Optimisation and evaluation of 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) and Alkyl Derivative of P-Phenylene Diamine (6PPD) and characterisation of Rubber Valcanisates

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Abstract

Natural and synthetic rubbers are widely used for various applications because of their unusual properties such as high elasticity, extensibility, resiliency. Natural rubber and synthetic rubbers have an unsaturation in their repeating unit of polymer chain. Due to this they get degraded by influence of heat, light, oxygen, ozone, fatigue, metal ions poisons and flexing. Antioxidants are mainly amine derivatives such as 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) and they function by reacting with oxides or broken polymer chain ends caused by reaction with oxygen. They therefore prevent the propagation of oxidative degradation, enabling the retention of the physical properties of the elastomer. Used polymers are generally disposed to the environments or in some case are being recycled. Therefore, optimization of additives is required for the performance of the characteristic properties of the rubber and to control the release of various additives to the environment.

The present work is focused on studying the effect of concentration of 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) with alkyl derivative of p-Phenylene diamine on the physical and mechanical properties of natural rubber like tensile strength, fatigue to failure and ozone resistant capacity. Concentration of TMQ was varied from 0 to 2.5 phr to study the optimization rubber characteristic.

Keywords: TMQ, 6PPD, Antioxidant, Ozone resistant, Natural rubber, Environment.

Introduction

Natural rubber and synthetic rubber are used for manufacturing most types of rubber products, but natural rubber represents the basic constituent of some rubber products, therefore the rubber materials are being used in many fields. The vulcanization system requires accelerators to increase both the rate of cross-linking and the density of cross-links[1-3]. Anti-degradants are being added to prevent the rubber from degradation by oxygen, ozone and heat. However, a wide range of different chemicals are also used as protective agents and processing aids[4-6].

Polymers will change over time when exposed to radiation, excessive heat and/or corrosive environments. These changes are the result of oxidative degradation caused by free radicals which form through hydrogen abstraction or hemolytic scission of carbon-carbon bonds. During polymerization, processing or service of the rubber product, the formation of free radicals ($R^{\cdot}$) is the first stage of polymer degradation and is called as the initiation of the degradation process. Propagation is the second stage of degradation when atmospheric oxygen reacts with the free radicals ($R^{\cdot}$) to form peroxy ($ROO^{\cdot}$) radicals. Labile hydrogen atom of the polymer reacts with peroxy radical to form unstable hydroperoxides (ROOH). Homolytic cleavage of hydroperoxides forms alkoxy and hydroxyl radicals and they further propagate the degradation mechanism[7].

Degradative reaction is interrupted by the addition of an antioxidant (AH). At the initiation stage, antioxidants inhibit the formation of free radicals ($R^{\cdot}$) and interrupt the propagation cycle by reacting with ($R^{\cdot}$) and ($ROO^{\cdot}$) radicals and thus introduce new termination reactions.

These changes can have a dramatic effect on the service life and properties of the polymer. To prevent or slow down degradation, antioxidants are often added. Antioxidants and antiozonants are used to protect the polymers from degradation. Antioxidants are highly effective ingredients and have a dramatic impact on the service life of the rubber product.

Dihydroquinolines differ in the degree of polymerization, thus influencing migratory and long-term durability properties[8-10]. They are good general antioxidants and are effective against heavy metal pro-oxidants such as nickel and copper ions oxidation. The polymeric nature of dihydroquinolines results in low volatility and migratory properties in a vulcanizate[11-14].

The aim of this study is to characterize and measure the effect of variation in dosage levels of 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) with alkyl derivative of p-Phenylene diamine (6-PPD) antiozonant on the viscosity, Mooney scorch property, cure properties, hardness, tensile strength, elongation at break, tear strength, modulus at different strain amplitudes and cyclic fatigue life of various cured compounds, ozone degradation resistance property etc.[15-20]

Material and Methods

Rubber compounding formulations for tyre tread compound of various technical grade ingredients as per table 1 are prepared with variations in 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) concentration from 0 to 2.5 phr. with constant N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine (6PPD) content. Eight number of samples were prepared as tabulated in table 2. These samples were mixed in Banbury mixer and two roll mixing mills.

a) Tyre tread compound formulations: The aim was to evaluate the effect of 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) with alkyl derivative of p-phenylene diamine (6-PPD) antioxidant in tread compound by changing the antioxidant contents. A formulation used to manufacture tyre treads by milling process was selected as a suitable formulation in this study with variation of TMQ content.

b) Compound Processing and Sample Preparation: Laboratory scale Banbury mixer (1st stage) and two roll mill mixers (2nd stage) were used for the compounding stage. Banbury mixer Farrel Bridge Limited, Rochdale, England was used for compound mixing, Method used was ASTM D-3182. Rotor speeds were maintained at 77 rpm constant during the experiments. Compound ingredients except sulfur and pilcure CBS given in table 2 were mixed and sequence of addition in Banbury mixture is as per table 3 at mixing cycle 1st stage.

