The Effect of Inorganic Peroxide on Natural Rubber–Carbon Black System

INTRODUCTION

The idea of obtaining reinforcement in rubber compound is rather old and its aim is to obtain vulcanisates with improved physical properties. Carbon black is the most important reinforcing agent for rubber in all its products where color is not important. The reinforcing characteristics of black filler depend on the colloidal morphology (structure of black) and surface properties.[1] It is mainly guided by their surface complexity and by the presence of surface-active groups like hydroxyl, carbonyl, quinone, etc., which are formed during the manufacturing process. It has been reported earlier that the better reinforcing effect between natural rubber and black filler is observed when they are mixed at elevated temperature with extended heating period.[2] Similar improvement is observed using certain chemicals (promoters) like dinitrosobenzene, quinone dioxime, inorganic sulfur, etc. at a comparatively lower temperature and with less time. The chemical used for enhancing the polymer-filler interaction prior to or during mixing results in improved green strength and thus yield vulcanisates with better physical properties.[3,4] In this paper we are reporting the results of our studies on the effect of inorganic peroxide on carbon black–rubber interaction during mixing. Both hydrogen peroxide (H_2O_2) and solid zinc peroxide were used in HAF-black (N330) and GPF-black (N660) in natural rubber systems. The effect of peroxide on steel cord–rubber adhesion has also been studied.

EXPERIMENTAL

The carbon black was treated with H_2O_2 and NH_3 before mixing. The treatment of black was done at different H_2O_2 and NH_3 proportions and compound mixing was done at different period intervals after treatment. Zinc peroxide was added directly in the mill along with black. Mixing was done on a conventional laboratory mill (15 × 33 cm) at 60–70°C according to ASTM D15-70. The treated black was added in the mill after zinc oxide and stearic acid at relatively higher temperature (~ 80°C). Oil was added after maximum portion of black incorporated into the rubber. All physical testings were done in the regular way.[5,6] Wire adhesion testing was done according to ASTM D1871-68 both before and after aging. H_2O_2 in black sample was estimated iodometrically.

RESULTS AND DISCUSSIONS

Table I shows the effect of hydrogen peroxide and ammonia loadings on black filler (N330). All mixing was done after 3 days of treatment. Increase of H_2O_2 and NH_3 increases 300% modulus and abrasion resistance. The enhancement of these properties is considerable up to 2.5 mL of H_2O_2 and 4 drops of NH_3 per 100 g of carbon black. Further increase of H_2O_2 and NH_3 does not further improve properties. The process is repeated with GPF-black (N660) and similar observations were made (Table II). This may be due to the fact that H_2O_2, in presence of NH_3 decomposes and forms oxygen. The alkyl radicals react with oxygen to give peroxy radicals. These peroxy radicals could be stable when they are trapped in the crosslink network.

$$RM^{\cdot} + O_2 \rightarrow RM{-}O \stackrel{\cdot}{-} O$$

These peroxy radicals interact with the active sites (*) located on the carbon black surface to give that weak bond, "rubber ··· carbon black"

$$RM{-}O \stackrel{\cdot}{-} O + {}^{*}\text{Carbon black} \rightarrow RM{-}O \stackrel{\cdot}{-} O \cdots {}^{*}\text{carbon black}$$

which is responsible for the reinforcing effect as well as for the improved physical–mechanical properties.

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TABLE I
Physical Properties of Rubber Vulcanisates with Different Hydrogen Peroxide–Ammonia Loadings

Mix	mL of H_2O_2 in 100 g black	Drop of NH_3 in 100 g black	300% Modulus, MPa	Elongation at break, %	Tensile strength, MPa	Tear strength, kN/m	Resilience, %	Abrasion index, (DIN)	Hardness, shore A
1	0	0	8.48	500	22.96	92.8	37	105	60
2	1.25	2	8.44	540	18.95	81.9	36	100	60
3	2.50	4	10.33	510	23.58	98.8	38	86	60
4	3.75	6	9.94	550	18.64	100.0	39	93	62
5	5.00	8	10.24	520	21.35	87.6	39	95	63

Formulations: Natural rubber 100; zinc oxide 5; stearic acid 3; HAF-black (N330) 45; *N*-phenyl-*N*-(1,3-dimethyl butyl)-*p*-phenylene diammine 2.5, polymerized trimethyl-dihydro quinoline 0.75; aromatic oil 7; *N*-oxy diethylene benzothiazole 2-sulfenamide 0.5; sulfur 2.25; *N*-cyclohexyl thiophthalimide 0.3. All samples were cured at 141°C for 30 min.

