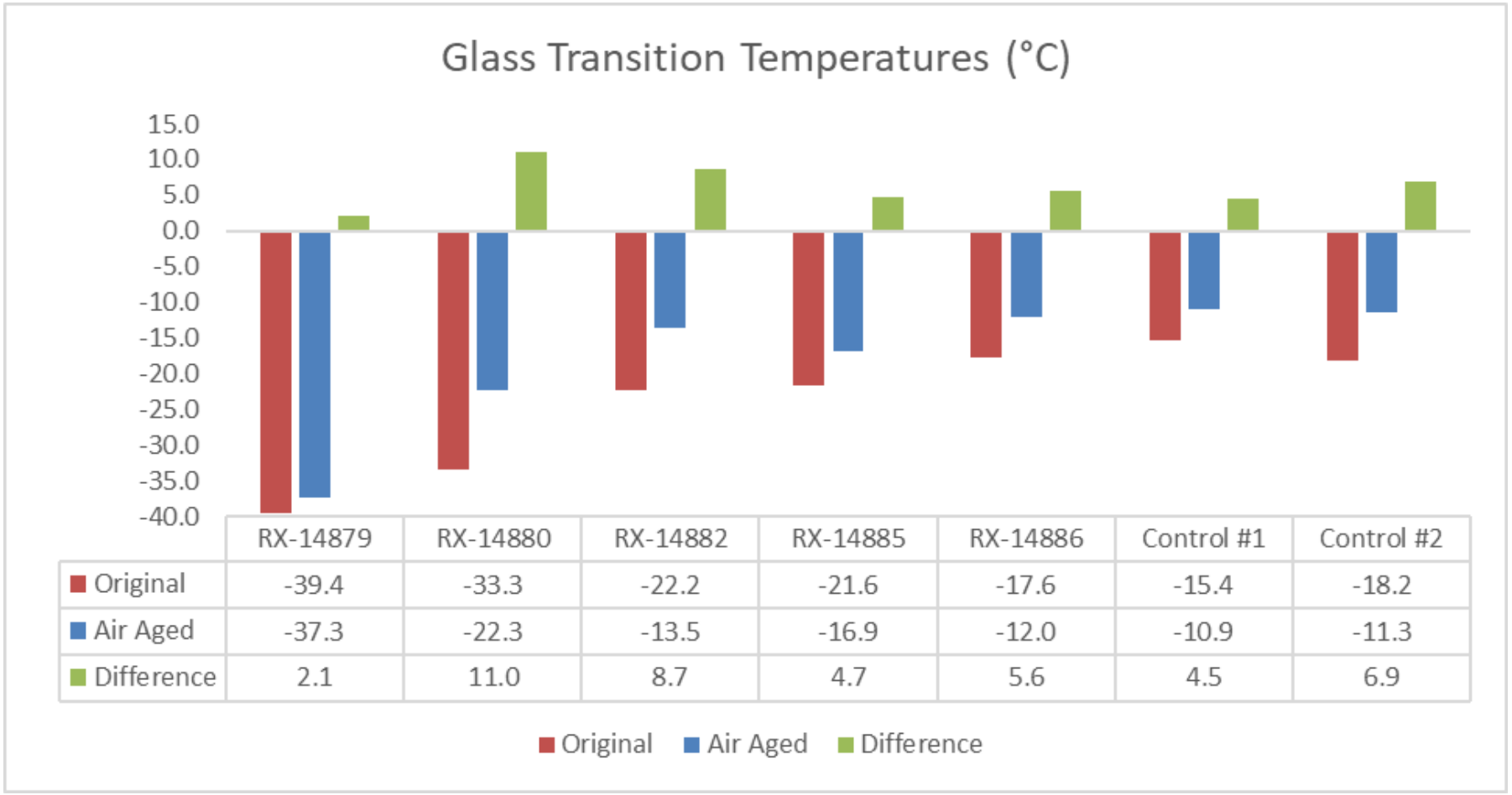
Glass Transitions Before and After Air Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Original	-39.4	-33.3	-22.2	-21.6	-17.6	-15.4	-18.2
Air Aged	-37.3	-22.3	-13.5	-16.9	-12.0	-10.9	-11.3
Difference	2.1	11.0	8.7	4.7	5.6	4.5	6.9

- Renewable polyester plasticizers RX-14879 and RX-14880 exhibited the lowest initial and aged Glass Transitions
- RX-14879 polyester plasticizer was the best in retaining the low temperature Tg after ageing with only 2.1°C increase after ageing

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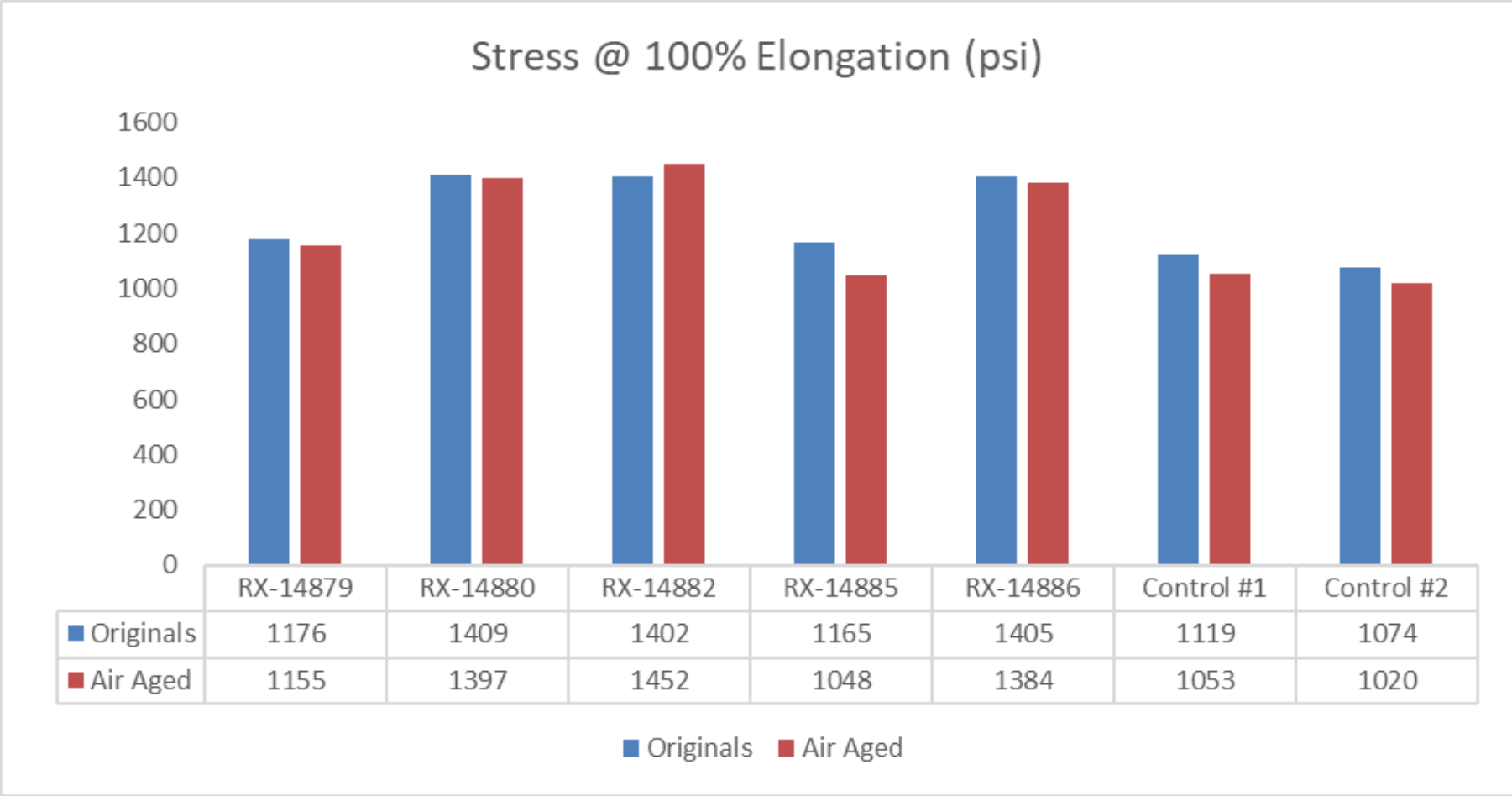
Stress @ 100% Elongation After Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	1176	1409	1402	1165	1405	1119	1074
Air Aged	1155	1397	1452	1048	1384	1053	1020