Table 1
Formulation of Tyre tread compound

S.N.	Ingredients	phr level	Function	Source used
1	Natural Rubber	100	Polymer	Harrisons Malayalam Ltd.
2	Zinc Oxide	4	Activator for accelerator	Navbharat Ind Ltd
3	Steric Acid	2	Activator for ZnO	Godrej Ind. Ltd.
4	N 330, HAF black	50	Reinforcing Filler	Philips Carbon
5	Naphthenic Oil- E-540	5	Process aid	Hindustan Petroleum
6	M C WAX	1.5		Raj Petro
7	TMQ	As per Table No. 2	Anti-oxidant	NOCIL LTD
8	6PPD	As per Table No. 2	Anti-degradant	NOCIL LTD
9	Pilcure CBS	0.7	Accelerator	NOCIL LTD
10	Sulphur	2.3	Cross linking agent	Oriental Carbon & Chem.
	Total	**165.5**		

Table 2
Tyre tread formulations with variation of TMQ for determination physical and mechanical properties

S. N.	Compounds	1	2	3	4	5	6	7	8
	Ingredient	**PHR**							
1	Natural Rubber-RMA-4	100	100	100	100	100	100	100	100
2	Zinc Oxide	4	4	4	4	4	4	4	4
3	Steric Acid	2	2	2	2	2	2	2	2
4	N 330 black	50	50	50	50	50	50	50	50
5	Naphthenic Oil- E-540	5	5	5	5	5	5	5	5
6	M C WAX	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
7	TMQ	------	1.0	-----	0.5	1	1.5	2.0	2.5
8	6PPD	------	.-------	1	1	1	1	1	1
9	Pilcure CBS	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
10	Sulphur	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
	Total	**165.5**	**166.5**	**166.5**	**167**	**167.5**	**168**	**168.5**	**169**

Table 3
Tyre tread formulations with variation of TMQ for determination physical and mechanical properties

S.N.	Ingredient	Time	Temperature (°C)
1	NR Polymer	Zero min	75
2	Zn O	1/2 min	75
3	Half Carbon + TDQ+ 6 PPD	1.0 min	90
4	Half Carbon + STEARIC ACID + OIL	3.5 min	120
5	SWEEP	4.0 min	135
6	Dump	4.5 min	150

Mixing in Two roll mills: Two roll mill mixers of Modern make were used for mixing cycle at 2nd stage, the set temperature of the two roles was 70 ± 5°C. Sulfur and pilcure CBS were added in 2nd stage mixing.

Experimental

Characterization and performance of physical properties of vulcanized rubber:

Moony viscometer: Mooney viscosity is measured on Mooney viscometer, equipment make: Monsanto USA, method used was ASTM D-1646. Test temperature was 100^0C on both platens, rotor dimension was 1.5 inch and 0.218-inch thickness, rotation of rotor was 2 RPM and pre-heat time was 60 seconds, Myler film was on top and bottom. Test specimen was at room temperature for at least 30 minutes. The temperature of both dies was set at to 100 °C and stabilizes within 0.5 °C. 25 ± 3 gm was weight of specimen, the platens were opened, the rotor was removed and the compound was fed by inserting its stem through the center of one piece. and keeping the rotor in its position, the second specimen was placed above the rotor and the platen was closed. The cellophane paper was used below and above the test specimen. The test was run and the reading were recorded.

Mooney Scorch time: Mooney scorch time was measured by equipment Mooney viscometer, Make and Model: Mooney Viscometer (Monsanto); Method used was ASTM D-1646. Test temperature: 121 °C on both platens, Rotor dimensions: Large 1.500 ± 0.001inch diameter of rotor and 0.218 ± 0.001inch thickness. Rotation of rotor: 2 RPM Pre-heat time: 60 seconds, Type of film used: Myler film on both sides (top and bottom). Size of test specimen: Two specimens each of 10 mm thick and 45 mm diameter were used and combined volume was 25 ± 3 cm^3. Test specimen was at room temperature for at least 30 minutes.

The temperature of both dies was set at 121 °C and stabilizes within 0.5°C. 25 ± 3 gm specimen was weighed, the platens were opened, the rotor was removed and the compound was fed by inserting its stem through the center of one piece and keeping the rotor in its position. The second specimen was placed above the rotor and the platen was closed. Cellophane paper was used below and above test specimen. The test was run and the readings were recorded.

Cure Characteristic: Cure time was measured by equipment Rheometer R-100 ODR (Oscillating Disc Rheometer), Make and Model: Monsanto Rheometer ODR (Oscillating Disc Rheometer)-R-100) Reference Standard: ASTM D-2084 Temperature of dies: 150 °C ± 0.5 Chart time: 30 min Torque 100 dN-m Amplitude of oscillation: 3^0 Frequency of oscillation: 100 cycles per min. The temperature was set at 150^0C and stabilized. 10 gm of compound was weighed (equivalent to 9 cc volume, circular test specimen of diameter 30 mm and thickness of 11.5 mm). The platen of equipment was opened and the compound was fed to rotor. Cellophane paper was placed on the rotor and close the platen. When the run was complete, the various parameters were noted.

Tensile strength: Tensile strength is the force per unit area (of the original cross-sectional area), which is applied at the time of the rupture of a specimen. Tensile strength was measured of unaged samples and after aging of sample at 100^0C for 48hrs, 85^0 at 96 hrs. 85^0 at 168 hrs. Tensile strength property was measured for tensile strength, elongation at break and modulus at % elongation. Test specimen used were of Dumbbell shaped and straight specimen, rate of grip specimen 500mm/minute, Dumbbell die type ASTM D-412 Die C was having width of specimen 6 mm. Also measure Angel Tear strain using ASTM D-624 and Durometer hardness of specimen using method ASTM D-2240

Fatigue to Failure test: The process in which growth of cracks occurs under repeated deformation is known as fatigue. It can lead to catastrophic failure. Standard Ref. ASTM-D-4482, Fatigue life (sample): The mean value of the number of cycles required to cause failure for several specimens of the sample. Make and Model: Fatigue to failure tester (Monsanto), Test sheet cured at 150°C for 9.0 min. Cam No:8, Extension Ratio: 1.8, Strain Produced :80% Extension Ensure the proper cam is installed that will give the desired extension ratio, adjust the distance between the flat, inner surface of grips to 60 mm, using a gauge length. Manually set the cam position to the minimum crosshead separation. Mount test specimens 6 dumbbells each of a rubber.

