IMPROVED NATURAL RUBBER COMPOSITIONS

Field of the Invention

The present invention relates to improved natural rubber compositions. More particularly, the present invention relates to improved natural rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the nanocarbon is uniformly pre-dispersed within the rubber component.

Background of the Invention

The rubber industry is the second largest industry in the world after iron and steel, with 92% of global supplies of natural rubber from Asia, and its major use in commercial terms relating to the manufacture of tyres with a recent projection of global demand to reach 3.3 billion units creating a market of $220 billion by 2012. As such, the drive to provide products for all sectors within this market, high-performance, heavy duty, automobile, truck, bus and such like is extremely high.

Following the discovery of nanosized carbon structures, also referred to as nanocarbon/nanotubes, and their unique combination of extraordinary strength, for example tensile strength greater than steel with only one sixth of its weight, and efficient heat conductivity properties, there has been great interest in using such materials, such as for example carbon nanotubes (CNTs) also sometimes referred to as buckytubes which are allotropes of carbon, as reinforcing agents in polymer structures.

It has been postulated that CNTs may have greater affinity, and therefore potential to improve strength, in unsaturated hydrocarbon-based polymer matrices, rather than saturated systems. Early studies by Qianet. al., Applied Physics Letters, 2000: 76(20), p. 2868-2870 confirmed that addition of relatively low amounts of CNTs to the unsaturated polystyrene polymer matrix led to significant improvements in tensile strength and stiffness and has contributed to the desire to incorporate CNTs into other polymer systems.

There are numerous publications relating to the utility of nanoparticles as reinforcing agents for various thermoplastic polymers but relatively few relating to the utility of nanocarbon in unsaturated hydrocarbon-based polymer natural rubber (NR), *cis*-polyisoprene.

It is thought that the combination of the specific nature of natural rubber and in particular it's inherent high viscosity, and the difficulties associated with delivering nanocarbon in particulate form into the desired mixing environment have made effective

incorporation, also referred to as dispersion, of nanocarbon into natural rubber a challenge. Thus it would be desirable to provide rubber compositions having nanocarbon dispersed within the rubber component(as a masterbatch) thereof.

Carbon black has been used as a reinforcing agentfor rubber products, and in particular to increase tread wear resistance for over a century. In the 1940s carbon black use was complemented by the introduction of highly active silicas. Carbon black or silicone-based materials (silicas or silanes) are now commonly used as reinforcing agents, or fillers, to improve the tensile strength and mechanical properties of rubber products, and in particular rubber for use in tyres. Carbon black is generally considered to be more effective for reinforcing rubber tyre treads than silica unless a coupling agent to enhance the bonding between the silica particles and the rubber is also used. Typically, tyres utilise relatively high levels of carbon black (20 – 50 parts per hundred rubber, pphr) depending upon the tyre type. As reported by Carretero-Gonzalez et al., "Effect of Nanoclay on Natural Rubber Microstructure", Macromolecules, 41 (2008), p6763, use of large amounts of such mineral fillers can lead to heavy final products and replacement with nanoparticles may have advantages for filler distribution within the rubber.

It has long been an objective in tyre design to provide a tyre which has desirable (low) rolling resistance whilst delivering desirable (high) wet grip and wear resistance. A proven approach to resolving this dichotomy has been to replace some (or all) of the carbon black reinforcing agent in the tyre tread with a silica reinforcing agent. This has resulted in tyres capable of higher performance, but with a correspondingly higher cost due to inclusion of the silica and coupling components.

It has also been proposed that nanomaterials, such as CNTs, may have potential as replacement mineral fillers because of their small size, high surface area and excellent aspect ratio. Abdul-Lateef et al., "Effect of MWSTs on the Mechanical and Thermal Properties of NR", The Arabian Journal for Science and Engineering, Vol 35, No. 1C, (2010), p 49, reported that tensile strength, elasticity and toughness were linearly improved with increasing levels of CNT.

WO 03/060002 disclosed rubber compositions comprising low-purity CNTs as potential replacement reinforcing agents for either all or part of the carbon black component and demonstrated that replacing an equivalent amount of the carbon black component with multi-walled, MWCNT, in a rubber composition suitable for use in tyres, led to improved tensile strength and elasticity.

~~It is an object of at least one aspect of the present invention to obviate or mitigate at~~ least one or more of the aforementioned problems.

It is a further object of at least one aspect of the present invention to provide improved natural rubber compositions having nanocarbon and carbon black as reinforcing agents suitable for use in vehicle tyres for the automotive industry.

Summary of the Invention

The Applicant has now developed a novel rubber composition suitable for use in tyres with nanocarbon and carbon black as reinforcing agents and which includes a unique ratio of rubber : nanocarbon : carbon black wherein the nanocarbon is uniformly pre-dispersed within the rubber component. The novel and inventive formulations developed by the Applicant provide both processing advantages such as longer cure time and performance advantages such as longer blow out time and low heat build-up in addition to demonstrating desirable physical properties such as tensile strength, hardness, elasticity, resilience and the like.

Until recently it has not yet been possible to fully explore and exploit the potential of nanocarbon as a rubber reinforcing agent due to dispersion associated difficulties in processing. The Applicant has also developed a novel process for the provision of masterbatches comprising nanocarbon pre-dispersed in rubber. Formulations according to the invention utilise such masterbatches for the rubber and nanocarbon component.

The Applicant has found that it is possible to provide rubber compositions, suitable for use in tyres, having improvements in wear abrasion and rolling resistance, reduced heat build-up (HBU) and longer blowout times, as well as providing desirable strength, hardness and resistance, when compared to conventional rubber compositions, by utilising particular mixtures of nanocarbon, uniformly pre-dispersed within natural rubber, and carbon black as reinforcing agents.

Thus, according to a first aspect of the present invention there is provided rubber compositions comprising a mixture of natural rubber, nanocarbon and carbon black wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component.

The present invention therefore provides rubber compositions having improved ~~thermal and heat resistance properties and desirable strength, hardness and reduced rolling~~

resistance as provided by utilising particular mixtures of nanocarbon, which has been uniformly pre-dispersed within natural rubber, and carbon black as reinforcing agents.

The relative ratio of nanocarbon to carbon black may be in the range of any of the following: about 1 : 30 to about 1 : 3; about 1 : 20 to about 1 : 5 or about 1 : 18 to about 1 : 6.

The relative ratio of nanocarbon to natural rubber may be in the range of any of the following: about 1 : 100 to about 8 : 100; about 2 : 100 to about 6 : 100; about 2 : 100 to about 5 : 100.

The rubber component may contain from about 1 to 10, about 1 to 8, about 1 to 6 or about 2 to 5 pphrnanocarbon.

The carbon black may be present at a level of from about 10 to 50 or about 20 to 40 pphr.

As detailed hereinbefore, it is an object of the compositions of the invention to provide rubber products, and in particular tyres having desirable physical characteristics such as to provide a tyre which has desirable (low) rolling resistance in combination with delivering desirable (high) wet grip and wear resistance. Surprisingly, the Applicant has now found that compositions of the invention achieve desirable resilience, and in particular desirable rolling resistance and wear resistance performance,in the absence of silica, or a silica-containing filler component, and of an optional, additional Si-coupling component. Specific embodiments of the present invention therefore do not contain any silica and Si-coupling agent.

