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Research Article

OPTIMISATION & EVALUATION OF N-(1,3-DIMETHYLBUTYL)-N′-PHENYL-1,4-PHENYLENEDIAMINE (6-PPD)-AN ANTIDEGRADANT IN TREAD COMPOUND AND CHARACTERISATION OF RUBBER VALCANISATES FOR ITS PERFORMANCE

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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, durability, high abrasion resistance, high strength. The automobile industry is a key consumer, for both tyre and non-tyre sectors and has emerged as the single-largest consumer of vulcanized rubber, in the form of auto tyres, tubes, and other parts and accessories. In some applications different additives are also used along with polymers. Used polymers are generally disposed to environments or in some case it is being recycled. Therefore, the optimization of additives is required for the performance of the characteristic properties of the rubber and to control the release of various additives in the environment. N-(1,3-Dimethylbutyl)-N′-phenyl-1,4-phenylenediamine (6PPD) is widely used as antidegradent due to its property of fast migration to the surface of the polymer. The present work is focused on studying the effect of concentration of N-(1,3-Dimethylbutyl)-N′-phenyl-1,4-phenylenediamine on the physical, mechanical properties like tensile strength, fatigue to failure and ozone resistant capacity. Concentration of 6PPD was varied from 0 to 2.5 phr to study the optimization of rubber characteristics.

Keywords: 6-PPD, Antioxidant, Ozone Resistant, Natural Rubber, Environment.

1. INTRODUCTION

The synthetic rubber is used for manufacturing of rubber products, but natural rubber represents the basic constituent of some rubber products, therefore the natural rubber materials are being used in many fields which includes industrial products such as rubber bands, fuel resistant parts, electrical insulation, drive belts, conveyor belts, floor coverings, elevator belts, rafts, foam rubber, hoses, tubes, paints, and bridge bearings. Natural rubber is used in sports field such as golf balls, bowling balls, football balls, sport goods, and toys balloons. Natural rubber is used in medical field such as catheters, gloves, surgical purposes, medical implants, and medical equipments. Natural rubber is also used in consumer products such as raincoats, sponges, pencil erasers, soap, shoes, and adhesives, transport field such as automotive (truck or bus) tires, bicycle tires, and aircraft tires. Most commonly, tyre [1, 2] consist of both natural rubber and synthetic rubber. Natural rubber [3, 4] has higher gum tensile properties [5] and adhesion strength compared to synthetic rubber, therefore tire products account for more than 50% of natural rubber usage.

There are various types of elastomers that can be cured by sulfur vulcanization process [6] and if desired they can also be cured by non-sulfur vulcanization.

The vulcanization system requires accelerators to increase the rate of cross-linking and the density of cross-links. Antidegradants are being added to prevent the rubber from degradation [7] by e.g. oxygen, ozone, and heat. However, a wide range of different chemicals [8-11], are also been used as protective agents and processing aids.

Natural rubber and Synthetic rubbers have an unsaturation in their repeating unit of the polymer chain, due to this, it gets degraded by the influence of heat, light, oxygen, ozone, fatigue, metal ions poisons, flexing etc. Oxidative degradation is caused by free radicals that form through hydrogen abstraction or hemolytic scission of carbon-carbon bonds. To prevent or slow down degradation, antioxidants are often added.

Paraphenylene Diamine antidegradants (PPDs) [12-14] are used as primary antioxidants and are known as the most powerful class of chemical antiozonants, Antiflexcracking agents [15], and Antioxidants. Antioxidants & Antiozonants are recognized for protecting the polymers from degradation. Antioxidants & antiozonant are used in low concentration, since they are extremely effective ingredients and have a remarkable impact on the service life of the rubber product. Antioxidants of different types and with various combinations are used for protecting the polymer for the entire phase of the product's life cycle.

During polymerization, processing or service of the rubber product, the formation of free radicals ($R^\bullet$) is the first stage of polymer degradation and is called as the initiation of the degradation process [16, 17]. Propagation is the second stage when atmospheric oxygen reacts with the free radicals ($R^\bullet$) to form peroxy ($ROO^\bullet$) 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 further propagates the degradation mechanism.

Degradative reaction is interrupted by the addition of an Antioxidant (AH). At the initiation stage, Antioxidants inhibit the formation of free radicals ($R^\bullet$) and interrupt the propagation cycle by reacting with ($R^\bullet$) and ($ROO^\bullet$) radicals and thus introduces new termination reactions [18].

Three types of PPDs are used in the Rubber Industry, N, N'-dialkyl-p-phenylenediamine, N-alkyl-N'-aryl-p-phenylenediamine and N, N'-diaryl-p-phenylenediamine [19]. Compared to all other PPD's, N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) gives an all-round performance as Antidegradants against all degradative forces [18-21]. It has excellent antioxidant, anti-flex cracking, static & dynamic ozone resistance properties. The presence of the bulky aromatic ring on one side and a branched alkyl chain on the other side exhibits an optimum migration rate, lower losses during processing, storage, & cure and hence presents long-term protection to rubber vulcanizates [20, 21]. It is slightly basic in nature and hence has a good impact on scorch & cure characteristics. It shows high solubility in rubber hence do not show blooming tendencies

In this study, we characterized seven number of compounding formulations with the variation in 6PPD content. We checked these compounds for physical and mechanical properties like Mooney viscosity, Mooney scorch, cure characteristic, hardness, tensile strength, tear strength, elongation at break, Fatigue to failure test and ozone resistant capacity.

The aim of this study was to characterize and measure the effect of variation in dosage levels of N-(1,3-Dimethylbutyl)-N′-phenyl-1,4-phenylenediamine anti - ozonant [22-24] on the viscosity, Mooney scorch property, cure properties, hardness, tensile strength, elongation at break, tear strength, modulus at different strain amplitudes, cyclic fatigue life of various cured compounds and ozone resistance property. This antidegradent will protect the rubber from degradation phenomenon and in turn, will increase life of rubber articles to a great extent. In present work, the effect of variation in dosage of 6PPD, an antioxidant, on the mechanical and physical properties of rubber treads have been studied.

