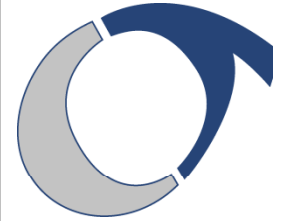


CHEM TECHNOLOGIES, LTD.

Beyond the obvious from innovation to application



Advancure™ with DOTG Replacements

Vamac® G Compound

Technical Report: CTR-09001

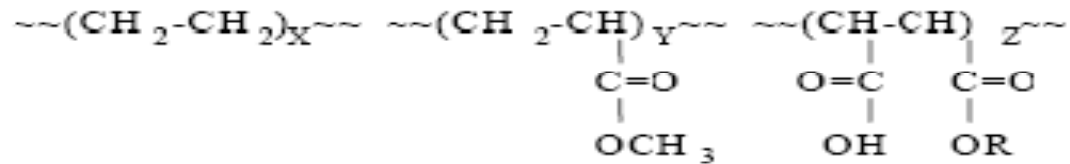
January 8, 2009

Background



- **DuPont Vamac[®] ethylene acrylic elastomers are designed to withstand high and low temperatures and aggressive new automotive fluids in under hood automotive applications such as seals, gaskets, ducts, hoses, boots and dampers.**
- **The most often cure system used in Vamac[®] compounds is a combination of HMDC (hexamethylenediamine carbamate) with DOTG (di-*o*-tolylguanidine) or DPG (diphenylguanidine).**
- **During the vulcanization process the HMDC breaks down into HMDA (hexamethylene diamine) which is the active curing agent.**
- **The HMDC curative is the second highest cost component of Vamac[®] compounds.**

Hexamethylenediamine Cure Mechanism

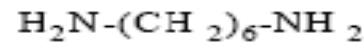


Ethylene

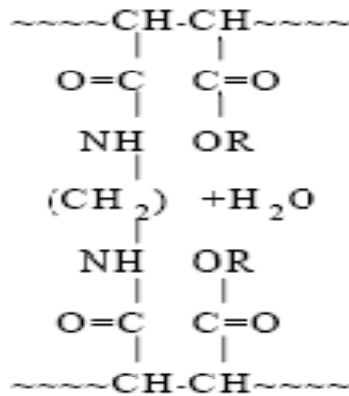
Methyl Acrylate

Cure Site

+

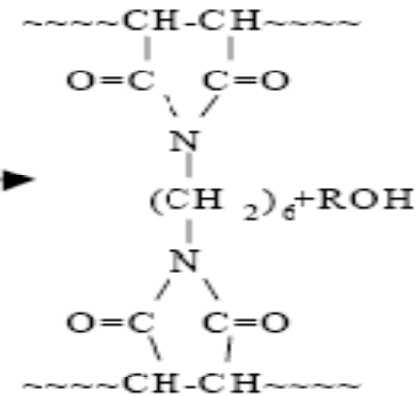


Hexamethylene Diamine



Amide Crosslink

Postcure



Imide Crosslink

Advancure



- **Advancure is a 47% active liquid concentrate of hexamethylenediamine (HMDA) absorbed on amorphous silica in powder form.**
- **Advancure is based on patented curing technology from DuPont and is enhanced with an innovative dispersion technology from Chem Technologies.**
- **Advancure is a free-flowing, dust-free beaded powder that can be used to cure the majority of Vamac[®] products at a lower cost compared to traditional curing technologies.**
- **Advancure HMDA (hexamethylene diamine) is a lower cost alternative to HMDC (hexamethylenediamine carbamate) types.**
- **For the same activity level, replace 1 phr of hexmethylenediamine carbamate with 1.56 phr of Advancure.**

DOTG Replacements



- **The European Union under R.E.A.C.H. is going to ban the use of guanidine curatives such as DPG and DOTG.**
- **Either DOTG or a combination of DOTG with DPG are used with HMDA (Advancure) or HMDC (Diak 1 types and equivalents).**
- **Two different chemicals are considered safe replacements for DOTG or DPG under R.E.A.C.H. regulations:**
 - **Safic Alcan's ACT 55, a tertiary amine complex, 70% active on a silica carrier**
 - **Lanexess' XLA-60, a proprietary amine complex**
- **Studies in the literature have shown salicylic acid (Akrochem's Retarder SAX) also acts as a retarder with the ACT 55 complex.**

Replacement Formulations



- **The following model cure systems were taken from the literature promoting ACT 55 and XLA-60 (see references at the end of the presentation).**
- **Control Formulations:**
 - #1 HMDC (Diak 1) 1.5 phr / DOTG 4 phr
 - #4 HMDA (Advancure) 2.3 phr / DOTG 4 phr
- **Replacement A Study:**
 - #5 HMDC (Diak 1) 1.2 phr / ACT 55 2 phr
 - #6 HMDA (Advancure) 1.85 phr / ACT 55 2 phr
 - #7 HMDC (Diak 1) 1.2 phr / ACT 55 2 phr / SAX 0.75 phr
 - #8 HMDA (Advancure) 1.85 phr / ACT 55 2 phr / SAX 0.75 phr
- **Replacement B Study:**
 - #9 HMDC (Diak 1) 1.5 phr / ACT 55 2 phr
 - #10 HMDA (Advancure) 2.3 phr / ACT 55 2 phr
 - #11 HMDC (Diak 1) 1.5 phr / ACT 55 2 phr / SAX 0.75 phr
 - #12 HMDA (Advancure) 2.3 phr / ACT 55 2 phr / SAX 0.75 phr
- **Replacement C Study:**
 - #13 HMDC (Diak 1) 1.5 phr / XLA-60 4 phr
 - #14 HMCA (Advancure) 2.3 phr / XLA-60 4 phr

Formulation



● Vamac[®] G	100.00
● N774 Carbon Black	90.00
● Stearic Acid	2.00
● Polyoxyethylene octadecyl ether phosphate	1.50
● 1-ocadecanamine	0.50
● Di(2-ethylhexyl) sebacate	10.00

Testing Procedures



- **Mixing was done in a Moriyama 1.5 L lab mixer with a dump temperature of 200°F.**
- **MDR Rheometer at 350°F and 370°F, ASTM D 5289.**
- **Mooney at 250°F, ASTM D 1646.**
- **Physical Properties (hardness, tensile, modulus, elongation).
Press-cured 5 minutes at 350°F, post cured 4 hours at 350°F.
ASTM D 412.**
- **Mixing and physical properties were tested at Gold Key Processing. Rheometer testing was performed at Chem Technologies.**