TABLE II
Physical Properties of the Rubber Vulcanisates with Different Hydrogen Peroxide–Ammonia Loadings

Mix	mL of H_2O_2 in 100 g black	Drop of NH_3 in 100 g black	300% Modulus, MPa	Elongation at break, %	Tensile strength, MPa	Hardness, shore A	Tear strength, kN/m	Resilience, %	Abrasion index, (DIN)
1	0	0	7.75	550	19.19	60	68.1	43	146
2	1.25	2	8.74	500	19.52	60	75.29	48	122
3	2.50	4	9.43	500	20.83	60	69.51	50	114
4	3.75	6	9.61	500	20.24	61	72.49	50	119
5	5.00	8	9.47	500	22.12	60	79.49	49	124

Formulations: Same as Table I except GPF-black (N660) is used instead of HAF-black.

The treated black was kept at room temperature and mixing was done at different time intervals (Table III) to measure the effect of treatment of black with time. In all cases, the presence of undecomposed H_2O_2 was estimated iodometrically. The titration value shows that H_2O_2 stays as absorbent in the black which decreases with time. After 13 days of treatment the effect disappears completely and it behaves as a normal carbon black. So the treatment of black with H_2O_2 and NH_3 is a temporary physical absorption process where H_2O_2 acts only as an oxygen donor. During mixing, the decomposition of H_2O_2 in rubber-black medium helps to form

TABLE III
Variation of Physical Properties of the Rubber Vulcanisates with Treated Black Mixed after Different Interval of Time

Mix	Time interval, days at 23°C	300% Modulus, MPa	Elongation at break, %	Tensile strength, MPa	Hardness, shore A	Resilience, %	Tear strength, kN/m	Abrasion index, (DIN)
1	untreated	7.75	550	19.17	60	43	68.1	146
2	3	9.07	490	20.37	60	46	70.6	115
3	8	8.30	530	21.37	60	45	77.0	126
4	13	7.72	525	19.52	59	46	65.1	136

Formulations: Same as Table II.

