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TECHNICAL BULLETIN

Tire Curing Bladders

Background

Cancarb has introduced the concept of high loadings of thermal black in halobutyl inner liners to the tire industry. This concept can theoretically be applied to other similar applications, including curing bladders, inner tubes and sports ball inner liners. This technical bulletin provides the results of Cancarb's evaluation of Thermax® N990 in butyl tire curing bladders.

Tire Curing Bladders: General Information

Tire curing bladders are sealed flexible rubber bags inflated inside of uncured tires during the vulcanization process. Curing bladders are one of the most severe rubber applications in terms of heat and flex resistance. Bladder compounds have some of the most stringent and exacting requirements of any rubber compound. These requirements can be summarized as follows:

1. Mix well and process easily
2. Satisfactory molding
3. Good physical properties
4. Good aging properties
5. Good flex and tear resistance
6. Low tension set
7. Excellent steam aging properties
8. Good thermal conductivity

Standard Curing Bladder Formulation

The carbon black loading in butyl curing bladders has typically been 50 or 55 parts of N330, high abrasion furnace type. The HAF type provides the necessary tear strength and has been well accepted over GPF or FEF grades. A typical formulation is as follows:

Butyl 268	100 phr	Exxon
Neoprene WRT	5 phr	Dupont[1]
N330 Carbon Black	50 phr	
Castor Oil	5 phr	
Zinc Oxide	5 phr	
Reactive Phenol Formaldehyde Resin	10 phr	butyl curing resin, Schenectady SP1045

To achieve optimum performance of the bladder compound, good dispersion of the Neoprene, carbon black, zinc oxide and curing resin is critical.

Based on the above formulation, compounds with the following filler loadings were tested at the BFGoodrich Laboratory in Breckville, Ohio. This lab is an American Association for Labratory Accreditation (A2LA) accredited lab and is ISO 9001 certified.

Compound #1 - 50 phr N330 (control)
Compound #2 - 110 phr Thermax® N990
Compound #3 - 90 phr Thermax® N990, 20 phr N660
Compound #4 - 80 phr Thermax® N990, 30 phr N330
Compound #5 - 90 phr Thermax® N990, 20 phr N330
Compound #6 - 40 phr Thermax® N990, 40 phr N330
Compound #7 - 50 phr Thermax® N990, 40 phr N330
Compound #8 - 60 phr Thermax® N990, 40 phr N330
Compound #9 - 90 phr Thermax® N990 Ultra Pure[2], 20 phr N330

Results are as attached in Table 1.

[1] 5 phr of Neoprene is added in resin cured butyl compounds activate the resin cure reaction by donating halogen.
[2] Compound #9 is identical to Compound #5, except that the Ultra Pure grade of Thermax® N990 was used so that the effect of the lower pH thermal black on the cure time could be evaluated. Thermax® N990 Ultra Pure has a typical pH of 5 compared to 10 for standard Thermax® N990.

Comments

All results are indicative of the typical effects of using Thermax® in a rubber Thermax® compound. Due to the large particle size and low structure, N990 is in general a non-reinforcing carbon black and while it will enhance the dynamic properties of rubber, it does not provide the strength or reinforcement that the furnace grades do. Furthermore, the higher pH will in general lead to longer cure times.

Test compound #2, with 110 phr of Thermax® N990, had the lowest viscosity, as expected. The similarity of the modulus to the control compound may be interest to some bladder producers.

Test compounds #5, #6 and #8 are similar to the control compound. Processing properties for #5 are generally equal to the control compound except the time to a 5pt. rise (T_s5)indicates a longer cure time. This is also evident in the other compounds that are loaded with Thermax®, as N990 provides more scorch safety than other carbon blacks. This was confirmed with test compound #9, which had 90 phr of Thermax® N990 Ultra Pure, the low pH thermal carbon black.

Tensile properties – original, aged and elevated temperature – for the Thermax® N990 compounds are in general lower than the control but are considered to be sufficient for this application. Elongation, however, is noticeably lower than the control and is a point of concern. However, test compound #6 should have sufficient elongation.