- RX-14880, RX-14882 and RX-14886 exhibited the highest original and aged moduli of all plasticizers
- RX-14885 and both Control plasticizers exhibited the lowest moduli before and after air ageing

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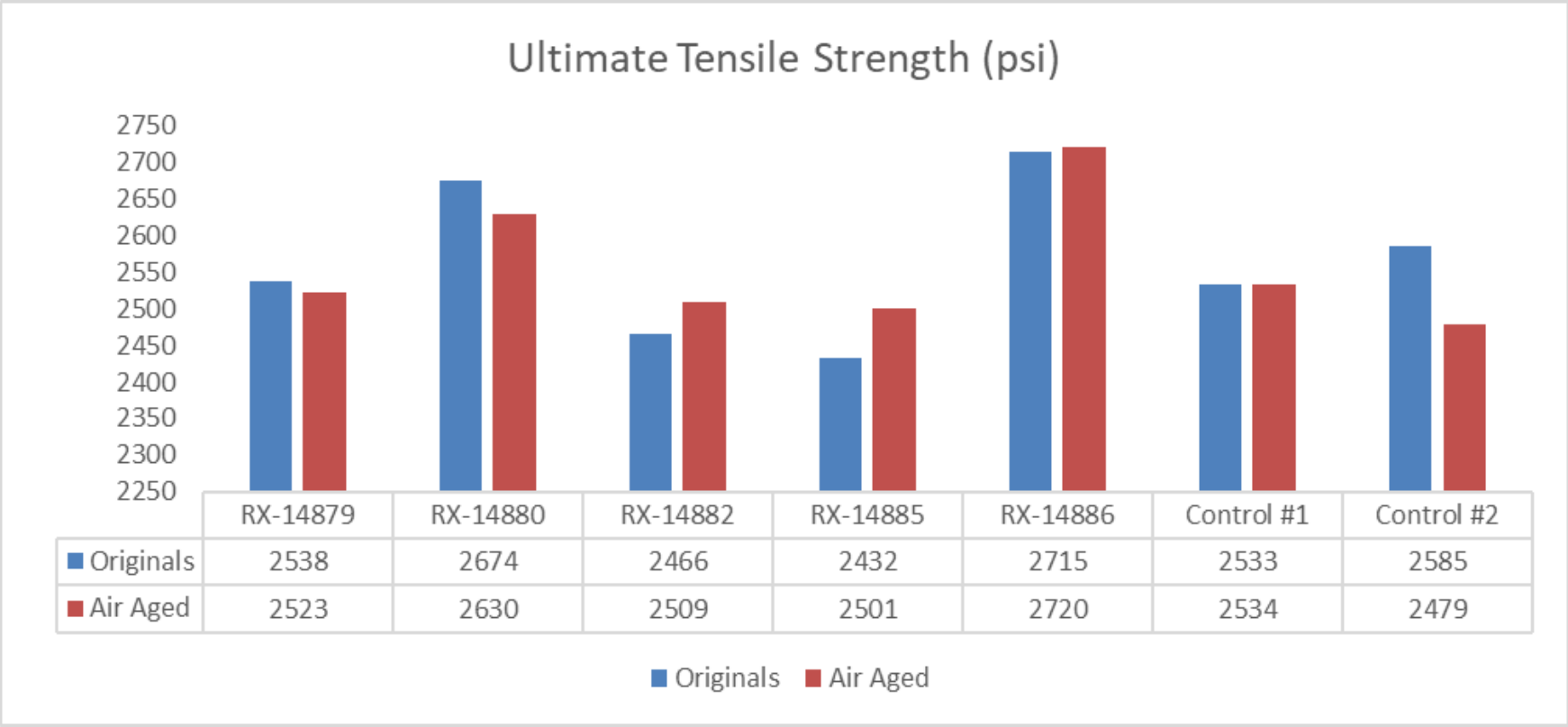
Tensile Strength Change After Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	2538	2674	2466	2432	2715	2533	2585
Air Aged	2523	2630	2509	2501	2720	2534	2479

- RX-14880 and RX-14886 polyesters exhibited the highest original and aged tensile strength of all plasticizers
- RX-14882 and RX-14885 plasticizers exhibited the lowest original tensile strengths while also exhibiting increase in tensile strength after heat ageing