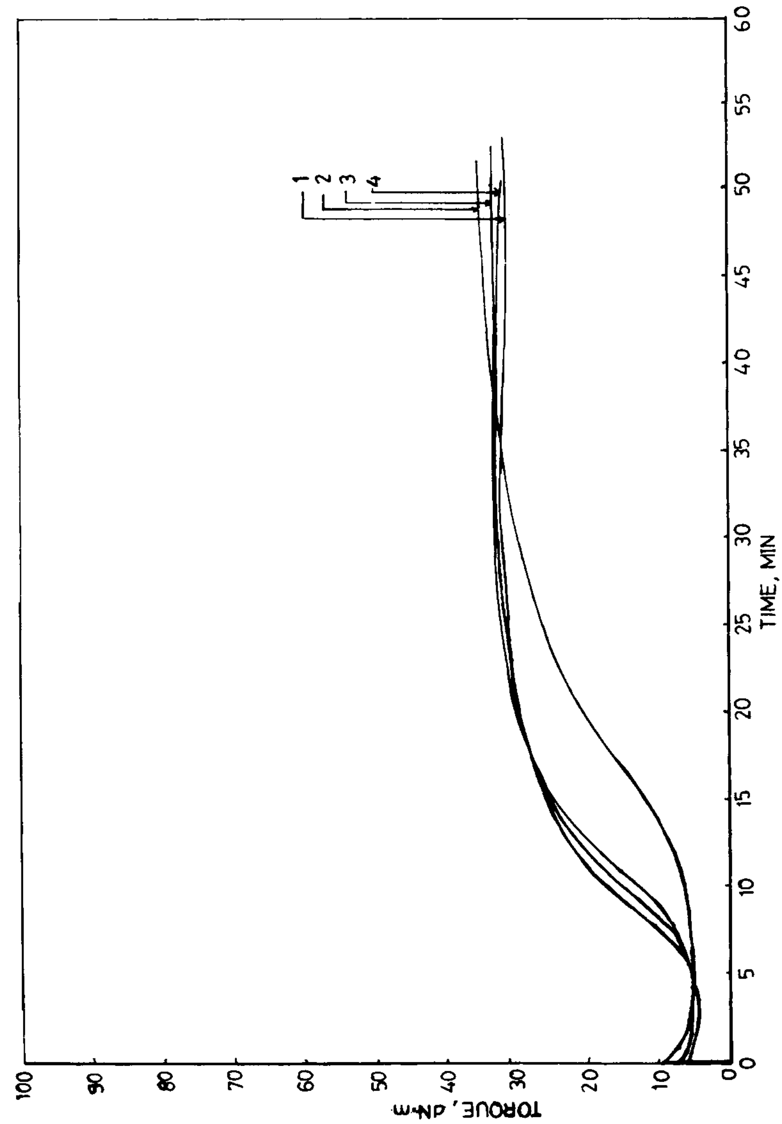

Fig. 1. Rheographs of the mixes with both treated and untreated HAF-black (N330).

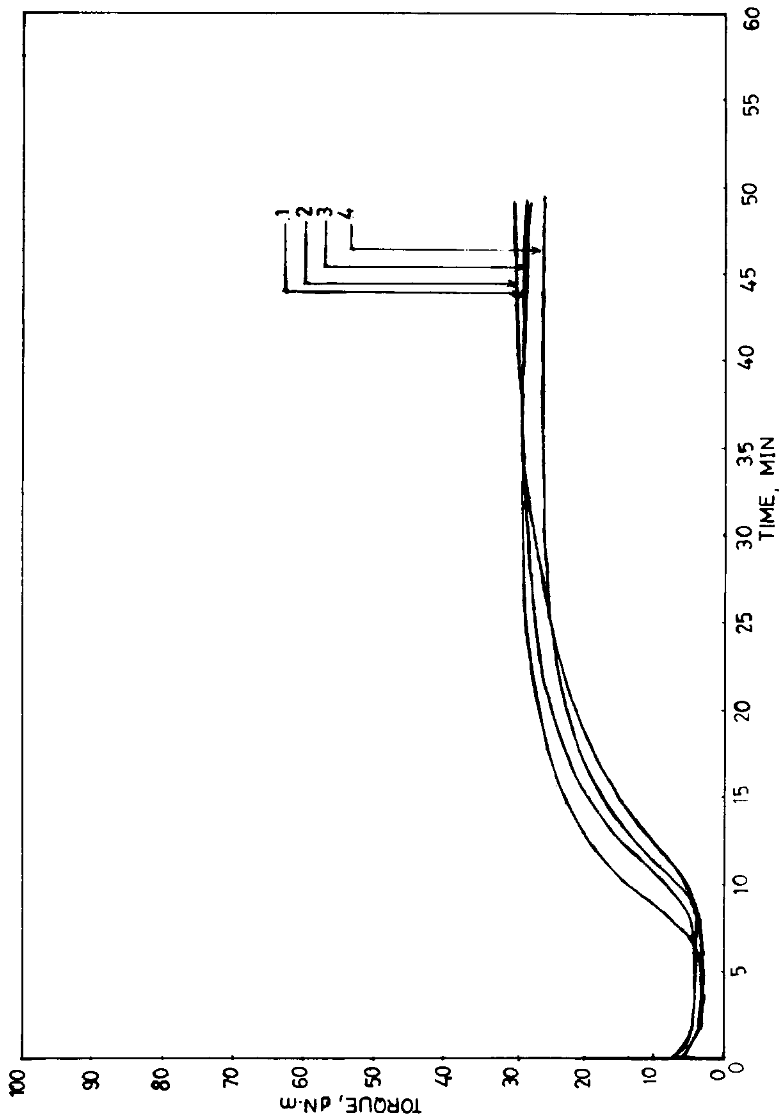

Fig. 2. Rheographs of the mixes with both treated and untreated GPF-black (N660).

