(12) PATENT APPLICATION PUBLICATION
(19) INDIA
(22) Date of filing of Application :09/11/2020

(21) Application No.202041048775 A
(43) Publication Date : 16/04/2021

(54) Title of the invention : A RUBBER COMPOSITION FOR A HIGHLY IMPERMEABLE TYRE INNERLINER AND METHOD THEREOF

(51) International classification	:B60C0001000000, C08K0003040000, C08L0007000000, B60C0005140000, B29D0030060000
(31) Priority Document No	:NA
(32) Priority Date	:NA
(33) Name of priority country	:NA
(86) International Application No Filing Date	:NA :NA
(87) International Publication No	: NA
(61) Patent of Addition to Application Number Filing Date	:NA :NA
(62) Divisional to Application Number Filing Date	:NA :NA

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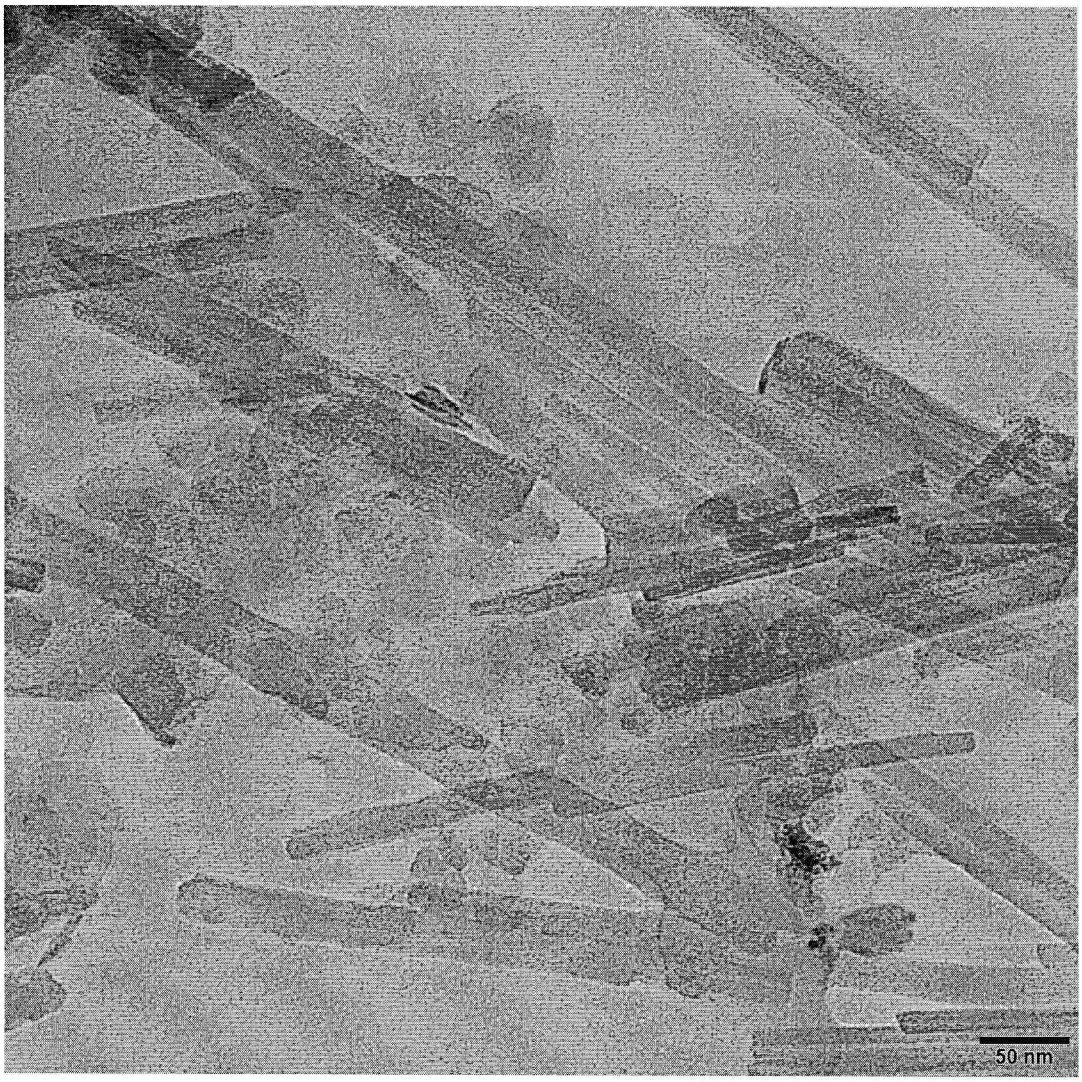
(57) Abstract :
The present invention provides a tyre inner liner nanocomposite and its method of preparation, capable of providing lower modulus, improved barrier and processability characteristics. The rubber composition of tyre inner liner includes 100 phr of rubber selected from natural rubber (NR), non-oil extended styrene butadiene rubber, poly butadiene rubber, reinforcing filler such as carbon black, naturally occurring, unmodified fuller™s earth nanoclay. It further discloses a tyre comprising the inner liner nanocomposite.