Start the fatigue tester at 1000 cycles, stop the tester and manually adjust the drive mechanism to produce minimum crosshead separation. At this stage, using grip adjustment, increase the distance between the grips until the specimen is under tension, then relieves the tension until a slight bow is just perceptible in the specimen. The specimen is thus adjusted for permanent set. Restart the tester, readjust the permanent set at 10,000 additional cycles and then every 24 hrs. thereafter.

Ozone resistant property: Study of effect of exposure of specimen under surface tensile strain conditions in either dynamic or static in an atmosphere containing specified levels of ozone concentration. Make and Model: Ozone resistance test equipment from OREC, USA. Ozone Resistance of Rubber Samples is tested using ASTM 1149 test method. Ozone generating source UV tube (for low concentration) or silent arc discharge (for high concentration) is located outside the ozone chamber. Ozone chamber generates ozone at constant concentration which is circulated and the samples are exposed to the atmosphere. The temperature of the chamber is maintained at the desired level as per the test method by means of a regulator.

Ozone concentration is measured using the electronic devices where ozonized air from the chamber is subjected to detection of its concentration and controlled to the desired setpoint by controlling voltage applied to the ozone generating source. Study of effect of exposure of specimen under surface tensile strain conditions, in either dynamic or static, in an atmosphere containing specified levels of ozone concentration.

Results and Discussion

Mooney viscosity: Mooney viscosity with variation of TMQ is given in table 4. Initially, an increase in viscosity is believed to be caused by a reduction in the degree of chemical mastication during mixing. This could also have happened as a result of efficient antioxidant synergistic effect. In general, efficient antioxidant makes its influence to stabilize rubber molecules during high shear mixing, resulting in relatively high molecular weight with a high Mooney viscosity.

Mooney Scorch time: With the increase of TMQ, there is no significant change in scorch time (Ts5), the marginal increase in scorch time compared to blank is desirable. Scorch time is given in table 5. Scorch is premature vulcanization in which the rubber becomes partly vulcanized before the product is in its final form and ready for vulcanization. This reduces the plastic properties of the compound; therefore, further processing of the compound is restricted. All the compounds with anti-degradant did not show any adverse impact on either ML or Ts5. Therefore, it was evident that anti-degradant loading has no adverse impact on premature crosslinking.

Cure Characteristic: The effect of cure time is tabulated in table 6. During the curing process, crosslinks are formed. It is found that Tc90, the optimum cure time, is not affected by antioxidant loadings. MH, the maximum torque an indication of the crosslinking density of the compound and it did not show a significant variation with type of loading of the antioxidant. With the increase of TMQ, there is a marginal increase in scorch time Ts1 compared with blank. With increase of TMQ, there is a marginal increase in scorch time Tc10 compared with blank. With increase of TMQ, there is a decrease in cure time Tc90 compared with blank. With increase of TMQ, there is a decrease in torque value (MH-ML) compared with blank. Increase in scorch time, decrease in cure time and decrease in torque value are the sound parameters for compounded rubber.

Tensile strength: Effect of variation of TMQ content on unaged tensile strength is shown in table 7. Tensile strength, elongation at break, hardness and tear strength before and after aging were measured. The results obtained are tabulated.

Table 4
Effect of different loading of TMQ on Mooney viscosity

Test ID	MI	ML	ML 1+4
1	94.52	60.32	60.32
2	96.10	60.46	60.46
3	96.75	58.96	58.96
4	95.38	57.63	57.63
5	95.45	57.66	57.66
6	96.12	58.70	58.70
7	96.42	57.94	57.94
8	96.20	54.66	54.66

There is an increase in viscosity (ML1+4) with the introduction of TMQ, compared to blank. Viscosity is marginal higher in all compounds containing antioxidant TMQ, compared to blank.

Table 5
Effect of different loading of TMQ on Mooney scorch

Test ID	MI	ML	Ts5	Ts35	Ts (35)-Ts (5)
1	75.13	50.51	17.79	20.24	2.45
2	74.69	51.46	17.90	20.56	2.65
3	71.09	46.95	18.38	20.88	2.50
4	70.64	48.51	17.73	20.17	2.44
5	68.84	49.47	16.95	19.24	2.29
6	69.53	48.64	17.57	19.95	2.38
7	70.11	49.45	18.10	20.60	2.50
8	67.35	47.34	17.72	20.09	2.37

As shown in figure 1, effect of variation of TMQ loading on physical properties of unaged compounds is as follows: Tear strength was found to be increased by 10 to 15 kg/ cm^2 among compounds from 2 to 8 compared to blank. Elongation at break was found to be increased by 10 to 15 %, among compounds from 2 to 8, compared to blank. 300 % Modulus was found to be decreased by 10 to 16 kg/ cm^2 among compounds from 2 to 8 compared to blank. There is no variation observed in hardness among compounds from 2 to 8 compared to blank.

Effect of variation of TMQ content on after aging @85/96 hrs is shown in table 8. Elongation at break, hardness and tear strength before and after aging were measured. The results obtained are tabulated.

As shown in figure 2, the effect of variation of TMQ loading on physical properties after hot air aging @ 85°C/96 hrs is as follows: There is an increase in % retention of tensile strength 2-fold times, among compounds 2 to 8, compared to blank. Retention of tensile strength value is 96 % against blank value of 55%. There is an increase in % retention of elongation at break 1.5-fold times, among compounds 2 to 8, compared to blank.

