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Redesigning OTR Compounds With Anti-Reversion Chemistry for Reduced Heat-Build Up and Improved Performance

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ABSTRACT

During service, large off-the-road tires (OTR) undergo severe compressive and shear deformation. As rubber compounds are viscoelastic, the deformation generates heat. Since thick sections of the tire dissipate heat slowly, tires operating under severe conditions reach high operating temperatures. Network reversion during cure exacerbates the hysteretic character. Large tires are manufactured using extended-low temperature cure to reduce network reversion. Anti-reversion agents (**ARA**) further reduce reversion thereby producing significantly improved networks. Mechanically and/or heat damaged networks inherently generate more heat under dynamic loads than the original "non-damaged" networks. OTR tires manufactured using compounds prepared with anti-reversion agents throughout a majority of the tire exhibit significantly reduced heat generation. Total network retention in improved in tires containing ARA. Such tires have lower running temperatures and provide better durability under severe conditions. This paper will explore the benefits of using **ARA** containing components to thick composite rubber parts.

INTRODUCTION

Natural rubber (NR) is the elastomer of choice for heavy duty applications such as "off-the-road", aircraft, or truck tires. While NR provides exceptional strength characteristics controlling the extent and uniformity of vulcanization is difficult in thick rubber sections. Optimal properties such as high strength and low hysteresis are exhibited in parts cured to approximately 90%-100% of the "maximum" cure (or torque levels as measured in a moving die or oscillating disk rheometer.) Uniform cure of thick rubber articles to optimum cure is virtually impossible. Rubber near mold surfaces experiences longer heat history (overcure) while centrally located rubber in the thickest parts may be somewhat under-cured at the end of the curing cycle. Overcure, or reversion, leads to degradation of properties via the loss of crosslink density and the accompanying main chain modifications.

Network reversion during cure exacerbates the hysteretic character or the rubber compound. Low temperatures and extended cure times are commonly employed in manufacturing large tires in order to reduce network reversion. Thermally reverted, mechanically and/or heat damaged networks generate more heat under dynamic loads than the original "non-damaged" networks. Anti-reversion agents (**ARA**) protect or repair the network during cure and service thereby producing significant improvements.

In rubber, heat generated during service dissipates slowly. Large tires can reach high operating temperatures leading to network degradation or ultimately blow-out failures. Employing ARA's in multiple compounds significantly reduces heat generation. Total network retention is improved after extended cure and service. Such tires have lower running temperatures and provide better durability under severe conditions.

Understanding the balance of heat generation as a function of network properties, service conditions, and tire geometry becomes a very complex engineering problem. Since heat dissipation is slow in rubber, small improvements in heat build up properties as measured in small rubber parts in the lab can be very meaningful in large tires. This paper will explore the comparative benefits of **ARA's** in small single component and larger composite rubber parts.

Reversion Review

Reversion is the thermal degradation of polysulfidic crosslinks, leading to a reduction of crosslink density, a change in the distribution of crosslink types, and an introduction of main chain modifications. It leads to a decline in compound physical properties such as modulus, tensile and elongation and in performance characteristics such as tear, fatigue and hysteresis. These network and backbone changes translate into reduced tire performance and /or shorter service life.

Reversion occurs when vulcanizates are over-cured or exposed to high temperature-anaerobic conditions. In practice, reversion is caused by:

* Overcure in the press.

* Overcure at the belt edge of steel belted radial tires during service. Steel belt coat compounds are particularly susceptible to reversion due to high sulfur to accelerator ratios.
* Severe operating conditions. High ambient temperatures, excessive loads and under-inflation lead to high internal temperatures and reversion.
* Higher temperature cure.

The rate of vulcanization and reversion are governed by different activation energies. Reversion requires higher temperatures to reach high rates of reaction. Since thermal conductivity of rubber is low and reversion is significantly worse at higher temperatures, cure of thick rubber parts is often done at low temperatures for long time. Comparing cures at different temperatures demonstrates this effect.

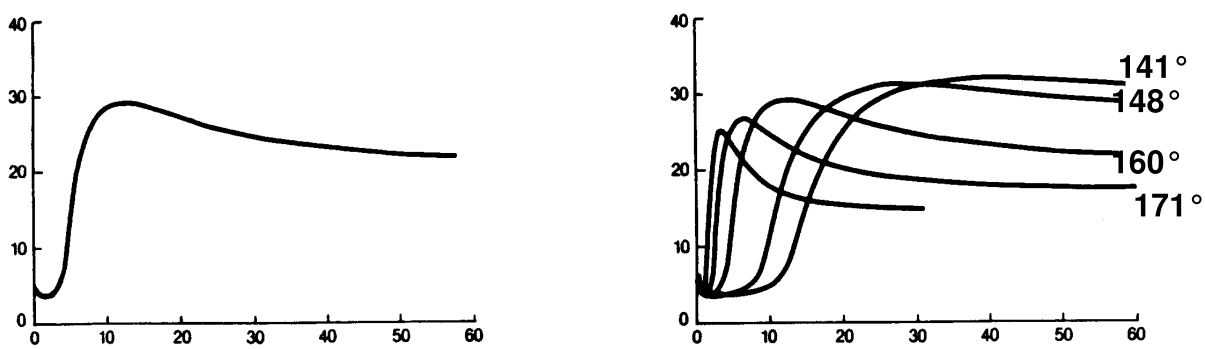

Figure 1 The effect of temperature and time in reversion.