No. of Pages : 28 No. of Claims : 10

NAME OF THE APPLICANT: TVS SRICHAKRA LIMITED
PROVISIONAL SPECIFICATION NO.: 202041048775 dated November 09, 2020

FIGURE 1:

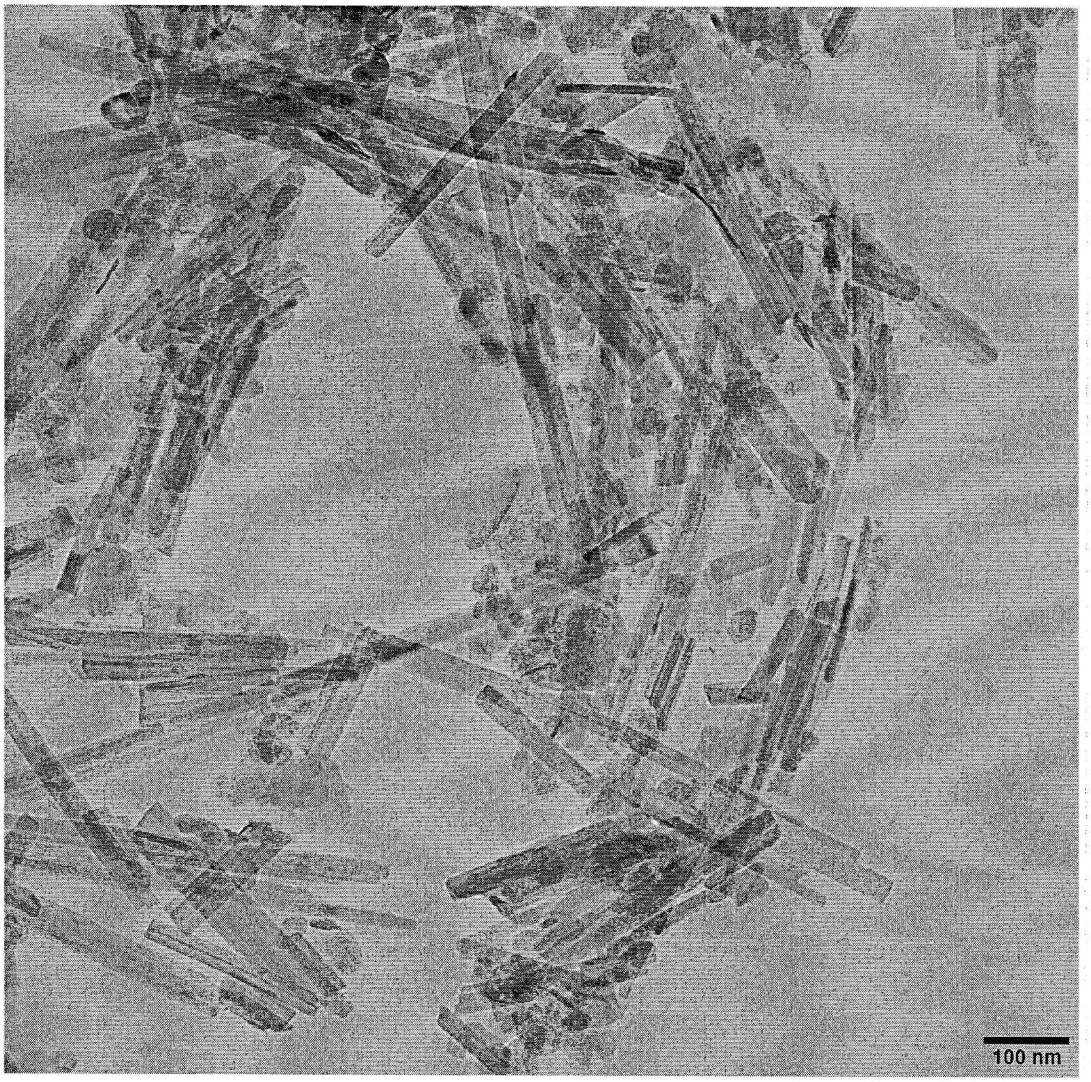


Dated this 8th day of April 2021

Durgumahanthi Sai Meera [IN/PA – 3410]
Agent for Applicant

NAME OF THE APPLICANT: TVS SRICHAKRA LIMITED
PROVISIONAL SPECIFICATION NO.: 202041048775 dated November 09, 2020

FIGURE 2:



Dated this 8th day of April 2021

Durgumahanthi Sai Meera [IN/PA – 3410]
Agent for Applicant

FORM 2

THE PATENTS ACT, 1970
(39 of 1970)
&
The Patents Rules, 2003

COMPLETE SPECIFICATION

(See section 10; rule 13)

1. TITLE OF THE INVENTION

"A RUBBER COMPOSITION FOR A HIGHLY IMPERMEABLE TYRE INNERLINER AND METHOD THEREOF"

2. APPLICANT (S)

(a) NAME:	TVS SRICHAKRA LIMITED
(b) NATIONALITY:	A Company Registered under the Indian Companies Act, 1956
(c) ADDRESS:	Vellarippatti, Melur Taluk, Madurai - 625122, Tamil Nadu, India.

3. PREAMBLE TO THE DESCRIPTION

The following specification particularly describes the invention and the manner in which it is to be performed.

A RUBBER COMPOSITION FOR A HIGHLY IMPERMEABLE TYRE INNERLINER AND METHOD THEREOF

FIELD OF THE INVENTION

The present invention relates to the field of tyres. More particularly, the present invention relates to tyre inner liner nanocomposite and its method of preparation. The present invention relates to a tyre inner liner nanocomposite capable of providing lower modulus, improved barrier and processability characteristics using naturally occurring unmodified Fuller's Earth nanoclay.