Elongation at break value after aging is 88 %, against blank value of 62 %. 300 % Modulus was found in the range 209 kg/ cm^2 to 190 kg/ cm^2, among compounds from 2 to 8, compared to blank. Here, blank does not have a 300 % modulus value. It indicates poor flexibility of blank compared to compounds (2-8) with anti-degradants.

Effect of variation of TMQ content on after aging @85/168 hrs is shown in table 9, Elongation at break, hardness and tear strength before and after aging were measured. The results obtained are tabulated.

Table 6
Effect of different loading of TMQ on Cure characteristic

Test ID	ML	MH	MH-ML	Ts1	Ts2	Tc10	Tc50	Tc80	Tc90	Tc100	CRI (90/2)
1	14.33	75.98	61.65	3.61	4.01	4.67	5.76	8.14	10.09	16.59	15.11
2	14.86	75.21	60.35	3.64	4.04	4.67	5.68	7.95	9.84	17.01	15.64
3	13.34	73.20	59.86	3.58	4.02	4.68	5.72	7.76	9.45	16.59	16.87
4	13.96	72.68	58.73	3.59	4.00	4.62	5.63	7.71	9.43	16.38	16.82
5	14.22	73.97	59.57	3.48	3.85	4.47	5.46	7.67	9.44	17.72	16.34
6	14.19	71.66	57.46	3.54	3.93	4.52	5.47	7.49	9.12	16.18	17.62
7	14.71	69.85	55.15	3.78	4.19	4.77	5.71	7.59	9.13	16.89	18.28
8	13.70	70.16	56.46	3.59	3.98	4.57	5.55	7.57	9.25	16.70	17.26

Table 7
Effect of different loading of TMQ on Tensile strength property (Before aging).

Unaged Tensile Property (Before any aging).								
Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
100 % Modulus (Kg / cm^2)	39.5	35.30	36.5	35.6	35.8	32.7	33.1	34.5
200 % Modulus (Kg / cm^2)	101.8	89.2	92.2	90.8	91.15	85	85.0	87.6
300 % Modulus (Kg / cm^2)	185.5	167.8	171.2	169	168.9	159.3	159.3	161.7
Tensile Strength (Kg / cm^2)	266.3	270.5	285.4	285	275.7	269.6	268.3	267.6
Elongation at Break, %.	394	421	439.4	444	433	438.1	437.9	428.4
Tear St., Kg/cm	46	52	57	55	57	59	55	60
Hardness, SH A	68	68	68	68	68	66	67	68

Table 8
Effect of different loading of TMQ on Tensile strength property (After aging @ 85 / 96 hrs)

Compound	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
100 % Modulus (Kg / cm^2)	43.2	48.3	48.9	48.7	47.9	44.13	45.9	44.2
200 % Modulus (Kg / cm^2)	113.2	123.6	124.4	123.6	122.4	112.7	117.6	110.9
300 % Modulus (Kg / cm^2)	---	209.6	209	208.3	207.3	192.6	199.5	189.1
Tensile Strength (Kg / cm^2)	148.5	235.0	245	255.6	258.8	253.6	256.9	248.2
Elongation at Break, %.	247	334	347	362	368	382	377	380
SH °A, Hardness.	70	72	71	72	71	69	70	72
% Retention in TS	55.76	86.89	85.73	89.69	93.88	94.05	95.73	92.75
% Ret. in Elongation at Break	62.60	79.24	79.08	81.65	84.83	87.12	86.02	88.73