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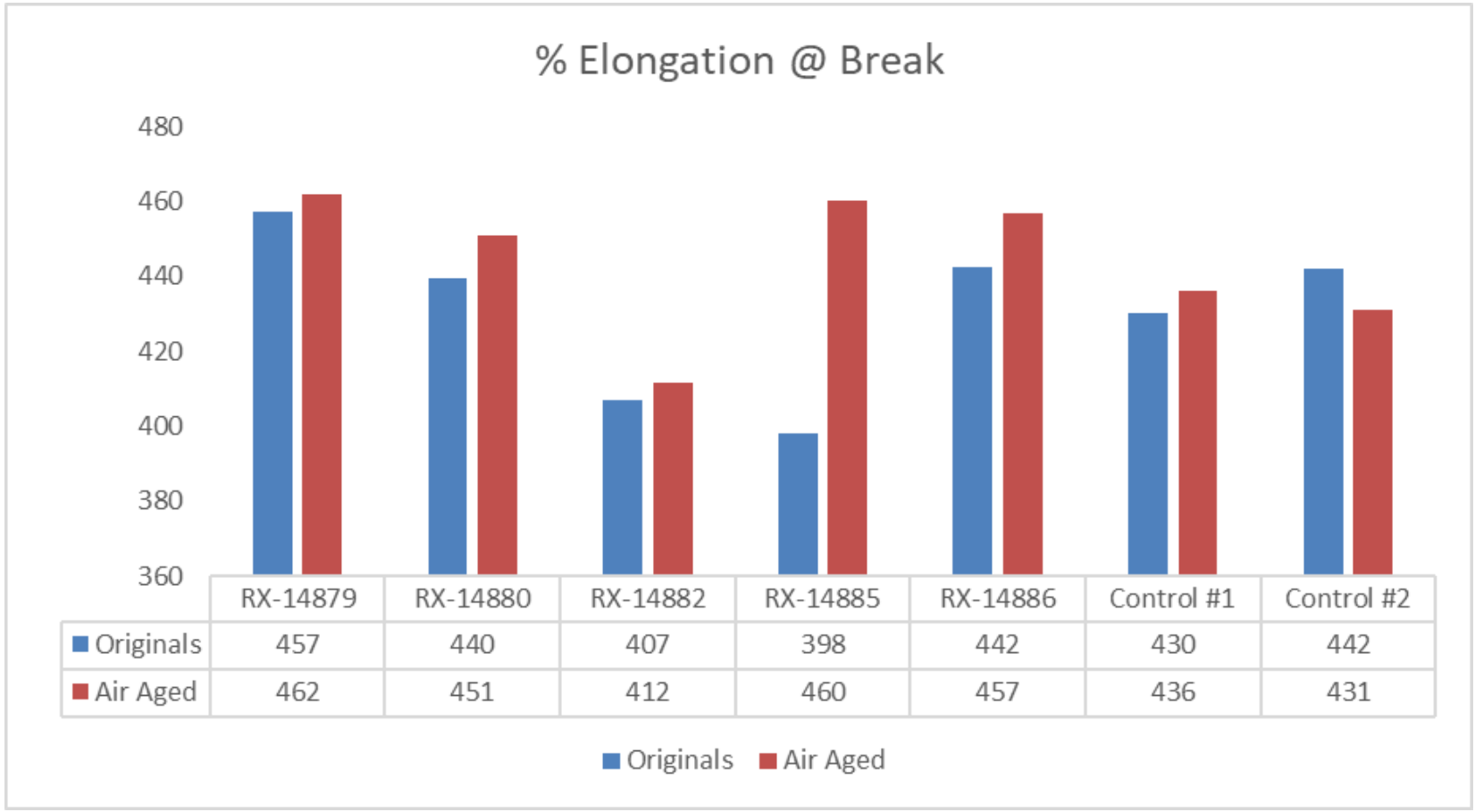
Elongation @ Break Change After Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	457	440	407	398	442	430	442
Air Aged	462	451	412	460	457	436	431

- RX-14879 polyester exhibited the highest elongation before and after air ageing along with excellent retention of elongation after ageing
- RX-14882 and RX-14885 exhibited the lowest original elongation

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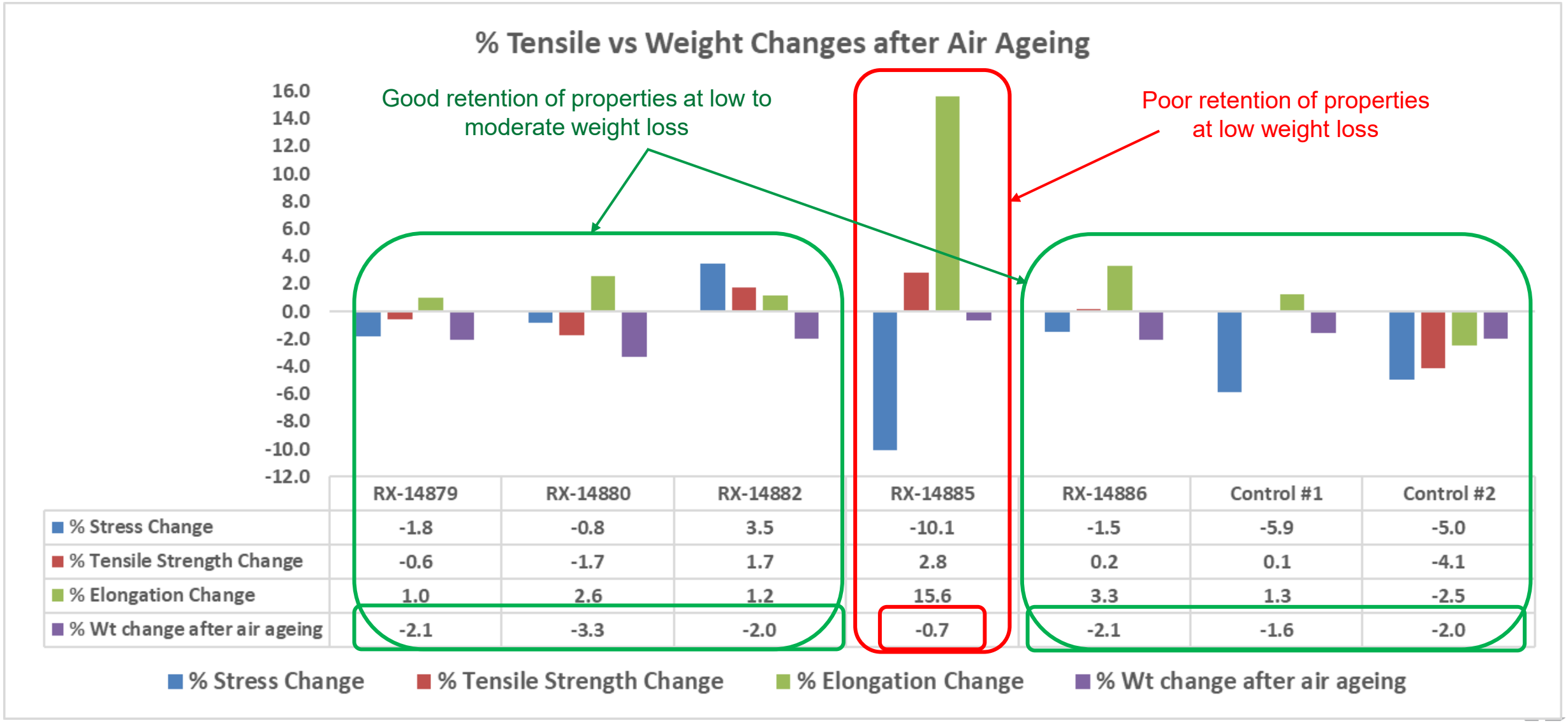
Tensile Performance Changes After Air Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
% Stress Change	-1.8	-0.8	3.5	-10.1	-1.5	-5.9	-5.0
% Tensile Strength Change	-0.6	-1.7	1.7	2.8	0.2	0.1	-4.1
% Elongation Change	1.0	2.6	1.2	15.6	3.3	1.3	-2.5
% Wt change after air ageing	-2.1	-3.3	-2.0	-0.7	-2.1	-1.6	-2.0