2. MATERIAL & METHODS

2.1. Experimental

Rubber compounding formulation for tyre tread compound of various ingredients were prepared with variation in N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine from 0 to 2.5 phr. Seven numbers of compound formulation samples were prepared using technical grade ingredients as per tabulated in Table 1. These samples were mixed in Banbury mixer and two roll mixing mill.

Table 1: Technical grade ingredients

Ingredients	phr level	Function	Source used
Natural Rubber	100	Polymer	Harrisons Malayalam Ltd.
Zinc Oxide	4	Activator for accelerator	White Seal
Stearic Acid	2	Activator for ZnO	Godrej Ind. Ltd.
N 330, Carbon black	50	Reinforcing Filler	Philips Carbon
Naphthenic Oil-E-540	5	Process aid	Hindustan Petroleum
M C Wax	1.5	Process aid	Raj Petro
TMQ	As shown in Table 2.2	Antioxidant	NOCIL LTD
6-PPD	As shown in Table 2.2	Antidegradant	NOCIL LTD
Pilcure CBS	0.7	Accelerator	NOCIL LTD
Sulphur	2.3	Cross-linking/Vulcanising agent	Oriental Carbon & Chemicals Ltd.
Total	**165.5**		

2.1.1. Tyre tread compound formulations

The aim was to evaluate the effect of N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylenediamine in tread compound by changing its concentrations. A formulation was used to manufacture tyre treads using ingredients with the variation of 6-PPD content as mentioned in Table 2. Compound Processing and Sample Preparation, Laboratory scale Banbury mixer (1st stage) and two roll mill mixer (2nd stage) were used for the compounding stage.

2.1.2. Mixing in Banbury mixer

Banbury mixer, Farrel Bridge Limited, Rochdale, England was used for compound mixing. Method used was ASTM D-3182. Rotor speed was maintained at 77 rpm constant during the experiments. Compound ingredients are given in Table 2 and sequence of addition in Banbury mixture is as per Table 3 at mixing cycle at 1st stage.

Table 2: Tyre tread formulations with variation of 6-PPD for determination physical & mechanical properties

Compounds	P1(Blank)	P2	P3	P4	P5	P6	P7
Ingredients				**Phr**			
Natural Rubber	100	100	100	100	100	100	100
Zinc Oxide	4	4	4	4	4	4	4
Stearic Acid	2	2	2	2	2	2	2
N 330 carbon black	50	50	50	50	50	50	50
Naphthenic Oil- E-540	5	5	5	5	5	5	5
M C Wax	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	-------	1	1	1	1	1	1
6-PPD	-------	-------	0.5	1	1.5	2	2.5
Pilcure CBS	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulfur	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Total	**162.5**	**163.5**	**164**	**164.5**	**165**	**165.5**	**166**

Table 3: Sequence of addition in Banbury mixer: 1st stage

Ingredients	Time	Temperature (°C)
Natural rubber	Zero min	75
Zn Oxide	1/2 min	75
Half Carbon + TMQ+ 6 PPD	1.0 min	90
Half Carbon + Stearic Acid + Oil + Wax	3.5 min	120
Sweep	4.0 min	135
Dump	4.5 min	150

2.1.3. Mixing in Two roll mill

Two roll mill Mixer, Modern make was used for mixing cycle at 2nd stage, and the set temperature of the two roles was 70±5°C. Sulfur and Pilcure CBS were added in masterbatch of Banbury mixer (1st stage) in the two-roll mixer (2nd stage mixing). These compounds were used for the characterization of mechanical and physical properties.

2.2. Equipment and Experimental work

2.2.1. Characterization mechanical and physical properties of vulcanized rubber

Characterization of vulcanized rubber for its properties like Mooney viscosity, Mooney scorch, Rheometric properties was done on various equipment. Physical properties like tensile strain, fatigue to failure test and ozone resistant capacity were also studied.

2.2.2. Mooney viscometer

Equipment makes Monsanto USA, Method of analysis used was ASTM D-1646. Test temperature was 100°C on both platens, Rotor dimension was 1.5 inch and 0.218 inch thickness. Rotation of rotor was 2 RPM and preheat time was 60 seconds, Myler film on top and bottom. For system check, Torque was measured at zero Mooney when rotor turning empty and 100 Mooney when torque was 8.3 Nm on the rotor. The test specimen was at room temperature for at least 30 minutes. The temperature of both dies was set at 100°C and stabilized within 0.5°C. 25±3 gm of the specimen was weighed, the platens were opened, the rotor was removed and the compound was fed by inserting its stem through the centre of one piece. 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 the test specimen. The test was run, and the readings were recorded.

2.2.3. *Mooney Scorch time*

Mooney Scorch time was measured by equipment Mooney viscometer, Make and Model: Mooney Viscometer (Monsanto). The method of analysis was used as ASTM D-1646.

Test temperature was 121ºC on both platens. Rotor dimensions: Large 1.500 ± 0.001inch diameter of rotor and 0.218 ± 0.001inch thickness. Rotation of rotor: 2 RPM, Preheat time: 60 seconds. Type of film used: Myler film on both sides (top and bottom). System check, Torque measurement: Zero Mooney where rotor turning in empty cavity and 100 Mooney when torque is 8.3 Nm on the rotor. Size of test specimen: Two specimens each of 10 mm thick and 45 mm diameter and combined volume 25 ± 3 cm^3. The 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 of the specimen was weighed, the platens were opened, the rotor was removed, and the compound was fed by inserting its stem through the centre of one piece. 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 the test specimen. The test was run, and the readings were recorded.

2.2.4. *Cure Characteristic*

Cure time was measured by equipment Make and Model: Monsanto Rheometer ODR (Oscillating Disc Rheometer R-100) Method of analysis was used as ASTM D-2084. Temperature of dies: 150ºC±0.5 Chart time: 30 min Torque range: 100 dN-m, the Amplitude of oscillation: 3^0, Frequency of oscillation: 100 cycles per min., The temperature was set at 150ºC and stabilized.