The effects of reversion at various temperatures (figure 1.) were shown in the classic work by C. T. Loo [1]. In general, the reactions of reversion result in the reduction of rank of the sulfur crosslinks, i.e. polysulfidic crosslinks are converted to monosulfidic and disulfidic crosslinks. A portion of the crosslinks are cleaved leaving behind cyclic sulfides and conjugated unsaturation in the polymer backbone.

The extend and damage of reversion can be controlled using two approaches, formation of a stable network less prone toward reversion and repair of damaged crosslinks. Hexamethylene-1,6-bisthiosulfate disodium dihydrate (Flexsys Duralink® HTS) alters the rate of both vulcanization and reversion.[2] The rate of reversion is slowed because this chemical generates a high concentration of "hybrid" crosslinks during vulcanization. The hybrid crosslink is effectively the hexamethylene moiety of the HTS linking two chains via mono- or disulfidic bonds (Figure 2.)

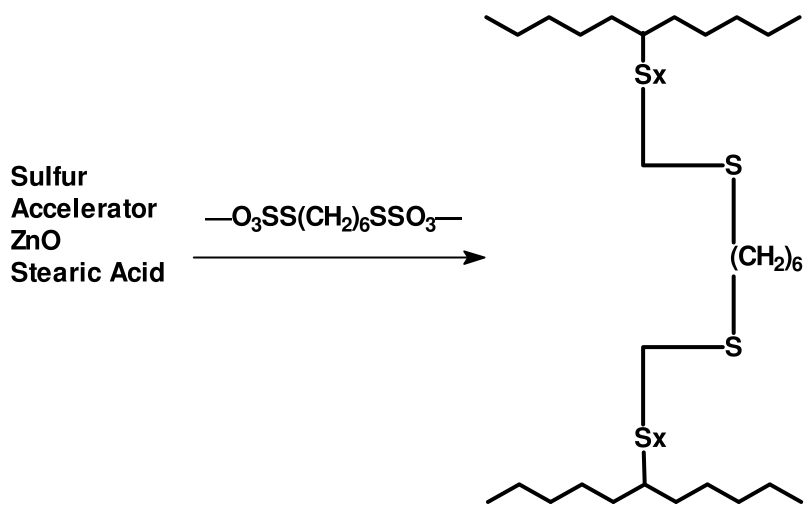

Figure 2 The Hybrid Crosslink**.**

The signature of reversion, conjugated unsaturation in the backbone serves as the reaction site for crosslink repair via the Diels-Alder reaction using the dienophile 1,3 bis(citraconimidomethyl) benzene (BCI-MX.[3])

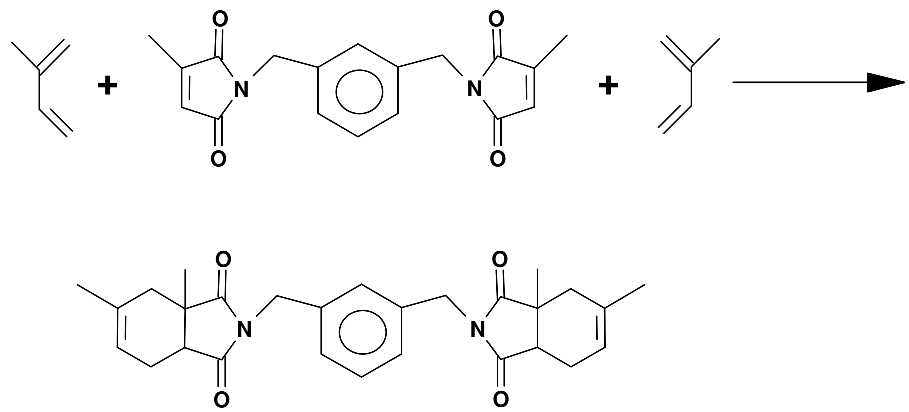

Figure 3 Diels-Alder crosslink repair using BCI-mX

<u>**The Goals of the Study**</u>

These ARA's function by uniquely different mechanisms[4] and each provide different levels of performance improvements. This article focuses on compounding combining the features of both BCI-MX and HTS to improve reversion resistance, heat build up and crack growth properties. Experimental design and response surface methodology were employed to generate desirable formulations based on the following criteria:

- Target moduli at optimal cure or upon over cure should be close to the optimal cure of the control compound. Slight increase or decrease is acceptable. Target compression moduli values were dynamic moduli measured at 20-30% strain.
- Heat build-up characteristics of the ARA containing formulations should be minimized.

- Crack growth characteristics of the compounds should be equal to or better than the control cured to t90 or optimal cure.

Formulations studied included carcass, steel skim, tread base and tread compounds. The formulations were in-line compounds provided by an anonymous manufacturer. Formulations were optimized using DOE adjusting variables of sulfur, accelerator, HTS and BCI-MX.

Finally, the heat-build up characteristics of the individual compounds are compared to the heat build-up behavior of a larger composite part.

Experimental

BCI-MX (Perkalink ®900) and HTS (Duralink ®HTS), were commercial grade materials supplied by Flexsys America LP.

Masterbatch mixes were production masterbatches obtained from the manufacturer. Accelerator, sulfur, antidegradant, BCI-MX and HTS were added on a two roll mill.

Vulcanization characteristics were measured using Alpha Technologies Moving Die Rheometer Model 2000 and Alpha Technologies Rubber Process Analyzer. Cure times were taken at t90 and 22 hrs at 137 C for small samples and 4 hrs at 150C for the large composite cylinders.