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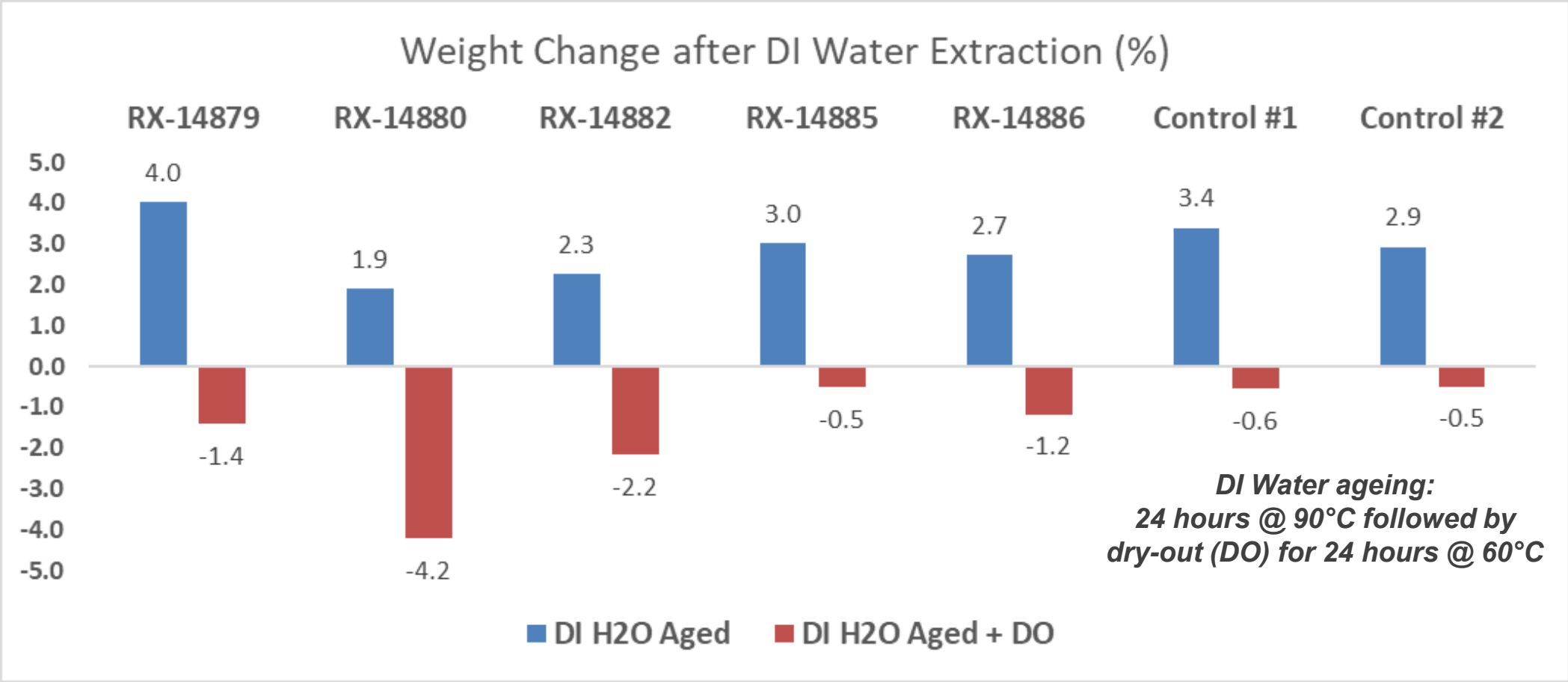
% Weight Change After DI Water Ageing



- RX-14879 polyester had the highest water pickup of all plasticizers while other RX polyesters had lower water pickups than the Controls
- RX-14885 renewable polyester was in-line with both water swell and DO performance of both Controls
- RX-14880 exhibited the highest DO weight loss of all plasticizers

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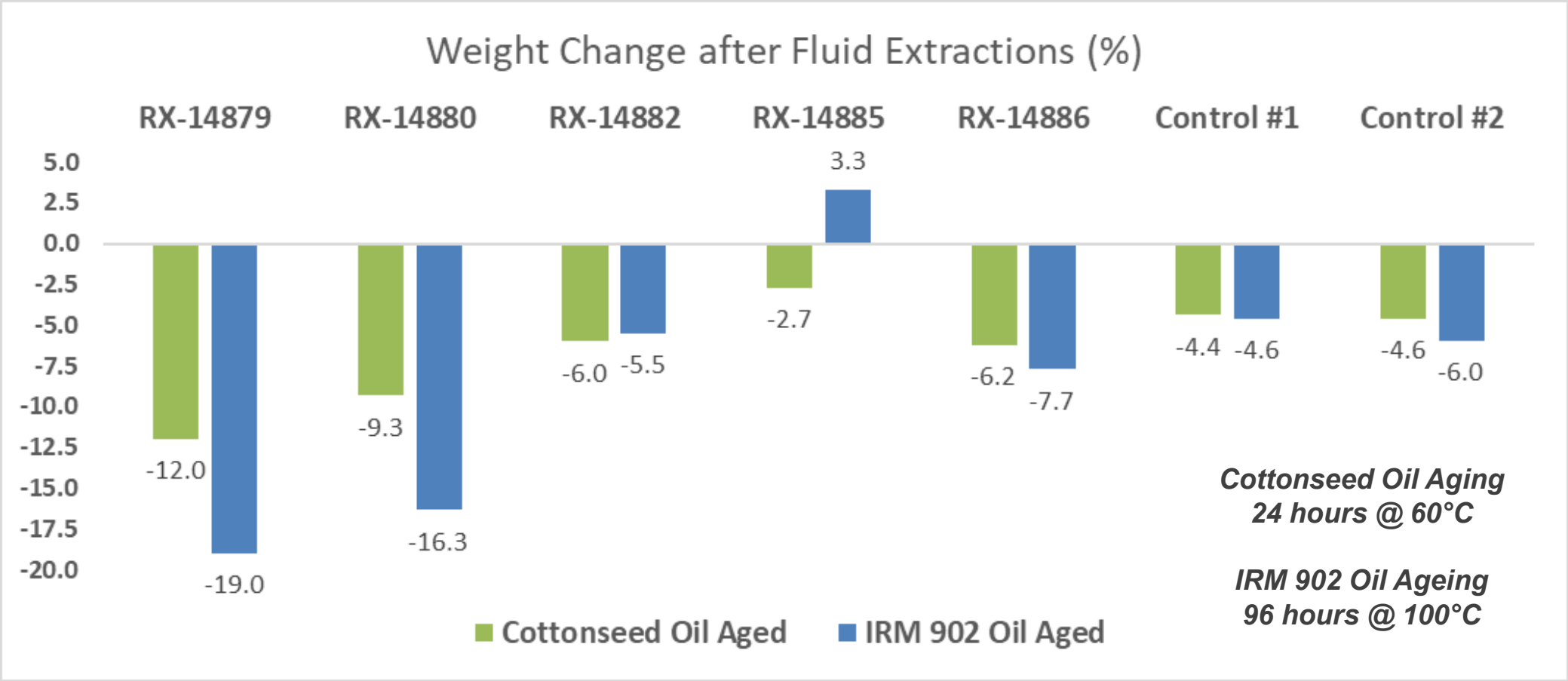
% Weight Change After Low Polarity Fluid Extractions