Thus, according to a further aspect of the present invention there is provided rubber compositions comprising a mixture of natural rubber, nanocarbon and carbon black wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component and optionally wherein there is no silica or silica containing reinforcing components.

According to a further aspect there is provided rubber compositions as described hereinbefore wherein the reinforcing component does not contain silica or silica based agents.

~~According to a further aspect there is provided rubber compositions as described~~ hereinbefore wherein the reinforcing component consists of one or more carbon based agents.

According to a further aspect there is provided rubber compositions as described hereinbefore wherein nanocarbon and carbon black are the only reinforcing components.

Any natural sourced rubber product may be used in the compositions according to the invention including: unprocessed and processed latex products such as ammonia containing latex concentrates; RSS, ADS or crepes; TSR, SMR L, SMR CV; or speciality rubbers SP, MG, DP NR; or field grade (cup lump) rubber products such as TSR, SMR 10, SMR 20, SMR 10 CV, SMR 20 SV, SMR GP. Further examples of natural rubbers suitable for use herein include chemically modified natural rubber products including: epoxidized natural rubbers (ENRs) such as for example ENR 25 and ENR 50. For the avoidance of doubt, all references to rubber in relation to the compositions according to the invention are to natural rubber as defined herein.

Preferred for use in the compositions herein are rubbers from a masterbatch having a pre-determined amount of nanocarbon pre-dispersed therein wherein the rubber is produced from a latex concentrate such as for example high ammonia natural rubber (HA NR) or low ammonia natural rubber (LA NR) and especially HA NR.

Nanocarbon (NC) as defined herein relates to nanosized carbon structures and includes: all types of single, double, or multi-wall carbon nanotubes (CNTs) and mixtures thereof; carbon nanotubes (CNTs), all types of carbon nanofibres (CNFs) and mixtures thereof; all types of graphite nanofibres (GNFs) and mixtures thereof; and mixtures of different nanosized carbon structures. CNTs or GNFs suitable for use herein include for example helical, linear or branched type.

Any nanocarbon (NC) as defined herein may be used for the preparation of a rubber-nanocarbonmasterbatch according to the process outlined hereinafter. CNTs and GNFs are preferred. CNTs having a length of < 50 μm and/or an outer diameter of < 20nm are preferred and especially CNTs having a C-purity of > 85% and non-detectable levels of free amorphous carbon. The concentration of nanocarbon, and in particular CNT or GNF, pre-dispersed in the natural rubber masterbatchmay preferably be about 5g or less of nanocarbon per 100g of rubber. In other words the masterbatch may preferably contain no more than about 5 parts by weight (pphr) nanocarbon per 100 parts by weight of rubber. Masterbatches suitable for use herein may, for example, include from about 2 to about 5 ~~pphrnanocarbon. Preferred masterbatches for use may herein include: from about 2 toabout~~

~~-5 pphr CNT, preferably from about 2.5 to about 4.5 pphr CNT, more preferably from about 3~~ to about 4 pphr CNT; from about 2 to about 5 pphr PGNF, preferably from about 3 to about 5 pphr PGNF, more preferably from about 4 to about 5 pphrGNF; and mixtures thereof. Particularly preferred masterbatches include about 3 pphr CNF and about 5 pphrGNF.

Thus the present invention provides rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about from about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber componentwherein the rubber is produced from a HA NR latex concentrate

Typically, the nanocarbonmay be pre-dispersed into the natural rubber according to the process described in Malaysian Patent Application XXXXXX filing date YY/07/2012, the disclosures of which are incorporated herein by reference and in particular according to the specific process described at Example 1 (which is reproduced herein as Process Example).

Thus according to a second aspect of the present invention there is provided rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about from about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber componentand wherein said rubber component is from a masterbatch produced via:

(a) formation of an aqueous slurry containing a dispersion of nanocarbon, at a level of from about 2% to 10%by weight of the aqueous slurry, and a surfactant and optionally a stabiliser;

(b) grinding of the aqueous nanocarbon containing slurry;

(c) combination of the aqueous slurry with a natural rubber latex concentrate or diluted latex solution and mixing until a uniform mixture is obtained;

(d) coagulation of the mixture followed by aqueous washing, and removal of excess surfactant, water and excess optional stabilisers by coagulate squeezing or suitable ~~alternative method;~~

(e) formation of dried rubber nanocarbonmasterbatches by either direct drying of the coagulate from step (d) or by coagulate cutting to granulate size and subsequent drying

wherein the pH of the slurry and latex are similar or equivalent prior to combination, and wherein the pH of the nanocarbon may be adjusted using a suitable base to align it to the pH of the rubber latex.

Typically, the pH of the slurry and latex may be within about 2, 1 or 0.5 pH units prior to combination.

Moreover, the formation of the aqueous slurry may contain a dispersion of nanocarbon at a level of from about 3% to about 5% by weight of the aqueous slurry and a surfactant and optionally a stabiliser.

Any carbon black suitable for reinforcing natural rubber may be used in the formulations according to the invention. Examples of suitable carbon black include: super abrasion furnace (SAF N110); intermediate SAF IN220; high abrasion furnace (HAF N330); easy processing channel (EPC N300); fast extruding furnace (FEF N550); high modulus furnace (HMF N683); semi-reinforcing furnace (SRF N770); fine thermal (FT N880); and medium thermal (MT N990).

Carbon black may be included at a level of from about 10 pphr to 50 pphr; 20pphr to 40 pphr, preferably from 25 pphr to 35 pphr and preferably from 30 pphr to 35 pphr in compositions according to the invention. ISAF N220 is a preferred form of carbon black for use in compositions according to the invention. The Applicant has found that the compositions of the invention, which use it are possible to significantly reduce levels of carbon black, versus standard rubber compositions, as demonstrated in the Examples hereinafter, are capable of delivering both improvements in key processing attributes, such as for example cure time, as well as improvements in highly desirable performance attributes, such as for example increased blowout time, increased resilience. In particular the compositions of the invention include carbon black at from about 20% to less than about 40%, and preferably from about 25% to about 35% and more preferably from about 30% to about 35% of carbon black to 100% of rubber.

The Applicants has also found that particular combinations of reinforcing agents are valuable for the delivery of desirable properties in the compositions according to the invention. Such combinations are illustrated in the Examples hereinafter.

For the avoidance of doubt where amounts of any materials or components are referred to herein as pphr this means parts per hundred rubber.

Further agents which may be incorporated into the rubber compositions include: one or more curing agents; one or more activators; one or more delayed-accelerators; one or more antioxidants; one or more processing oils; one or more waxes; one or more scorch inhibiting agents; one or more processing aids; one or more tackifying resins; one or more reinforcing resins; one or more peptizers, and mixtures thereof.

Examples of suitable vulcanization agents for inclusion to the rubber compositions of the invention include sulphur or other equivalent "curatives". Vulcanization agents, also referred to as curing agents, modify the polymeric material (polyisoprene) in the natural rubber containing component to convert it into a more durable material for commercial utility, and may be included at a level of from about 1 pphr to about 4 pphr, preferably from about 1 pphr to about 3 pphr and preferably from about 1.5 pphr to about 2.5 pphr in formulations according to the invention. Sulphur is the preferred vulcanization agent for incorporation into the compositions according to the invention.