Heat build-up was determined using the Doli Flexometer according to ASTM D-623. Dynamic compression moduli were measured using an MTS 831

Elastomer Testing System at room temperature. Crack growth was measured using pierce samples for the DeMattia Flex-Crack tester.

After optimization of the modulus, crack growth, and heat build up characteristics on small parts (Doli cylinders 19 x 25 mm and DeMattia samples 25 x 3 mm,) composite cylinders (57 x 64 mm) were prepared using all control compounds or ARA containing compounds. The composite cylinders weighed approximately 200 gr were prepared using equal weights (about 50 gr) of each compound. The cylinders were prepared by rolling the compounds along the longitudinal axis in the following order:

1. Steel Skim compound
2. Carcass compound
3. Tread base
4. Tread Cap

Large cylinders for heat build-up testing were cured for 4 hrs @ 150. Thermography was used to measure the surface temperature of the composite samples during the Heat build-up test. Imagining and analysis were performed by Thermo Guard, Inc. using a FLIR long wave infrared camera.

Results:

Individual Doli samples were tested for heat build-up in the Doli Flexometer according to ASTM D-623. After testing in the Doli Flexometer, a transverse cut at the midpoint of the longitudinal axis of each sample provided a surface at the geometric center of the sample. Those surfaces were “modulus” profiled using micro-indentation modulus testing by Akron Rubber Development Laboratories (ARDL.) The representative results of the carcass compound are shown in figure 4.

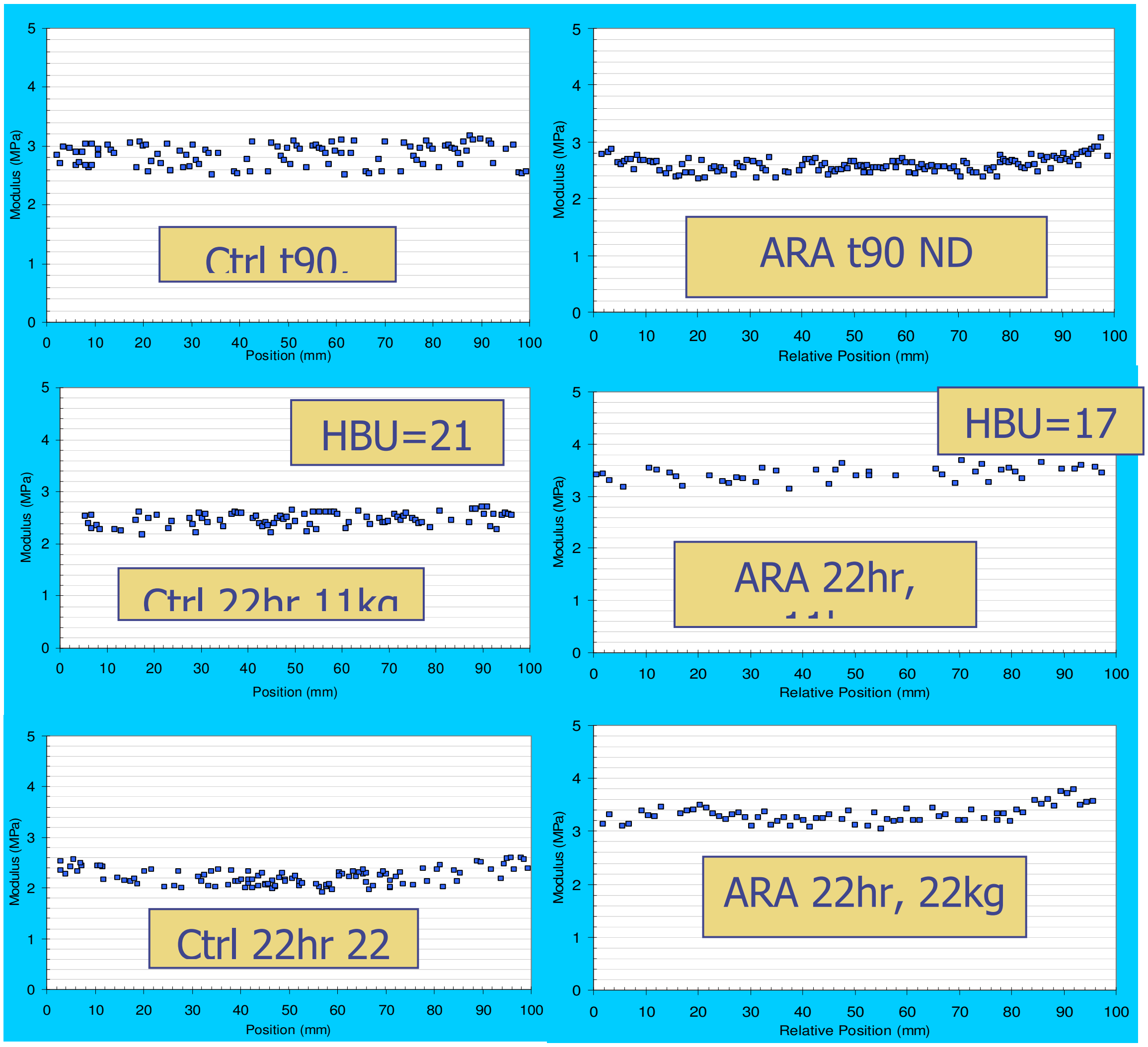

Figure 4 Micro-indentation modulus profiling for Doli Flexometer samples. Control samples are on the left, ARA samples are on the right with the appropriate annotation describing the sample cure and test condition.