- Weight losses for both cottonseed and IRM 902 oils follow very similar trend with RX-14885 being the best performer of all plasticizers in the study
- RX-14885 renewable polyester surprisingly exhibited small weight gain (swell) in IRM 902 oil whiles all other polyesters experienced weight losses
- RX-14882 and RX-14886 could be described as having similar performance while RX-14879 and RX-14880 could be described as having poorer performance to Controls

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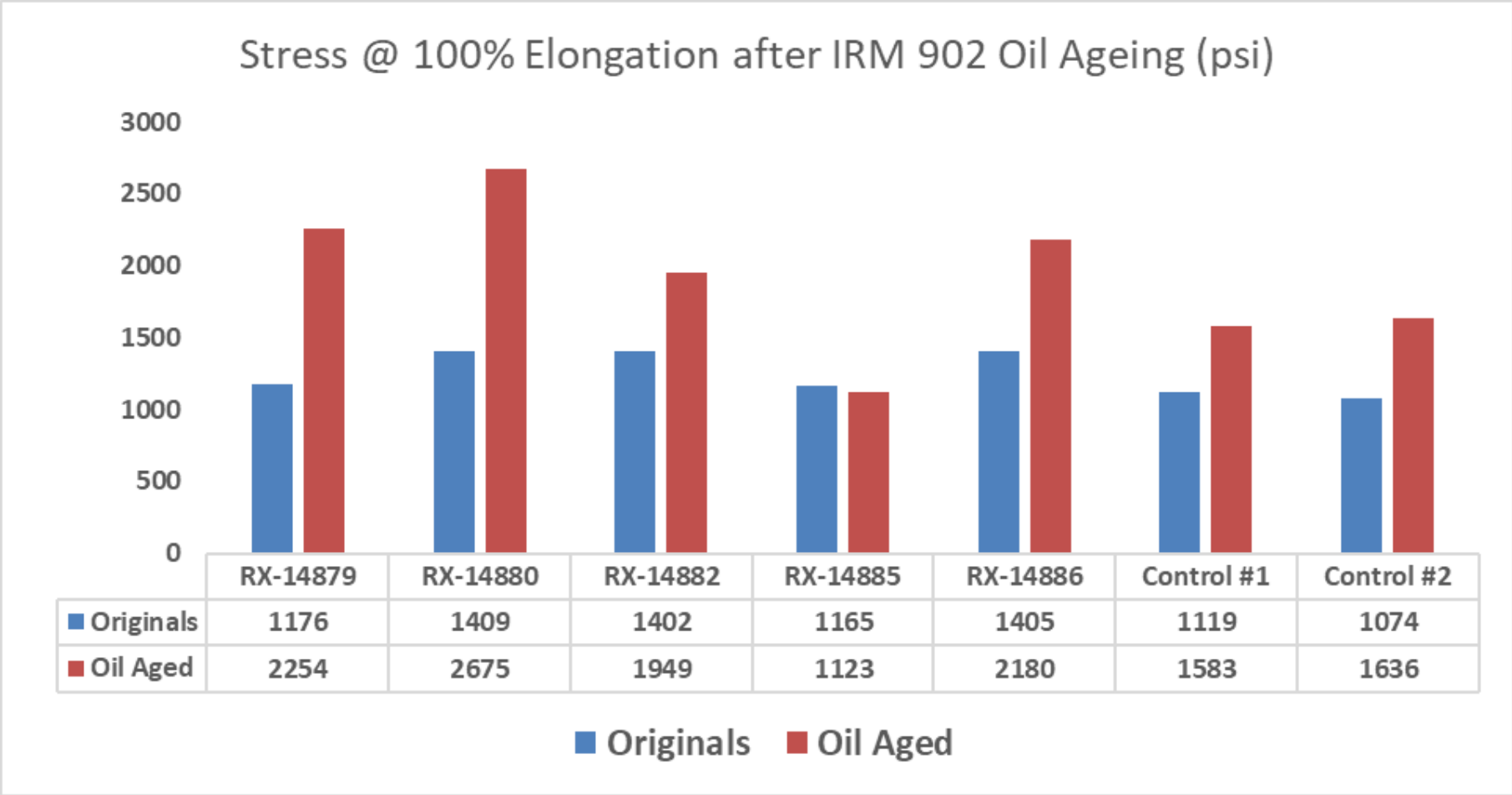
Change in Modulus After IRM-902 Oil Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	1176	1409	1402	1165	1405	1119	1074
Oil Aged	2254	2675	1949	1123	2180	1583	1636

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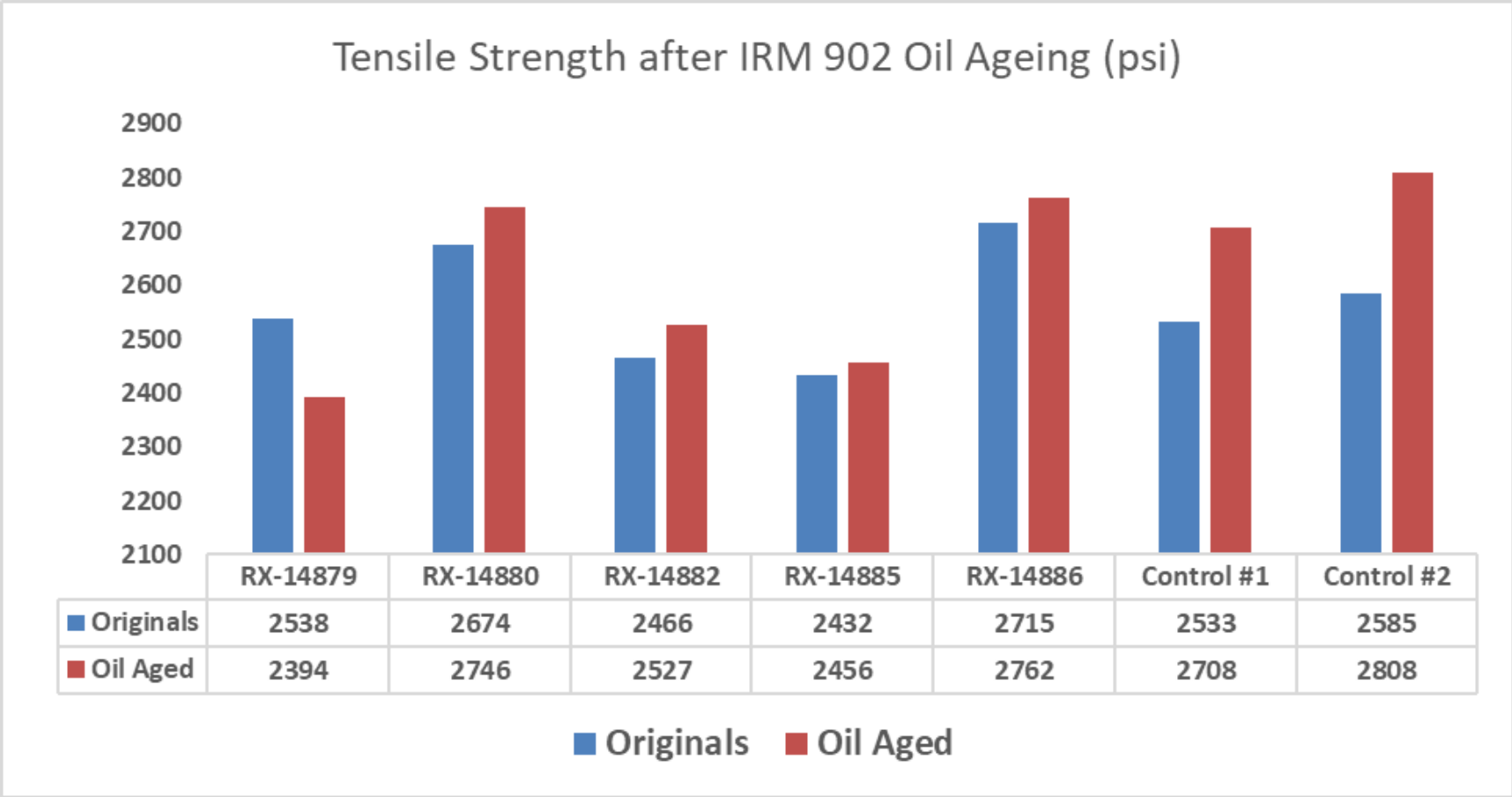
Change in Ultimate Tensile Strength After IRM-902 Oil Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	2538	2674	2466	2432	2715	2533	2585
Oil Aged	2394	2746	2527	2456	2762	2708	2808