Examples of suitable vulcanization activating agentsfor inclusion to the rubber compositions of the invention include zinc oxide (ZnO), stearic acid (octadecanoic acid), stearic acid/palmitic acid mixture, or other suitable alternatives.It is thought that vulcanization activating agents essentially accelerate the vulcanization process by promoting the effectiveness of the curing agent. Vulcanization activating agents can be included at a total level of from about 2 pphr to about 10 pphr, preferably from about 3 pphr to about 7 pphr and preferably from about 4 pphr to about 6 pphr. Zinc oxide and stearic acid are preferred vulcanization activating agents for incorporation into the compositions according to the invention at individual levels of zinc oxide at a level of from about 1.5 pphr to about 6 pphr, preferably from about 2 pphr to about 4 pphr and preferably about 3 pphr and stearic acid at from about 0.5 pphr to about 4 pphr, preferably from about 1 pphr to about 3 pphr and preferably about 2 pphr.

Examples of suitable vulcanization delayed-acceleratorsfor inclusion in the rubber compositions of the invention include any one or combination of the following:N-tertiary-butyl-benzothiazole-sulphenamide (TBBS);2.2'-Dibenzothiazole Disulfide (MBTS); 2-(2,4-Dinitrophenylthio) benzothiazole (DNBT);Diethyldiphenylthiuram disulphide;Tetramethylthiuram disulphide;N,N-dicyclohexyl-2-benzothiazole sulfenamide (DCBS);N-oxydiethylenethiocarbamyl-N'-oxydiethylenesulphenamide (OTOS) and the like. It is thought that vulcanization delayed-accelerators essentially assist the vulcanization process by increasing the vulcanization rate at higher temperatures. Vulcanization delayed-accelerators agents can be included at a level of from about 0.5 pphr to about 3 pphr, preferably about 1 pphr toabout 2 pphr, and especially about 1.5 pphr. TBBS is preferred as

a vulcanization delayed-accelerator for incorporation into the compositions according to the invention.

Examples of suitable antioxidants for inclusion to the rubber compositions of the invention include any one of or combination of the following: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD);2-mercaptobenzimidazole compounds; 2-benzimidazolethiol;Dialkylateddiphenylamines;octylated diphenylamine; Nickel dibutyldithiocarbamate; N-isopropyl-N'-phenyl-p-phenylenediamine;4'-diphenyl-isopropyl-dianiline and 2,2'-Methylenebis(6-tert-butyl-4-methylphenol). Antioxidantscan be included at a level of from about 0.5 pphr to about 3 pphr, preferably from about 0.5 pphr to about 1.5 pphr, and especially about 1 pphr. 6PPD is preferred as antioxidant in the compositions according to the invention.

Examples of suitable processing oilsfor inclusion in the rubber compositions of the invention include napthanlenic oils such as Shellflex 250MB.Processing oils can be included at a level of from about 2 pphr to about 6 pphr, preferably from about 3 pphr to about 5 pphr, and especially about 4 pphr.Shellflex 250MB is preferred as processing oil in the compositions according to the invention.

Examples of suitable optional additional reinforcing agents for inclusion in the rubber compositions of the invention include one or more silicas and/orsilanes, such as for example: silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhodia, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2, VN3, VN3 GR; silanes commercially available from Evonik such as Si 363® and Si 69® (Bis[3-(triethoxysilyl)propyl]tetrasulfide). Where an optional, additional silica based reinforcing agent is used then a suitable coupling agent, such as a silane may also be included.

Additional agents which can be included into the compositions also include peptizers (e.g. AP - zincPentachlorobenzenethiol zinc, WP-1, HP).

The composition of the present invention may be used in a range of component parts of heavy vehicle tyres such as truck tyres, bus tyres,car tyres, aircraft tyres or tyres for an earth moving vehicle.

The composition of the present invention may therefore be used in a range of tyre components suitable for use in the manufacture of tyres for heavy duty vehicles, such as

~~truck or bus tyres, light duty vehicles, such as car tyres, vehicles for use in earth moving,~~ construction or engineering, civil engineering, or for use on aircraft.

The rubber composition of the present invention may also be used in any part of the tyre such as the tread, inner liner, sidewall and shoulder where the tread makes its transition to ~~the sidewall.~~

Detailed Description - Experimental Methods

The various physical properties of the compositions exemplified can be measured according to any of the standard methodologies as are known in the art. For example, onset of vulcanisation can be detected via an increase in viscosity as measured with a Mooney viscometer (V_c). Similarly viscosity measurements can be used to measure incipient cure (scorch) times and the rate of cure in early stage vulcanisation.In particular, cure characteristics can be measured using a rheometer such as a Monsanto Rheometer. These measurements can be made according to various internationally accepted standard methods ASTM D1616-07(2012) (http://www.astm.org/Standards/D1646.htm). Density (specific gravity), elasticity (M100, M300), tensile strength as measured according to (ISO 37) ASTM D412-06ae2 (http://www.astm.org/Standards/D412.htm).Elongation at break (EB) as measurable by the method described in http://www.scribd.com/doc/42956316/Rubber-Testing.Hardness (International Rubber Hardness Degree, IRHD) as measured according to (ISO 48) ASTM D1415-06(2012) (http://www.astm.org/Standards/D1415.htm).Resilience (%)as measured according to ASTM D7121-05 (http://www.astm.org/Standards/D7121.htm). Abrasion resistance index (ARI), tan delta as measurable by the methods described in (http://findarticles.com/p/articles/mi_hb6620/is_5_241/ai_n53029843/).

Heat build-up and blowout as measurable by the methods described in http://www.dtic.mil/dtic/tr/fulltext/u2/a193058.pdf.

Process Example

As described hereinbefore, nanocarbon may be pre-dispersed into the natural rubber according to the process described in Malaysian Patent Application XXX filing date YY/07/2012. Masterbatches suitable for use in the compositions according to the invention have levels of pre-dispersed nanocarbon contained within the rubber component produced according to this process of from about 1 to 10, about 1 to 8, about 1 to 6 or about 2 to 5 pphrnanocarbon. Process Example 1 illustrates the production of a 2pphr masterbatch. Masterbatches containing other nanocarbon levels can be made via appropriate adjustment of the components.

Part 1 - PreparationofNanocarbonSlurryandNanocarbonDispersion

A 1%nanocarbondispersionwaspreparedas follows:3gofnanocarbonwasputintoa glassbeaker(500ml)containing15gofasurfactantand282gofdistilledwater.The mixturewasstirredbymeansof mechanicalstirrerat80rpmforabout10minutesto

obtainananocarbonslurry.Theslurry wastransferredtoaballmillforgrindingtobreak downany agglomeratesofnanocarbon.Ballmillingwasdonefor24hourstoobtaina nanocarbondispersion,whichwasthentransferredintoaplasticcontainer. Thesurfactantwasusedintheformofa10%to20%solution.

Inananalogousmanner,a3%nanocarbondispersionwaspreparedfrom9gof nanocarbon,45gofsurfactantand246gofdistilledwater. ThepHofdispersionwasadjusted(byaddingKOH)tothatofthelatextowhichitwasto beadded.