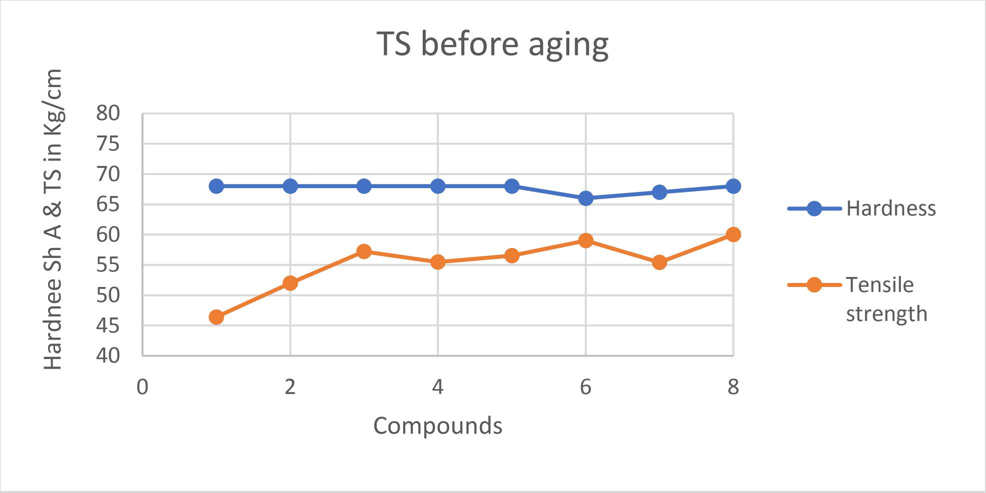

Figure 1: Effect of variation TMQ loading on hardness and tensile strength

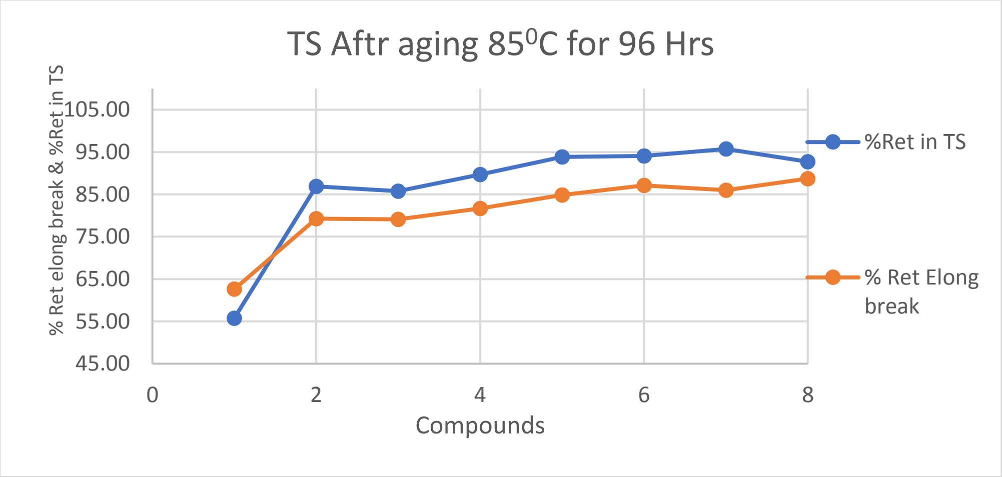

Figure 2: Effect of variation TMQ loading on tensile strength and elongation break at 85 °C for 96 Hrs.

Table 9
Effect of different loading of TMQ on Tensile strength property (After aging @ 85 / 168 hrs).

Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
100 % Modulus (Kg / cm^2)	42.8	53.9	57.2	56.9	55.0	49.7	50.1	53.1
200 % Modulus (Kg / cm^2)	------	136	139.7	140.1	136	122.8	124.9	129.8
300 % Modulus (Kg / cm^2)	-------	------	-----	-----	---	202.6	204.4	207
Tensile Strength (Kg / cm^2)	72.8	198.2	207.7	206	212.3	226.2	225.4	229.1
Elongation at Break, %.	154	271	281.2	281	286	332.4	331.2	335
SH °A, Hardness.	65	71	73	71	72	72	70	71
% Retention in TS	27.34	73.30	72.79	72.29	77.02	83.92	83.99	85.63
% Ret. in Elongation at Break	39.14	64.33	63.99	63.42	65.98	75.85	75.63	77.00

As shown in figure 3, the effect of variation of TMQ loading on physical properties after hot air aging at 85°C/168 hrs. are given. It is more severe aging than 85^0-96 hrs. There is an increase in % retention of tensile strength (TS) almost 3-fold times higher in compounds 2 to 8 compared with blank. TS value is 80% against blank value of 27 %. It indicates a very powerful aging resistance with anti-degradant.

There is an increase in % retention of elongation at break 1.5 to 2-fold times higher in compounds 2 to 8, compared to blank. % Retention of elongation at break value is 77% against a blank value of 39%. It indicates much better flexibility even after severe aging.

300 % Modulus is found in the range 202 kg/ cm^2 to 170 kg/ cm^2 among compounds from 6 to 8, compared to blank. Here, blank and 2 to 5 compounds does not have a 300 % modulus value. It indicates optimization of antioxidant required in the compound for prolong period. It indicates rubber products with less or without antioxidant showing a severe loss of flexibility of rubber products.

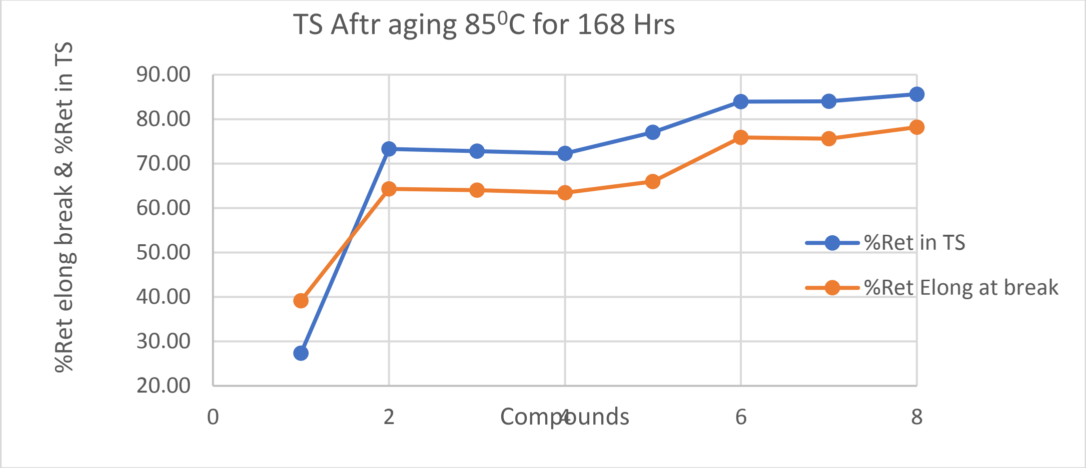

Figure 3: Effect of variation TMQ loading on tensile strength and elongation break at 85°C for 168 Hrs.

Table 10
Effect of different loading of TMQ on Tensile strength property (After aging @ 100 / 48 hrs.)