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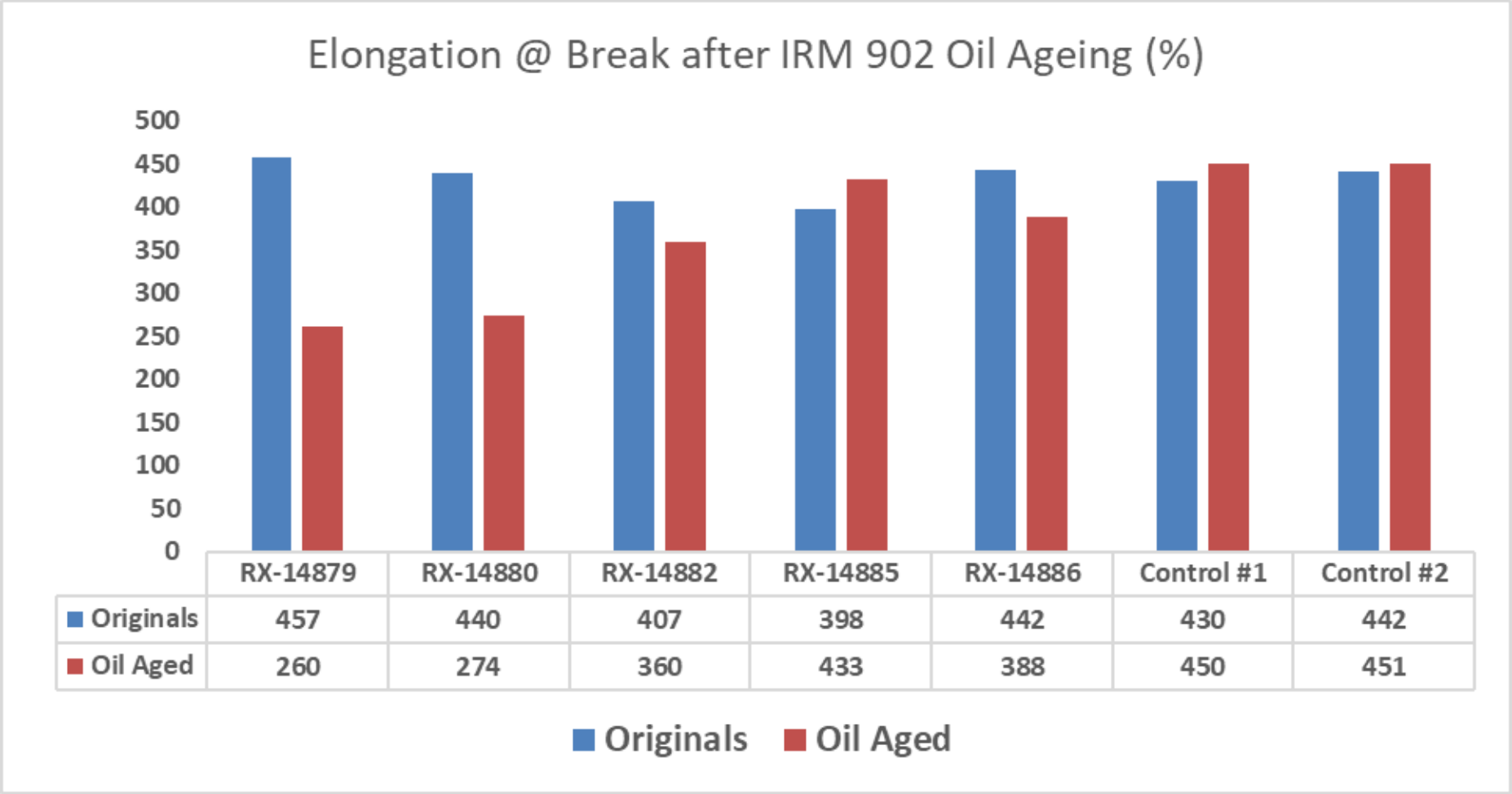
Change in Elongation @ Break After IRM-902 Oil Ageing



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Originals	457	440	407	398	442	430	442
Oil Aged	260	274	360	433	388	450	451