TABLE IV
Physical Properties of the Vulcanisates

Mix	300% Modulus, MPa	Elongation at break, %	Tensile strength, MPa	Hardness, shore A	Resilience, %	Tear strength, kN/m	Monsanto fatigue to failure, KCl	Abrasion index, (DIN)	Goodrich heat build-up ΔT (°C) at 50°C
1	11.28	500	21.94	65	38	90.7	76.4	95	75
		(150)	(8.25)	(68)	(32)	(33.3)			
2	14.19	410	20.60	65	39	127.6	89.8	83	55
		(140)	(7.64)	(68)	(32)	(29.1)			
3	13.00	450	21.99	64	38	95.6	62.7	85	80
		(130)	(7.00)	(71)	(30)	(21.7)			
4	12.93	480	21.23	65	36	100.7	54.9	88	67
		(120)	(6.65)	(68)	(31)	(17.5)			

Formulations: Same as Table I except filler is 50 phr instead of 45 phr. Mix: 1. Untreated N330 black; Mix: 2. Untreated N330 alongwith 6 phr Inorganic peroxide in place of 5 phr ZnO; Mix: 3. Untreated N339; Mix: 4. Carbon black (N330) treated with 2.5 mL of H_2O_2 and 4 drops of NH_3. Values in parentheses are aging values at 105°C for 72 h.

peroxy radicals which in turn improve properties through the formation of better polymer-filler interaction.

To eliminate the step for pretreatment of black surface, solid zinc peroxide was used instead of hydrogen peroxide and ammonia. High structure black was used for comparison of effects found with treated black. Addition of zinc peroxide improves the 300% modulus and lowers the elongation at break (Fig. 1 and Table IV). The modulus is even higher than high structure black and abrasion resistance and heat build-up are better than high structure black (mix 2 vs. mix 3). A similar effect is observed in the case of GPF-black (Fig. 2 and Table V). The effect of zinc peroxide is better than hydrogen peroxide and ammonia combination (mix 2 vs. mix 4). The main advantage of using zinc peroxide in normal black is that the properties of heat build-up keep other physical properties identical. All samples were treated with methyl iodide and show better polymer-filler attachment.

Improvement of Steel Cord–Rubber Adhesion Using Inorganic Peroxide

Adhesion between steel cord and rubber is dependent on brass-coating composition and also the compounding of rubber. Different authors[7,8] have reported a number of works to improve the steel cord–rubber adhesion. Here we have used the phenomenon of inorganic peroxide in carbon

TABLE V
Physical Properties of Vulcanisates

Mix	300% Modulus, MPa	Elongation at break, %	Tensile strength, MPa	Hardness shore A	Resilience, %	Tear strength, kN/m	Abrasion Index (DIN)	Monsanto fatigue to failure, KCl	Goodrich heat build-up ΔT (°C) at 50°C
1	10.07	450	20.42	63	44	62.51	137	35.7	72
		(155)	(7.67)	(63)	(38)	(37.65)			
2	12.98	410	23.52	65	48	64.61	122	46.5	50
		(158)	(7.37)	(65)	(37)	(37.65)			
3	11.97	470	20.26	63	46	72.67	118	43.8	80
		(158)	(8.42)	(67)	(35)	(37.82)			
4	11.38	480	19.92	61	47	66.88	130	57.2	67
		(160)	(7.94)	(64)	(34)	(23.11)			

Formulations: Same as Table IV except N660 is used instead of N330.