Part 2 - PreparationofNanocarbon-ContainingNaturalRubberMasterBatches

Thenanocarbondispersionpreparedasdescribedabovewasmixedwithhighammonia naturalrubberlatexconcentrate(HANRlatex).Thelatexconcentratewasfirstdilutedwithdistilledwa tertoreduceitsconcentrationinordertoreducetheviscosityofthelatexto facilitatemixingwiththenanocarbondispersion.Themixingwiththenanocarbon dispersionwasthendoneinthepresenceofabout5pphrofsurfactant(employedasa 5%to20%solution).

Thenanocarbondispersionandthesurfactantweredischargedintoabeakercontaining thenaturalrubber(NR)latex.Themixturewassubjectedtomechanicalstirring. TheNRlatexwasthencoagulatedwithaceticacid.Thecoagulumformed waswashedwithwaterandsqueezedtoremoveexcess surfactantsandwater.Thecoagulumwascutintosmallgranulesandwashedwithwater.Thesegran uleswerethendriedinanelectricallyheatedovenuntiltheywerefullydriedtoobtainananocarbon-containingnaturalrubbermasterbatch.

Theamountofnanocarboninthedispersionandtheamountofthedispersionandthe latexarechosensoastoobtainapredeterminedratioofnanocarbontorubber (expressedhereinintermsofpphr).Morespecificallythemasterbatch contained 2pphrofnanocarbon.

The following non-limiting examples are representative of the compositions of the invention.

Example Formulations 1 to 5

Formulations 1 to 5 are suitable for use in heavy duty vehicular applications such as truck and bus tyre treads.

Formulations 3 to 5 are representative of the compositions of the invention and formulations 1 and 2 are comparative examples based upon a commercially available Standard Malaysian Rubber (SMR10). All components are expressed as pphr rubber, for example CNT MB 103 means that there are 3 pphr of CNT in 100 parts of rubber masterbatch MB (dried NR latex) and stearic acid "2" means that there are 2 parts of stearic acid per 100 parts of rubber.

Ingredients	**1**	**2**	**3**	**4**	**5**
Rubber, SMR10	100	100	-	-	-
Rubber-CNT MB	-	-	*103	-	-
Rubber-CNT MB	-	-	-	*105	**105
Activator, Zinc oxide	3	3	3	3	3
Activator, Stearic acid	2	2	2	2	2
Antioxidant, 6PPD	1	1	1	1	1
Carbon Black, N220	52	40	35	30	30
Oil, Shellflex 250MB	4	4	4	4	4
Accelerator, TBBS	1.4	1.4	1.4	1.4	1.4
Curing agent, Sulfur	1.5	1.5	1.5	1.5	1.5
Reinforcer, Silica (VN3)	-	12	-	-	-
Silica coupling agent, Si69	-	1.0	-	-	-
Polyethylene glycol, PEG	-	0.5	-	-	-

* Carbon nanotubes havingalengthof havingalengthof <50μmandanouterdiameterof<20nm;ithadaC-purityof>85%andnon-detectable free amorphous carbon.Employedas suppliedi.e.asagglomeratedbundlesofCNTswithaveragedimensionsof0.05to1.5mm.

** GNF, platelet graphite nanofibers

Experimental Results

As illustrated in Table 1, the uncured rubber compositions according to the invention were demonstrated to have lower Mooney viscosity and improved cure times compared to that of comparator compositions 1 and 2.

TABLE 1

Properties related to Curing	1	2	3	4	5
V_c (M_L (1+4), 100°C)	62.3	66.1	38.4	54.3	34.4
Scorch time, t2 (minutes) at 150°C	2.6	2.5	2.5	2	2.3
Cure time, t95 (minutes) at 150°C	8	8.4	11.5	12	12

As illustrated in Table 2, all cured formulations according to the invention demonstrated improved blowout time versus comparator formulation 1, and, a cured formulation according to the invention demonstrated improved thermal and blow out properties, when compared to the comparator formulations. All the formulations according to the invention demonstrate either the same as, or lower Tan δ values than Comparator Formula 2 which indicates that formulations of the invention are capable of delivering desirable low rolling resistance performance without the use of silica. Formulation 5 delivered improved (higher) resilience than comparator formula 2 which is a yet further indicator of the desirable rolling resistance performance achievable by formulations according to the invention. All formulations according the invention demonstrated improved ARI values versus Comparator formula 1 and either comparable or improved values, versus Comparator Formula 2 which is an indication of their ability to provide desirable wear performance without the use of a silica reinforcing agent.

TABLE 2

Property	1	2	3	4	5
Elongation at break, EB (%)	569	584	523	523	532
Resilience (%)	58	63	57	61	70
tan δ (°) at 60°C	0.11	0.09	0.09	0.09	0.07
Abrasion Resistance Index, ARI (%)	103.9	108.1	109	114	107
Heat build-up, HBU, at 55°C (minutes)	20.4	16	20.4	20.4	13.5
Blowout time at 100°C (minutes)	11.0	Not tested	24	14.0	60

Resilience is an important property of tread rubber compound since it affects rolling resistance and heat build-up. The higher the resilience, the lower the rolling resistance and

heat build-up (HBU). The lower the rolling resiliance the less fuel is required to propel the vehicle forward. Formulations 4 and 5 demonstrated the highest resilience.

Tan δ is a measure of rolling resistance of a rubber compound. Formulations 5 gave the lowest rolling resistance.

Abrasion resistance (ARI) is a measure of associated with potential wear resistance of tyre treads.

Heat build-up (HBU) is an important property in tyre tread formulations. Failure known as blowout occurs in the shoulder region of the tread if excessive HBU is generated in the shoulder region. Formulation 5 gave the lowest HBU.

Formulations 3, 4 and 5 all took longer time to blowout than the comparator formulation 1. The longer the time it takes for blowout failure to occur, the longer is the service life and the safer is the tyre.

As illustrated in Table 3, formulations of the invention display desirable strength and hardness properties.

TABLE 3

Physical Property	1	2	3	4	5
Density ($Mgcm^{-3}$)	1.1138	1.1206	1.0891	-	1.0807
M100 (MPa)	2.4	2.2	2.93	2.93	2.09
M300 (MPa)	12.6	11.7	12.17	12.2	10.6
Tensile strength (MPa)	29.4	29.0	29.0	28.0	27.0
Elongation at Break (%)	569	584	523	523	532
Hardness (IRHD)	69	64	74	74	64

Whilst specific embodiments of the present invention have been described above, it will be appreciated that departures from the described embodiments may still fall within the scope of the present invention. For example, any suitable type of nanoparticle and carbon black may be used. Moreover, any type of natural rubber may be used.

Claims

1. A rubber composition comprising a mixture of natural rubber, nanocarbon and carbon black reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component.

2. A rubber composition according to claim 1, wherein the relative ratio of nanocarbon to carbon black in pphr is in the range of any of the following: about 1 : 30 to about 1 : 3; about 1 : 20 to about 1 : 5 or about 1 : 18 to about 1 : 6.

3. A rubber composition according to any of claims 1 or 2, wherein the relative ratio of nanocarbon to natural rubber in pphr isin the range of any of the following: about 1 : 100 to about 8 : 100; about 2 : 100 to about 6 : 100 or about 2 : 100 to about 5 : 100.