10 gm of the compound was weighed (equivalent to 9 cc volume, circular test specimen of diameter 30 mm and thickness of 11.5 mm). The platen was opened, and the compound was fed to the rotor. The cellophane paper was placed on the rotor and the platen was closed.

The run was completed, and the various parameters were noted.

2.2.5. *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.

Equipment Tensiometer Dak System Inc., Test Bench was used. Tensile strength was measured of unaged samples and after aging of the sample at 100ºC for 48hrs, 85ºC at 96 hrs. and 85ºC at 168 hrs. Tensile strength property was measured for Tensile strength, Elongation at break & Modulus at % elongation. Test specimens used were of Dumbbell shaped and straight specimen, rate of grip specimen 500mm/minute, Dumbbell die type ASTM D-412 Die C and width of specimen 6 mm. Angel Tear strain using ASTM D-624 and Durometer hardness of specimen using method ASTM D-2240 was also measured.

2.2.6. *Fatigue to Failure test*

The process in which the growth of cracks occurs under repeated deformation is known as fatigue. It can lead to catastrophic failure.

Make and Model: Fatigue to failure tester (Monsanto), Method of analysis was used as ASTM-D-4482, Fatigue life (sample): The mean value of the number of cycles required to cause failure for a number of specimens of the sample. Test sheet cured at 150ºC 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.

Started the fatigue tester at 1000 cycles, stopped the tester and manually adjusted the drive mechanism to produce minimum crosshead separation. At this stage, using grip adjustment increased the distance between the grips until the specimen was under tension, and then relieved the tension until a slight bow was just perceptible in the specimen. The specimen was thus adjusted for permanent set. Restarted the tester, readjusted the permanent set at 10,000 additional cycles and then, every 24 hrs., thereafter.

2.2.7. *Ozone resistant property*

Make and Model: Ozone resistance test equipment, from OREC, USA. Study of the effect of exposure of specimen under surface tensile strain conditions, in either dynamic or static, in an atmosphere containing specified levels of ozone concentration.

Ozone Resistance of Rubber Samples was 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. The ozone chamber generates ozone at a constant concentration which is circulated, and the samples are exposed to the atmosphere. Temperature of the chamber was maintained at 40°C as per the test method by means of a regulator. Ozone concentration was measured using the electronic device where ozonized air from the chamber was subjected to the detection of its concentration and controlled to the desired setpoint by controlling the voltage applied to the ozone generating source.

Study of the effect of exposure of specimen under surface tensile strain conditions, in either dynamic or static, in an atmosphere containing specified levels of ozone concentration.

3. RESULTS AND DISCUSSION

In this study, we characterized seven number of compounding formulations with the variation in 6PPD content. We checked these compounds for Mooney viscosity, Mooney scorch, Rheometric properties, hardness, Tensile strength, tear strength, elongation at break, Fatigue to failure test, ozone resistant capacity.

3.1. Mooney viscosity

Mooney viscosity with a variation of 6-PPD 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 (Fig.1).

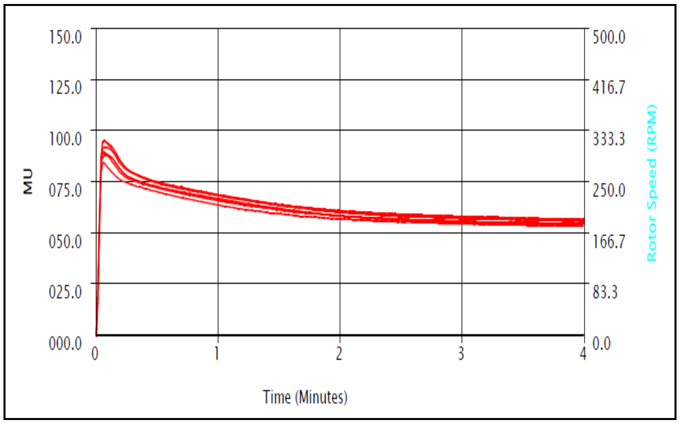

Fig. 1: Mooney viscosity graph

This could also happen as a result of an 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 and result with a high Mooney viscosity.

MI: Initial Viscosity

ML: Minimum Viscosity

ML 1+4: M - Mooney (It is viscosity and its unit are Mooney), L- Size of rotor - Large,

1-1 minute preheat time, 4: At 4-minute viscosity of compound

Increase in viscosity (ML1+4) with the introduction of 6-PPD content in compound P2 to P7 as compared to blank compound P1. Viscosity is marginally higher in all compounds P2 to P7 containing 6-PPD as compared to blank compound P1.

Table 4: Effect on Mooney viscosity

Compounds	Mooney viscosity		
	MI	ML	ML 1+4
P1	84.63	53.90	53.90
P2	88.21	54.63	54.63
P3	95.01	58.12	58.12
P4	91.88	58.43	58.43
P5	95.45	56.42	56.42
P6	89.92	55.68	55.68
P7	89.20	54.61	54.61

3.2. Mooney Scorch time

With the increase of 6-PPD, 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.

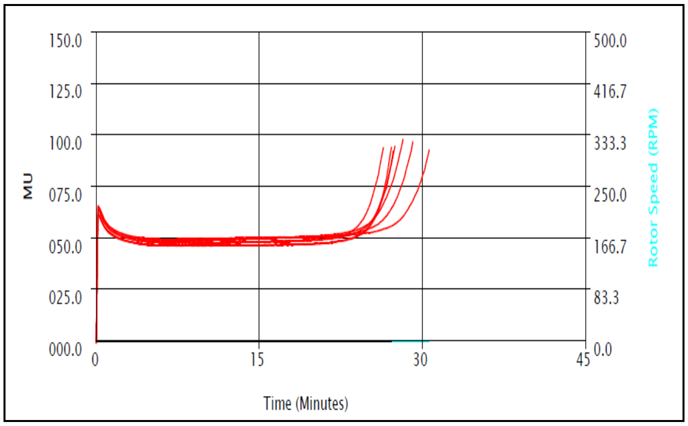

Fig 2: Mooney viscosity graph: Mooney Scorch time

Scorch is premature vulcanization in which the rubber becomes partly vulcanized before the product is in its final form and ready for vulcanization (Fig.2).