BACKGROUND OF THE INVENTION

Tyre inner liners must be constructed of materials which are relatively low in air permeability and yet flexible. General purpose rubbers do not possess the required low air permeability. The rubbers which have been almost exclusively used for this purpose are butyl rubbers, particularly the halogenated butyl rubbers. Until recently, only these polymers possessed the necessary traits to be useful in the manufacture of tyre inner liners and tyre inner tubes.

Published International Application PCT/US91/04896 discloses the use of isomonoolefin/para-alkyl styrene copolymers (IPMS) for the manufacture of tyre inner liners. Tyre inner liners made from these copolymers exhibit very low air permeability.

The addition of clays to rubber is well-known in the art. Clays have been added to rubber compositions to improve their strength. For example, U.S. Pat. No. 4,889,885 discloses the preparation of a composite material by adding a layered silicate to rubber to improve the mechanical properties. The resulting products, however, are relatively stiff and therefore are unsuitable for the use as tyre inner liners.

KR20020044199 relates to provided is an inner liner rubber composition for tyre, which maintains its physical property and has an improved anti-porosity by using nanoclay. The composition comprises 2-10 parts by weight of nanoclay with respect to 100 parts by weight of halobutyl rubber, natural rubber, or mixed rubber of halobutyl rubber and natural rubber as rubber material. The nanoclay consists of 10-20 wt% of clay and 90-80 wt% of resin, and has a specific gravity of 1.5±0.2. The clay consists of 20-80 wt% of Al_2O_3 and 80-20 wt% of SiO2, and has a specific gravity of 2.3±0.5, interlayer height of 1.0-4.0 nm, and average particle diameter of 1.0-7.0 micrometer. The resin is an alkylphenol-based resin.

US5665183 relates to a tyre inner liner, comprising a solid rubber and a complex, said complex comprising a reactive rubber and layered silicate clay uniformly dispersed therein. The complex comprising the clays significantly improves the low air permeability of the tyre inner liner without adversely affecting the rubber composition.

KR20070122068 relates to a rubber composition for tyres comprising silane-treated clay is provided to ensure good physical properties of rubber, particularly excellent gas barrier property, while improving thermal stability and dimensional stability. A rubber composition for tyres comprising silane-treated clay comprises 100 parts by weight of base rubber and 1-70 parts by weight of silane-treated clay. The silane-treated clay has a clay content of 50-90 wt%, a silane content of 5-50 wt and a specific gravity of 2.5+/-0.2. The clay in the silane-treated clay has a specific gravity of 2.5+/-0.2, an average particle diameter of 0.5+/-0.4 micrometers, an Al2O3 content of 35 wt% of less, and a SiO2 content of 56 wt% or less. The silane-treated clay is treated with mercaptosilane, aminosilane or glycidylsilane.

IN Publication No. 201621013899 relates to an inner liner system for pneumatic tubeless tyre comprising a single inner liner layer, said layer being air-impermeable and compatible with inner ply eliminating the need for additional layers in inner liner systems. The secondary components comprised in the inner liner include fillers and other adjuncts. Fillers are selected from at least one of nano-sized exfoliated kaolin clay in about 14-24%w/w of the composition, carbon black in about 10-20%w/w of the composition, mica and calcium carbonate.

US2014116594 relates to an inner liner rubber composition that enables improvements in handling stability, fuel economy, elongation at break, sheet processability, air barrier properties, and compounding cost in a balanced manner; and a pneumatic tyre including an inner liner formed from the rubber composition. The rubber composition includes: a reclaimed butyl rubber; a halogenated butyl rubber other than the reclaimed butyl rubber; at least one semi-reinforcing filler selected from the group consisting of finely ground bituminous coal, talc, mica, and hard clay; and carbon black having a specific N2SA and/or silica having a specific N2SA.

JP2002088208 relates to a rubber composition for use in inner liners of pneumatic tyres with excellent air permeation resistance and improved processability, and to provide, by using the composition, a pneumatic tyre that allows its inner liner to reduce the gauge to a great extent, while preserving the inner pressure preserving characteristics. A rubber component comprising 40-100 wt. % of a halogenated butyl rubber and <60 wt. % of a diene rubber is compounded with a layered or planar mineral such as kaolin or clay to form a rubber composition for use in inner liners of pneumatic tyres.

CN104710634 relates to nanocomposite composition that includes the nano composite, the nano composite made in such that its air-retention properties are much improved over what is known, while maintaining desirable elasticity and processability. In a particular aspect, an air-retention article such as an inner liner if formed by first contacting a desirable elastomer, especially a functionalized poly(isobutylene-co-p-methylstyrene) elastomer, with one or more layered fillers such as a clay described further below, and also contacting one or more processing aids, and one or more solvents to form an nano composite composition. The nano composite composition is then precipitated to form the solid nano composite composition which can be dried and further blended with other suitable ingredients such as, for example, curative agents, thus forming an inner liner suitable for a tyre or other article.

JP2010013543 provides a rubber composition for use in tyre inner liners which simultaneously satisfies both the air-permeability resistance and the flexural fatigue resistance, and to provide a pneumatic tyre using it. The rubber composition for use in tyre inner liners, comprising a blend of 100 pts. mass of a rubber component (but, the rubber component accounts for 50 pts. mass or more of a butyl-based rubber), 5-25 pts. mass of an oil-extended china clay, 10 pts. mass or more of an inorganic filler and 30 pts. mass or more of a carbon black, is characterized in that the sum total blending quantity of the above oil-extended china clay, inorganic filler and carbon black is 45-100 pts. mass.