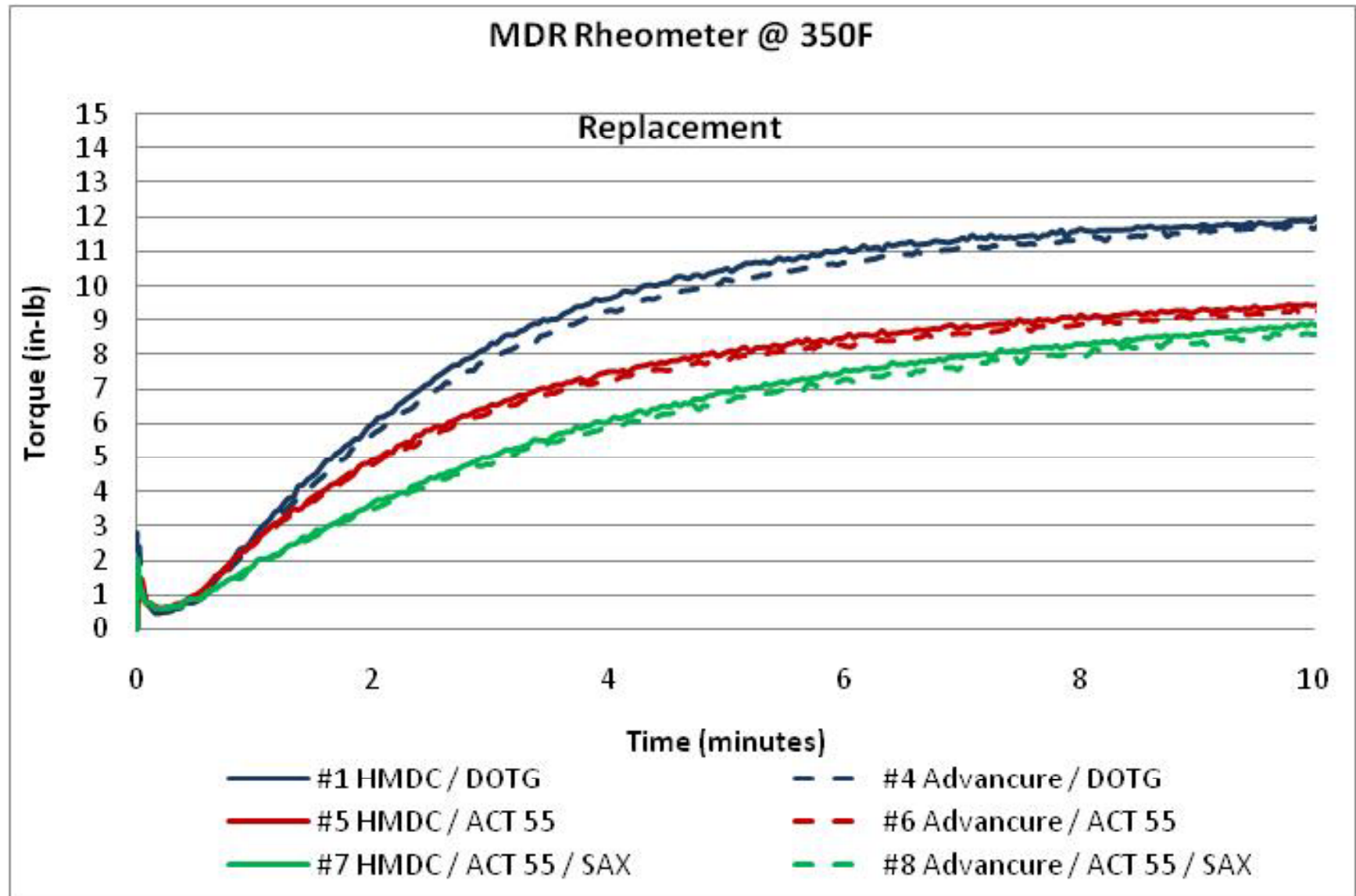
Replacement A Study

HMDC 1.2 phr or HMDC 2.3 phr

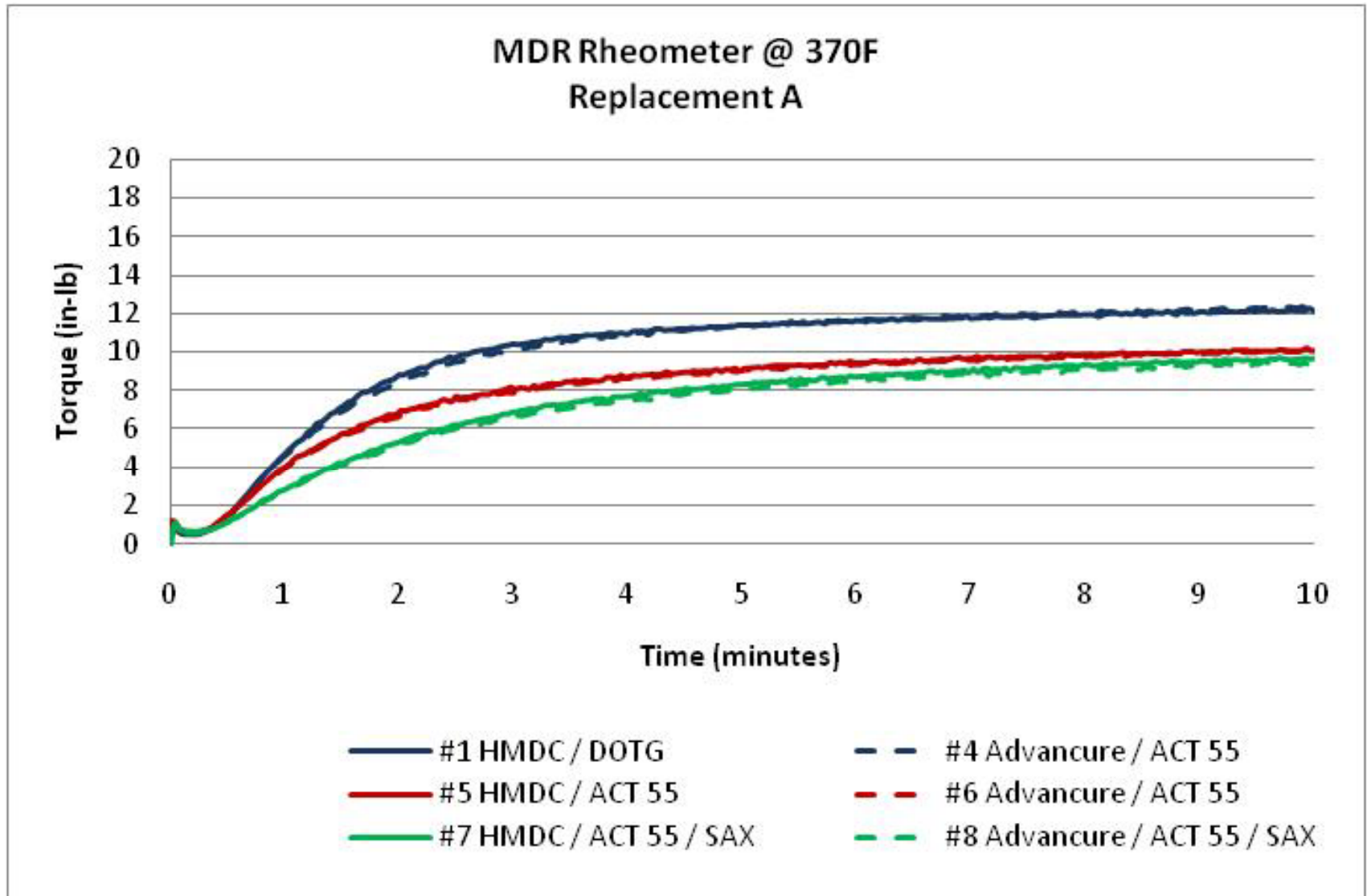
ACT 55 2 phr

Retarder SAX 0 or 0.75 phr

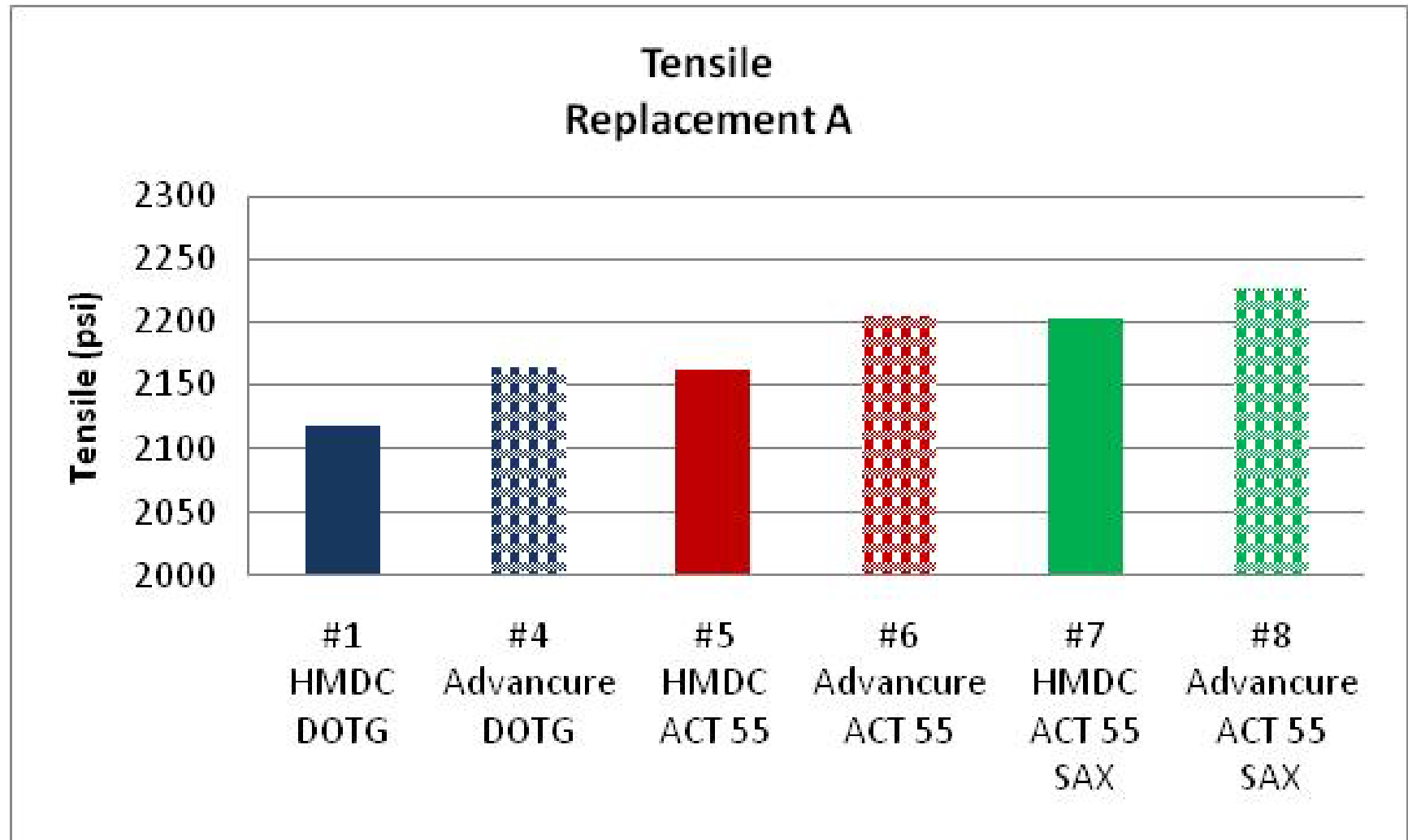
The Advancure compounds had rheometer curves similar to the HMDC compounds. The ACT 55 compounds had similar scorch but a slower rate of cure and a lower state of cure than the DOTG controls. Adding SAX salicyclic acid further slowed the cure rate and lowered the state of cure.



The Advancure compounds had rheometer curves similar to the HMDC compounds. The ACT 55 compounds had similar scorch but a slower rate of cure and a lower state of cure than the DOTG controls. Adding SAX salicylic acid further slowed the cure rate and lowered the state of cure.

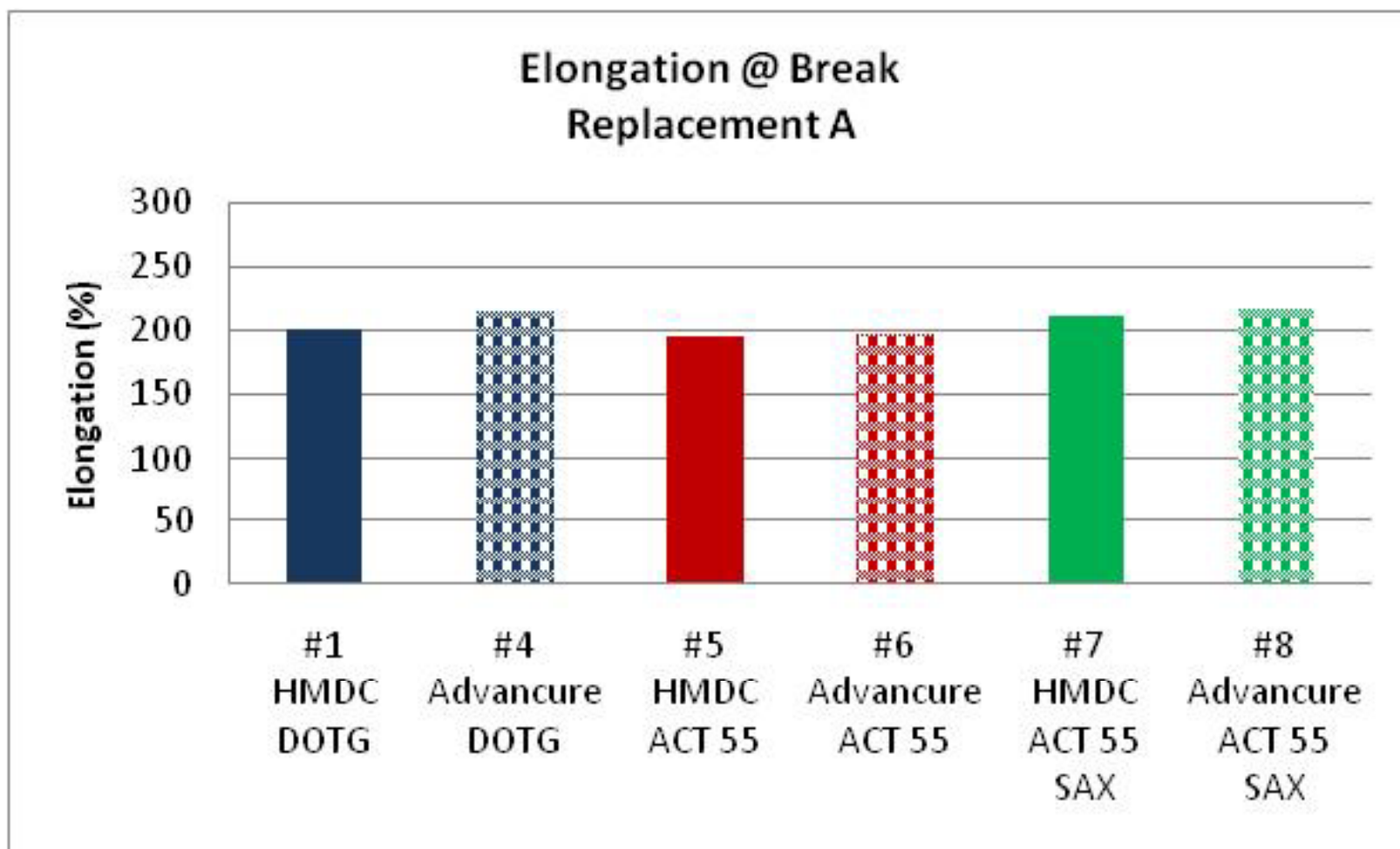


The Advancure compounds had slightly higher tensile than the HMDC compounds. The ACT 55 compounds had higher tensile than the DOTG compounds. SAX increases the tensile.