It is clearly seen in Figure 4 that the ARA samples maintain modulus significantly better than the control. The mean modulus of the control in first condition, t90 cure “not Doli Tested” is about 2.8 MPa. After 22 hr cure and Doli testing using a 22 kg load (to simulate both long cure and high intensity service conditions) the average modulus is on the order of 2.2 MPa, a drop of more than 20%. In addition, the shape of the modulus profile clearly shows that the center section of the sample has more significant modulus deterioration than the edges. We attribute the modulus drop to an accumulation of heat at the center of the sample inducing more reversion than at the edges.

An important concern in using any crosslinking agent which imparts carbon-carbon crosslinks is resistance to tearing or crack growth. The following experiments were designed to address the combined concerns of maintaining modulus, minimizing heat build-up, and crack growth behavior simultaneously. The results are given for the steel skim compound which by nature of its function and modulus is prone to failure via either a crack growth or heat buld-up mechanism. In this series of experiments we seek to minimize the change in modulus over several cure and simulated service conditions. The compression modulus was measured using the MTS 831 Elastomer Testing System at optimal t90 cure, 22 hr cure with no service, 22 hr cure with 30 minutes of 11 kg load Doli Flexometer (low severity) service condition, and finally 22 hr cure with 22 kg load (high severity) service condition. The results are provided in Figure 5. The control compound shows the greatest range of dynamic moduls, from about 5.75 to 8.6 or an average of 7.15 +/-1.4 MPa, a range of nearly /-20%. The ARA samples typically show an average deviation about the mean modulus value of only about +/- 0.5 MPa or an average deviation of about +/-7%.

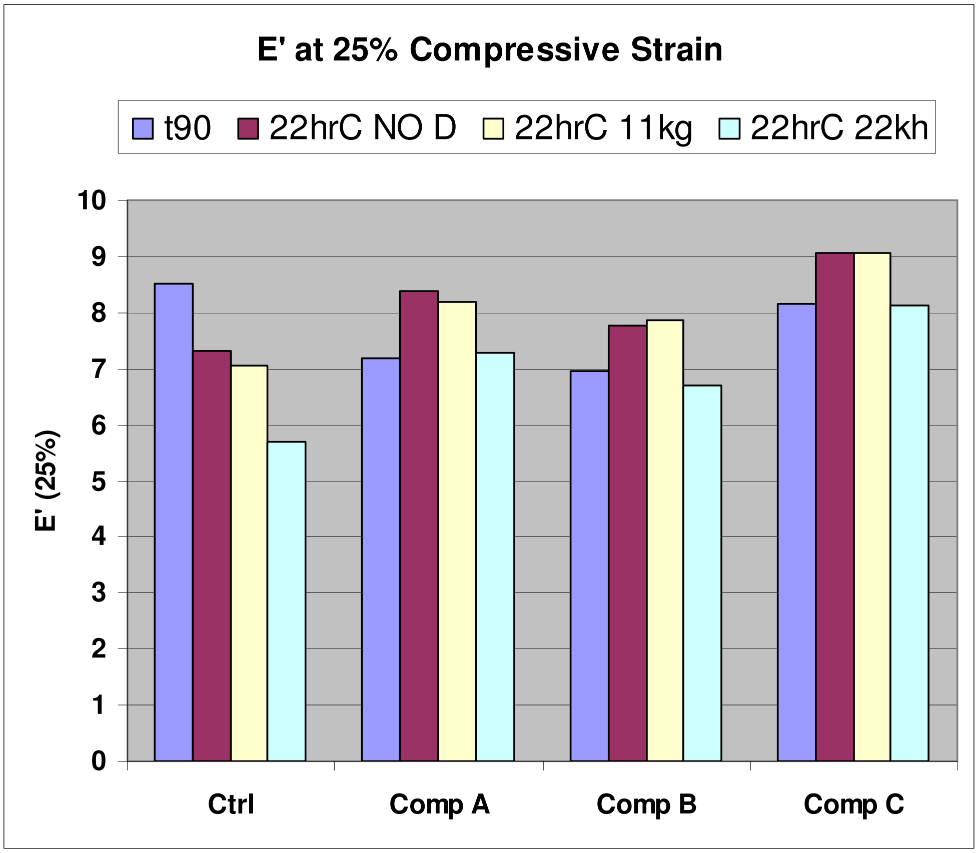

Figure 5 Residual modulus after optimal and extended cure followed by various simulated service conditions.

Heat build-up is improved in the ARA samples significantly relative to the controls. Figure 6 shows the ARA samples have significantly reduced changes in the Delta T compared to the control. These results suggest that the load rating of the ARA samples could be increased on the order of 50-80% compared to the control and still provide a similar level of heat generation during service.