Compounds	**1 Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
100 % Modulus (Kg / cm^2)	36.82	48.5	52.3	50.5	50.2	46.1	48.3	49.5
200 % Modulus (Kg / cm^2)	-------	121.1	127.9	125.5	124.2	113.4	120.3	121.7
300 % Modulus (Kg / cm^2)	-------	-------	------	102.5	136.6	191.5	131.9	198.6
Tensile Strength (Kg / cm^2)	72.32	182.1	194.6	209.4	208.2	206.2	206.4	209.2
Elongation at Break, %.	169.7	271.2	281.4	302.6	302.5	321.5	310.3	315.1
SH °A, Hardness.	71	72	73	73	73	71	71	73
% Retention in TS	27.15	67.31	68.19	73.47	75.51	76.49	76.90	78.18
% Retention in Elong. at Break	43.10	64.38	64.04	68.23	69.79	73.36	70.87	73.55

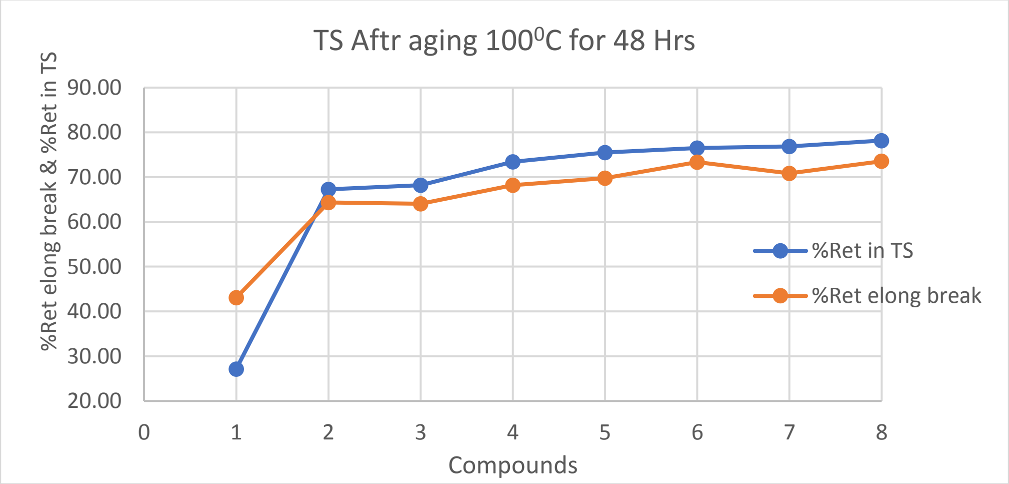

Figure 4: Effect of variation TMQ loading on tensile strength and elongation break at 100 °C for 48 Hrs

Effect of variation of TMQ content on after aging @100/48 hrs is shown in table 10, Elongation at break, hardness and tear strength before and after aging were measured. The results obtained are tabulated.

As shown in figure 4, effect of variation of TMQ loading on physical properties after aging @ 100°C/48 hrs is given. It is severe aging even than 85^0-168 hrs. There is an increase in % retention of tensile strength almost 2 to 2.5-fold times higher in compounds 2 to 7 compared to blank. TS value is 78% against blank value of 27%. It indicates prominent anti-degradant effect. There is an increase in % retention of elongation at break, almost 1.5-2.0-fold times higher in compounds 2 to 7 compared to blank. % retention of elongation at break value is 74 % against a blank value of 43 %. It indicates better flexibility after severe aging. 300 % modulus was found in the range of 102 to 198 kg/ cm^2 among compounds from 4 to 8 compared to blank.

Here, blank and single antioxidant does not have a 300 % modulus value. The combination of antioxidant TMQ and 6PPD protects the compounded rubber from higher heat and prolong period. It indicates without proper combination of antioxidant. There is a significant loss of flexibility in rubber compounds. These observations after aging at various temperatures for specific duration show that the introduction of both TMQ and 6PPD increases retention of physical properties in all compounds and are improved to a great extent.

Fatigue to Failure test: Effect of loading of 6PPD on fatigue to failure test (table 11) was measured for aged and unaged compounds and results obtained are tabulated. Unaged fatigue to failure value is from 144 to 291 kc for compounds having TMQ, compared to blank which has only 71 kc (figure 5). This is almost 3 to 4 times higher.

Aged at 85 / 4 days fatigue to failure value ranges from 87 to 275 kc for compounds having TMQ compared with blank which has only 26 kc. This increase is almost 3 to 10 times. It indicates the combination of TMQ and 6PPD dramatically improves fatigue to failure properties. It is also observed that 6PPD is more effective than TMQ in improvement in fatigue to failure property. This is the key property for automobile tyres.

Ozone resistant property: Effect of variation of TMQ content with constant 6PPD concentration on ozone resistance test (Static mode) is shown in table 12. Study of effect of exposure of specimen under surface tensile strain conditions in either dynamic or static mode in an atmosphere containing specified levels of ozone concentration is made.

As shown in figure 6, the ozone test at 50 pphm is a very severe condition as the atmospheric ozone concentration is much below 10 pphm. Ozone is the most powerful degradation factor for unsaturated rubbers. Hence protection against ozone is very important for rubber particularly tyre compounds. TMQ dosages have synergistic effect and as dosages increases, the ozone resistance slightly improves. At 1.0 pphm TMQ concentration, no ozone cracks were observed even after prolong ozone exposure of 144 hrs. Ozone test at 50 pphm is a very severe condition as the atmospheric ozone concentration is much below 10 pphm.