Tear strength for the test compound #5 is also noticeably lower than the control compound. However, with 40 phr N330 and 60 phr Thermax® N990, test compound #8 has equivalent tear strength.

Thermal conductivity improved (i.e was higher) with the higher black loadings in all of the test compounds. Test compound #8 showed exceptional results. This is more a function of the higher carbon loading which is allowed with Thermax®, rather than a property specific to thermal carbon black. Higher thermal conductivity is a beneficial in bladder compounds allowing higher heat flow resulting in faster tire cure times. Estimates of the increase in cure times range from 10 – 20 seconds per tire.

The DeMattia crack growth results, for all compounds including the control, were poor and showed insufficient crack growth resistance. Experience with this test suggests that more than two samples should be used for a valid indication of the true crack growth resistance.

The compounds containing Thermax® had slower cure rates than the control. One possible explanation for the slower cure is the surface activity of thermal black, or that the high pH of the thermal blacks inhibited the rate of resin cure in the butyl rubber. The T_{95} results confirm this, with test compound #9, the low pH compound, having the shortest cure time of the thermal black compounds. Adding more Neoprene or Stannous Chloride to the formulation should increase the cure rate.

Cost Benefit Analysis

Calculations of cost savings should theoretically include the material costs, tire cure time, press downtime and any increase (or decrease) in productivity due to the changes in throughput.

For raw materials cost savings, Table 2 provides an estimate of savings of approximately US $0.94 per curing bladder. This is due to the substitution of the higher cost butyl rubber with Thermax® N990.

Conclusion

Test compounds #6 and #8 provide the best balance of physical properties compared to the control compound. The main advantages seen thus far would be the improved thermal conductivity and reduced compound cost. Final judgment on the above results will naturally be subject to bladder life.

Supplementary Notes

Thermal conductivity is measured according to ASTM C518-91, Vol. 04.06. Q is the heat flow through the rubber test piece at a thickness of approximately 13 mm (0.51 in.). K is the measurement of thermal conductivity expressed in BTU•in/(ft.2•hr.•°F). it is normally expressed in degrees Kelvin. mV is a milli-volt value of the heat flow meter output. This value is not converted to temperature. The results have been indexed based on the control compound for ease of understanding. BFGoodrich used a Dynatech Rapid-k meter and a Haskris recirculating chiller.

For further information please contact Cancarb.