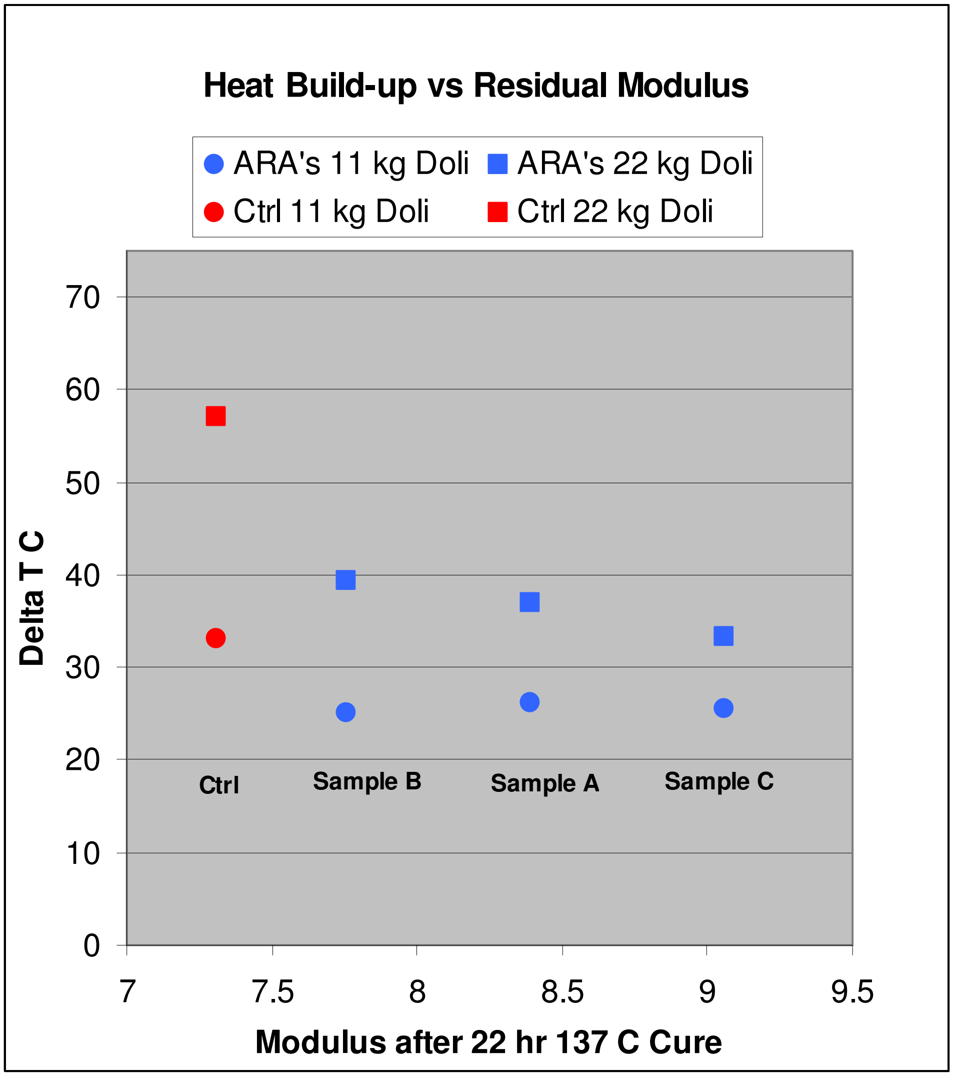

Figure 6 Heat build-up of Steel Skim stock samples cured 22 hrs at 137 C and tested either with an 11 or a 22kg load.

Crack growth resistance is a very important concern in OTR compounding. While it is easy to reduce heat build-up by increasing the modulus this improvement in HBU is often accompanied by a concomitant drop in crack growth resistance or tear strength. The optimized compounds above were tested on the DeMattia crack growth tester using two cure conditions. The first was the "optimal" cure or t90. In this case, we would like to see the crack growth of the ARA samples be at least as low as the control sample. The second condition (highly reverted samples 22 hr Cure) were tested for Crack growth resistance. In this case, we would like to see all the samples perform at least as well as the control compound cured at t90. The results are provided in Figure 7.