JP2011074142 relates to a rubber composition in which inconvenience such as rubber cutting and boring of sheet is hardly generated even when thin gauge is performed as an inner liner and a manufacturing method therefore, and to provide an inner liner comprising such a rubber composition and a pneumatic tyre using the inner liner. The rubber composition is characterized in that the shrinkage at a temperature of 40°C at

non-vulcanization is 15% or less. Further, the inner liner is characterized in that it comprises the rubber composition, and the pneumatic tyre is characterized in that the inner liner is used. Further, in the rubber composition, air permeability-proof can be enhanced by formulating an inorganic clay mineral.

JP2012125969 relates to a polymer laminate, which is reduced in thickness and excellent in air permeation resistance and adhesiveness with adjacent rubber, and a pneumatic tyre with an inner liner using the same. The polymer laminate includes: a first layer containing SIBS and 0.1-50 pts. mass of an organized clay mineral based on 100 pts. mass of the SIBS; and a second layer including at least one of a styrene-isoprene-styrene triblock copolymer and a styrene-isobutylene diblock copolymer.

JP2008266517 relates to a rubber composition for tyre inner liner causing no decline in its rupture properties while improving its gas-barrier tendency. The rubber composition comprises a butyl rubber matrix phase and a dispersed phase of natural rubber and/or isoprene rubber, wherein the distribution ratio for clay mineral contained in the dispersed phase and the matrix phase (the clay mineral level per area in the dispersed phase/that in the matrix phase) stands at 1.5-2.5.

JP2014024998 relates to a rubber composition (in particular a rubber composition for inner liner) in which a clay mineral such as mica, clay and the like is blended at high blending quantity and which is characterized in that the air permeability thereof is decreased without causing a strength deterioration of the unvulcanized rubber composition by blending a particular amount of carbon black and butyl- based rubber having a specific Mooney viscosity, and a pneumatic tyre using the same with improved molding work efficiency.

Still, there is a need to develop tyre inner liner nanocomposite capable of providing lower modulus, improved barrier and processability characteristics.

The present invention aims to provide a tyre inner liner nanocomposite and its method of preparation which is capable of providing lower modulus, improved barrier and processability characteristics using naturally occurring Fuller's Earth nanoclay.

OBJECT OF THE INVENTION

It is primary object of the present invention to provide a rubber composition for tyre inner liner.

It is primary object of the present invention to provide a highly impermeable tyre inner lining comprising of a nano-composite.

It is another object of the present invention to provide a method of preparation of rubber tyre composition.

It is another object of the present invention to provide a rubber tyre inner liner composition which is capable of providing lower modulus, improved barrier and processability characteristics.

It is another object of the present invention to provide a rubber composition for tyre inner liner, particularly a nanocomposite using Fullers Earth nanoclay in NR: SBR: BR tri blend and NR: SBR blend.

It is another object of the present invention to provide tyre inner liner rubber nanocomposite having high elongation properties.

It is another object of the present invention to provide cost effective and environmental friendly tyre inner liner nanocomposite.

SUMMARY OF THE INVENTION

One or more of the problems of the conventional prior arts may be overcome by various embodiments of the present invention.

It is primary aspect of the present invention to provide a rubber composition for tyre inner liner, comprising of:

one or more rubbers – 100 phr;
reinforcing filler – 35 – 85 phr;
nanofiller – 0.1 – 40 phr;
process aid – 1- 10 phr;
vulcanization activators – 2 – 10 phr;
vulcanization agent – 1 – 3.5 phr;
anti-degradants – 1 – 2 phr; and
primary accelerators – 1- 3 phr,

wherein the nanofiller is naturally occurring unmodified fuller's earth nanoclay with acicular particles in diameter 1 to 5 nm and length 10 – 5000 nm with the aspect ratio in the range between 5 and 45 measured in HR TEM image at 50 nm magnification.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the rubbers are selected from natural rubber (NR), non-oil extended styrene butadiene rubber, poly butadiene rubber and combinations thereof.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the reinforcing filler is carbon black.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the processing aid is aromatic oil.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the vulcanization activators are selected from zinc oxide, stearic acid and combinations thereof.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the vulcanization activator comprises of zinc oxide and stearic acid preferably in a weight ratio of 2-5: 2-5 phr.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the vulcanization agent is sulphur.

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the primary accelerator is CBS (N-cyclohexyl-2-benzothiazolesulfenamide).

It is another aspect of the present invention to provide a rubber composition for tyre inner liner, wherein the anti-degradants are selected from TMQ-2,2,4-trimethyl-1,2-dihydroquinoline.

It is another aspect of the present invention to provide a method for preparation of rubber composition for tyre inner liner, comprising of steps:

preparation of master batch by:

initially mixing of rubber;

mixing and reacting with reinforcing filler, nanofiller:

processing aid, vulcanization activators; anti-degradants;

sweeping down in the orifice, mixing and dumping of the rubber compound;

sheet out the rubber compound;

preparation of final batch by:

mixing and reacting of master batch compounds with vulcanization agent and primary accelerator and dumping at a temperature range of 85 degree celsius and 110 degree Celsius; and

sheet out the rubber compound,

wherein the nanofiller is naturally occurring unmodified fuller's earth nanoclay with acicular particles in diameter range between 1 and 5 nm and length in the range between 10 and 5000 nm with the aspect ratio is in the range between 5 and 45 measured in HR TEM image at 50 nm magnification, and

wherein the preparation of master batch is carried out in a temperature range between 85 degree Celsius and 90 degree Celsius.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 illustrates acicular particles of unmodified fuller's earth nanoclay analyzed with HR TEM at 50 nm.

