Vulcanizing Nitrile Rubber

DI-CUP® dicumyl peroxide and **VUL-CUP®** peroxide [*a,a*'-bis(*tert*-butylperoxy) diisopropylbenzene] are effective vulcanizing agents for all types of NBR (nitrile rubber). These peroxides produce vulcanizates with better heat-aging and lower compression set than sulfur-accelerator systems.

The vulcanizates in this bulletin were compounded with Di-Cup® 40KE dicumyl peroxide and Vul-Cup® 40KE peroxide. Other forms of Di-Cup® and Vul-Cup® can be used with similar results.

Peroxide vs. Sulfur Cure

NBR compounds cured with Di-Cup® dicumyl peroxide and Vul-Cup® peroxide exhibit better heat resistance and lower compression set than the same compounds cured with a sulfur-accelerator system. Table I on page 2 shows a comparison of the performance of sulfur-cured NBR with that of Di-Cup® and Vul-Cup®. The peroxide levels were chosen to yield vulcanizates with elongation and modulus values equivalent to those of the sulfur-cured stock.

The most significant differences between the stocks are the better heat resistance, lower compression set, and improved low-temperature flexibility of those cured with peroxides.

Basic Formulation

The following basic formulation is suggested as a starting point in developing a new compound. If an existing formulation is to be modified to include a peroxide, remove all ingredients associated with the previous cure system and add Di-Cup® dicumyl peroxide or Vul-Cup® peroxide as indicated.

Formulation	Parts by Weight	
NBR	100	
Filler	Variable	
Zinc oxide	5.0	
Antioxidant	0.5	
Peroxide	Di-Cup® 40KE	2.5-5.0 phr
	Vul-Cup® 40KE	1.5-3.0 phr

Typical results using this formulation are shown in Table II. All compounds contain 50 phr HAF black and can be cured as follows:

		Cure Conditions	
Peroxide	**Peroxide, phr**	**Time, min.**	**Temperature, °F (°C)**
Di-Cup® 40KE peroxide	3.4	25	330 (166)
Vul-Cup® 40KE peroxide	2.1	25	340 (171)

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Table I - Performance of Peroxide vs. Sulfur-Cured Nitrile Rubber

Formulation	Sulfur Cure	Vul-Cup® Peroxide Cure	Di-Cup® Peroxide Cure
Nipol® 1032	100	100	100
HAF black	50	50	50
ZnO	5.0	5.0	5.0
Antioxidant	1	1	1
Stearic acid	1	--	--
MBTS	1.5	--	--
Sulfur	1.5	--	--
Vul-Cup® 40KE	--	1.6	--
Di-Cup® 40KE	--	--	2.5
Cure temperature,°F (°C)	310 (154)	240 (171)	330 (166)
Cure time, min.	30	25	25
Original Properties			
100% modulus, psi (MPa)	460 (3.1)	440 (3.0)	460 (3.2)
200% modulus, psi (MPa)	1,150 (7.9)	1,250 (8.6)	1,435 (9.9)
Tensile strength, psi (MPa)	2,800 (19.3)	3,100 (21.4)	3,080 (21.2)
Elongation, %	380	395	345
Shore A hardness, points	65	64	65
$T_{10,000}$, °C	-18	-22	-22
Compression Set, %			
70 hrs at 212°F (100°C)	66	20	20
70 hrs at 257°F (125°C)	82	30	30
Air-Oven Aging, 70 hrs at 257°F (125°C)			
100% modulus, psi (MPa)	--	1,260 (8.7)	1,215 (8.4)
200% modulus, psi (MPa)	--	3,060 (21.1)	--
Tensile strength, psi (MPa)	1,980 (13.7)	3,350 (23.1)	3,000 (20.7)
Elongation, %	80	215	195
Shore A hardness, points	70	77	75
ASTM No. 3 Oil-Aging, 70 hrs at 257°F (125°C)			
100% modulus, psi (MPa)	700 (4.8)	520 (3.6)	485 (3.3)
200% modulus, psi (MPa)	--	1,680 (11.7)	1,650 (11.4)
Tensile strength, psi (MPa)	870 (6.0)	2,400 (16.6)	2,620 (18.1)
Elongation, %	107	240	285
Shore A hardness, points	60	53	56
Volume swell, %	10.8	16.6	16.6

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Table II - Performance of Peroxide-Cured Nitrile Rubber