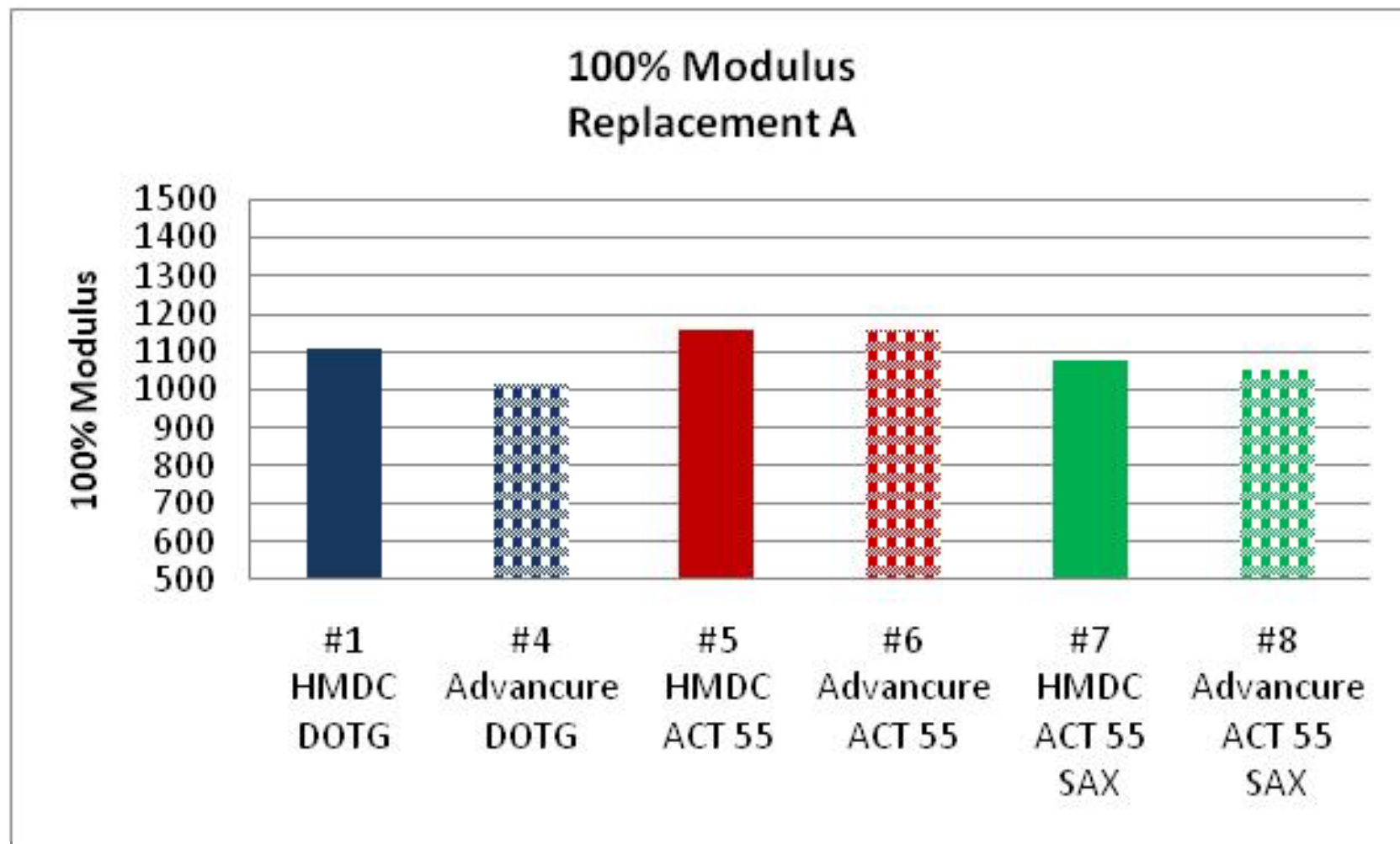


The compounds did not differ significantly for elongation at break

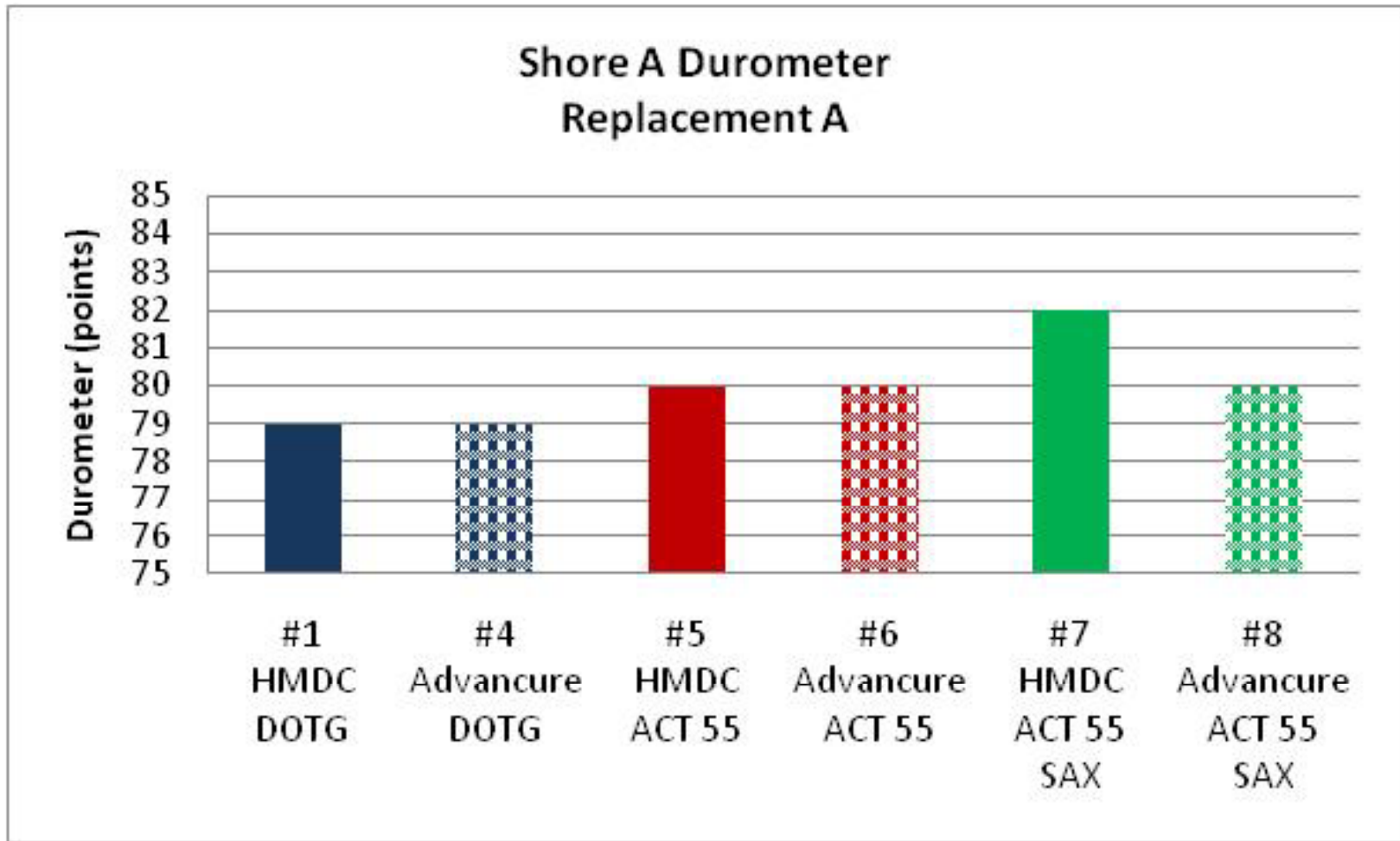




The compounds did not differ significantly for 100% modulus.



The HMDC / ACT 55 / SAX compound had slightly higher durometer than the other compounds.