Figure 2 illustrates acicular particles of unmodified fuller's earth nanoclay analyzed with HR TEM at 100 nm

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a tyre inner liner nanocomposite and its method of preparation which is capable of providing lower modulus, improved barrier and

processability characteristics. The invention also relates to tyres comprising the inner liner composition of the present invention.

The rubber composition of tyre inner liner includes 100 parts by weight of a rubber, selected from natural rubber (NR), non-oil extended styrene butadiene rubber (SBR), poly butadiene rubber (PBR), or with the blend of natural rubber and styrene butadiene rubber. The filler comprises a reinforcing filler such as carbon black between dosage of 35 to 85 phr with the iodine surface area of 31to 41 mg/gm, and 0.1 to 40 phr of naturally occurring unmodified fuller's earth nanoclay preferably acicular particles in diameter 1 to 5 nm and length 10 to 5000 nm with the aspect ratio is in the range of 2 to 45 measured in HR TEM image at 50nm magnification.

In accordance with the present invention, there is provided a rubber composition for tyre inner liner which further consists of process aid, vulcanization activators, vulcanization agent, anti-degradants, and primary accelerators.

In accordance with the present invention there is provided a rubber composition for tyre inner liners preferably consist of carbon black as reinforcing filler; aromatic oil as process aid; zinc oxide, stearic acid and combinations thereof as vulcanization activators; sulphur as vulcanization agent; CBS (N-cyclohexyl-2-benzothiazolesulfenamide) as primary accelerator; and TMQ-2,2,4-trimethyl-1,2-dihydroquinoline as anti-degradants.

A rubber tyre inner liner nanocomposite according to an embodiment of the present invention, essentially consists of process aid – 1- 10 phr; vulcanization activators - 2-10 phr; vulcanization agent - 1-3.5 phr; anti-degradants – 1- 2 phr; and primary accelerators – 1-3 phr.

Method of preparation of a rubber composition for tyre inner liner nanocomposite:

Another embodiment of the present invention discloses a method for preparation of rubber composition for tyre inner liner nanocomposite with diene based rubber, tri-blend comprises a non-oil extended styrene butadiene rubber, natural rubber and poly butadiene rubber, a reinforcing filler comprising of carbon black, and an unmodified fuller's earth nanoclay as a nano filler and also a method of a rubber composition for tyre inner liner nanocomposite with diene based rubber blend comprising a non-oil extended styrene butadiene rubber and natural rubber, a reinforcing filler comprising of carbon black, and an unmodified fuller's earth nanoclay as a nanofiller. The formulation (in phr) is given in table 1 and table 2 as follows.

For the purpose of exemplification the rubber composition is prepared by thermo-mechanical process which is carried out using a Banbury mixer.

The method of preparation of rubber composition includes following steps:

a) method of preparation of master batch comprising of the steps:

Step1:

Preparation of master batch has been performed with the rotation speed of the mixer between 50 to 60 rpm and with the head temperature of the Banbury mixer maintained between 85 degree Celsius and 90 degree Celsius.

i) mixing chamber has been charged with the natural rubber; non-oil extended styrene butadiene rubber (SBR) and polybutadiene rubber (PBR), and allowed to mix for 0 to 30 seconds.

ii) addition of the reinforcing filler carbon black, unmodified fuller's earth nanoclay, aromatic oil, zinc oxide, stearic acid, TMQ the anti-degradant, and allowed to mix for 168 to 196 seconds.

iii) sweeping down in the orifice and allowed to mix for 102 to 120 seconds and the master batch rubber compound has been dumped. The master batch rubber compound has been sheeted out in the laboratory two-roll mill,

b) Method of preparation of final batch comprising of the steps:

Mixing chamber charged with the master batch and the curatives sulphur, CBS (N-cyclohexyl-2-benzothizolesulfenamide) are added, and allowed to mix for 50 to 80 seconds and dumped at the temperature range of 85 degree Celsius and 110 degree Celsius. Final batch sheet out has been done in the laboratory two roll mill.

Table 1: According to one embodiment of the present invention, there is provided a formulation of tri blend NR: SBR: BR based tyre inner liner nanocomposite in phr.

Ingredients	Control C1, phr	Formulation related to invention	
		F1, phr	F2, phr
RSS 3[3]	45.00	45.00	45.00
SBR 1502[4]	40.00	40.00	40.00
BR[5]	15.00	15.00	15.00
N660[6]	60.00	60.00	60.00
Fullers Earth[7]		10.00	15.00
Aromatic oil[8]	6.00	6.00	6.00
Zinc oxide[9]	3.00	3.00	3.00
Stearic acid[10]	2.00	2.00	2.00

TMQ[1]	0.50	0.50	0.50
Sulphur[11]	2.25	2.25	2.25
CBS[2]	1.35	1.35	1.35
Total	175.10	185.10	190.10

Table 1A:

According to another embodiment of the present invention, there is provided a formulation of NR: SBR based tyre inner liner nanocomposite in phr.