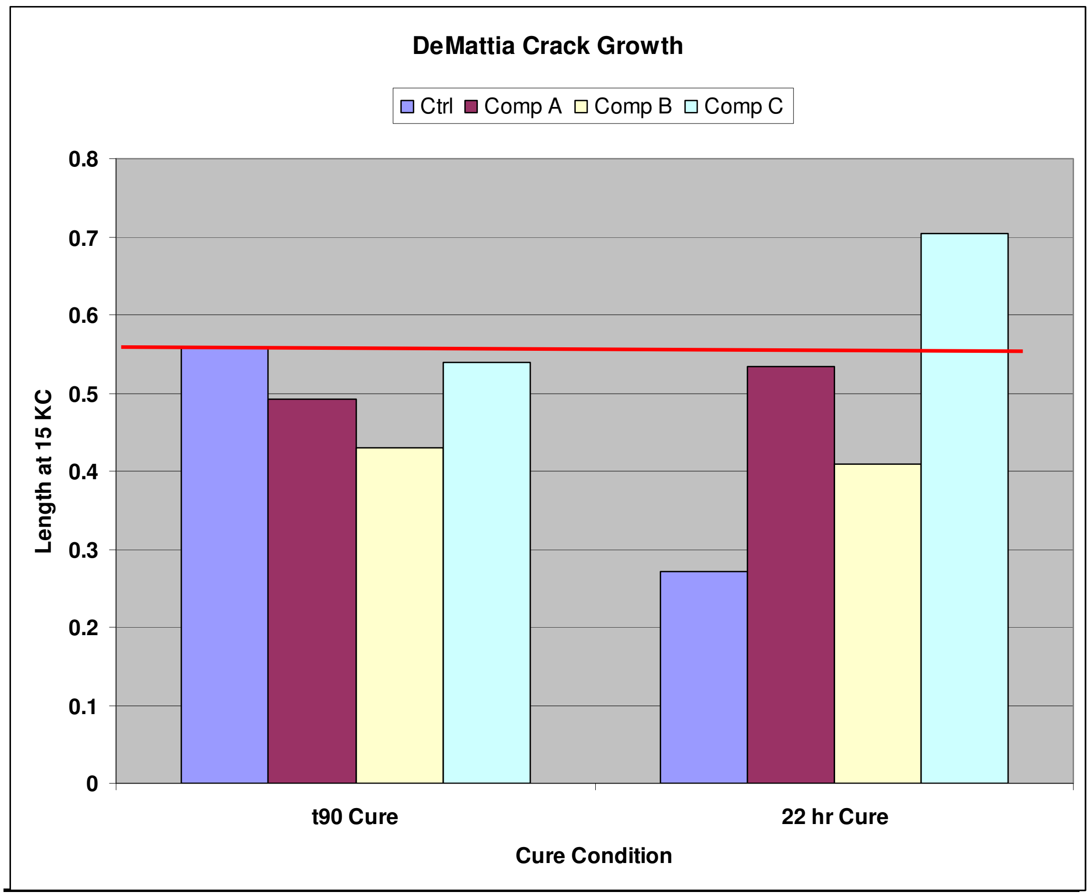

Figure 7 DeMattia Crack Growth behavior of Steel Skim Compounds cured at either t90 (optimal cure) or 22 hrs (highly reverted.) The control is much lower in crack growth. The ARA samples show very little change in crack growth behavior.

While Figure 7 shows a dramatic improvement in crack growth resistance of the control compound, Figure 6 shows this compound is severely compromised for heat build-up. The best performance is demonstrated in the ARA materials where little change in either Heat Build-up or crack growth behavior is observed. This is consistent with the very low change in modulus of these materials upon "overcure" or after "overcure + service."

Heat build-up comparison Doli Pellet vs Composite sample.

Heat flow in small samples is easy to manage; on the other hand, large body composites represent a significant engineering challenge. We have demonstrated the ability to prepare "small sample" compounds which have resistance to change in modulus, heat build-up and crack growth resistance when subjected to intense overcure and service conditions. The greatest benefit will be realized when combining all of these benefits into multiple compounds in a large composite structure. Here we aim to demonstrate the larger scale benefit of reduced heat build-up without rigorous mathematical treatment in a larger composite construction.

Doli Flexometer samples were prepared and run according to ASTM D-623. The improvement in heat build-up (HBU ctrl – HBU test sample) cured for 22 hrs and tested under loads of 11 or 22 kg is given in Figure 8. The largest Delta T values are observed under the most servere conditions (22 kg load). The average delta T at low loads is 2 kg and for high loads about 22 kg,

	11 kg	**22 kg**
Carcass	2.4	6.9
Steel Skim	3.6	20.9
Tread Base	2.7	7.8
Tread Cap	1.2	2.1
Average	2	9

Table 1 Heat build-up values of 22 and 22 kg samples.

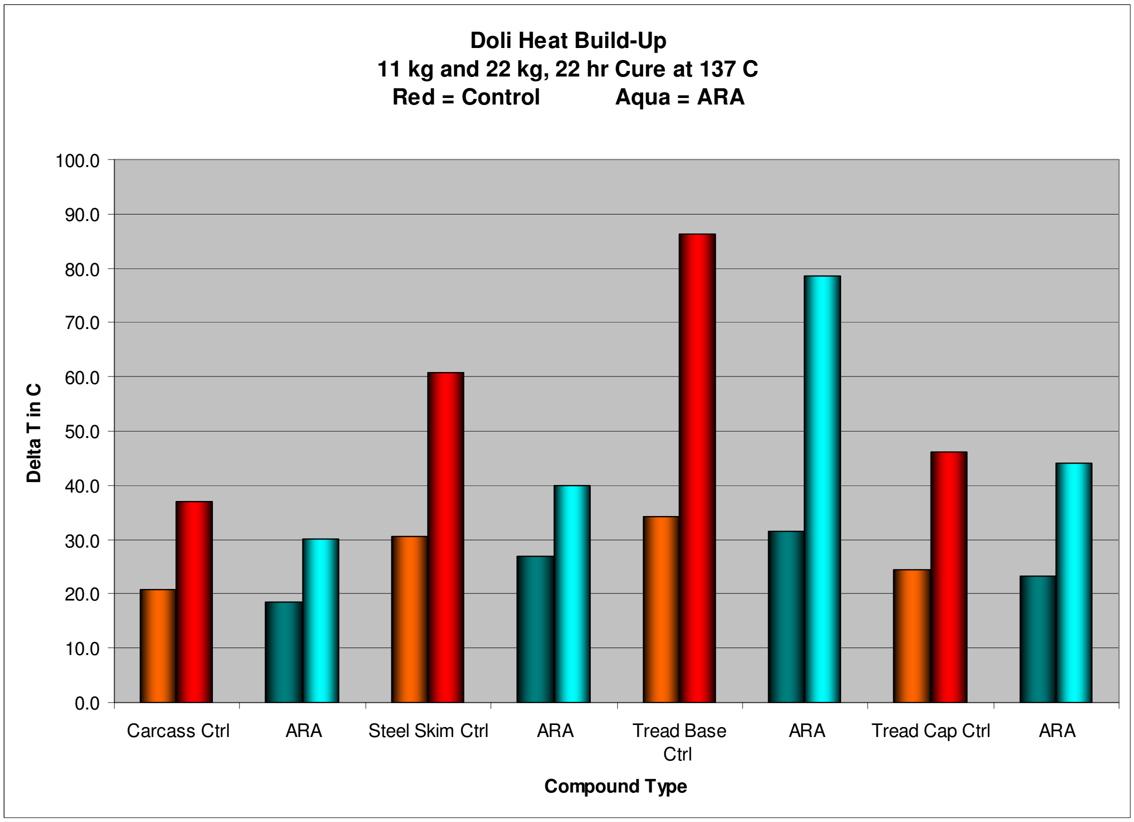

Figure 8 The difference in heat build-up of samples tested after optimal cure, t90 at low temp, and t90 tested at high temo.