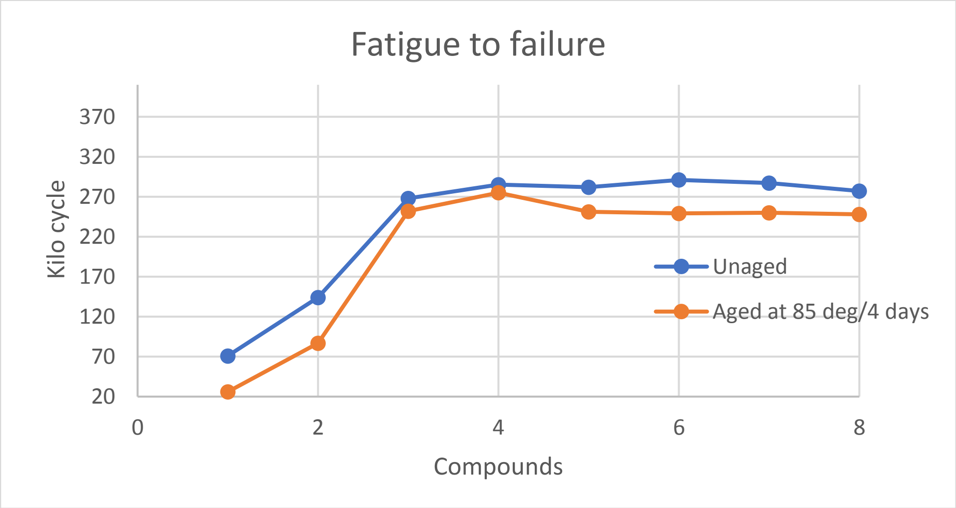

Figure 5: Effect of variation TMQ loading on Fatigue to failure Unaged and Aged

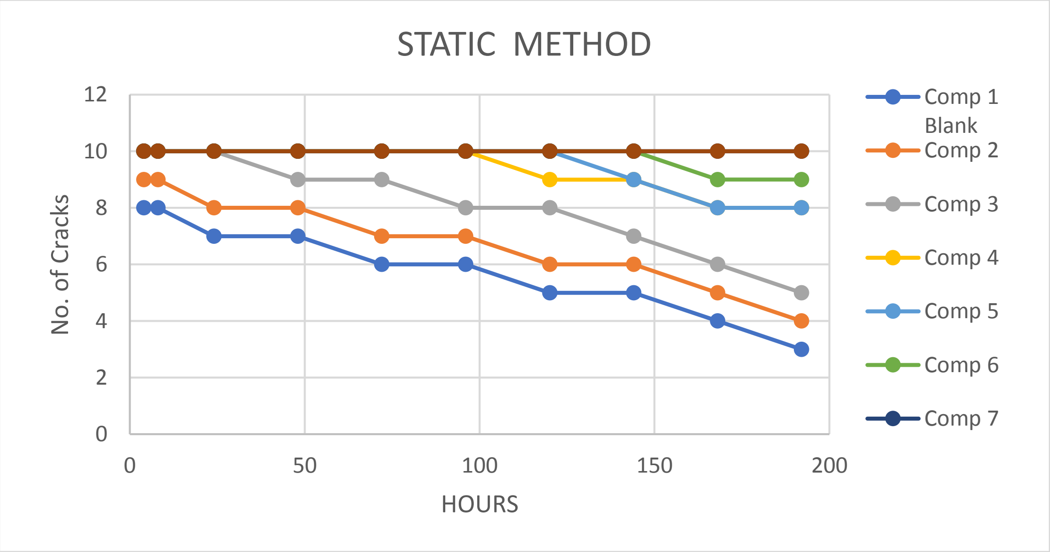

Figure 6: Effect of variation TMQ loading on a static method

Effect of variation of TMQ content on ozone resistance test (Loop mode) is shown in table 13. Study of effect of exposure of specimen under surface tensile strain conditions in either dynamic or static, in an atmosphere containing specified levels of ozone concentration is made.

Effect of variation of TMQ content on Ozone resistance test (10 % dynamic mode) is shown in table 14. Study of effect of exposure of specimen under surface tensile strain conditions in either dynamic or static condition, in an atmosphere containing specified levels of ozone concentration is made.

Table 11
Effect of different loading of TMQ on Fatigue to failure test

Fatigue to failure Properties (Cure Time: T max at 150 deg. C)								
Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Unaged Kilo cycle	71	144	268	285	282	291	287	277
Aged at 85 / 4 days Kilo cycle	26	87	252	275	251	249	250	248

Table 12
Effect of different loading of TMQ on Ozone resistance test (Static method)

Hours/Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
4	8	9	10	10	10	10	10	10
8	8	9	10	10	10	10	10	10
24	7	8	10	10	10	10	10	10
48	7	8	10	10	10	10	10	10
72	6	7	10	10	10	10	10	10
96	6	7	8	10	10	10	10	10
120	5	6	8	9	10	10	10	10
144	5	6	7	9	9	9	9	9
168	4	5	6	8	9	9	9	9
192	3	4	5	8	8	8	9	9

Table 13
Effect of different loading of TMQ on Ozone resistance test (Loop method)

Hours/ Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
4	7	8	10	10	10	10	10	10
8	7	8	10	10	10	10	10	10
24	6	7	10	10	10	10	10	10
48	6	7	10	10	10	10	10	10
72	5	6	9	10	10	10	10	10
96	5	6	8	9	9	10	10	10
120	4	5	8	9	9	9	10	10
144	4	4	7	9	9	9	9	9
168	3	4	6	8	8	8	9	9
192	3	3	6	8	8	8	8	8

Table 14
Effect of different loading of TMQ on Ozone resistance test (10% Dynamic method)

Hours/Compounds	**1-Blank**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
4	6	7	7	8	10	10	10	10
8	6	6	7	8	9	10	10	10
24	5	6	6	8	9	9	10	10
48	5	6	6	7	9	9	9	9
72	5	5	5	7	8	9	9	9
96	4	5	5	6	8	9	9	9
120	4	4	4	6	8	8	8	8
144	4	4	4	5	7	8	8	8
168	3	3	3	5	7	8	8	8
192	2	3	3	4	6	7	7	7