Ingredients	C2, Control, phr	Formulation related to invention			
		F3, phr	F4, phr	F5, phr	F6, phr
RSS 3[3]	50.00	50.00	50.00	50.00	50.00
SBR 1502[4]	50.00	50.00	50.00	50.00	50.00
PBR 1220[5]	-	-	-	-	-
N660[6]	60.00	60.00	60.00	60.00	60.00
Fullers Earth[7]	-	5.00	10.00	15.00	20.00
Aromatic oil[8]	6.00	6.00	6.00	6.00	6.00
Zinc oxide[9]	3.00	3.00	3.00	3.00	3.00
Stearic acid[10]	2.00	2.00	2.00	2.00	2.00
TMQ[1]	0.50	0.50	0.50	0.50	0.50
Sulphur[11]	2.25	2.25	2.25	2.25	2.25
CBS[2]	1.35	1.35	1.35	1.35	1.35
Total	175.10	180.10	185.10	190.10	195.10

1. TMQ - 2,2,4-trimethyl-1,2-dihydroquinoline from Lanxess India Private Limited. It is an anti-degradant excellent resistance to thermo-oxidative ageing of elastomers.
2. CBS (N-cyclohexyl-2-benzothiazolesulfenamide) from Nocil Limited, India. It is a delayed action accelerator suitable for diene rubbers.

3. RSS 3 (Natural Rubber - Ribbed Smoke Sheet) from Southland Global PTE Ltd, Thailand with the Mooney Viscosity, ML (1+4) at 100°C is 74 MU.
4. SBR 1502 from Pottekkattu Rubbers Pvt Ltd, India with the unmassed viscosity, ML(1+4) @ 100°C is in the range of 45 to 54 MU.
5. PBR 1220 from Reliance Industries Ltd, India with the Mooney viscosity, ML(1+4)@ 100°C in the range of 41 to 49.55MU.
6. ASTM Grade N660 from Birla Carbon, India. It is the reinforcing filler (GPF) general purpose furnace having the iodine adsorption number (IAN No.) value between 31 to 41 mg/gm, oil absorption number (OAN) value between 85 to 95 cc/100gm, compressed oil absorption no. (COAN) value between 69 to 79 cc/100gm, nitrogen surface area (N_2SA) value between 30 to 40 m^2/gm and the statistical thickness surface area (STSA) value between to 29 to 39 m^2/gm.
7. Fuller's Earth from Prakash & Co, India. It is unmodified nanoclay with the acicular particles in diameter 1 to 5 nm and length 10 to 5000 nm with the aspect ratio is in the range of 5 to 45 measured in HR TEM image at 50nm magnification.
8. Aromatic Oil from Indian Oil Corporation Limited, India.
9. Zinc oxide from POCL Enterprises Limited, India. It is used as an activator for the sulphur vulcanization of rubbers enhances the vulcanization efficiency and reduces the vulcanization time.
10. Stearic acid from 3F Industries Ltd., India. Stearic acid activates accelerators in presence of zinc oxide forming zinc stearate incitu.
11. Sulphur from the Standard Chemical Co. Pvt Ltd, India. It is the vulcanizing agent.

Results:

Characterization of Cured Rubber Vulcanizate and Uncured Rubber Compound:

The compound properties are listed in Table 2 & Table 2A below:

The purpose of these tests is to measure the improved properties of the formulation related to the invention against control formulation. For this, two NR: SBR: BR tri blend based tyre inner liner nanocomposite F1, F2 reinforced by carbon black grade N660 and unmodified fullers earth nano clay with the acicular particles in diameter 1 to 5 nm and length 10 – 5000 nm with the aspect ratio is in the range of 2 to 45 measured in HR TEM image at 50nm magnification are prepared against NR: SBR: BR triblend based tyre inner liner rubber composition reinforced by carbon black grade N660 with the iodine surface area 31 to 41 mg/gm is prepared and evaluated.

Also, four NR: SBR blend based tyre inner liner nanocomposite F3, F4, F5, F6 reinforced by carbon black grade N660 and unmodified fullers earth nano clay with the acicular particles in diameter 1 to 5 nm and length 10 – 5000 nm with the aspect ratio is in the range of 2 to 45 measured in HR TEM image at 50nm magnification are prepared against NR: SBR blend based tyre inner liner rubber composition reinforced by carbon black grade N660 with the iodine surface area 31 to 41 mg/gm is prepared and evaluated.

Measurements and Tests:

Better processability (Process Requirements) of a Rubber Compound:

M1. Mooney Scorch Characteristics (pre vulcanization characteristics using large rotor) for processability:

The Mooney Scorch measurements are carried out with a Mooney Viscometer (MV 2000 Alpha technologies, USA) according to ASTM D1646. MV indicates the minimum viscosity, t_5 indicates the time to scorch (MV+5) which indicates the processing properties (process safety) and t_{35} indicates the time to cure (MV+35)

Tensile Properties of a Rubber Vulcanizate:

M2. Tensile properties are carried out in a universal testing machine (UTM) (Instron Make, Model 5966, USA). 300% modulus and elongation at break are measured in accordance with ASTM D412.

Barrier Properties of a Rubber Vulcanizate:

M3. Oxygen transmission rate of a rubber vulcanizate is measured in Mocon Make, Model MH 2/21, USA in accordance with ASTM F1927 and Water vapour transmission rate is carried out in a Mocon Make, Model MG 3/33 in accordance with ASTM F 1249.

The present invention provides a tyre inner liner F1, F2, NR: SBR: BR tri-blend based nano composite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 10 phr gave process safety, $t_{5\&}t_{35}$ values improved by 9.96% and 13.07 % when compared to NR: SBR: BR triblend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control).