This reduces the plastic properties of the compound; therefore, further processing of the compound is restricted. All the compounds with Antidegradants did not show any adverse impact on either ML or Ts5. Therefore, it was evident that Antidegradants loading has no adverse impact on premature crosslinking.

Ts 5 Scorch time - Time required for 5 Mooney rise above minimum viscosity

Ts 35 Scorch time - Time required for 35 Mooney rise above minimum viscosity

Table 5: Effect on Mooney scorch

Compounds	Mooney viscosity		Scorch time		
	MI	ML	Ts5	Ts35	Ts (35)-Ts (5)
P1	62.17	46.33	23.26	26.77	3.51
P2	64.51	48.09	25.62	30.20	4.58
P3	65.67	48.75	24.75	28.54	3.80
P4	65.01	49.30	24.15	27.63	3.49
P5	63.93	47.60	23.27	26.01	2.74
P6	61.69	46.05	24.15	29.97	2,82
P7	61.24	46.40	24.15	26.95	2.80

Table 6: Effect on Cure characteristic

Comps.	Torque dN-m			Scorch time		Cure time				
	ML	MH	MH-ML	Ts1	Ts2	Tc10	Tc50	Tc80	Tc90	Tc100
P1	15.38	86.0	70.6	4.13	4.83	5.98	7.6	10.58	13.00	23.99
P2	16.27	81.6	65.3	4.29	5.18	6.49	8.0	11.12	13.65	25.07
P3	16.51	79.4	62.8	4.24	4.99	6.15	7.6	10.45	12.85	23.28
P4	16.76	79.0	62.2	4.23	4.99	6.11	7.51	10.46	12.88	23.77
P5	16.33	77.8	61.4	4.25	4.85	5.73	6.98	9.67	11.88	20.70
P6	15.90	76.1	60.2	4.39	5.01	5.95	7.24	10.00	12.29	22.13
P7	16.03	74.2	58.2	4.58	5.21	6.07	7.31	9.85	11.94	21.15

3.3. Cure Characteristic

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 (Fig.3).

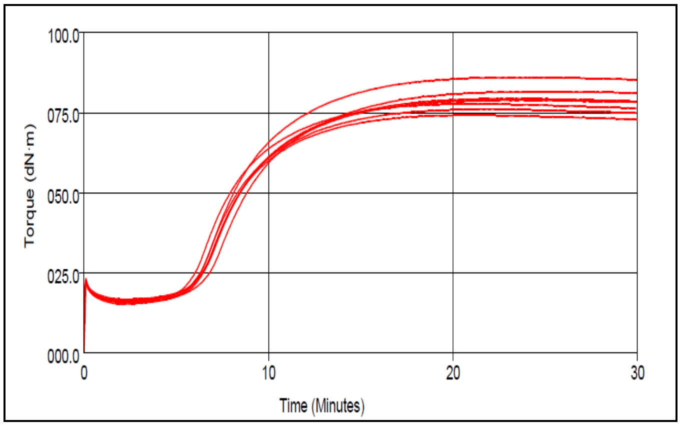

Fig. 3: Oscillating Disc Rheometer graph

MH, the maximum torque, which is an indication of the crosslinking density of the compound and it did not show significant variation with type of loading of the antioxidant. With the increase of 6-PPD, there is a marginal increase in scorch time Ts1 compared with blank. With the increase of 6-PPD, there is a marginal increase in scorch time Tc10 compared with blank. With an increase of 6-PPD, there is a decrease in cure time Tc90 compared with blank. With the increase of 6-PPD, 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.

ML: Minimum torque dN-mMH: Maximum Torque dN-m

Ts 1 is Scorch Time - Time required for 1 dN-m rise above ML, Ts 2 is Scorch Time - Time required for 2 dN-m rises above ML, Tc 90- It is the time at which 90% of cure has taken place

3.4. Tensile strength

The effect of 6-PPD content on tensile strength was studied at different temperatures 85°C to 100°C for the varied aging time of the rubber samples. The properties monitored are Elongation at break, Hardness, and Tear strength before and after aging. 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. Elongation, or strain, is defined as the extension between benchmarks produced by tensile force applied to the specimen and expressed as a percentage of the original distance between the marks. Elongation is the elongation at the moment of rupture. Tensile stress commonly called "Modulus" is the stress in Kg per square cm (of original cross-section) required to produce a certain elongation.

Effect of variation of 6-PPD content on tensile strength property (Before aging) are tabulated and given in table 7.

Table 7: Effect on Tensile strength property (Before aging)

Test	Compounds						
	P1-Blank	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**
100 % Modulus (Kg/cm^2)	29.9	28.2	26.6	27.3	27.8	26.9	27.2
200 % Modulus (Kg/cm^2)	76.7	72	69.9	71.8	72.4	70	69.7
300 % Modulus (Kg/cm^2)	142.9	135.3	130.5	131.8	133.6	129.6	127.2
Tensile Strength (Kg/cm^2)	251.8	265.3	259.7	260.9	268.4	265.8	277.9
Elongation at Break, %.	460	490	500	500	500	510	540
Tear St., Kg/cm	66.2	77	78.1	75.4	76.5	80	79.5
Hardness, SH A	64	62	62	62	61	60	60