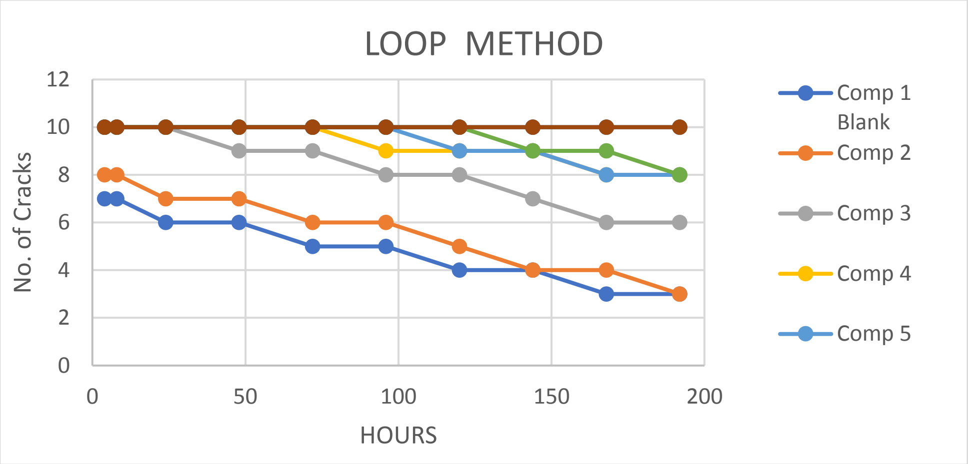

Figure 7: Effect of variation TMQ loading on loop

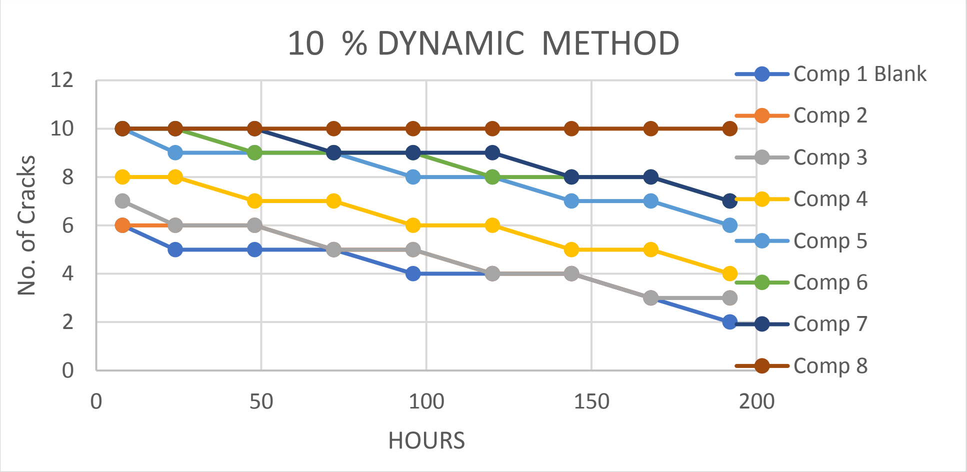

Figure 8: Effect of variation TMQ loading on dynamic mode

Effect of TMQ loading on Ozone resistance capacity: Introduction of TMQ with 6PPD in formulation increases ozone resistance property. In static (Figure 7) and loop (Figure 8) method until 72 and 48hrs respectively, compounds 3 shows no crack whereas compounds 4 and 5 show no crack till 72 hrs and compounds 6,7 and 8 show no crack till 120 hrs. In the dynamic method, this being a very severe test, compounds 6, 7 and 8 show no crack tills 8 to 24 hrs. Blank is showing cracks at 4 hrs in all the above tests. It is observed that 6PPD is more effective in improving ozone resistant capacity of rubber compound.

Conclusion

1. With increased dosages of TMQ with constant 6PPD content an antioxidant, there is marginal increase of Mooney viscosity in all compounds compared with blank. The increase in viscosity is believed to be caused by a reduction in the degree of chemical mastication during mixing. This could also have happened as a result of an efficient antioxidant synergistic effect.

2. With an increase of TMQ with constant 6PPD content, there is no significant change in scorch time (Ts5). All the compounds did not show any significant variation of either ML or Ts5. Therefore, it was evident that the time required for the beginning of the process of crosslinking is not significantly influenced by loading of antioxidants.

With an increase of TMQ with constant 6PPD content, there is an increase in scorch time, a decrease in cure time and decrease in torque value which are the sound parameters for compounded rubber.

3. Tensile strength properties and elongation at break observations after aging at various temperatures for specific duration show that the introduction of TMQ with constant 6PPD content increases retention of physical properties in all compounds which are improved to a great extent.

4. Unaged and aged fatigue to failure properties increased with the introduction of TMQ with constant 6PPD content an antioxidant in the compounds which shows TMQ and 6PPD's anti-cracking property. Fatigue to failure property is important for tyre. Values of fatigue to failure show increasing trend means TMQ and 6PPD protect the rubber compound from cracking with increase in concentration specifically as 6PPD is more effective.

5. With the increase of TMQ with constant 6PPD content, ozone resistant capacity of the compounds also increased in

all three static, loop and dynamic methods. The increasing concentration of 6PPD shows higher ozone resistant capacity. All three methods static, loop and dynamic methods show that TMQ and 6PPD protect the rubber compound from ozone and heat exposure with increase in their concentration, specifically TMQ gives heat protection and 6PPD gives ozone resistant capacity to the rubber.

Considering the above study, it is revealed that a combination of 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) and N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine (6PPD), an anti-degradant is playing a crucial role in improving physical properties along with fatigue to failure and ozone resistance to a great extent. Thus, with the use of anti-degradants, the polymer can be protected during the entire phase of the product's life cycle to a great extent. Based on these observations we can conclude that the 6PPD and TMQ can be used between 1.0 to 1.5 phr. for better performance.

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