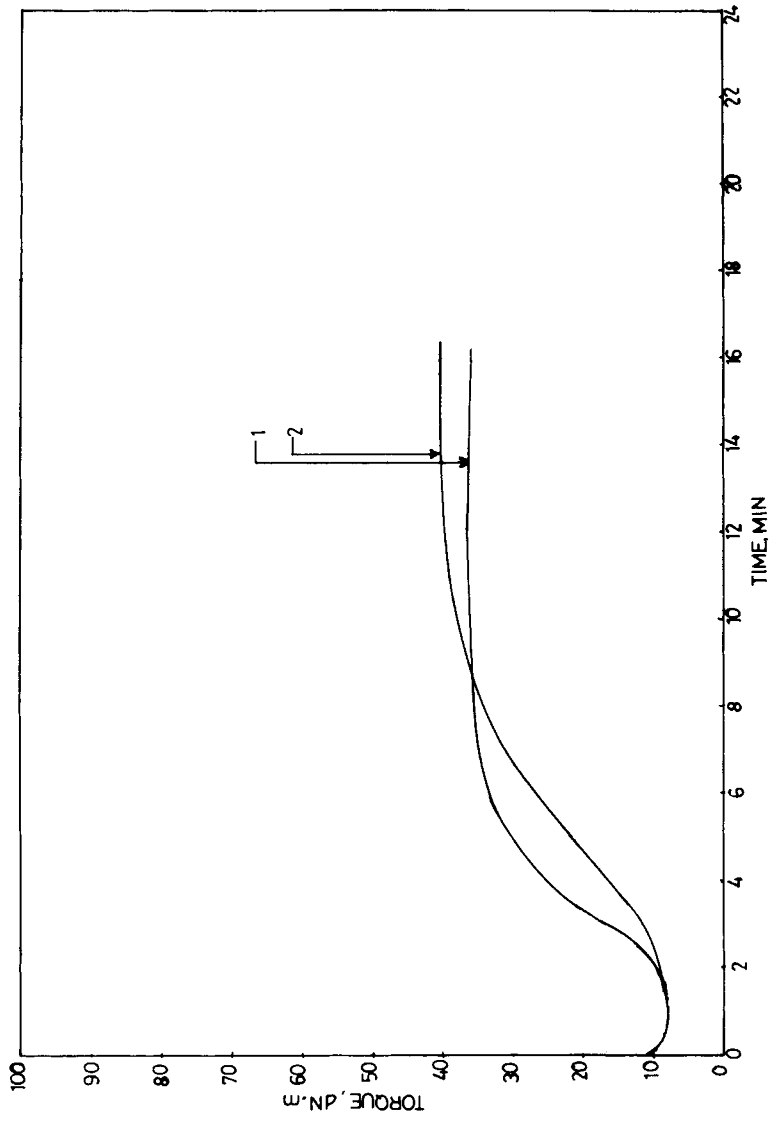

Fig. 3. Rheographs of highly loaded black without and with inorganic peroxide.

TABLE VI
Adhesion Values of Both Normal and Aged Condition

Sample no.	Properties	Cured at 180°C, min 4	6 (Normal)	9	Aged at 105°C, days 3	5
1	Hardness, Shore A	72	75	76	85	90
	Adhesion, kg	73.5	74.8	73.9	83.9	72.6
2	Hardness, Shore A	68	73	74	85	90
	Adhesion, kg	111.1	110.2	81.6	119.3	91.6

Formulations: Mix 1. SBR 1502 100; zinc oxide 3; stearic acid 1; PF resin 8; HAF (N326) black 57; FEF black (N660) 57, aromatic oil 22; antioxidant 2; *N*-oxy diethylene benzothiazole 2-sulfenamide 1; sulfur 3.0. Mix 2. Contains additional 5 g of zinc peroxide in 250 g of mix 1.

black compounding and studied the effect of bonding between steel cord used in tire bead and rubber. Figure 3 shows the curing characteristics of highly black-loaded rubber compounds. Table VI shows the effect of 5 parts of zinc peroxide in highly black-loaded compound. The presence of inorganic peroxide improves the bond strength to a considerable extent in both aged and unaged conditions.

CONCLUSION

Hydrogen peroxide–ammonia system activates the peroxy radical formation, and this improves the polymer-filler interaction under mixing condition. This effect is minimized with conditioning time after black treatment. Zinc peroxide shows better effect than hydrogen peroxide–ammonia system. The similar effect is observed in both HAF (N330) and GPF (N660). Use of zinc peroxide in normal black gives better effect on properties than does high structure black. Addition of inorganic peroxide also improves the adhesion between steel cord and rubber compound. Further work is needed in this field.

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