4. A rubber composition according to any preceding claim, wherein the rubber component contains from about 1 to 10, about 1 to 8, about 1 to 6 or about 2 to 5 pphrnanocarbon.

5. A rubber composition according to any preceding claim, wherein carbon black is present at a level of fromabout 10 to 50 or about 20 to 40 pphr.

6. A rubber composition according to any preceding claim, wherein nanocarbon and carbon black are the only reinforcing agents.

7. A rubber composition according to any preceding claim, wherein there is no silica and Si-coupling agent.

8. A rubber composition according to any preceding claim, wherein the natural rubber is selected from any one of or combination of the following: unprocessed and processed latex products such as ammonia containing latex concentrates; RSS, ADS or crepes; TSR, SMR L, SMR CV; speciality rubbers SP, MG, DP NR; or field grade (cup lump) rubber products such as TSR, SMR 10, SMR 20, SMR 10 CV, SMR 20 SV, SMR GP.

9. A rubber composition according to any preceding claim, wherein the natural rubber is selected from chemically modified natural rubber products including: epoxidized natural rubbers (ENRs) such as for example ENR 25 and ENR 50.

10. A rubber composition according to any preceding claim containing a vulcanizing agent.

11. A rubber composition according to any preceding claim containing one or more delaying accelerators.

12. A composition according to any preceding claim containing one or more activating agents.

13. A rubber composition according to any preceding claim containing one or more antioxidants.

14. A tyre comprising at least one component part made from a rubber composition as defined in any of claims 1 to 13.

15. A tyre according to claim 14, wherein the rubber composition as defined in any of claims 1 to 13 is used in the tread of the tyre.

16. A tyre according to claim 14, wherein the rubber composition as defined in any of claims 1 to 13 is used in tyre components such as the inner liner, sidewall and shoulder where the tread makes its transition to the sidewall.

17. A tyre according to any of claims 14 to 16, wherein the tyre is a heavy vehicle tyre such as a truck tyre, a bus tyre, a car tyre, an aircraft tyre or a tyre for an earth moving vehicle.

18. Use of a rubber composition according to any claims 1 to 11 for in the manufacture of component parts for tyres such as the treads,inner liner, sidewall and shoulder where the tread makes its transition to the sidewall.

19. A rubber composition having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about from about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber componentand wherein said rubber component is from a masterbatch produced via:

(a) formation of an aqueous slurry containing a dispersion of nanocarbon, at a level of from about 2% to 10%by weight of the aqueous slurry, and a surfactant and optionally a stabiliser;

(b) grinding of the aqueous nanocarbon containing slurry;

(c) combination of the aqueous slurry with a natural rubber latex concentrate or diluted latex solution and mixing until a uniform mixture is obtained;

(d) coagulation of the mixture followed by aqueous washing, and removal of excess surfactant, water and excess optional stabilisers by coagulate squeezing or suitable alternative method;

~~(e) formation of dried rubber nanocarbonmasterbatches by either direct drying of~~ the coagulate from step (d) or by coagulate cutting to granulate size and subsequent drying;

wherein the pH of the slurry and latex are similar or equivalent prior to combination, and wherein the pH of the nanocarbon may be adjusted using a suitable base to align it to the pH of the rubber latex.

20. A rubber composition according to claim 15, wherein the formation of the aqueous slurry contains a dispersion of nanocarbon at a level of from about 3% to 5% by weight of the aqueous slurry and a surfactant and optionally a stabiliser.

~~21. A rubber composition according to any of claims 15 and 16, wherein the pH of the slurry and latex are within about 2, 1 or 0.5 pH units prior to combination.~~

IMPROVED NATURAL RUBBER COMPOSITIONS

Field of the Invention

The present invention relates to improved natural rubber compositions. More particularly, the present invention relates to improved natural rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the nanocarbon is uniformly pre-dispersed within the rubber component.

Background of the Invention

The rubber industry is the second largest industry in the world after iron and steel, with 92% of global supplies of natural rubber from Asia, and its major use in commercial terms relating to the manufacture of tyres with a recent projection of global demand to reach 3.3 billion units creating a market of $220 billion by 2012. As such, the drive to provide products for all sectors within this market, high-performance, heavy duty, automobile, truck, bus and such like is extremely high.

Following the discovery of nanosized carbon structures, also referred to as nanocarbon/nanotubes, and their unique combination of extraordinary strength, for example tensile strength greater than steel with only one sixth of its weight, and efficient heat conductivity properties, there has been great interest in using such materials, such as for example carbon nanotubes (CNTs) also sometimes referred to as buckytubes which are allotropes of carbon, as reinforcing agents in polymer structures.

It has been postulated that CNTs may have greater affinity, and therefore potential to improve strength, in unsaturated hydrocarbon-based polymer matrices, rather than saturated systems. Early studies by Qianet. al., Applied Physics Letters, 2000: 76(20), p. 2868-2870 confirmed that addition of relatively low amounts of CNTs to the unsaturated polystyrene polymer matrix led to significant improvements in tensile strength and stiffness and has contributed to the desire to incorporate CNTs into other polymer systems.

There are numerous publications relating to the utility of nanoparticles as reinforcing agents for various thermoplastic polymers but relatively few relating to the utility of nanocarbon in unsaturated hydrocarbon-based polymer natural rubber (NR), cis-polyisoprene.

It is thought that the combination of the specific nature of natural rubber and in particular

it's inherent high viscosity, and the difficulties associated with delivering nanocarbon in particulate form into the desired mixing environment have made effective incorporation, also referred to as dispersion, of nanocarbon into natural rubber a challenge. Thus it would be desirable to provide rubber compositions having nanocarbon dispersed within the rubber component (as a masterbatch) thereof.

Carbon black has been used as a reinforcing agent for rubber products, and in particular to increase tread wear resistance for over a century. In the 1940s carbon black use was complemented by the introduction of highly active silicas. Carbon black or silicone-based materials (silicas or silanes) are now commonly used as reinforcing agents, or fillers, to improve the tensile strength and mechanical properties of rubber products, and in particular rubber for use in tyres. Carbon black is generally considered to be more effective for reinforcing rubber tyre treads than silica unless a coupling agent to enhance the bonding between the silica particles and the rubber is also used. Typically, tyres utilise relatively high levels of carbon black (20 - 50 parts per hundred rubber, pphr) depending upon the tyre type. As reported by Carretero-Gonzalez et al., "Effect of Nanoclay on Natural Rubber Microstructure", Macromolecules, 41 (2008), p6763, use of large amounts of such mineral fillers can lead to heavy final products and replacement with nanoparticles may have advantages for filler distribution within the rubber.

It has long been an objective in tyre design to provide a tyre which has desirable (low) rolling resistance whilst delivering desirable (high) wet grip and wear resistance. A proven approach to resolving this dichotomy has been to replace some (or all) of the carbon black reinforcing agent in the tyre tread with a silica reinforcing agent. This has resulted in tyres capable of higher performance, but with a correspondingly higher cost due to inclusion of the silica and coupling components.

It has also been proposed that nanomaterials, such as CNTs, may have potential as replacement mineral fillers because of their small size, high surface area and excellent aspect ratio. Abdul-Lateef et al., "Effect of MWSTs on the Mechanical and Thermal Properties of NR", The Arabian Journal for Science and Engineering, Vol 35, No. 1 C, (2010), p 49, reported that tensile strength, elasticity and toughness were linearly improved with increasing levels of CNT.