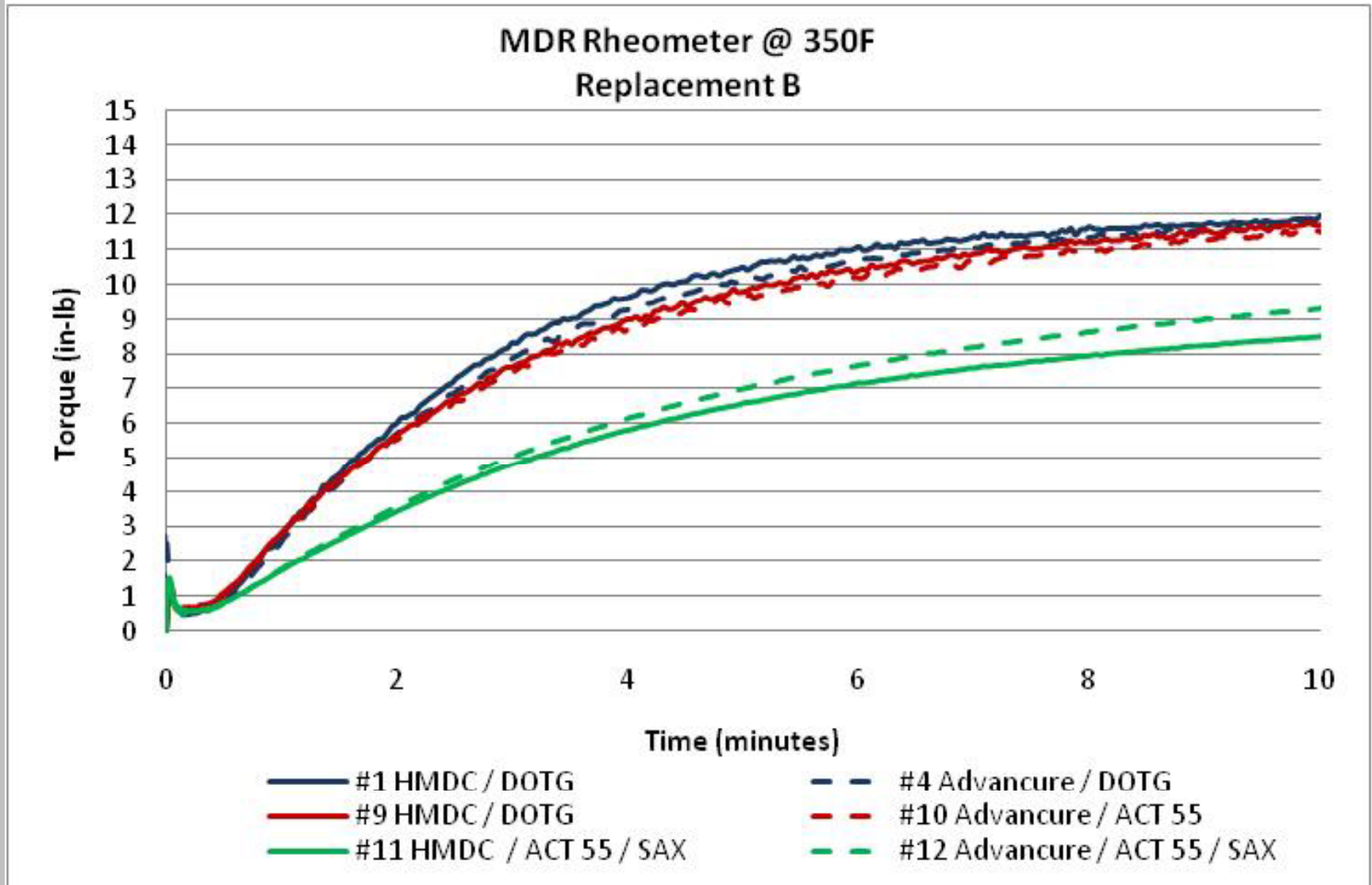
Replacement B Study

HMDC 1.5 phr or HMDC 2.3 phr

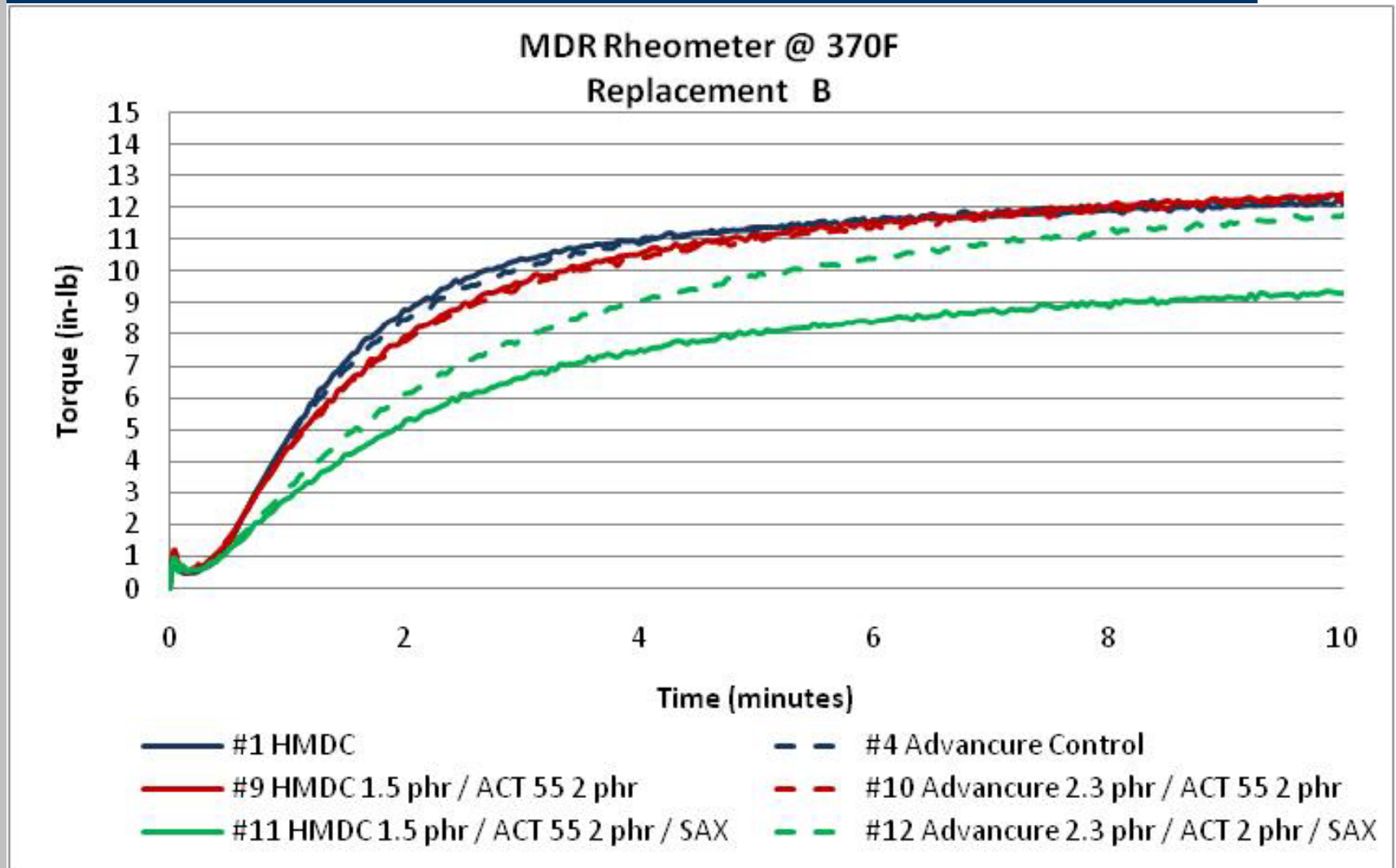
ACT 55 2 phr

Retarder SAX 0 or 0.75 phr

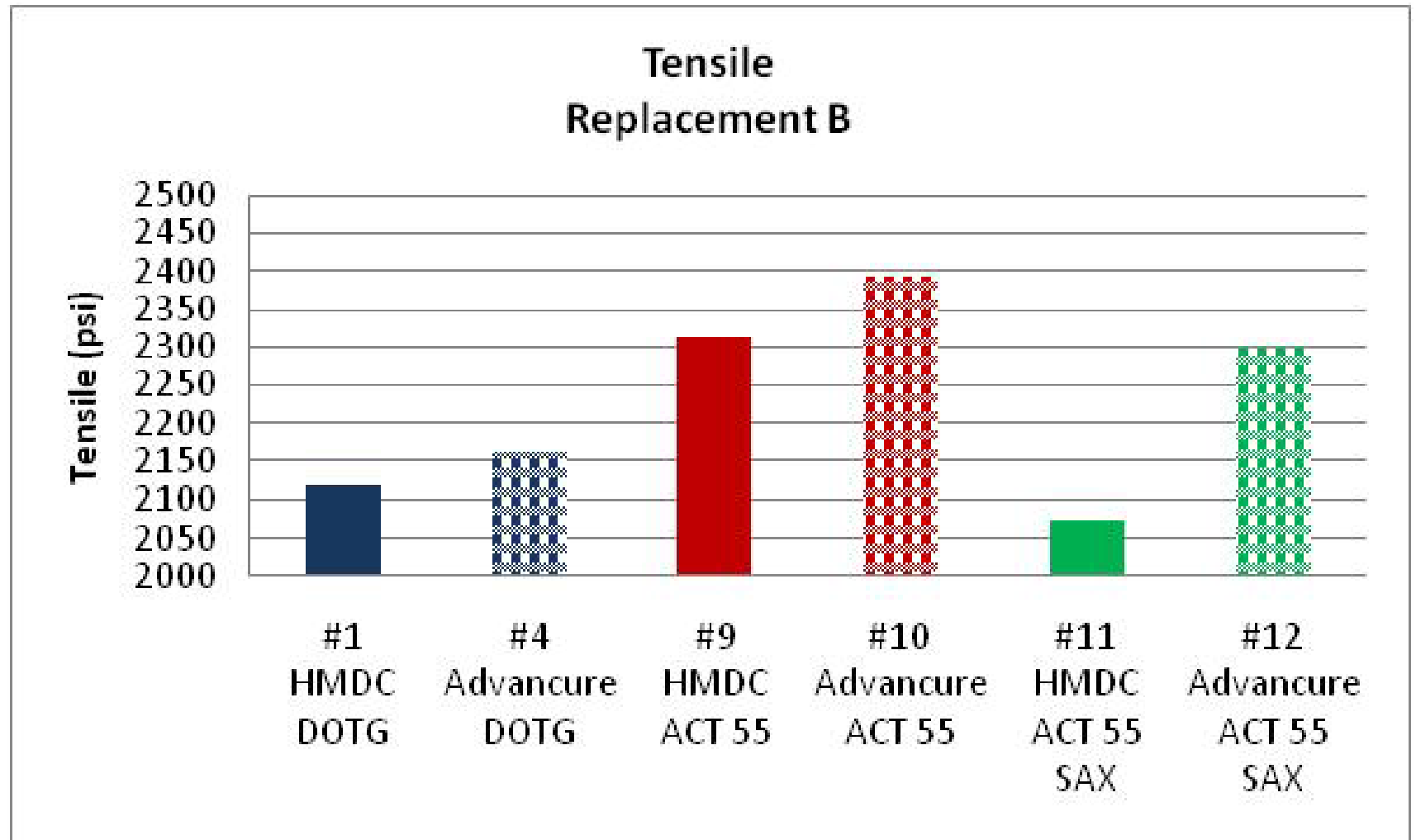
The Advancure compounds had rheometer curves similar to the HMDC compounds. The compounds with ACT 55 (without SAX) had very similar rheometer curves to the control compounds with DOTG. The addition of SAX to the ACT 55 compounds slows the rate of cure and lowers the state of cure.



The Advancure compounds had rheometer curves similar to the HMDC compounds. The compounds with ACT 55 (without SAX) had very similar rheometer curves to the control compounds with DOTG. The addition of SAX to the ACT 55 compounds slows the rate of cure and lowers the state of cure particularly in combination with HMDC.