Moreover, further addition of fuller's earth nanoclay from 10 to 15 phr NR: SBR: BR tri-blend based tyre inner liner nanocomposite F2, improved the process safety i.e., t_5 & t_{35} values to a greater extent 13.98% & 18.92 % respectively when compared to NR: SBR: BR tri-blend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control).

The present invention also relates a tyre inner liner F3, F4, F5 & F6 NR: SBR blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 5 to 20 phr gave process safety i.e., t_5&t_{35} values improved by 10.45 to 21.42 % and 4.07 to 16.60% when compared to NR: SBR blend tyre inner liner rubber composition C2 reinforced by N660 carbon black (Control).

The present invention also relates to a tyre inner liner F1, F2, NR: SBR: BR tri-blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 10 phr gave 3.53 % lowered 300 % modulus when compared to NR: SBR: BR tri-blend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control). Further addition of fuller's earth nanoclay from 10 to 15 phr in NR: SBR: BR tri-blend based tyre inner liner nanocomposite F2, gave 2.77 % lower 300 % modulus when compared to NR: SBR: BR triblend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control).

The present invention also relates a tyre inner liner F3, F4, F5, F6 NR: SBR blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 5 to 20 phr gave 14.10 to 24.20 % lower 300% modulus when compared to NR:SBR blend tyre inner liner rubber composition C2 reinforced by N660 carbon black (Control).

The present invention relates to a tyre inner liner F1, F2, NR: SBR: BR tri-blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 10 phr provides 5.17% higher elongation at break. Further addition of fuller's earth nanoclay from 10 to 15 phr NR: SBR: BR tri-blend based tyre inner liner nanocomposite F2, gave 0.5% higher elongation at break when compared to NR: SBR: BR tri-blend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control).

The present invention also relates a tyre inner liner F3, F4, F5, F6 NR: SBR blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 5 to 20 phr gave 2.65 to 9.97 % higher elongation at break when compared to NR: SBR blend tyre inner liner rubber composition C2 reinforced by N660 carbon black (Control).

The present invention relates to a tyre inner liner F1, F2, NR: SBR: BR tri-blend based nanocomposite reinforced by N660 carbon black and unmodified fuller's earth nano clay with 10 phr provides lower oxygen and water vapour transmission rate 6.12 & 11.04% when compared to NR: SBR: BR tri-blend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control). Further addition of fuller's earth nanoclay from 10 to 15 phr NR: SBR: BR triblend based tyre inner liner nanocomposite F2, gave 28.14% lowered oxygen transmission rate (OTR) which is significant and 2.5% lower water vapour transmission rate (WVTR) when compared to NR: SBR: BR triblend tyre inner liner rubber composition C1 reinforced by N660 carbon black (Control).

The present invention also relates to a tyre inner liner F3, F4, F5 and F6 NR: SBR blend based nanocomposite reinforced by N660 carbon black and unmodified fullers earth nano clay with 5 to 20 phr gave 4.98 to 9.82% lower oxygen transmission rate, i.e., good and 15.72 to 20.02% lower water transmission rate which is significant when compared to NR: SBR blend tyre inner liner rubber composition C2 reinforced by N660 carbon black (Control).

Hence, both the NR: SBR blend & NR: SBR: BR tri blend based tyre inner liner composite provides excellent barrier properties i.e., lower oxygen transmission rate (lower air permeability) and lower water vapour transmission rate when compared to control compounds C1 & C2.

Table 2: Characterization of cured rubber vulcanizate & uncured rubber compound of NR: SBR: BR triblend based tyre inner liner nanocomposite

Properties	**C1, Control**	**Formulation related to invention**	
		F1	**F2**

Better processability:			
Mooney Scorch @ 125°C			
t_5, minutes: minutes	27.90	30.68	31.80
t_5, Index (Higher the index value is better)	100	109.96	113.98
t_{35}, minutes: minutes	34.03	38.48	40.47
t_{35}, Index (Higher the index value is better)	100	113.07	118.92
Tensile Properties			
300 % Modulus, Mpa	14.43	13.92	14.03
300% Modulus, Index (Lower the index value is better)	100	96.47	97.23
Elongation at Break, %	329.47	346.49	331.13
Elongation at Break, Index (Higher the index value is better)	100	105.17	100.5
Barrier Properties:			
Oxygen Transmission Rate, OTR	110.222	103.481	79.203
OTR, Index (Lower the index value is better)	100	93.88	71.86
Water Vapour Transmission rate, WVTR	2.655	2.362	2.587
WVTR, Index (Lower the index value is better)	100	88.96	97.44

Table 2A: Characterization of cured rubber vulcanizate & uncured rubber compound of NR: SBR blend based tyre inner liner nanocomposite

Properties	**C2, Control**	**Formulations related to invention**			
		F3	**F4**	**F5**	**F6**
Better processability:					

Mooney Scorch @ 125°C					
t_5, minutes: minutes	26.30	31.87	30.50	29.50	29.05
t_5, Index (Higher the index value is better)	100	121.2	115.97	112.17	110.45
t_{35}, minutes: minutes	34.68	40.14	40.44	38.99	36.09
t_{35}, Index (Higher the index value is better)	100	115.74	116.6	112.42	104.07
Tensile Properties:					
300 % Modulus, Mpa	16.74	14.38	13.81	14.33	12.69
300% Modulus Index (Lower the Index value is better)	100	85.9	82.5	85.6	75.8
Elongation at Break, %	329.63	347.82	338.37	346.50	362.51
EB%, Index (Higher the index value is better)	100	105.5	102.65	105.1	109.97
Barrier Properties:					
Oxygen Transmission Rate (OTR), $cc/m^2.gm$	136.605	123.190	129.414	129.799	112.327