WO 03/060002 disclosed rubber compositions comprising low-purity CNTs as potential replacement reinforcing agents for either all or part of the carbon black component and demonstrated that replacing an equivalent amount of the carbon black component with multi-

walled, MWCNT, in a rubber composition suitable for use in tyres, led to improved tensile strength and elasticity.

It is an object of at least one aspect of the present invention to obviate or mitigate at least one or more of the aforementioned problems.

It is a further object of at least one aspect of the present invention to provide improved natural rubber compositions having nanocarbon and carbon black as reinforcing agents suitable for use in vehicle tyres for the automotive industry.

Summary of the Invention

The Applicant has now developed a novel rubber composition suitable for use in tyres with nanocarbon and carbon black as reinforcing agents and which includes a unique ratio of rubber : nanocarbon : carbon black wherein the nanocarbon is uniformly pre-dispersed within the rubber component. The novel and inventive formulations developed by the Applicant provide both processing advantages such as longer cure time and performance advantages such as longer blow out time and low heat build-up in addition to demonstrating desirable physical properties such as tensile strength, hardness, elasticity, resilience and the like.

Until recently it has not yet been possible to fully explore and exploit the potential of nanocarbon as a rubber reinforcing agent due to dispersion associated difficulties in processing. The Applicant has also developed a novel process for the provision of masterbatches comprising nanocarbon pre-dispersed in rubber. Formulations according to the invention utilise such masterbatches for the rubber and nanocarbon component.

The Applicant has found that it is possible to provide rubber compositions, suitable for use in tyres, having improvements in wear abrasion and rolling resistance, reduced heat build-up (HBU) and longer blowout times, as well as providing desirable strength, hardness and resistance, when compared to conventional rubber compositions, by utilising particular mixtures of nanocarbon, uniformly pre-dispersed within natural rubber, and carbon black as reinforcing agents.

Thus, according to a first aspect of the present invention there is provided rubber compositions comprising a mixture of natural rubber, nanocarbon and carbon black wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of

nanocarbon to natural rubber is in the range of about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component.

The present invention therefore provides rubber compositions having improved thermal and heat resistance properties and desirable strength, hardness and reduced rolling- resistance as provided by utilising particular mixtures of nanocarbon, which has been uniformly pre-dispersed within natural rubber, and carbon black as reinforcing agents.

The relative ratio of nanocarbon to carbon black may be in the range of any of the following: about 1 : 30 to about 1 : 3; about 1 : 20 to about 1 : 5 or about 1 : 18 to about 1 : 6.

The relative ratio of nanocarbon to natural rubber may be in the range of any of the following: about 1 : 100 to about 8 : 100; about 2 : 100 to about 6 : 100; about 2 : 100 to about 5 : 100.

The rubber component may contain from about 1 to 10, about 1 to 8, about 1 to 6 or about 2 to 5 pphr nanocarbon.

The carbon black may be present at a level of from about 10 to 50 or about 20 to 40 pphr.

As detailed hereinbefore, it is an object of the compositions of the invention to provide rubber products, and in particular tyres having desirable physical characteristics such as to provide a tyre which has desirable (low) rolling resistance in combination with delivering desirable (high) wet grip and wear resistance. Surprisingly, the Applicant has now found that compositions of the invention achieve desirable resilience, and in particular desirable rolling resistance and wear resistance performance, in the absence of silica, or a silica-containing filler component, and of an optional, additional Si-coupling component. Specific embodiments of the present invention therefore do not contain any silica and Si-coupling agent.

Thus, according to a further aspect of the present invention there is provided rubber compositions comprising a mixture of natural rubber, nanocarbon and carbon black wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component and optionally wherein there is no silica or silica containing reinforcing components.

According to a further aspect there is provided rubber compositions as described hereinbefore wherein the reinforcing component does not contain silica or silica based agents.

According to a further aspect there is provided rubber compositions as described hereinbefore wherein the reinforcing component consists of one or more carbon based agents.

According to a further aspect there is provided rubber compositions as described hereinbefore wherein nanocarbon and carbon black are the only reinforcing components.

Any natural sourced rubber product may be used in the compositions according to the invention including: unprocessed and processed latex products such as ammonia containing latex concentrates; RSS, ADS or crepes; TSR, SMR L, SMR CV; or speciality rubbers SP, MG, DP NR; or field grade (cup lump) rubber products such as TSR, SMR 10, SMR 20, SMR 10 CV, SMR 20 SV, SMR GP. Further examples of natural rubbers suitable for use herein include chemically modified natural rubber products including: epoxidized natural rubbers (ENRs) such as for example ENR 25 and ENR 50. For the avoidance of doubt, all references to rubber in relation to the compositions according to the invention are to natural rubber as defined herein.

Preferred for use in the compositions herein are rubbers from a masterbatch having a pre-determined amount of nanocarbon pre-dispersed therein wherein the rubber is produced from a latex concentrate such as for example high ammonia natural rubber (HA NR) or low ammonia natural rubber (LA NR) and especially HA NR.

Nanocarbon (NC) as defined herein relates to nanosized carbon structures and includes: all types of single, double, or multi-wall carbon nanotubes (CNTs) and mixtures thereof; carbon nanotubes (CNTs), all types of carbon nanofibres (CNFs) and mixtures thereof; all types of graphite nanofibres (GNFs) and mixtures thereof; and mixtures of different nanosized carbon structures. CNTs or GNFs suitable for use herein include for example helical, linear or branched type.

Any nanocarbon (NC) as defined herein may be used for the preparation of a rubber-nanocarbon masterbatch according to the process outlined hereinafter. CNTs and GNFs are preferred. CNTs having a length of < 50 pm and/or an outer diameter of < 20nm are preferred and especially CNTs having a C-purity of > 85% and non-detectable levels of free amorphous carbon. The concentration of nanocarbon, and in particular CNT or GNF, pre-dispersed in the natural rubber masterbatch may preferably be about 5 g or less of nanocarbon per 100g of rubber. In other words the masterbatch may preferably contain no more than about 5 parts by weight (pphr) nanocarbon per 100 parts by weight of rubber. Masterbatches suitable for use herein may, for example, include from about 2 to about 5 pphr nanocarbon. Preferred

masterbatches for use may herein include: from about 2 to about 5 pphr CNT, preferably from about 2.5 to about 4.5 pphr CNT, more preferably from about 3 to about 4 pphr CNT; from about 2 to about 5 pphr PGNF, preferably from about 3 to about 5 pphr PGNF, more preferably from about 4 to about 5 pphr GNF; and mixtures thereof. Particularly preferred masterbatches include about 3 pphr CNF and about 5 pphr GNF.

Thus the present invention provides rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about from about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component wherein the rubber is produced from a HA NR latex concentrate

Typically, the Nanocarbon may be pre-dispersed into the natural rubber according to the process described in Malaysian Patent Application XXXXXX filing date YY/07/2012, the disclosures of which are incorporated herein by reference and in particular according to the specific process described at Example 1 (which is reproduced herein as Process Example).