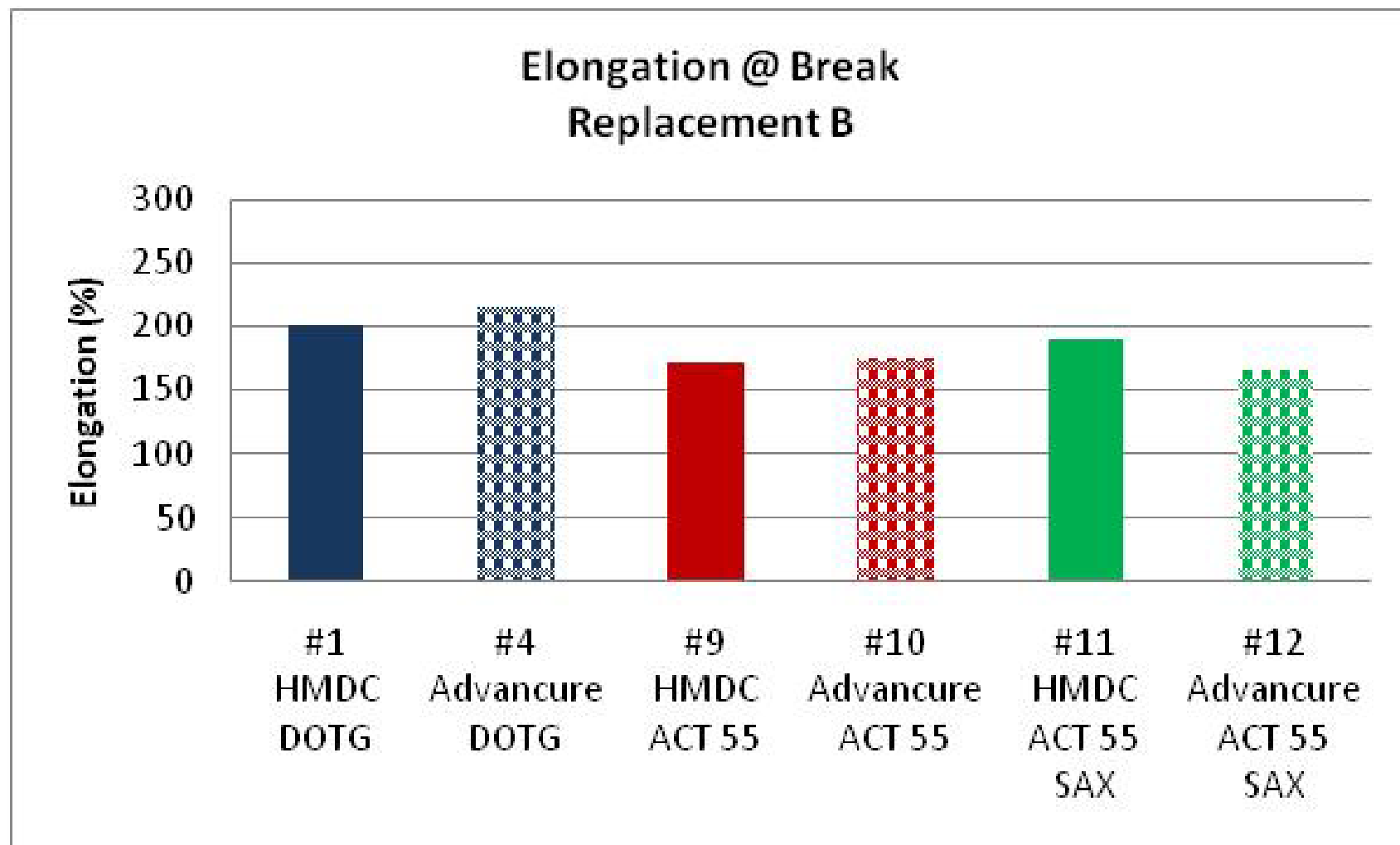


The Advancure compounds had higher tensile than the HMDC compounds. The ACT 55 compounds (without SAX) had higher tensile than the DOTG control compounds. Adding SAX to the HMDC/ACT 55 compounds lowers the tensile. Adding SAX to the Advancure / ACT 55 compound increased the tensile.

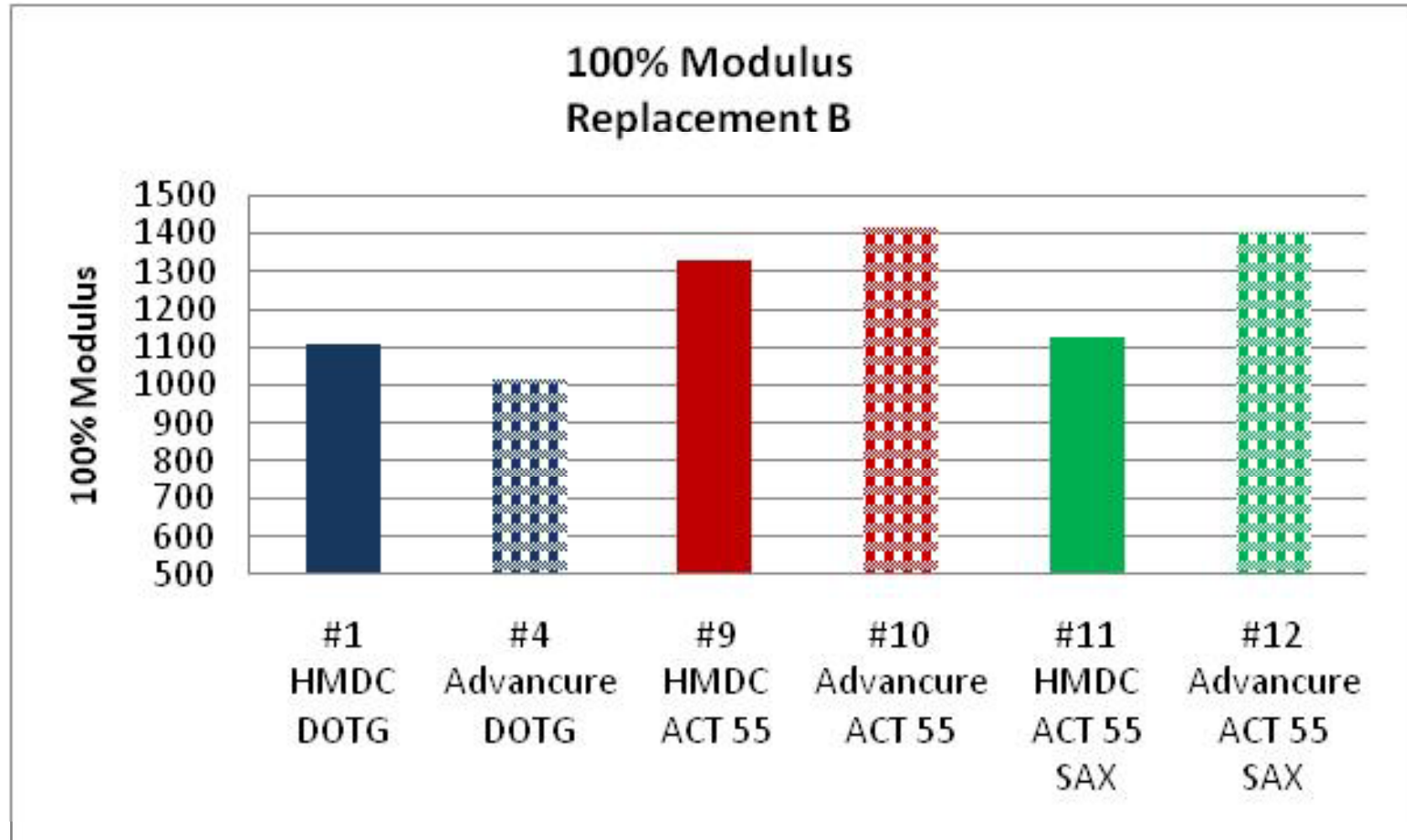




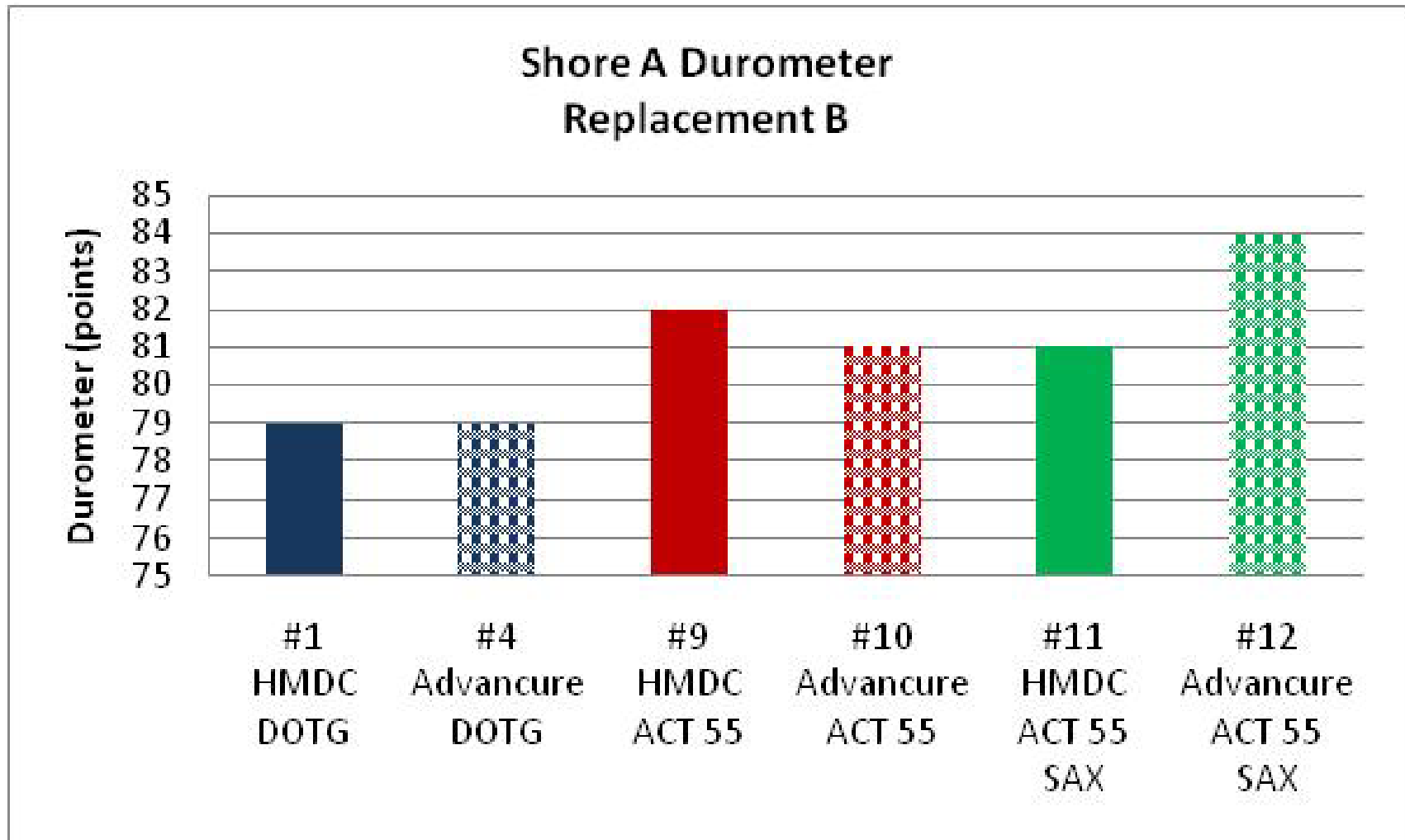
The compounds did not differ significantly for elongation at break.



The ACT 55 compounds had higher modulus than the DOTG control compounds. Adding SAX to the HMDC / ACT 55 compound lowers modulus.



The ACT 55 compounds had higher durometer values than the DOTG control compounds. Adding SAX to the HMDC / ACT 55 compound lowers durometer.