Large composite cylindrical compression buttons (5.72 x 6.4 cm) were prepared using equal weights of the four test compounds; steel skim, carcass, tread base, and tread cap compounds. Two large cylinders were prepared using all control formulations and two large cylinders were prepared using all ARA formulations. Approximately 50 grs of each mentioned compound were rolled in order into the composite cylinder. A schematic of the cross-sectional view of the composite material is given in Figure 8.

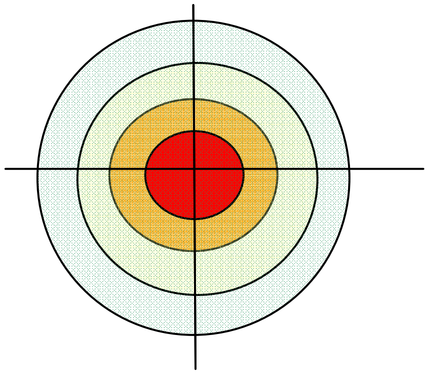

Figure 9 The cross sectional schematic of the composite "button". From center to edge, each circle represents a "cylinder" of steel skim, carcass, tread base, and tread cap compound.

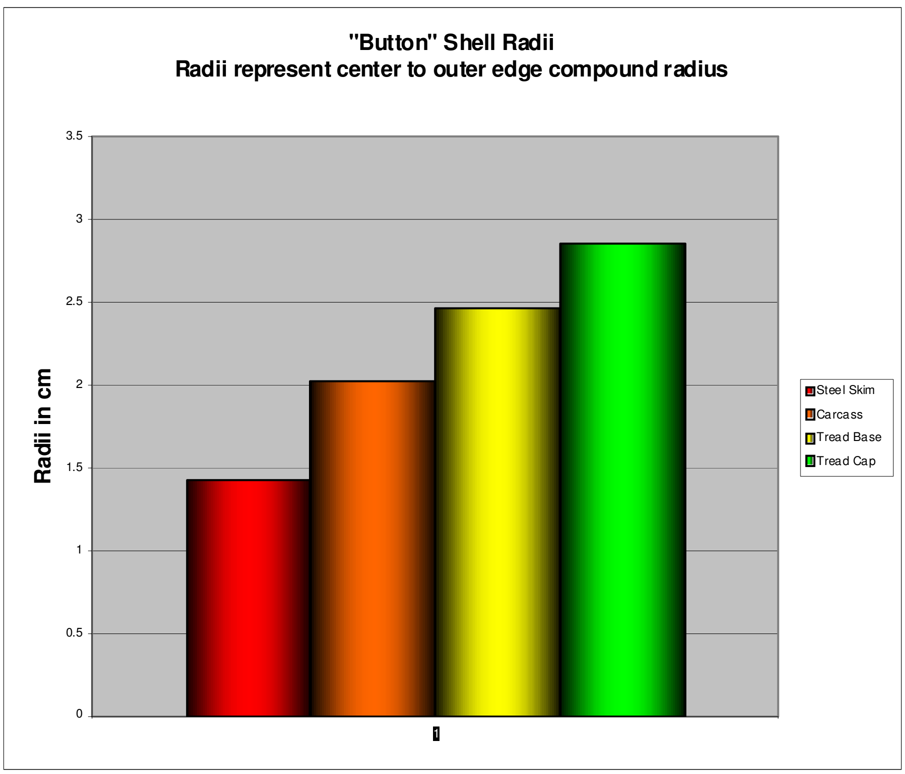

Figure 10 Cylindrical radii of the composite button.

The calculated cylindrical radii are given in Figure 9. Given the constant weight used for each segment, the graph demonstrates nicely the decreasing thickness of each shell progressing center to edge. The respective cylindrical samples were tested in the MTS 831 elastomers testing system. The MTS heat build- up experiment was run using conditions of lesser severity than those used in the 11kg, Doli experiment. A static load of 1000 N was applied. A dynamic load of +/- 750 N was superimposed on the static load at a frequency of 15 Hz. This load and frequency resulted in the large cylinder compression on the order of 15-18% strain. In addition to the lower load, the dynamic frequency was half that imposed in the Doli experiment (the Doli experiment employs a 30 Hz dynamic frequency.) The Doli experiment resulted in compressive strains generally equal to or greater than the strains observed in the MTS experiment. The ranges and average compressions observed in the Doli experiment are summarized in Table 2.

Table 2 Average and ranges of compression observed in 11 kg Doli experiment.

11 kg Doli experiment	Average	Min	Max
Static Compression	25.3	15.6	31.0
Init Flex Comp	17.2	8.0	22.9
Final Flex Comp	19.0	10.0	26.5

Thermographic video imaging was conducted to determine extremely precise and accurate information regarding the temperature of the cylinder surface. A Representative image is shown in Figure 11. Data from the image was used to generate the service temperature curves in Figure 12. Comparing the low load Doli experiment to the large cylinder shows the influence of part size on heat dissipation. The delta T between the control samples and the ARA samples in the low load experiment ranged from about 1 to 4 degrees. In the large cylinder MTS heat build-up experiment the ARA compounds runs about 8 degrees cooler than the control.