	Acrylonitrile Content					
	Low	Medium	Medium	High	High	Very High
	Krynac® 2750	Nipol® 1053	Nipol® 1032	Paracril® C	Chemigum® N-3	Krynac® 5075
Original Properties						
100% modulus, psi (MPa)	595 (4.1)	600 (4.0)	580 (4.7)	680 (5.1)	740 (5.6)	815 (5.6)
200% modulus, psi (MPa)	2045 (14.1)	1960 (13.5)	1810 (12.5)	2520 (17.4)	2270 (15.7)	1845 (12.7)
Tensile strength, psi (MPa)	3060 (21.1)	3150 (21.7)	3120 (21.5)	3420 (23.6)	3160 (21.7)	3255 (22.4)
Elongation, %	260	280	280	250	250	400
Shore A hardness, points	70	75	76	75	77	79
Air-Oven Aging, 70 hrs at 257°F (125°C)						
100% modulus, psi (MPa)	1015 (7.0)	1530 (10.6)	1460 (10.1)	1520 (10.5)	1730 (11.9)	1660 (11.4)
Tensile strength, psi (MPa)	2845 (19.6)	2070 (14.3)	2070 (14.3)	2780 (19.2)	3100 (21.4)	3020 (20.8)
Elongation, %	190	130	130	160	150	200
Shore A hardness, points	76	84	85	81	85	78
ASTM No. 3 Oil-Aging, 70 hrs at 257°F (125°C)						
100% modulus, psi (MPa)	465 (3.2)	610 (4.2)	520 (3.6)	650 (4.5)	900 (6.2)	855 (5.9)
200% modulus, psi (MPa)	1925 (13.3)	2190 (15.1)	1920 (13.2)	2600 (17.9)	2570 (17.7)	1865 (12.9)
Tensile strength, psi (MPa)	1925 (13.3)	2340 (16.1)	2350 (16.2)	2630 (18.1)	2730 (18.8)	2435 (16.8)
Elongation, %	200	210	220	205	190	260
Shore A hardness, points	57	63	64	67	73	82
Volume swell, %	22.6	30.2	24.7	17.2	9.0	5.4
Compression Set, % 70 hrs at 257°F (125°C)	16.0	22.7	29.6	18.0	24.6	34.0

Cure Time

The cure curves for Vul-Cup® peroxide in Hycar® 1032 polymer NBR are shown in Figure 1. Physical property data were determined from vulcanizates cured at 330°F (165°C) for varying lengths of time. The time to 95% cure (t_{95}) is shown.

The data presented in Figure 1 show that very little curing occurs after the first 20 min., but that the cure does not become flat until 40 min. Results of postcuring the press-cured samples in Figure 1 are shown in Figure 2. All compounds were post-cured 4 hours at 300°F (149°C) after an initial press cure for the indicated time. The response of tensile strength and compression set to post-cure demonstrates the effect of the high post-cure temperature. All samples were degraded by post-curing.

These results are not thought to be generic for all types of NBR. The experiments were carried out on a medium-high- acrylonitrile-content polymer. Higher- or lower-nitrile-content products will perform differently. It is suggested that the compounder carry out similar experiments if postcuring is considered.

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Figure 1 - Cure Curves -- Vul-Cup® Peroxide in NBR