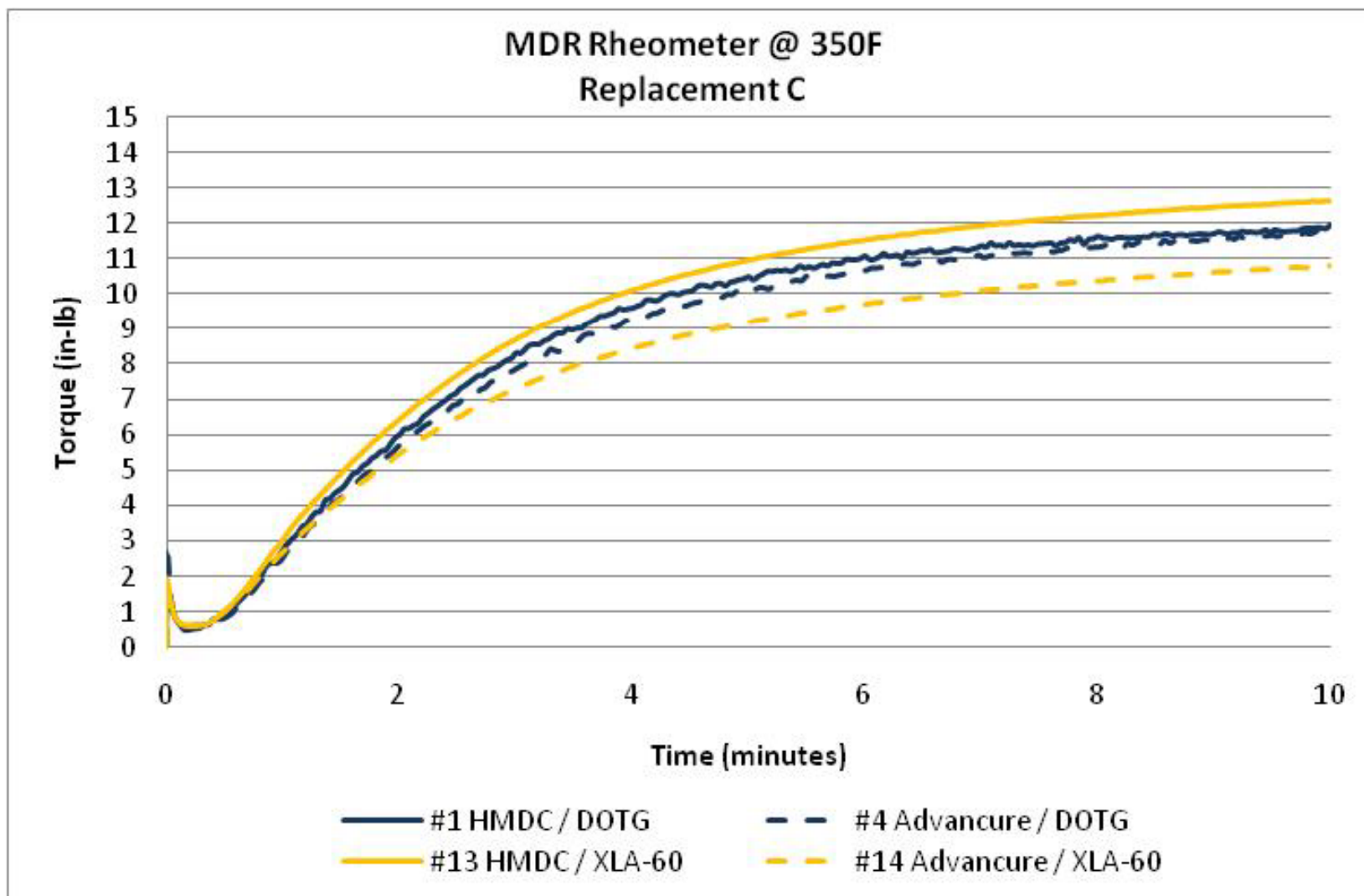


Replacement C Study

**HMDC 1.5 phr or HMDC 2.3 phr
XLA-60 4 phr**

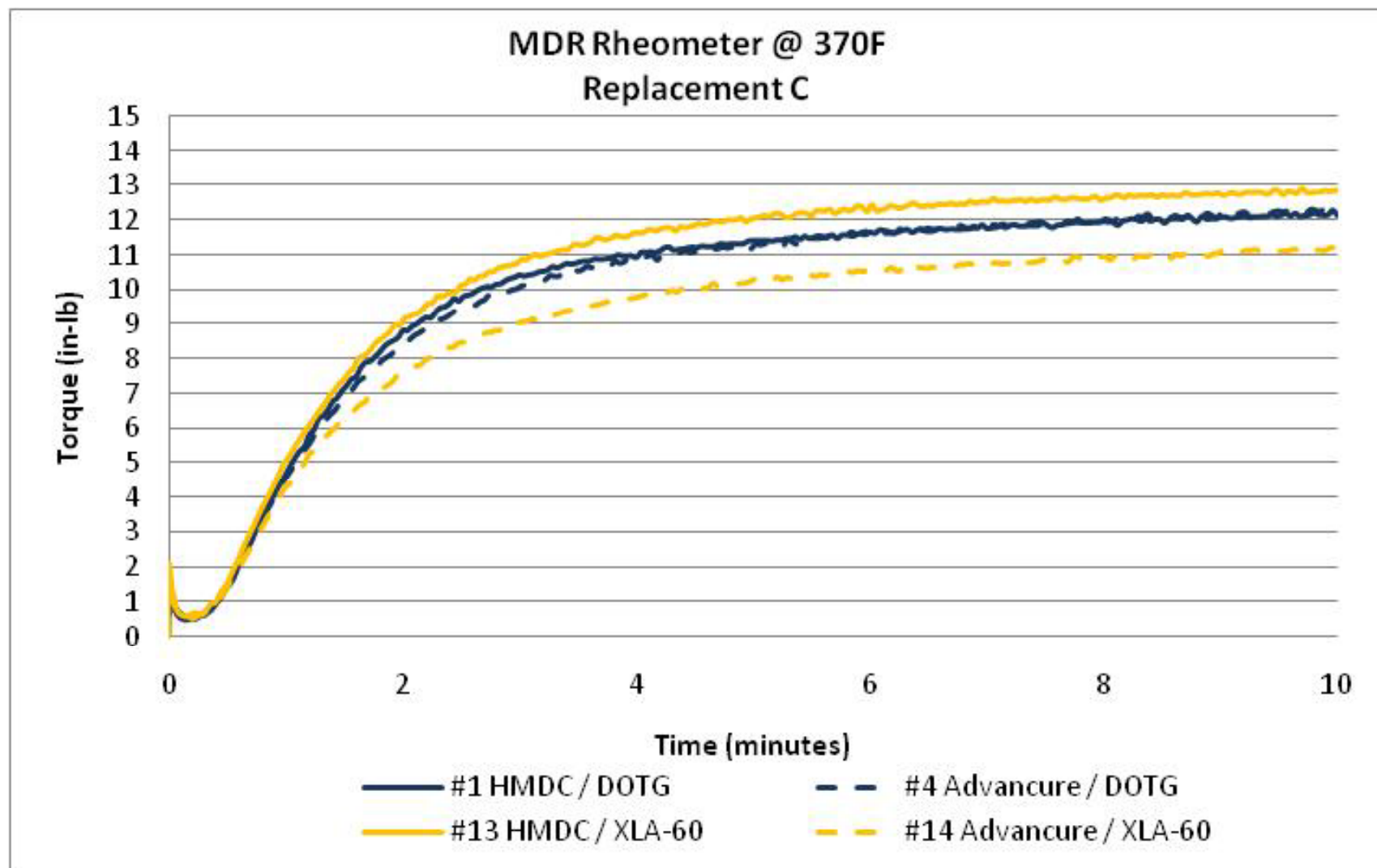


The HMDC / XLA-60 compound had a similar rheometer curve to the DOTG control compounds. The Advancure / XLA-60 compound had a lower state of cure than the other compounds.