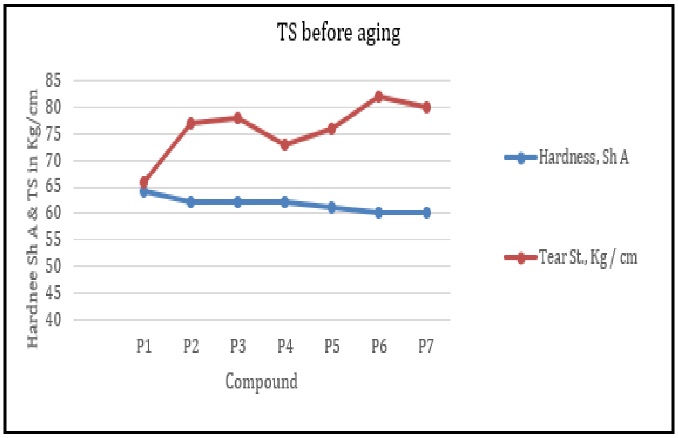

Fig. 4(a): Effect on hardness and tensile strength

As shown in Fig. 4(a), Effect of variation of 6-PPD loading on tensile strength property before aging as below,

It is seen in fig. 4(a), that Tensile strength increases by 10 to 25 kg/cm^2 and Hardness decreases by 2 to 4 SH°A with increasing 6 PPD content in unaged rubber samples P2 to P7 as compared to blank. This is further endorsed by the increase in Elongation at break or strain by 20 % and decrease in 300 % Modulus by 3 to 16 kg/cm^2.

Effect of variation of 6-PPD content on tensile strength property after aging at 85°C/96 hrs are tabulated and given in table 8.

Table 8: Effect on Tensile strength property after aging at 85°C/96 hrs

Tests	Compounds						
	P1-Blank	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**
100 % Modulus (Kg/cm^2)	33.87	40.32	40.44	41.35	41.27	41.95	40.52
200 % Modulus (Kg/cm^2)	87.23	103.93	103.75	105.94	105.4	104.42	103.19
300 % Modulus (Kg/cm^2)	-------	181.75	179.82	181.07	179.97	177.14	173.56
Tensile Strength (Kg/cm^2)	123.11	226.49	233.48	232.38	242.15	252.6	240.72
Elongation at Break, %.	260	360	380	380	420	410	410
SH °A, Hardness.	62	65	65	65	65	65	64
% Retention in TS	49.00	85.00	90.00	89.00	90.00	95.00	87.00
% Retention in elongation at break	57.00	73.00	76.00	76.00	84.00	80.00	76.00

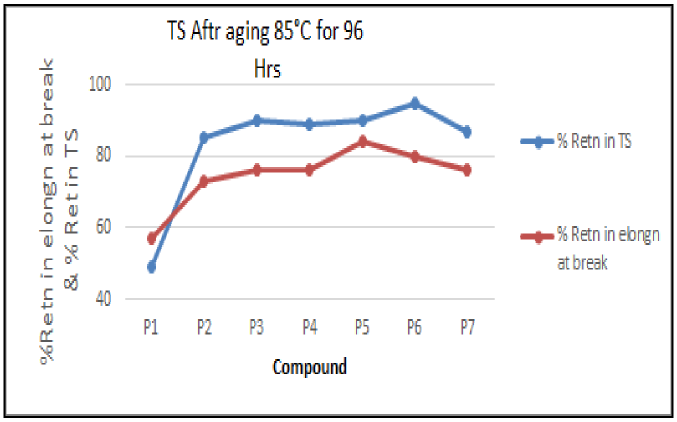

Fig. 4(b): Effect on tensile strength & elongation break at 85 °C for 96Hrs

As shown in Fig. 4(b), Effect of variation of 6-PPD loading on tensile strength property after aging at 85°C/96 hrs is as below,

In the hot air aging at 85°C/96 hrs samples, in the unaged samples, % Retention of tensile strength was found to increase by 95% as compared to blank 45% and % Retention of elongation at break value 84% as compared to blank 57%. This is further endorsed by the 300% modulus was found to be in the range of 173 kg/cm^2 to 181 kg/cm^2 as compared to blank doesn't have 300 % modulus value. It indicates a blank sample without antidegradants has no flexibility property at 300% modulus.

Table 9: Effect on Tensile strength property after aging at 85°C/168 hrs

Tests	Compounds						
	P1-Blank	P2	P3	P4	P5	P6	P7
100 % Modulus (Kg/cm^2)	31.27	42.79	43.44	42.52	41.38	41.21	40.1
200 % Modulus (Kg/cm^2)	80.59	107.52	109.43	107.79	104.68	103.95	100.63
300 % Modulus(Kg/m^2)	-------	183.93	184.49	181.92	176.68	177.41	170.09
Tensile Strength (Kg/cm^2)	88.47	211.39	216.18	209.11	209.81	203.41	208.79
Elongation at break, %.	210	340	350	340	350	340	360
SH °A, Hardness.	62	65	66	66	66	66	66
% Retention in TS	35.00	80.00	83.00	80.00	78.00	77.00	75.00
% Retention in elongation at break	46.00	69.00	70.00	68.00	70.00	67.00	67.00

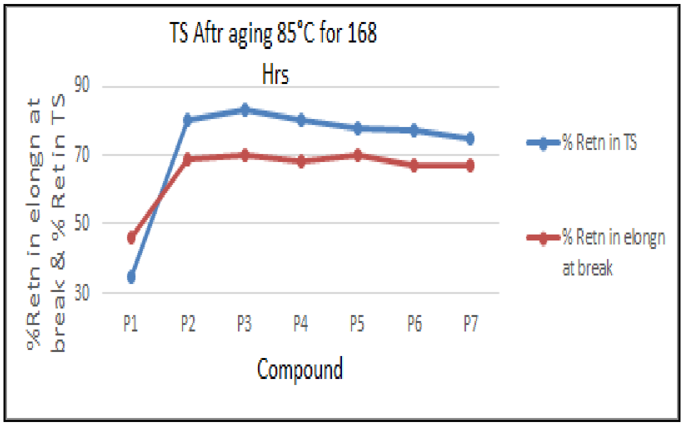

Fig. 4 (c): Effect on tensile strength & elongation break at 85°C/168 hrs

Effect of variation of 6-PPD content on tensile strength property after aging at 85°C/168 hrs are tabulated and given in table 9.