OTR, Index (Lower the index value is better)	100	90.18	94.74	95.02	82.23
Water Vapour Transmission rate(WVTR),	2.526	2.129	2.064	2.023	2.001
WVTR, Index (Lower the Index value is better)	100	84.28	81.71	80.09	79.22

Hence, NR: SBR: BR tri blend F3, F4, F5, F6 & NR: SBR blend F1, F2 based tyre inner liner nanocomposite reinforced with N660 carbon black and unmodified fuller's earth nano clay with the acicular particles in diameter 1 to 5 nm and length 10 – 5000 nmwith the aspect ratio is in the range of 5 to 45 measured in HR TEM image at 50nm magnification gave better barrier properties along with processing safety, lower 300% modulus and higher elongation at break when compared to NR:SBR:BR triblend C1, & NR: SBR blend C2 reinforced with N660 carbon black with iodine adsoprtion no. 31 to 41 mg/gm.

The present invention provides a tyre inner liner nanocomposite and its method of preparation, capable of providing lower modulus, improved barrier and processability characteristics. The rubber composition of tyre inner liner includes 100 parts by weight of a rubber, with the blend of natural rubber and styrene butadiene rubber, a reinforcing filler such as carbon black between dosage of 35 to 85 phr with the iodine surface area of 31 to 41 mg/gm, 0.1 to 40 phr of naturally occurring, unmodified fuller's earth nanoclay preferably acicular particles in diameter 1 to 5 nm and length 10-5000 nm with the aspect ratio is in the range of 2 to 45 measured in HR TEM image at 50nm magnification.

WE CLAIM:

1. A rubber composition for tyre inner liner, comprising of:

one or more rubbers – 100 phr;

reinforcing filler – 35 – 85phr;

nanofiller – 0.1 – 40 phr;

process aid – 1- 10 phr;

vulcanization activators – 2 – 10 phr;

vulcanization agent – 1 – 3.5 phr;

anti-degradants – 1 – 2 phr; and

primary accelerators – 1- 3 phr,

wherein the nanofiller is naturally occurring unmodified fuller's earth nanoclay with acicular particles in diameter 1 to 5 nm and length 10 – 5000 nm with the aspect ratio in the range between 5 and 45 measured in HR TEM image at 50 nm magnification.

2. The rubber composition for tyre inner liner as claimed in claim 1, wherein the rubbers are selected from natural rubber (NR), non-oil extended styrene butadiene rubber, poly butadiene rubber and combinations thereof.

3. The rubber composition for tyre inner liner as claimed in claim 1, wherein the reinforcing filler is carbon black.

4. The rubber composition for tyre inner liner as claimed in claim 1, wherein the processing aid is aromatic oil.

5. The rubber composition for tyre inner liner as claimed in claim 1, wherein the vulcanization activators are selected from zinc oxide, stearic acid and combinations thereof in a weight ratio of 2-5: 2-5 phr.

6. The rubber composition for tyre inner liner as claimed in claim 1, wherein the vulcanization agent is sulphur.

7. The rubber composition for tyre inner liner as claimed in claim 1, wherein the primary accelerator is CBS (N-cyclohexyl-2-benzothiazolesulfenamide).

8. The rubber composition for tyre inner liner as claimed in claim 1, wherein the anti-degradants are selected from TMQ-2,2,4-trimethyl-1,2-dihydroquinoline.

9. A tyre comprising an inner liner rubber composition as claimed in claim 1.

10. A method for preparation of rubber composition for tyre inner liner, comprising of steps:

preparation of master batch by:

initially mixing of rubbers;

mixing and reacting with reinforcing filler, nanofiller,

processing aid, vulcanization activators; anti-degradants;

sweeping down in the orifice, mixing and dumping of the rubber compound;

sheet out the rubber compound;

preparation of final batch by:

mixing and reacting of master batch compounds with vulcanization agent and primary accelerator and dumping at a temperature range of 85 degree Celsius and 110 degree Celsius; and

sheet out the rubber compound,

wherein the nanofiller is naturally occurring unmodified fuller's earth nanoclay with acicular particles in diameter range between 1 and 5 nm and length in the

range between 10 and 5000 nm with the aspect ratio is in the range between 5 and 45 measured in HR TEM image at 50 nm magnification, and

wherein the preparation of master batch is carried out in a temperature range between 85 degree Celsius and 90 degree Celsius.

Dated this 8th day of April 2021

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NAME OF THE APPLICANT: TVS SRICHAKRA LIMITED
PROVISIONAL SPECIFICATION NO.: 202041048775 dated November 09, 2020

A RUBBER COMPOSITION FOR A HIGHLY IMPERMEABLE TYRE INNERLINER AND METHOD THEREOF

ABSTRACT

The present invention provides a tyre inner liner nanocomposite and its method of preparation, capable of providing lower modulus, improved barrier and processability characteristics. The rubber composition of tyre inner liner includes 100 phr of rubber selected from natural rubber (NR), non-oil extended styrene butadiene rubber, poly butadiene rubber, reinforcing filler such as carbon black, naturally occurring, unmodified fuller's earth nanoclay. It further discloses a tyre comprising the inner liner nanocomposite.