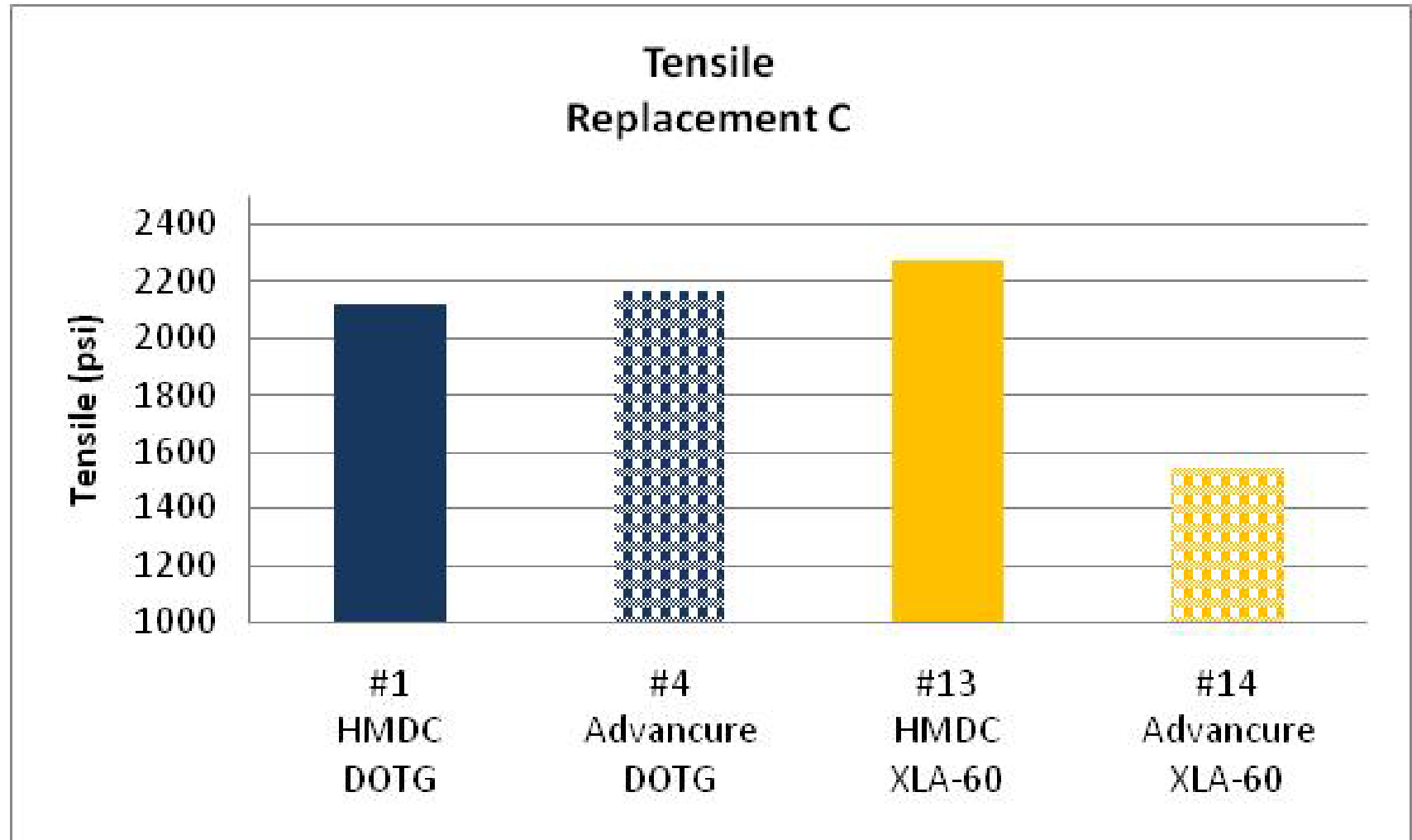




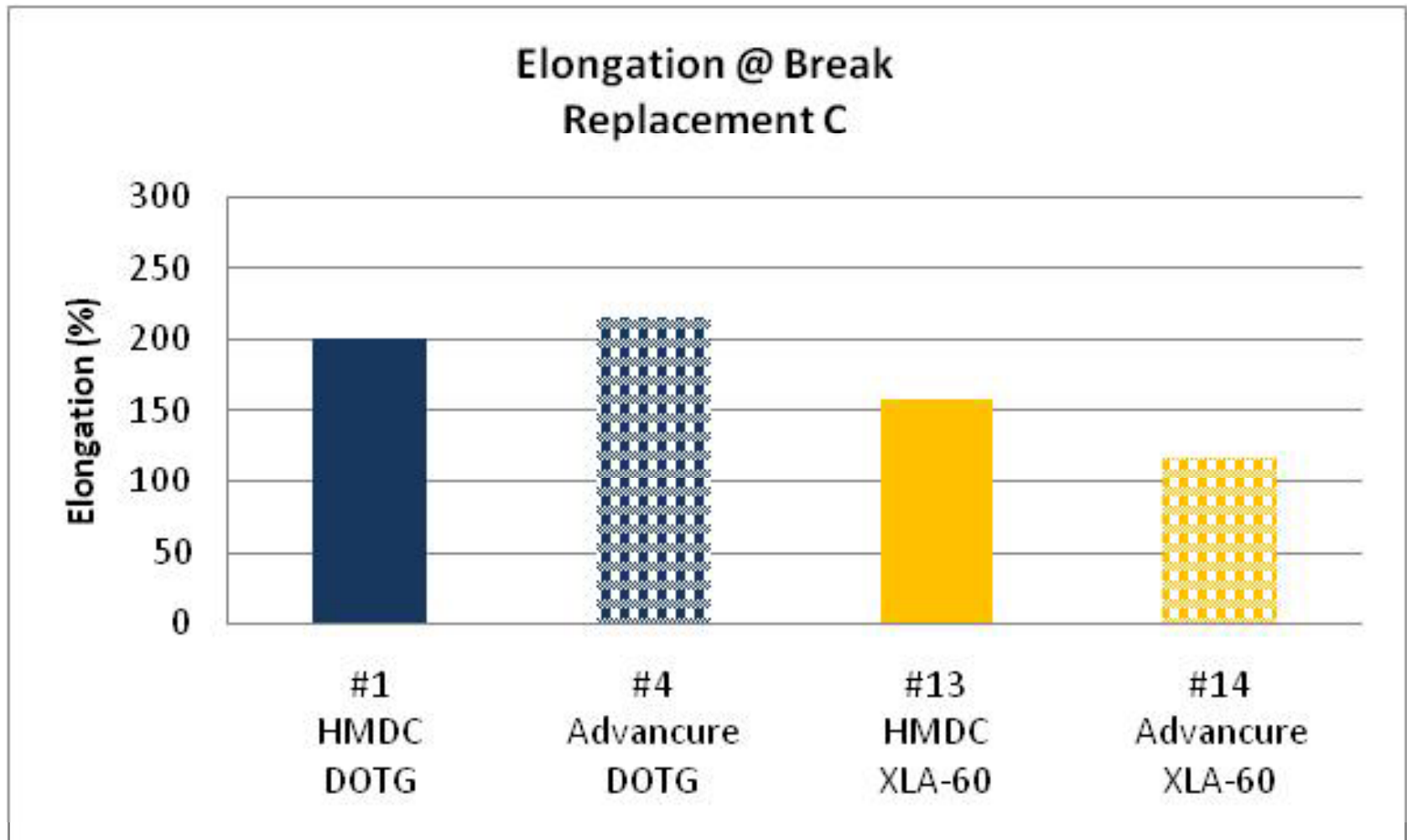
The HMDC / XLA-60 compound had a similar rheometer curve to the DOTG control compounds. The Advancure / XLA-60 compound had a lower state of cure than the other compounds.



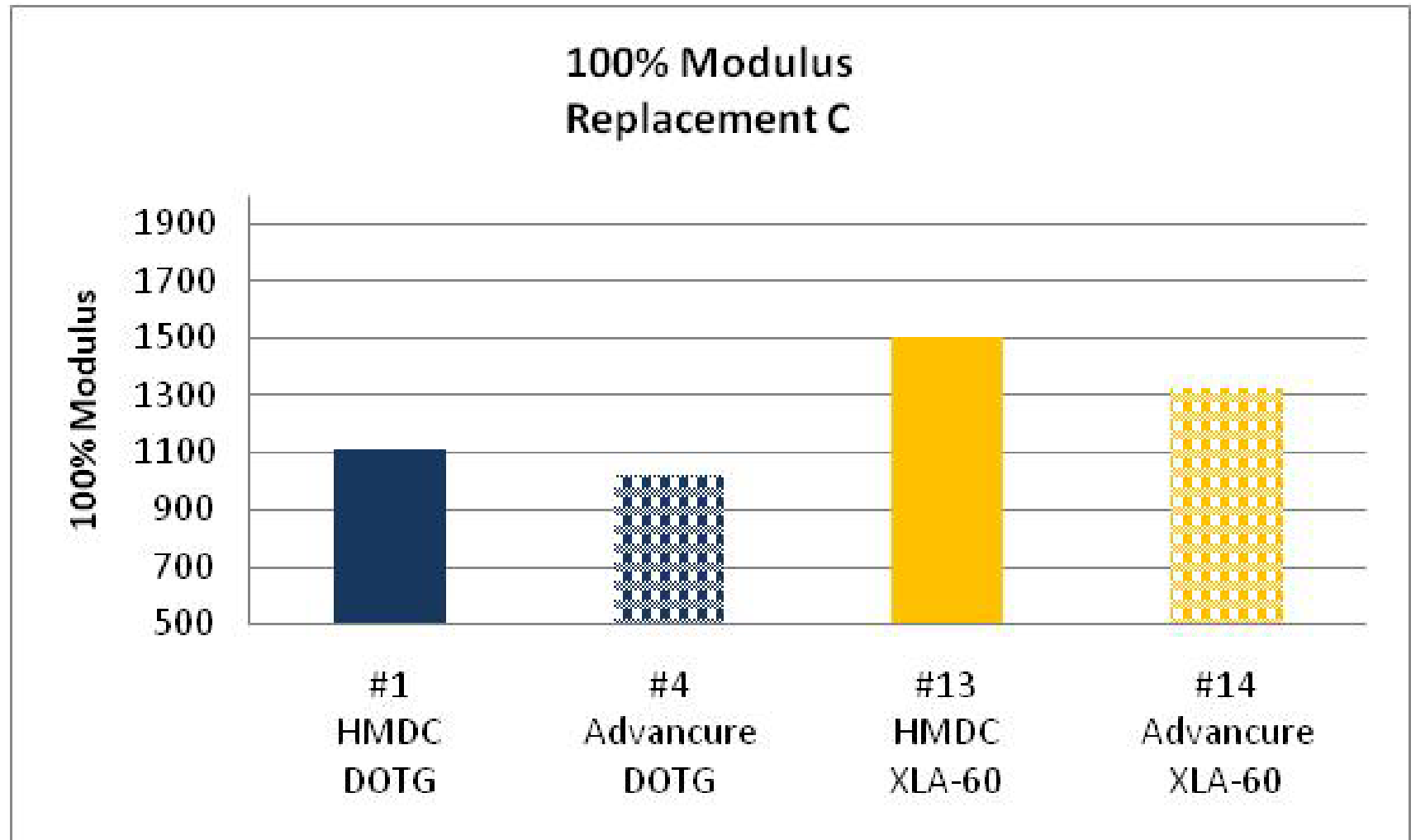
The HMDC / XLA-60 compound had similar tensile values to the DOTG control compounds. The Advancure / XLA-60 compound had lower tensile than the other compounds.



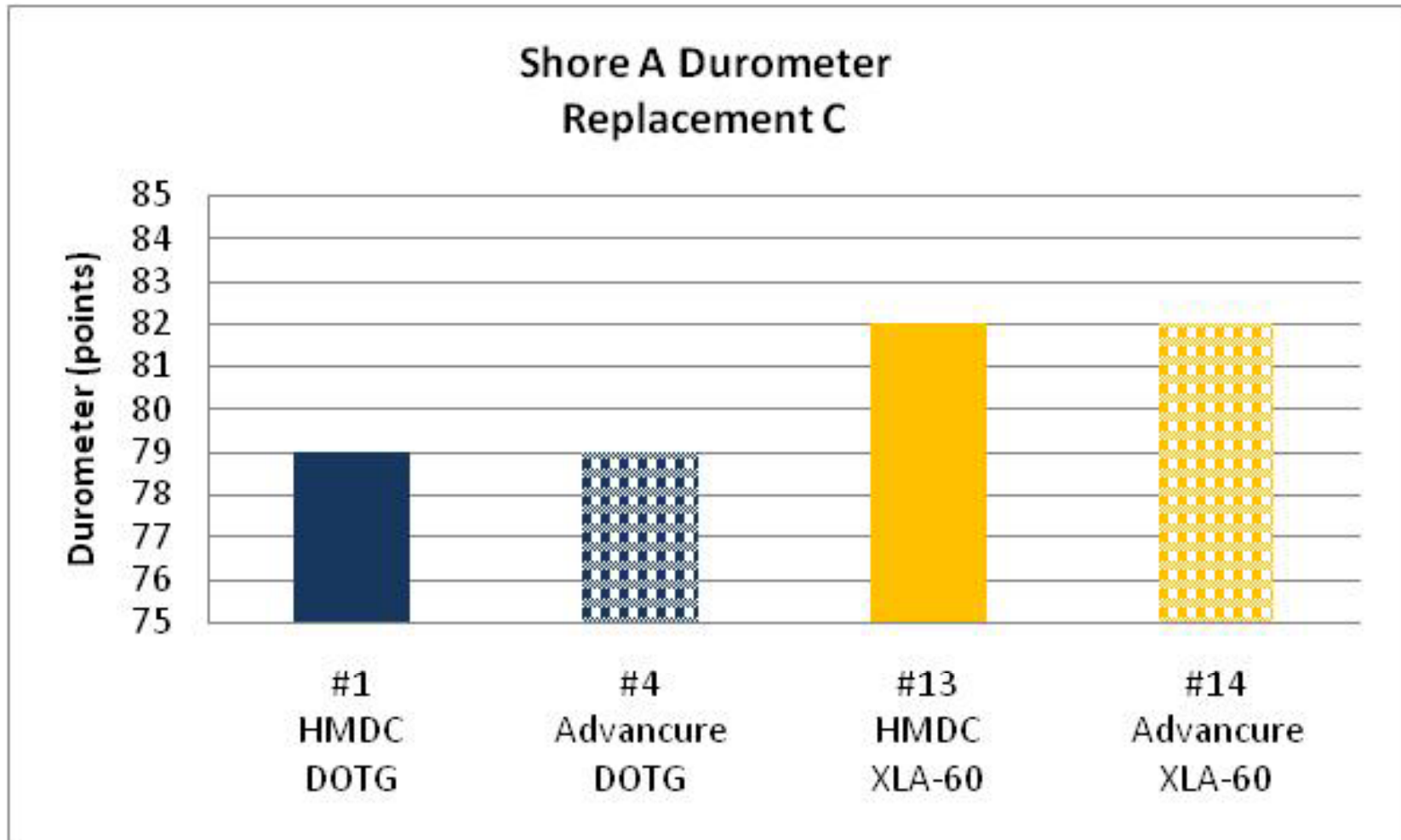
The XLA-60 compounds had lower elongation at break than the DOTG control compounds.