Thus according to a second aspect of the present invention there is provided rubber compositions having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of about from about 1 : 40 to about 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from about 1 : 100 to about 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component and wherein said rubber component is from a masterbatch produced via:

(a) formation of an aqueous slurry containing a dispersion of nanocarbon, at a level of from about 2% to 10%by weight of the aqueous slurry, and a surfactant and optionally a stabiliser;

(b) grinding of the aqueous nanocarbon containing slurry;

(c) combination of the aqueous slurry with a natural rubber latex concentrate or diluted latex solution and mixing until a uniform mixture is obtained;

(d) coagulation of the mixture followed by aqueous washing, and removal of excess surfactant, water and excess optional stabilisers by coagulate squeezing or suitable alternative

method;

(e) formation of dried rubber Nanocarbon masterbatches by either direct drying of the coagulate from step (d) or by coagulate cutting to granulate size and subsequent drying

wherein the pH of the slurry and latex are similar or equivalent prior to combination, and wherein the pH of the nanocarbon may be adjusted using a suitable base to align it to the pH of the rubber latex.

Typically, the pH of the slurry and latex may be within about 2, 1 or 0.5 pH units prior to combination.

Moreover, the formation of the aqueous slurry may contain a dispersion of nanocarbon at a level of from about 3% to about 5% by weight of the aqueous slurry and a surfactant and optionally a stabiliser.

Any carbon black suitable for reinforcing natural rubber may be used in the formulations according to the invention. Examples of suitable carbon black include: super abrasion furnace (SAF N110); intermediate SAF IN220; high abrasion furnace (HAF N330); easy processing channel (EPC N300); fast extruding furnace (FEF N550); high modulus furnace (HMF N683); semi-reinforcing furnace (SRF N770); fine thermal (FT N880); and medium thermal (MT N990).

Carbon black may be included at a level of from about 10 pphr to 50 pphr; 20 pphr to 40 pphr, preferably from 25 pphr to 35 pphr and preferably from 30 pphr to 35 pphr in compositions according to the invention. ISAF N220 is a preferred form of carbon black for use in compositions according to the invention. The Applicant has found that the compositions of the invention, which use it are possible to significantly reduce levels of carbon black, versus standard rubber compositions, as demonstrated in the Examples hereinafter, are capable of delivering both improvements in key processing attributes, such as for example cure time, as well as improvements in highly desirable performance attributes, such as for example increased blowout time, increased resilience. In particular the compositions of the invention include carbon black at from about 20% to less than about 40%, and preferably from about 25% to about 35% and more preferably from about 30% to about 35% of carbon black to 100% of rubber.

The Applicants has also found that particular combinations of reinforcing agents are valuable for the delivery of desirable properties in the compositions according to the invention. Such combinations are illustrated in the Examples hereinafter.

For the avoidance of doubt where amounts of any materials or components are referred to

herein as pphr this means parts per hundred rubber.

Further agents which may be incorporated into the rubber compositions include: one or more curing agents; one or more activators; one or more delayed-accelerators; one or more antioxidants; one or more processing oils; one or more waxes; one or more scorch inhibiting agents; one or more processing aids; one or more tackifying resins; one or more reinforcing resins; one or more peptizers, and mixtures thereof.

Examples of suitable vulcanization agents for inclusion to the rubber compositions of the invention include sulphur or other equivalent "curatives". Vulcanization agents, also referred to as curing agents, modify the polymeric material (polyisoprene) in the natural rubber containing component to convert it into a more durable material for commercial utility, and may be included at a level of from about 1 pphr to about 4 pphr, preferably from about 1 pphr to about 3 pphr and preferably from about 1.5 pphr to about 2.5 pphr in formulations according to the invention. Sulphur is the preferred vulcanization agent for incorporation into the compositions according to the invention.

Examples of suitable vulcanization activating agents for inclusion to the rubber compositions of the invention include zinc oxide (ZnO), stearic acid (octadecanoic acid), stearic acid/palmitic acid mixture, or other suitable alternatives. It is thought that vulcanization activating agents essentially accelerate the vulcanization process by promoting the effectiveness of the curing agent. Vulcanization activating agents can be included at a total level of from about 2 pphr to about 10 pphr, preferably from about 3 pphr to about 7 pphr and preferably from about 4 pphr to about 6 pphr. Zinc oxide and stearic acid are preferred vulcanization activating agents for incorporation into the compositions according to the invention at individual levels of zinc oxide at a level of from about 1.5 pphr to about 6 pphr, preferably from about 2 pphr to about 4 pphr and preferably about 3 pphr and stearic acid at from about 0.5 pphr to about 4 pphr, preferably from about 1 pphr to about 3 pphr and preferably about 2 pphr.

Examples of suitable vulcanization delayed-accelerators for inclusion in the rubber compositions of the invention include any one or combination of the following: N-tertiary-butyl-benzothiazole-sulphenamide (TBBS); 2.2-Dibenzothiazole Disulfide (MBTS); 2-(2,4-Dinitrophenylthio) benzothiazole (DNBT); Diethyldiphenylthiuram disulphide; Tetramethylthiuram disulphide;N,N-dicyclohexyl-2-benzothiazole sulfenamide (DCBS);N-oxydiethylenethiocarbamyl-N-oxydiethylene sulphenamide (OTOS) and the like. It is thought

that vulcanization delayed-accelerators essentially assist the vulcanization process by increasing the vulcanization rate at higher temperatures. Vulcanization delayed-accelerators agents can be included at a level of from about 0.5 pphr to about 3 pphr, preferably about 1 pphr to about 2 pphr, and especially about 1.5 pphr. TBBS is preferred as a vulcanization delayed-accelerator for incorporation into the compositions according to the invention.

Examples of suitable antioxidants for inclusion to the rubber compositions of the invention include any one of or combination of the following: N-(1 ,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD); 2-mercaptobenzimidazole compounds; 2-benzimidazolethiol; Dialkylated diphenylamines; octylated diphenylamine; Nickel dibutyldithiocarbamate; N-isopropyl-N'-phenyl-p-phenylenediamine; 4'-diphenyl-isopropyl-dianiline and 2,2'-Methylenebis(6-tert-butyl-4-methylphenol). Antioxidants can be included at a level of from about 0.5 pphr to about 3 pphr, preferably from about 0.5 pphr to about 1.5 pphr, and especially about 1 pphr. 6PPD is preferred as antioxidant in the compositions according to the invention.

Examples of suitable processing oils for inclusion in the rubber compositions of the invention include napthanlenic oils such as Shellflex 250MB. Processing oils can be included at a level of from about 2 pphr to about 6 pphr, preferably from about 3 pphr to about 5 pphr, and especially about 4 pphr. Shellflex 250MB is preferred as processing oil in the compositions according to the invention.

Examples of suitable optional additional reinforcing agents for inclusion in the rubber compositions of the invention include one or more silicas and/or silanes, such as for example: silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhodia, with, for example, designations of Z1 165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2, VN3, VN3 GR; silanes commercially available from Evonik such as Si 363® and Si 69® (Bis[3-(triethoxysilyl)propyl]tetrasulfide). Where an optional, additional silica based reinforcing agent is used then a suitable coupling agent, such as a silane may also be included.

Additional agents which can be included into the compositions also include peptizers (e.g. AP – zinc Pentachlorobenzenethiol zinc, WP-1, HP).