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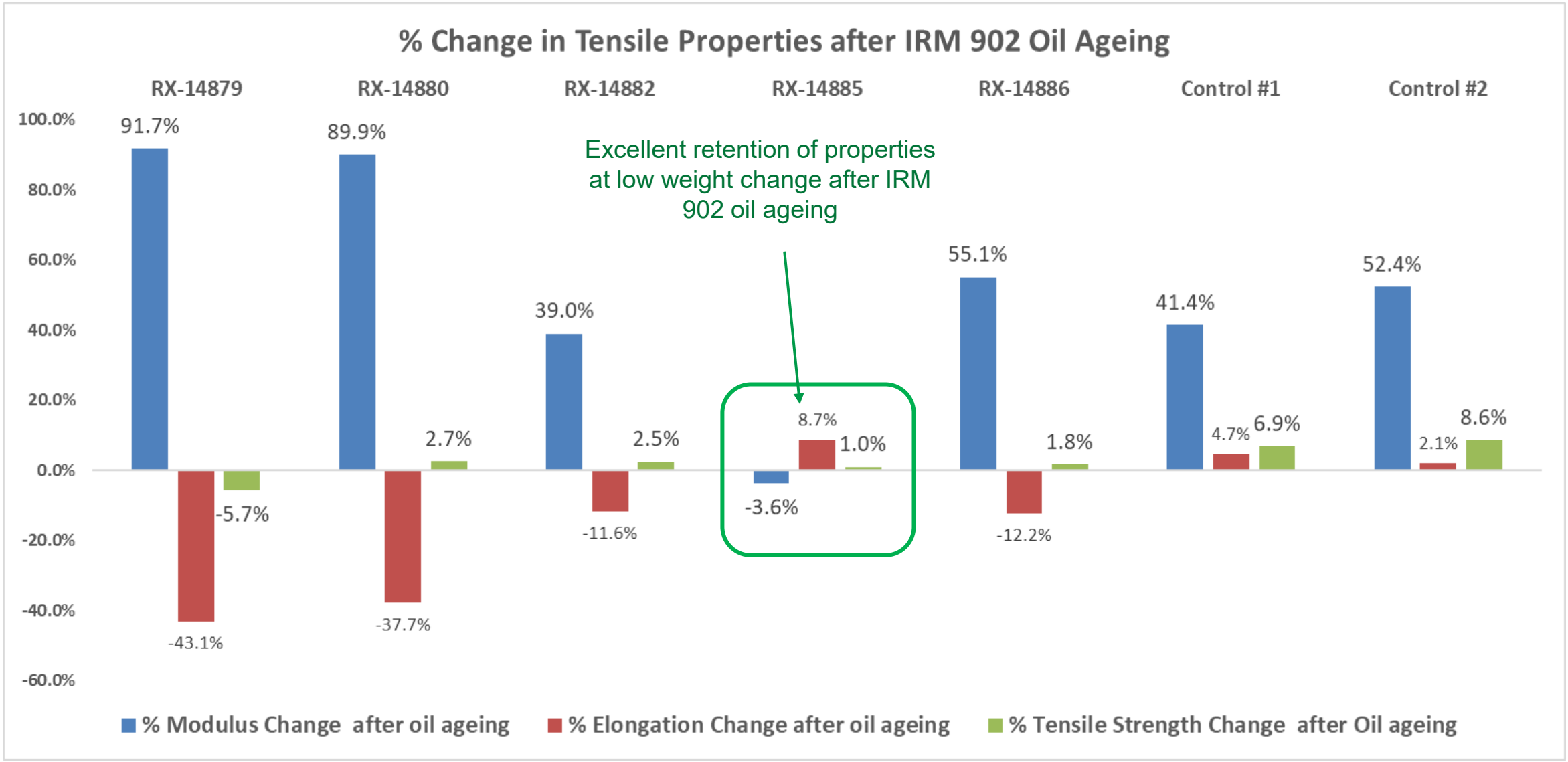
Change in Tensile Properties After IRM-902 Oil Ageing



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Performance Rating Calculations

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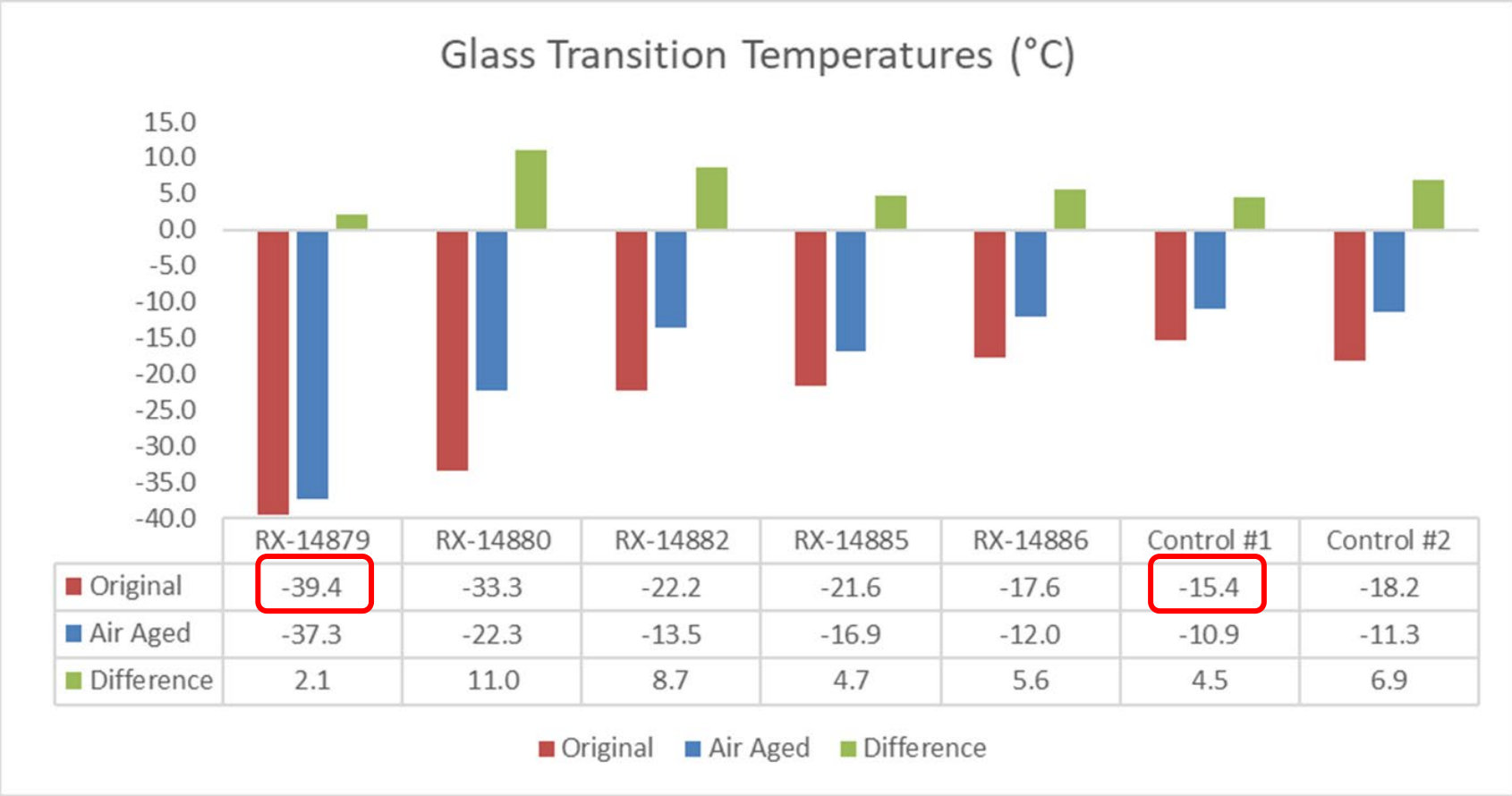
Examples of Performance Ratings Guidelines



	RX-14879	RX-14880	RX-14882	RX-14885	RX-14886	Control #1	Control #2
Original	-39.4	-33.3	-22.2	-21.6	-17.6	-15.4	-18.2
Air Aged	-37.3	-22.3	-13.5	-16.9	-12.0	-10.9	-11.3
Difference	2.1	11.0	8.7	4.7	5.6	4.5	6.9

Initial (Original) Tg		
-15.4	eq to -16 or higher	1
-39.4	< -16 and > -20	2
Range	< -20 and > -25	3
	< -25 and > -30	4
	eq to -30 or lower	5