The XLA-60 compounds had higher 100% modulus values than the DOTG control compounds.



The XLA-60 compounds had higher durometer values than the DOTG control compounds.



Conclusions



- **The best match for the traditional DOTG with HMDC or Advancure cure systems is as follows:**
 - **Keep the HMDC or Advancure level the same and substitute 2 phr of ACT 55 for the 4 phr of DOTG**
- **Advancure generally gives similar cure properties to HMDC with slightly higher tensile values.**

Final Comments



- **Advancure can be used either with DOTG or with ACT 55 and gives similar properties to HMDC cured compounds.**
- **Advancure's price is 50 to 70% less than HMDC which can result in final compound savings of over \$0.20/lb.**
- **Advancure is classified as a preparation under R.E.A.C.H. regulations. All of the ingredients in Advancure are registered under R.E.A.C.H.**
- **Additional data comparing Advancure to HMDC in Vamac compounds is available in Chem Technologies CTR-06001 technical report.**

TP-2008-006	1	4	5	6	7	8
	#1 HMDC DOTG	#4 Advancure DOTG	#5 HMDC ACT 55	#6 Advancure ACT 55	#7 HMDC ACT 55 SAX	#8 Advancure ACT 55 SAX
Replacement A						
Vamac G	100.0	100.0	100.0	100.0	100.0	100.0
N-774	90.0	90.0	90.0	90.0	90.0	90.0
Stearic Acid	2.0	2.0	2.0	2.0	2.0	2.0
Vanfre VAM	1.5	1.5	1.5	1.5	1.5	1.5
Armeen 18 D	0.5	0.5	0.5	0.5	0.5	0.5
DOS	10.0	10.0	10.0	10.0	10.0	10.0
DOTG	4	4				
Vulcofac ACT 55			2	2	2	2
Rhenogran XLA-60						
Diak 1	1.5		1.2		1.2	
Advancure Lot # 206223						
Advancure Lot # 108116						
Advancure Lot # 108305		2.3		1.85		1.85
Retarder SAX					0.75	0.75
Total Parts	209.5	210.3	207.2	207.9	208.0	208.6
MDR Rheometer @ 350F, Chem Technologies						
MH (in-lb)	11.98	11.81	9.44	9.38	8.9	8.6
ML (in-lb)	0.48	0.51	0.59	0.63	0.61	0.59
Ts1 (minutes)	0.98	0.72	0.69	0.72	0.88	0.92
Ts2 (minutes)	0.95	1	1.01	1.04	1.39	1.46
Tc50 (minutes)	2.11	2.18	2.06	2.09	2.79	2.76
Tc90 (minutes)	5.63	6.01	6.04	6.49	7.31	7.23
MDR Rheometer @ 370F, Chem Technologies						
MH (in-lb)	12.28	12.37	10.21	10.05	9.67	9.54
ML (in-lb)	0.69	0.57	0.58	0.61	0.56	0.62
Ts1 (minutes)	0.56	0.54	0.53	0.54	0.63	0.66
Ts2 (minutes)	0.7	0.69	0.72	0.73	0.91	0.93
Tc50 (minutes)	1.36	1.41	1.4	1.41	1.89	1.93
Tc90 (minutes)	4.21	4.59	5.23	5.19	6.13	6.13
MDR Rheometer @ 350F, Gold Key						
MH (in-lb)	11.91	11.61	9.54	9.05	7.99	7.61
ML (in-lb)	0.45	0.5	0.56	0.58	0.55	0.53
Ts2 (minutes)	0.93	0.96	1.02	1.05	1.36	1.44
Tc90 (minutes)	4.28	4.4	4.37	4.42	4.88	4.95
Mooney @250F						
MI	40.16	41.91	43.14	42.6	40.1	39.68
Viscosity ML 1+\$	33.16	33.43	35.17	34.46	31.38	30.87
Physical Properties:						
Tensile (psi)	2118	2164	2162	2204	2202	2227
Elongation (%)	201	216	196	198	212	218
25% Modulus (psi)	307	302	362	351	367	362
50% Modulus (psi)	513	489	573	573	563	549
100% Modulus (psi)	1108	1017	1158	1157	1078	1055
200% Modulus (psi)	2118	2024	0	0	2116	2078
300% Modulus (psi)	0	0	0	0	0	0
Shore A Durometer (pts)	79	79	80	80	82	80

TP-02008-006	1	4	9	10	11	12
	#1	#4	#9	#10	#11	#12
Replacement B	HMDC	Advancure	HMDC	Advancure	HMDC	Advancure
	DOTG	DOTG	ACT 55	ACT 55	ACT 55	ACT 55
					SAX	SAX
Vamac G	100.0	100.0	100.0	100.0	100.0	100.0
N-774	90.0	90.0	90.0	90.0	90.0	90.0
Stearic Acid	2.0	2.0	2.0	2.0	2.0	2.0
Vanfre VAM	1.5	1.5	1.5	1.5	1.5	1.5
Armeen 18 D	0.5	0.5	0.5	0.5	0.5	0.5
DOS	10.0	10.0	10.0	10.0	10.0	10.0
DOTG	4	4				
Vulcofac ACT 55			2	2	2	2
Rhenogran XLA-60						
Diak 1	1.5		1.5		1.2	
Advancure Lot # 206223						
Advancure Lot # 108116						
Advancure Lot # 108305		2.3		2.3		2.3
Retarder SAX					0.75	0.75
Total Parts	209.5	210.3	207.5	208.3	208.0	209.1
MDR Rheometer @ 350F, Chem Technologies						
MH (in-lb)	11.98	11.81	11.76	11.58	8.55	9.31
ML (in-lb)	0.48	0.51	0.66	0.58	0.58	0.49
Ts1 (minutes)	0.98	0.72	0.68	0.66	0.91	0.87
Ts2 (minutes)	0.95	1	0.96	0.92	1.47	1.39
Tc50 (minutes)	2.11	2.18	2.22	2.21	2.79	2.92
Tc90 (minutes)	5.63	6.01	6.35	6.32	7.36	7.53
MDR Rheometer @ 370F, Chem Technologies						
MH (in-lb)	12.28	12.37	12.46	12.32	9.36	11.86
ML (in-lb)	0.69	0.57	0.62	0.6	0.6	0.62
Ts1 (minutes)	0.56	0.54	0.53	0.51	0.66	0.6
Ts2 (minutes)	0.7	0.69	0.68	0.68	0.94	0.87
Tc50 (minutes)	1.36	1.41	1.53	1.52	1.92	2.08
Tc90 (minutes)	4.21	4.59	5.28	5.31	6.13	6.47
MDR Rheometer @ 350F, Gold Key						
MH (in-lb)	11.91	11.61	11.4	10.89	7.95	9.03
ML (in-lb)	0.45	0.5	0.55	0.57	0.53	0.55
Ts2 (minutes)	0.93	0.96	0.95	1	1.35	1.3
Tc90 (minutes)	4.28	4.4	4.59	4.52	4.9	4.97
Mooney @250F						
MI	40.16	41.91	43.47	44.53	39.69	39.92
Viscosity ML 1+\$	33.16	33.43	36.25	36.22	31.28	32
Physical Properties:						
Tensile (psi)	2118	2164	2313	2392	2072	2298
Elongation (%)	201	216	172	176	190	165
25% Modulus (psi)	307	302	371	366	366	426
50% Modulus (psi)	513	489	620	682	575	692
100% Modulus (psi)	1108	1017	1327	1416	1124	1404
200% Modulus (psi)	2118	2024	0	0	0	0
300% Modulus (psi)	0	0	0	0	0	0
Shore A Durometer (pts)	79	79	82	81	81	84

TP-02008-006	1	4	13	14
	#1	#4	#13	#14
Replacement C	HMDC	Advancure	HMDC	Advancure
	DOTG	DOTG	XLA-60	XLA-60
Vamac G	100.0	100.0	100.0	100.0
N-774	90.0	90.0	90.0	90.0
Stearic Acid	2.0	2.0	2.0	2.0
Vanfre VAM	1.5	1.5	1.5	1.5
Armeen 18 D	0.5	0.5	0.5	0.5
DOS	10.0	10.0	10.0	10.0
DOTG	4	4		
Vulcofac ACT 55				
Rhenogran XLA-60			4	4
Diak 1	1.5		1.5	
Advancure Lot # 206223				
Advancure Lot # 108116				
Advancure Lot # 108305		2.3		2.3
Retarder SAX				
Total Parts	209.5	210.3	209.5	210.3
MDR Rheometer @ 350F, Chem Technologies				
MH (in-lb)	11.98	11.81	12.65	10.82
ML (in-lb)	0.48	0.51	0.58	0.61
Ts1 (minutes)	0.98	0.72	0.67	0.7
Ts2 (minutes)	0.95	1	0.89	0.98
Tc50 (minutes)	2.11	2.18	2.07	2.12
Tc90 (minutes)	5.63	6.01	5.8	6.18
MDR Rheometer @ 370F, Chem Technologies				
MH (in-lb)	12.28	12.37	12.87	11.19
ML (in-lb)	0.69	0.57	0.57	0.51
Ts1 (minutes)	0.56	0.54	0.51	0.53
Ts2 (minutes)	0.7	0.69	0.64	0.7
Tc50 (minutes)	1.36	1.41	1.34	1.38
Tc90 (minutes)	4.21	4.59	3.99	4.65
MDR Rheometer @ 350F, Gold Key				
MH (in-lb)	11.91	11.61	12.86	10.43
ML (in-lb)	0.45	0.5	0.49	0.54
Ts2 (minutes)	0.93	0.96	0.85	0.96
Tc90 (minutes)	4.28	4.4	4.34	4.38
Mooney @250F				
MI	40.16	41.91	42.57	41.49
Viscosity ML 1+\$	33.16	33.43	34.33	33.4
Physical Properties:				
Tensile (psi)	2118	2164	2269	1544
Elongation (%)	201	216	158	117
25% Modulus (psi)	307	302	386	398
50% Modulus (psi)	513	489	684	652
100% Modulus (psi)	1108	1017	1505	1323
200% Modulus (psi)	2118	2024	0	0
300% Modulus (psi)	0	0	0	0
Shore A Durometer (pts)	79	79	82	82

References



- **Vulcofac ACT 55 certificate of analysis, product data sheet and msds**
- **Press Cure and Post Cure Optins for AEM Terpolymer by E.McBride of DuPont**
- **Vulcofac ACT 55 – A Replacement for Guanidine Accelerators by A.Kral of Safic Alcan.**
- **Rhenogran XLA-60 DOTG-free Curing Systems for ACM Compounds by C.Rosca of Rhein Chemie.**
- **Interim Study and Suggestions for Replacement of DOTD in Zeon HT-ACM Elastomers by Zeon.**
- **Replacement of DOTG in HT-ACM Elastomer – Safic Alcan Products – Accelerator and Retarder Study by Zeon.**
- **An Alternate Accelerator for Vamac Terpolymers: Vulcofac ACT 55 by DuPont.**
- **DOTG Replacement – Compounding Tips for Vamac Ethylene Acrylic Elastomer.**