Table 1: Curing Bladder Compound Data

Compound #	#1 (control)	#2	#3	#4	#5	#6	#7	#8	#9
Thermax® N990		110	90	80	90	40	50	60	
Thermax® N990 Ultra Pure									**90**
N330 Carbon Black	50			30	20	40	40	40	20
N660 Carbon Black									
Compound Properties (ASTM D1646-96a)									
Mooney Viscosity M_L (1 + 4) @ 100°C	66	59	65	76	69	76	75	77	70
Mooney Scorch @ 137.8°C (ASTM D1646-96a)									
Minimum	49	40	45	58	52	59	58	60	53
$T_{(min)}$ + 5 minutes	24.5	32.8	37.8	26.8	35.8	14.3	14	15.8	17.4
Monsanto R100 Oscillating Disk Rheometer @ 190°C, 1° arc (ASTM D2084-95)									
M_L (dNm)	9.9	7.6	8.7	10.2	9.9	11.9	11.3	11.5	10.2
M_H (dNm)	34.4	36.7	38.5	40.7	40.2	38	39.4	38.7	38.6
T_2 (min)	3.2	3.5	3.7	3.2	3.3	3.1	2.8	3	2.6
T_{90} (min)	29.2	36.5	40.7	37.1	37.6	33.6	34.5	34.9	30.7
T_{95} (min)	36.9	45.5	48.9	45.2	46.3	42.8	43.5	43.2	40.1
Stress-Strain, Originals @ RT, Cure Conditions T95 @ 190°C (ASTM D412-97)									
100% Modulus (MPa)	1.8	2.2	2.4	2.2	2.8	2.3	2.3	3.1	2.6
300% Modulus (MPa)	5.5	5.5	5.7	6.5	7.9	7.2	7.6	8.9	7.9
Tensile Strength (MPa)	15	6.5	6.7	7.9	8.9	11.2	10.5	10	8.9
Elongation (%)	647	414	403	425	415	490	450	420	400
Shore A Hardness	66	70	70	71	74	69	71	73	72
Stress-Strain, Originals @ 100°C, Cure Conditions T95 @ 190°C (ASTM D412-97)									
100% Modulus (MPa)	1.9	1.9	1.7	1.9	2.3	2.1	2.4	2.3	2.2
300% Modulus (MPa)	5.6	4.2	3.8	5.2	6.3	6.1	7.1	6.5	-
Tensile Strength (MPa)	9.1	4.3	4	5.7	6.3	6.7	7.1	6.7	6
Elongation (%)	460	315	325	335	305	330	310	310	290
Stress-Strain, Oven-Aged 48 hours @ 170°C, Cure Conditions T95 @ 190°C (ASTM D412-97)									
100% Modulus (MPa)	4.6	4.4	4.8	5	4.9	4.6	5.3	5.1	5.2
200% Modulus (MPa)	7.6	6.8	7.6	8.2	8.1	7.7	8.8	8.2	8.3
Tensile Strength (MPa)	10.3	7.5	8.1	8.7	9.1	9.4	6.9	8.9	8.3
Elongation (%)	280	240	215	205	230	255	155	220	200
Shore A Hardness	90	96	94	94	93	90	90	93	91
Tear Strength, Die C (ASTM D24-96), RT									
(kN/m)	38.9	34.0	33.6	35.1	33.1	34.5	33.9	40.7	32.3
Tension Set, 100% Elongation, @ 200°C – Held 10 minutes (ASTM D412-97)									
Tensile Set (%)	13.4	25.0	27.4	25.9	20.5	24.1	26.6	29.3	26.1
DeMattia Crack Growth: 23°C, aged 7 days @ 100°C; average of two samples, inches (ASTM D813-95)									
5,000 cycles	2.5	5.0	6.0	7.0	3.5	3.5	6.5	5.5	5.5
10,000 cycles	2.5	5.5	6.5	7.5	4.5	5.5	6.5	6.5	6.5
15,000 cycles	3.5	6.5	7.5	8.5	5.5	6.5	7.5	7.0	7.5
25,000 cycles	5.0	8.0	9.0	10.0	7.0	7.5	9.0	7.5	10+
Thermal Conductivity, 100°C (ASTM C518-91)									
Q: Heat Flow (mV)	3.610	3.953	4.153	4.200	4.157	4.095	4.282	4.440	4.420
K: Thermal Conductivity									
(BTU in/(hr.sq.ft iF))	0.786	0.844	0.892	0.900	0.891	0.856	0.885	0.910	0.917
Index	100	110	115	116	115	113	118	120	122

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Curing Bladder Formulation	Traditional Formulation Parts: By Weight	By Volume	Thermax® N990 Formulation Parts: By Weight	By Volume
Exxon Butyl 268	100.00	108.70	100.00	108.70
Neoprene W	5.00	4.00	5.00	4.00
N330 Carbon Black	50.00	27.78	20.00	11.11
Thermax® N990	0.00	0.00	90.00	50.00
Castor Oil	5.00	5.21	5.00	5.21
Zinc Oxide	5.00	0.89	5.00	0.89
Curing Resin SP 1045	10.00	9.52	10.00	9.52
TOTAL	**175.00**	**156.10**	**235.00**	**189.43**
Specific Gravity (calculated)	**1.121**	-	**1.241**	-
Compound Cost (USD)	1.99/kg	2.23/litre	1.76/kg	2.18/litre

Savings per curing bladder (USD), based on 4 kg compound: 0.94

Ingredient Cost Assumptions

Prices are listed in September 1997 Rubber World Compounding Ingredients Price List. Prices are used for bulk quantities.

	USD/kg	Spec. Gravity
Exxon Butyl 268	2.390	0.92
Neoprene W	4.09	1.25
N330 Carbon Black	0.83	1.80
Thermax® N990	0.99	1.80
Castor Oil	1.58	0.96
Zinc Oxide	2.18	5.60
Curing Resin SP 1045	2.88	1.05

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