As shown in Fig. 4(c), Effect of variation of 6-PPD loading on tensile strength property after aging at 85°C/168 hrs. is as below,

Hot air aging at 85°C/168 hrs is more severe aging condition than 85°C/96 hrs. In this aging condition, % Retention of tensile strength was found to increase by 85% as compared to blank 35% and % Retention of elongation at break value 70 % as compared to blank 46% with increasing 6 PPD content in rubber samples. This is further endorsed by the 300% modulus was found to be in the range of 170 kg/ cm^2 to 184 kg/ cm^2 as compared to blank doesn't have 300 % modulus value. It indicates a very powerful aging resistance and better flexibility even after severe aging in presence of antidegradant.

Effect of variation of 6-PPD content on tensile strength property after aging at 100°C/48 hrs are tabulated and given in table 10.

As shown in Fig.4(d), Effect of variation of 6-PPD loading on tensile strength property after aging at 100°C/48 hrs is as below:

The aging at 100°C/48 hrs is severe aging even than 85°C/168 hrs. In this aging condition, % Retention of Tensile strength was found to increase to 75% as compared to blank 27% and % retention of Elongation at break value is 70 % as compared to the blank value of 46 % with an increase of 6 PPD content in rubber samples. This is further endorsed by 300 % Modulus found in the range of 160 kg/ cm^2 to 171 kg/ cm^2 as compared to blank doesn't have 300% modulus value. It indicates that the Antidegradants effect is very prominent under severe aging conditions.

Tensile strength study at various aging conditions like 85°C/ 96 Hrs, 85°C/ 168 hrs, 100°C/48 Hrs. showed % Retention in Elongation at Break increased by 30 to 80 %, among compounds with an increase of 6-PPD. 300 % Modulus (Kg / cm^2) found in the range 163 kg/ cm^2 to 181 kg/ cm^2, among compounds having 6-PPD doses compared to blank. The blank doesn't have a 300 % modulus value. It indicates the blank compound has poor flexibility compared to compounds having Antidegradants. These above observations after aging at various temperatures for specific duration show that the introduction of 6-PPD increases the retention of physical properties in all compounds and is improved to a great extent.

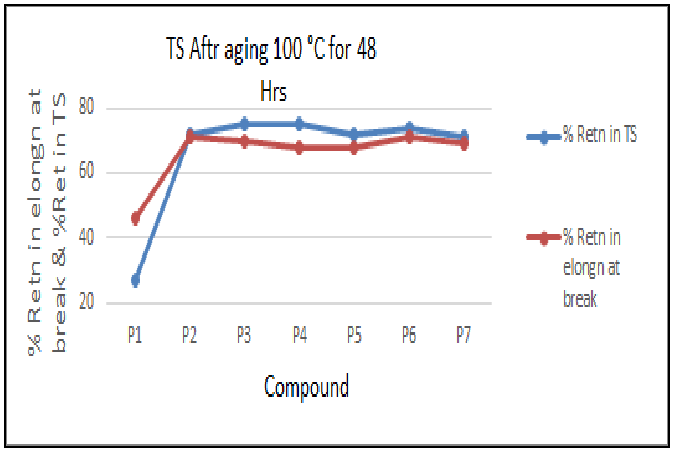

Fig. 4 (d): Effect on tensile strength & elongation break at 100°C/ 48 hrs

Table 10: Effect on Tensile strength property after aging at 100°C/48 hrs

Test	Compounds						
	P1 Blank	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**
100 % Modulus (Kg/cm^2)	26.63	35.92	38.7	40.35	40.44	37.38	39.59
200 % Modulus(Kg/cm^2)	58.42	91.63	96.94	100.65	102.05	94.63	100.05
300 % Modulus(Kg/cm^2)	--------	161.8	166.23	170.56	171.33	162.06	163.74
Tensile Strength(Kg cm^2)	68.66	192.3	193.71	194.7	193.67	197.43	197.16
Elongation at Break, %.	210	350	350	340	340	360	370
SH °A, Hardness.	60	65	65	65	65	65	64
% Retention in TS	27.00	72.00	75.00	75.00	72.00	74.00	71.00
% Retention in elongation at break	46.00	71.00	70.00	68.00	68.00	71.00	69.00

3.5. Fatigue to Failure test

Effect of loading of 6-PPD on Fatigue to failure test were measured for aged and unaged compounds and results obtained are tabulated (Table 11).

As shown in Fig. 5, Effect of variation of 6-PPD loading on fatigue to failure, Unaged and aged compounds as below:

Unaged Fatigue to failure value 3.5 is from 258 to 384 kc for compounds having 6-PPD, compared with blank which has only 88 kc. This is very high, almost 3 to 4 times.

Aged at 85°C/4 days Fatigue to failure value ranges from 141 to 261 kc for compounds having 6-PPD compared with blank compound which has only 48 kc. There is an increase of almost 3 to 5 times. Fatigue to failure study indicates that increasing the dose of 6-PPD in rubber compounds, fatigue to failure value changes great extent. This is the key property for automobile tyres.

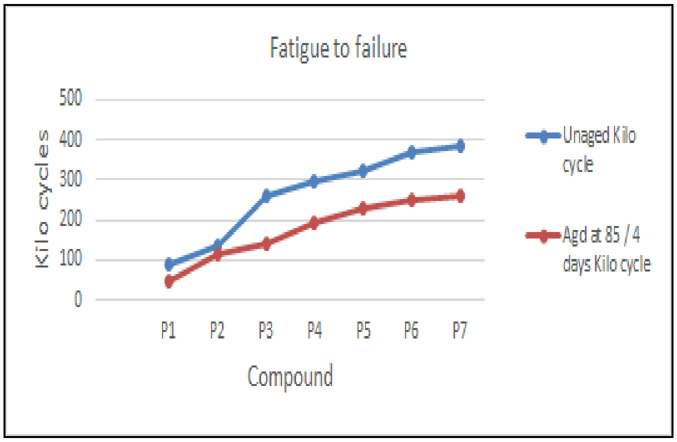

Fig. 5: Effect on Fatigue to failure Unaged & Aged

Table 11: Effect on Fatigue to failure test

Fatigue to failure Properties (Cure Time: T max at 150°C)							
Test	Compounds						
	P1-Blank	P2	P3	P4	P5	P6	P7
Unaged Kilo cycle	88	136	258	297	323	368	384
Aged at 85 / 4 days Kilo cycle	48	116	141	191	231	251	261