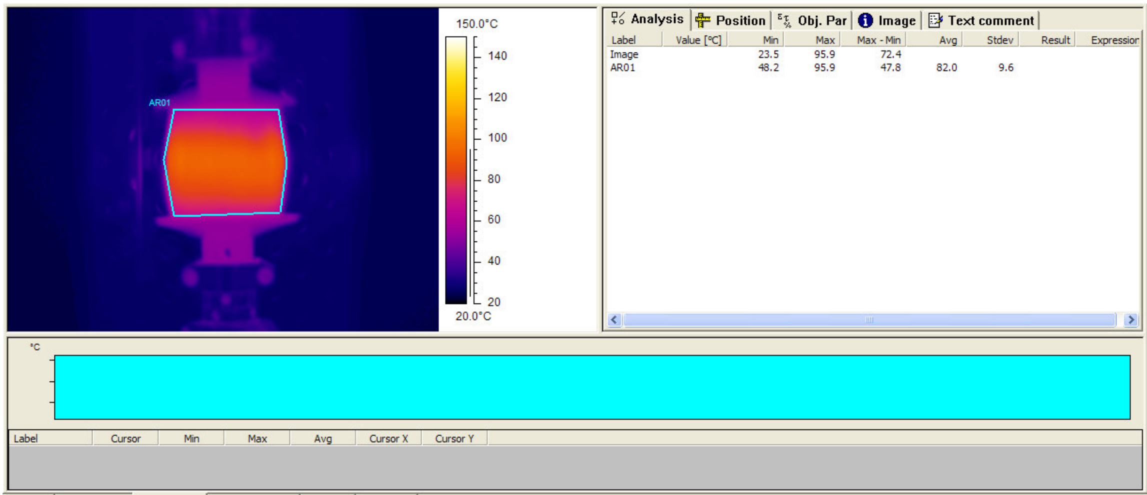

Figure 11 Example of thermographic image and analysis.

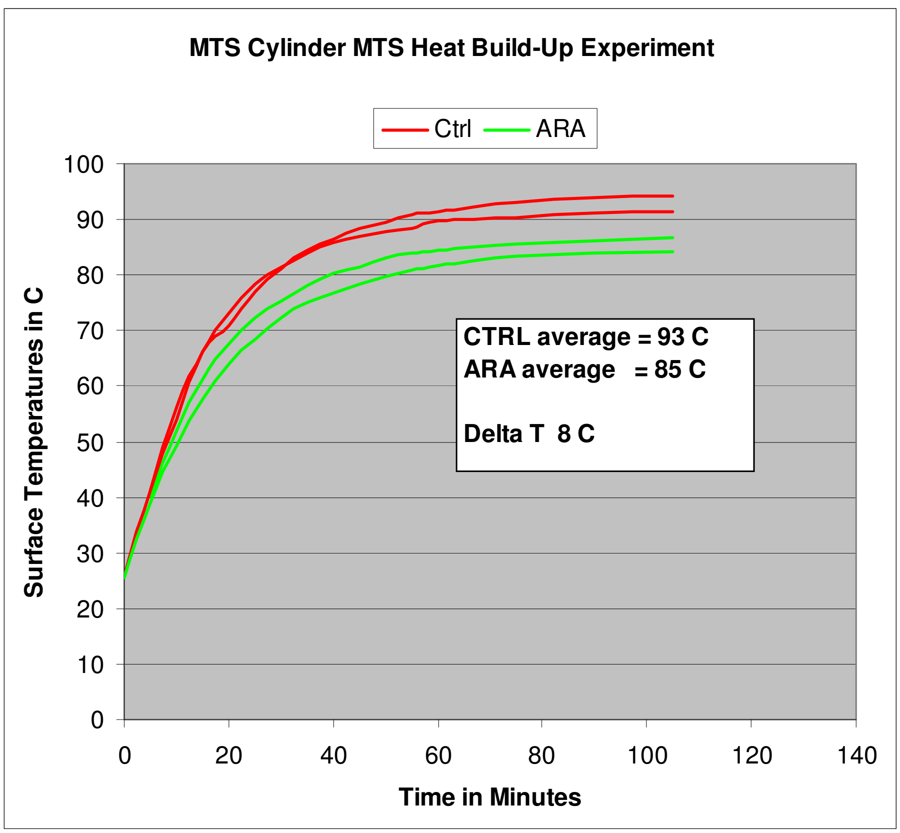

Figure 12 MTS Heat Build-Up experiment using large cyclinders.

Summary:

Both BCI-MX and HTS show improved resistance to reversion in conventionally compounded vulcanizates. The retained modulus shows that BCI-MX and HTS combinations preserve a high percentage of the original network upon upon overcure and after service. The crack growth characteristics of the vulcanizates equal to or better than the control materials cured to t90. The use of BCI-MX in combination with HTS results in vulcanizates having excellent retention of modulus and crack growth characteristics upon overcure and high severity service conditions.

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[2] F. Ignatz-Hoover et al., Rubber World, Vol 214, No.5, pp. 19-20,81-84.

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[4] W. F. Helt , B. H. To and W. E. Paris, Rubber World, 204, 18, 1991. . R. N. Datta, A. H. M. Schotman, A. J. M. Weber, F. G. H. Van Wijk, P. J. C. Van Haeren, J. W. Hofstraat, A. G. Talma, and A. G. Boevenkamp-Bouwman, Rubber Chem. Technol. 70, 129, 1997.