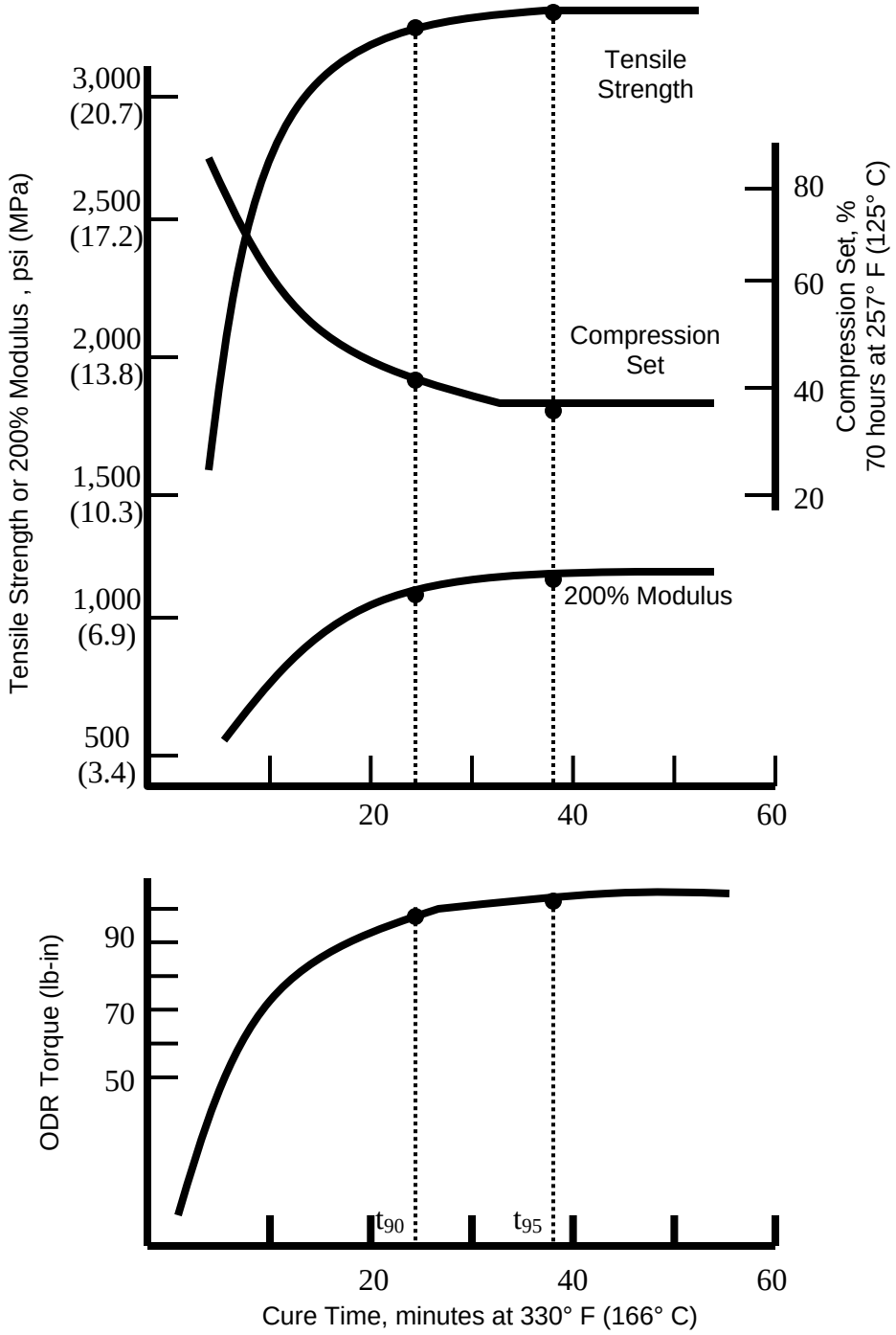

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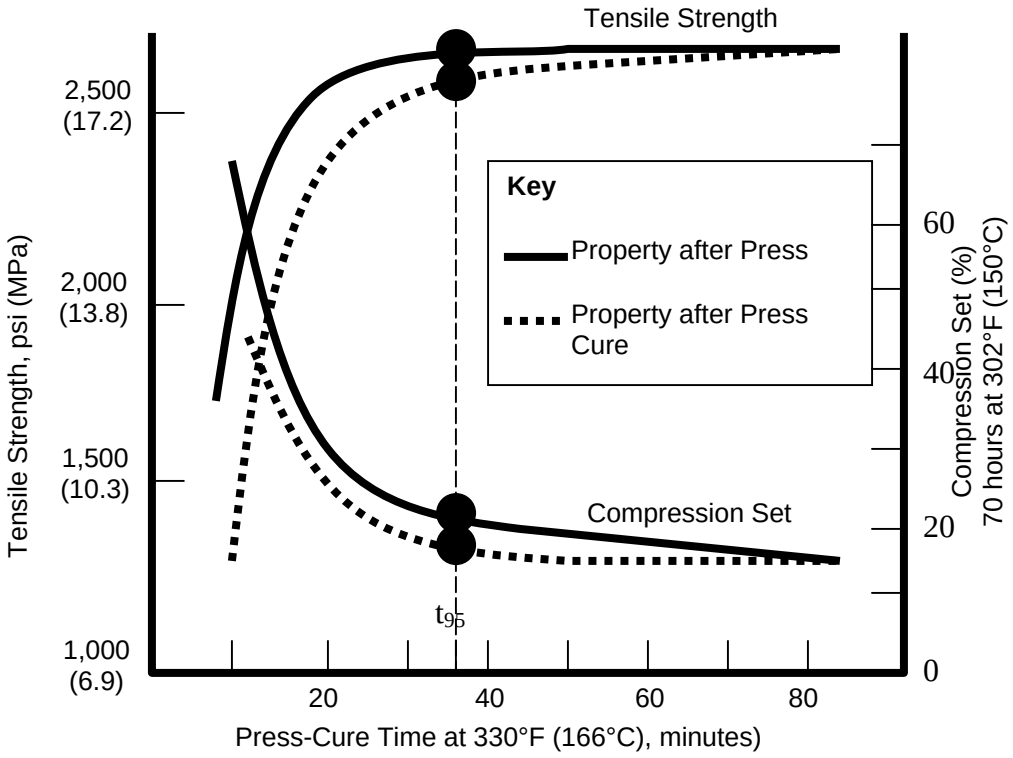
Figure 2
Effect of Postcure, 4 hrs at 300°F (149°C), on NBR Cured With Vul-Cup® Peroxide



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