Table 12: Ozone resistance test- Static method

Exposure to Ozone 50 pphm in hrs.	Compounds						
	P1-Blank	P2	P3	P4	P5	P6	P7
	No. of Cracks						
4	8	9	10	10	10	10	10
8	8	9	10	10	10	10	10
24	7	8	10	10	10	10	10
48	7	8	9	10	10	10	10
72	6	7	9	10	10	10	10
96	6	7	8	10	10	10	10
120	5	6	8	10	10	10	10
144	5	6	7	10	10	10	10
168	4	5	6	9	10	10	10
192	3	4	5	9	10	10	10

3.6. Ozone resistant property

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.

Effect of exposure of specimen under surface tensile strain was studied under three conditions static, loop and dynamic methods in an exposure to Ozone 50 pphm for 4 hrs to 192 hrs and development of cracks were observed.

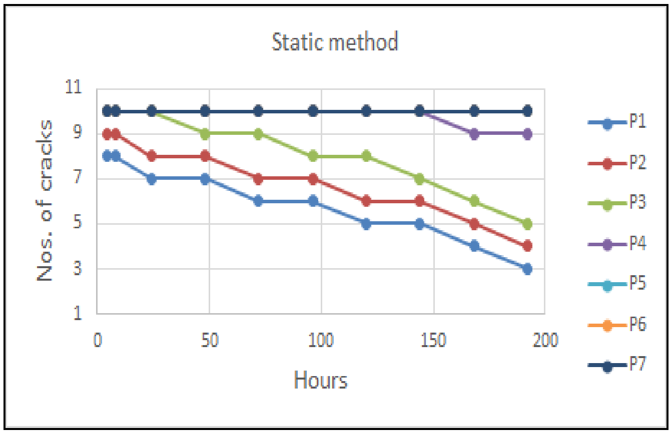

Fig. 6(a): Effect on Ozone resistant test (static method)

Effect of variation of 6-PPD content on Ozone resistance test in Static method is tabulated in table 12.

As shown in Fig. 6(a), Effect of variation of 6-PPD content on Ozone resistance test (Static method). 6-PPD dosages are very important and as dosages increase the ozone resistance improves.

In the static method, it was found that with increase 6-PPD content, the ozone resistant capacity of the compound increased. At 1.5 to 2.5 phr 6-PPD concentration, no ozone cracks observed even after prolonged ozone exposure of 192 hrs. as compared to blank has cracks within 4 Hrs.

Effect of variation of 6-PPD content on Ozone resistance test in Loop method is tabulated in Table 13 as below.

As shown in Figure 6 (b), Effect of 6-PPD content loading on Ozone resistance capacity (Loop method) is given below,

Loop method has higher tensile strain than a static method. In static method, it was found that with an increase in 6 PPD content, the ozone resistant capacity of the compound increased. At 1.5 to 2.5 phr 6-PPD concentration, no ozone cracks observed even after prolonged ozone exposure of 192 hrs as compared to blank sample that had cracks within 4 Hrs.

Table 13: Effect on Ozone resistance test (Loop method)

Exposure to Ozone 50 pphm in Hrs.	Compounds						
	P1-Blank	P2	P3	P4	P5	P6	P7
	No. of Cracks						
4	7	8	10	10	10	10	10
8	7	8	10	10	10	10	10
24	6	7	10	10	10	10	10
48	6	7	9	10	10	10	10
72	5	6	9	10	10	10	10
96	5	6	8	9	10	10	10
120	4	5	8	9	10	10	10
144	4	4	7	9	10	10	10
168	3	4	6	8	10	10	10
192	3	3	6	8	10	10	10

Table 14: Effect on Ozone resistance test (10% Dynamic method)

Exposure to Ozone 50 pphm in Hrs.	Compounds						
	P1-Blank	P2	P3	P4	P5	P6	P7
	No. of Cracks						
4	6	7	7	8	10	10	10
8	6	6	7	8	10	10	10
24	5	6	6	8	10	10	10
48	5	6	6	7	9	10	10
72	5	5	5	7	9	10	10
96	4	5	5	6	8	9	9
120	4	4	4	6	8	9	9
144	4	4	4	5	7	8	8
168	3	3	3	5	7	8	8
192	2	3	3	4	6	7	7

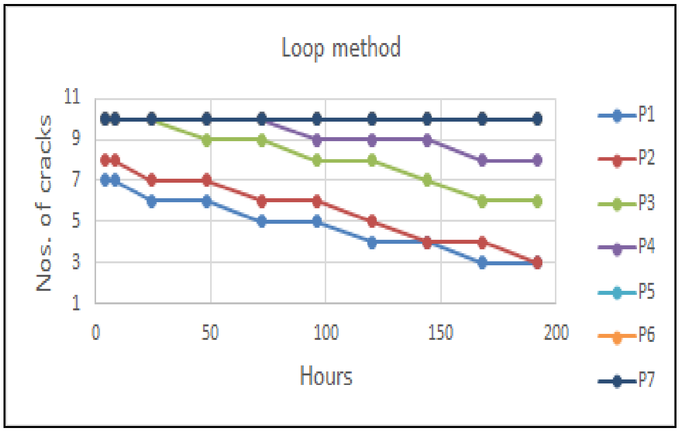

Fig. 6(b): Effect on Ozone resistant test (Loop method)

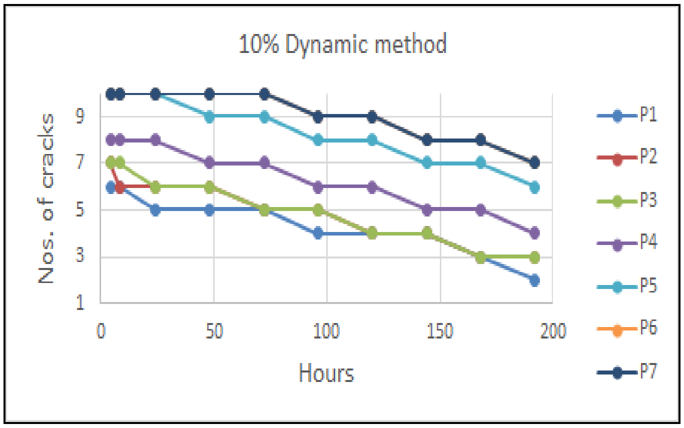

Fig. 6(c): Effect on Ozone resistant test (10% Dynamic method)

Effect of variation of 6-PPD content on Ozone resistance test in 10% Dynamic method is tabulated in Table 14.