- Lastly – simply assign ratings based on where the actual specimen values fit in the agreed upon performance ranges (“5” is best and “1” is worst)

- 1st - Pick the lowest and the highest Tg values to set the performance range
- 2nd – Split the range into section to allow for proper / effective rating assignments

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Examples of Performance Ratings Guidelines

		Recipe Variable	RX-14879	RX-14880	RX-14886	RX-14882	RX-14885	Control #1	Control #2
% Change of Stress @ 100% El (psi) after			91.66	89.93	55.11	39.01	-3.57	41.42	52.41
% Change of Elongation at Break (%)			-43.08	-37.71	-12.24	-11.64	8.65	4.65	2.12
% Change of Ultimate Tensile Strength			-5.70	2.67	1.76	2.46	0.98	6.91	8.62
		TOTAL Chang	**140.44**	**130.31**	**69.11**	**53.11**	**13.20**	**52.98**	**63.15**

NOTE: *Slide 19 uses this tabulated data for the graph*

- 1st – Add the absolute values of all the % differences for all tensile properties for each specimen
- 2nd – Use the total change row data to set the performance range
- 3rd – Split the range into section to allow for proper & effective rating assignments
- Lastly - simply assign ratings based on where the actual specimen values fit in the agreed upon performance ranges (“5” is best and “1” is worst)

retention of tensiles after IRM-902 oil ageing		
13.20	< 45	5
140.44	eq to 45 to 75	4
Range	eq to 75 to 105	3
	eq to 105 to 135	2
	> 135	1

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Overall Performance Ratings

The weighted percentage values are assigned by the customer based on their needs for performance for a given application

WEIGHT	10	5	10	15	10	10	10	10	5	10	5	100
PERFORMANCE CRITERIA	Initial Tg / low temp. flexibility	Tg / low temp. flexibility after heat ageing	Weight loss after heat ageing	Retention of tensile prop. after heat ageing	Weight pick-up/swell after DIW ageing	DO wt change after DIW ageing	Weight loss after cottonseed oil ageing	Retention of Hardness / Hardness Change	% wt change after IRM-902 oil ageing	retention of tensiles after IRM-902 oil ageing	Surface Energy Data (dynes)	TOTAL POINTS
RX-14879	5	5	3	5	1	3	1	5	1	1	3	310
RX-14880	5	3	2	4	5	1	1	3	1	2	5	295
RX-14882	3	1	4	4	4	2	3	3	3	4	2	320
RX-14885	3	2	5	1	2	5	5	2	5	5	5	345
RX-14886	2	1	3	4	3	3	3	3	3	4	3	305
Control #1	1	1	4	4	2	4	4	2	4	4	2	305
Control #2	2	1	4	3	3	5	4	1	3	4	2	305
Rating system: 5 best, 1 worst performance												

The performance values are determined based on the test data for the performance criteria deemed important

TOTAL score indicates final performance rating for all products tested for a given hypothetical application and the scoring/performance rating system jointly agreed upon

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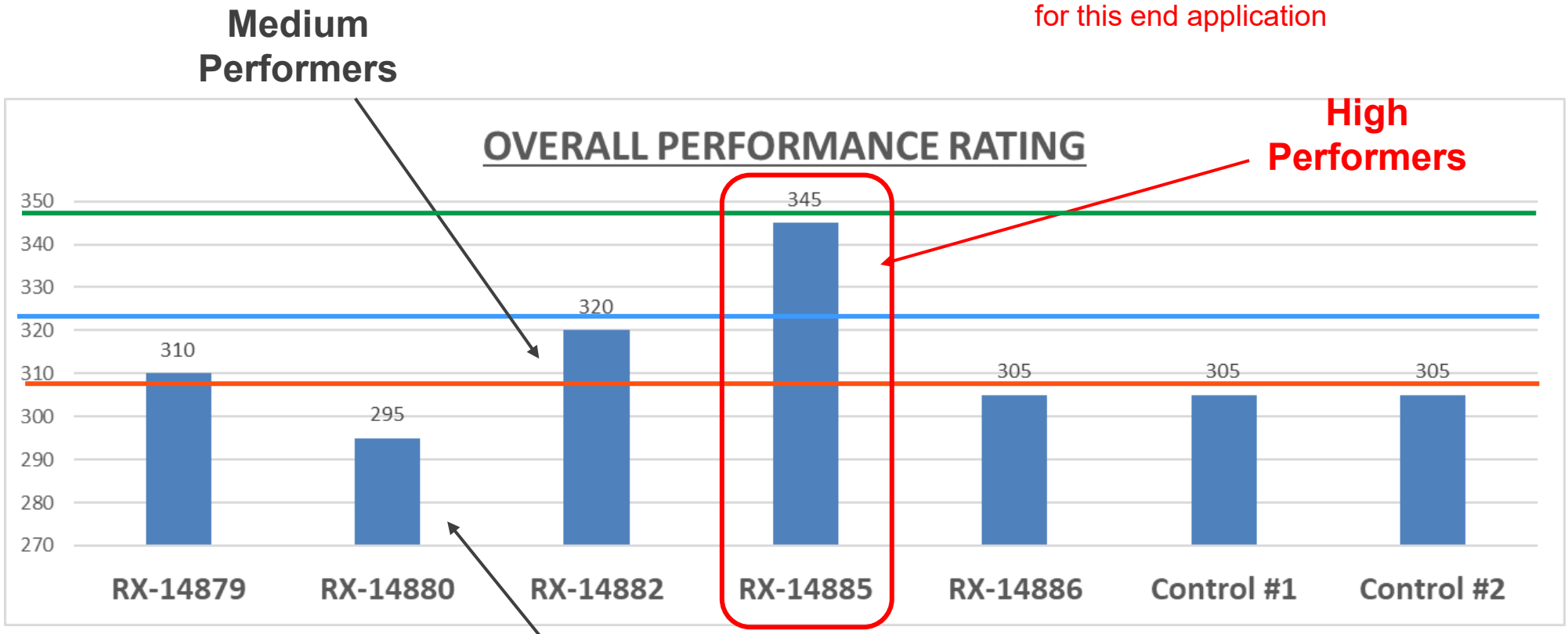
Performance Summary

Based on the FINAL performance score described in this example, RX-14885 polyester seems like the most suited for this end application



NOTE: The overall performance rating may change depending on desired weight placed on each key performance characteristic!

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Conclusions

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Conclusions

- Several new polymeric plasticizers made from 100% renewable resources were synthesized, compounded, and evaluated against selected control polymeric plasticizers
- Multitude of tests were performed, and data used for direct side-by-side comparisons against control plasticizers
- The overall performance rating was also calculated based on ratings assignments for key performance criteria for each plasticized compound based on a hypothetical end-application
- The highest performing polymeric plasticizer in this example was RX-14885 having performance ratings of 345 with the 2nd best in performance being RX-14882 polyester having 25 points lower score
- This example process emphasizes the importance of customer-focused and data-driven approaches Hallstar uses toward new product development