As shown in Fig. 6 (c), Effect of 6-PPD content loading on Ozone resistance capacity (10% Dynamic method).

10% Dynamic method has higher tensile strain than the static method and loop method. It is very severe ozone resistant condition. In the 10% Dynamic method, it was found that with increase 6 PPD content in compounds P1 to P7, the ozone resistant capacity of the compound increased. At 2.0 to 2.5 phr 6-PPD concentration P6 and P7 compounds, no ozone cracks observed even after prolonged ozone exposure of 72 hrs. as compared to blank has cracked at 4 hrs.

The Ozone resistant study reveals that the increase in 6-PPD doses in rubber compounds showed that the ozone resistant capacity of the polymer increases even in loop and dynamic mode testing.

4. CONCLUSIONS

1. With increased dosages of 6-PPD, there is a marginal increase of Mooney viscosity is observed 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 happen as a result of an efficient antioxidant synergistic effect.
2. With the increase of 6-PPD, 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 the loading of antioxidants.
3. With the increase of 6-PPD, increase in scorch time, a decrease in cure time and a decrease in torque value are the sound parameters for compounded rubber.
4. Tensile strength properties and Elongation at break observations after aging at various temperatures for specific duration shows that the introduction of 6-PPD increases the retention of physical properties in all compounds and is improved to a great extent.
5. Unaged and aged Fatigue to failure properties increased with the introduction of 6-PPD in compounds thatshows 6-PPD's anti-cracking property. Fatigue to failure property important for the tyre. Values of fatigue to failure show increasing trend means 6-PPD protects the rubber compounds from cracking with an increase in concentration.
6. With the increase of 6-PPD, Ozone resistant capacity of the compounds also increased in all three Static, Loop and Dynamic methods. The increasing concentration of 6-PPD shows higher ozone resistant capacity. All three methods static, loop and dynamic methods show that 6-PPD protects the rubber compound from ozone and heat exposure with an increase in its concentration.

Considering the above study, it is revealed that N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (6-PPD), an antidegradant 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 antidegradants, 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 6-PPD can be used in between 1.5 to 2.0 phr. for better performance.

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6. REFERENCES

1. Takizawa, Yoichi U.S. Pat. Appl. Publ, US 20100324168 A1 20101223(2010)
2. Pichugin AM. *Kauchuk i Rezina*, 2008;**5**:2-11.
3. Bristow GM. *Journal of Natural Rubber Research*, 1991; **6(3):**137-151.
4. Dragoni E, Medri G. *Theoretical and Applied Fracture Mechanics*, 1988; **10**:79-83
5. Marks AM, Adhikary A, Mukhopadhyay R. *Rubber World*, 2004; **231(2):** 29-32, 55.
6. Hopmann C, Lemke F, Moeckel J. *Kautschuk Gummi Kunststoffe*, 2017; **70(4):**20-24.
7. Li GY, Koenig JL. *Rubber Chemistry and Technology*, 2005; **78(3):**355-390.
8. Irina S, Nikolay P. *Polymer Aging at the Cutting Edge*, 2002;85-99.
9. Cossu G, Palumbi MC, Caliano L PCT. *Int. Appl.*, WO 2016075667 A1 20160519; 2016.
10. Dasgupta S, Agrawal SL, Bandyopadhyay S, Mukhopadhyay R, et al. *Polymer Testing*, 2009; **28(3):**251-263.

11. Joona M. *IndustriadellaGomma/Elastica*, 2004; **524**:35-37.
12. Ando Shinji, Fukamachi Shinji, Shibata Emiko, Tanabe Takeshi, *Jpn. Kokai Tokkyo Koho JP* 2010254579 A 20101111, 2010.
13. Kortisova I, Breza M, Cibulkova Z. *Chemical Papers*, 2007; **61(1):** 61-65.
14. Rublon P, Favier A. *Procedia Engineering*, 2015;**133**:161-170.
15. Cataldo F. *Polymer Degradation and Stability*, 2001; **72(2):**287-296.
16. Duh Yih-Shing, Ho Ta-Cheng, Chen Jenq-Renn, Kao Chen-Shan. *Polymers (Basel, Switzerland),* 2010; **2(3):**174-187.
17. Felix OA, Justice AI, Tochukwu UAN. *Journal of Materials Science and Chemical Engineering*, 2015; **3**:7-12.
18. Parley PS, Banthorpe DV, Porter M. *Journal of Natural Rubber Research*, 1992; **7(3):**157-167.
19. Saiki A, Minashima H, Yano Y, Shiina N, et al. *PCT Int. Appl.*, WO 2015178037 A1 20151126, 2015.
20. Li H, Yu Z, Liu, Jinfeng, Li Q, et al. *Faming ZhuanliShenqing* CN 108570173 A 20180925, 2018.
21. Kortisova I, Breza M, Cibulkova Z. *Chemical Papers*, 2007; **61(1):**61-65.
22. Breza M, Kortisova I, Cibulkova Z. *Polymer Degradation and Stability*, 2006; **91(12):**2848-2852.
23. Cibulkova Z, Klein E, Lukes V. *Petroleum and Coal*, 2004; **46(2):** 42-48.
24. Klein E, Cibulkova Z, Lukes V. *Polymer Stability*, 2005; **88(3):**548-554.