The composition of the present invention may be used in a range of component parts of heavy vehicle tyres such as truck tyres, bus tyres, car tyres, aircraft tyres or tyres for an earth moving vehicle.

The composition of the present invention may therefore be used in a range of tyre components suitable for use in the manufacture of tyres for heavy duty vehicles, such astruck or bus tyres, light duty vehicles, such as car tyres, vehicles for use in earth moving, construction or engineering, civil engineering, or for use on aircraft.

The rubber composition of the present invention may also be used in any part of the tyre such as the tread, inner liner, sidewall and shoulder where the tread makes its transition to the sidewall.

Detailed Description - Experimental Methods

The various physical properties of the compositions exemplified can be measured according to any of the standard methodologies as are known in the art. For example, onset of vulcanisation can be detected via an increase in viscosity as measured with a Mooney viscometer (V_c). Similarly viscosity measurements can be used to measure incipient cure (scorch) times and the rate of cure in early stage vulcanisation. In particular, cure characteristics can be measured using a rheometer such as a Monsanto Rheometer. These measurements can be made according to various internationally accepted standard methods ASTM D1616-07(2012) (http://www.astm.org/Standards/D1646.htm). Density (specific gravity), elasticity (M100, M300), tensile strength as measured according to (ISO 37) ASTM D412-06ae2 (http://www.astm.org/Standards/D412.htm).EIongation at break (EB) as measurable by the method described in http://www.scribd.com/doc/42956316/Rubber-Testing. Hardness (International Rubber Hardness Degree, IRHD) as measured according to (ISO 48) ASTM D1415-06(2012) (http://www.astm.org/Standards/D1415.htm).Resilience (%) as measured according to ASTM D7121-05 (http://www.astm.org/Standards/D7121 .htm). Abrasion resistance index (ARI), tan delta as measurable by the methods described in (http://findarticles.eom/p/articles/mi_hb6620/is_5_241/ai_n53029843/).

Heat build-up and blowout as measurable by the methods described in http://www.dtic.mil/dtic/tr/fulltext/u2/a193058.pdf.

Process Example

As described hereinbefore, nanocarbon may be pre-dispersed into the natural rubber according to the process described in Malaysian Patent Application XXX filing date YY/07/2012. Masterbatches suitable for use in the compositions according to the invention have

levels of pre-dispersed nanocarbon contained within the rubber component produced according to this process of from about 1 to 10, about 1 to 8, about 1 to 6 or about 2 to 5 pphr nanocarbon. Process Example 1 illustrates the production of a 2pphr masterbatch. Masterbatches containing other nanocarbon levels can be made via appropriate adjustment of the components.

Part 1 – Preparation of Nanocarbon Slurry and Nanocarbon Dispersion

A 1 % nanocarbon dispersion was prepared as follows:

3g of Nanocarbon was put into a glass beaker (500ml) containing 15 g of a surfactant and 282 g of distilled water. The mixture was stirred by means of mechanical stirrer at 80 rpm for about 10minutes to obtain a Nanocarbon slurry. The slurry was transferred to a ball mill for grinding to break down any agglomerates of nanocarbon.

Ball milling was done for 24 hours to obtain a Nanocarbon dispersion which was then transferred into a plastic container.

The surfactant was used in the form of a 10% to 20%solution.

In an analogous manner, a 3% Nanocarbon dispersion was prepared from 9g of nanocarbon, 45 g of surfactant and 246 g of distilled water.

The pH of dispersion was adjusted (by adding KOH) to that of the latex to which it was to be added.

Part 2 – Preparation of Nanocarbon-Containing Natural Rubber Master Batches

The Nanocarbon dispersion prepared as described above was mixed with high ammonia natural rubber latex concentrate (HA NR latex). The latex concentrate was first diluted with distilled water to reduce its concentration in order to reduce the viscosity of the latex to facilitate mixing with the Nanocarbon dispersion. The mixing with the Nanocarbon dispersion was then done in the presence of about 5pphr of surfactant (employed as a 5% to 20%solution).

The Nanocarbon dispersion and the surfactant were discharged into a beaker containing the natural rubber (NR) latex. The mixture was subjected to mechanical stirring. The NR latex was then coagulated with acetic acid. The coagulum formed was washed with water and squeezed to remove excess surfactants and water the coagulum was cut into small granules and

washed with water. These granules were then dried in an electrically heated oven until they were fully dried to obtain a nanocarbon containing natural rubber masterbatch.

The amount of Nanocarbon in the dispersion and the amount of the dispersed latex are chosen so as to obtain a predetermined ratio of Nanocarbon to rubber (expressed herein in terms of pphr). More specifically the masterbatch contained 2 pphr of nanocarbon.

The following non-limiting examples are representative of the compositions of the invention.

Example Formulations 1 to 5

Formulations 1 to 5 are suitable for use in heavy duty vehicular applications such as truck and bus tyre treads.

Formulations 3 to 5 are representative of the compositions of the invention and formulations 1 and 2 are comparative examples based upon a commercially available Standard Malaysian Rubber (SMR10). All components are expressed as pphr rubber, for example CNT MB 103 means that there are 3 pphr of CNT in 100 parts of rubber masterbatch MB (dried NR latex) and stearic acid "2" means that there are 2 parts of stearic acid per 100 parts of rubber.

Ingredients	**1**	**2**	**3**	**4**	**5**
Rubber, SMR10	100	100	-	-	-
Rubber-CNT MB	-	-	*103	-	-
Rubber-CNT MB	-	-	-	*105	**105
Activator, Zinc oxide	3	3	3	3	3
Activator, Stearic acid	2	2	2	2	2
Antioxidant, 6PPD	1	1	1	1	1
Carbon Black, N220	52	40	35	30	30
Oil, Shellflex 250MB	4	4	4	4	4
Accelerator, TBBS	1.4	1.4	1.4	1.4	1.4
Curing agent, Sulfur	1.5	1.5	1.5	1.5	1.5
Reinforcer, Silica (VN3)	-	12	-	-	-
Silica coupling agent, Si69	-	1.0	-	-	-
Polyethylene glycol, PEG	-	0.5	-	-	-

* Carbon nanotubes having a length of < 50 μm and an outer diameter of < 20 nm; it had a C-purity of > 85% and non-detectable free amorphous carbon. Employed as supplied i.e. as agglomerated bundles of CNTs with average dimensions of 0.05 to 1.5 mm.

** GNF, platelet graphite nanofibers

Experimental Results

As illustrated in Table 1, the uncured rubber compositions according to the invention were demonstrated to have lower Mooney viscosity and improved cure times compared to that of comparator compositions 1 and 2.

TABLE 1

Properties related to Curing	1	2	3	4	5
V_c (M_L (1+4), 100°C)	62.3	66.1	38.4	54.3	34.4
Scorch time, t2 (minutes) at 150°C	2.6	2.5	2.5	2	2.3
Cure time, t95 (minutes) at 150°C	8	8.4	11.5	12	12

As illustrated in Table 2, all cured formulations according to the invention demonstrated improved blowout time versus comparator formulation 1, and, a cured formulation according to the invention demonstrated improved thermal and blow out properties, when compared to the comparator formulations. All the formulations according to the invention demonstrate either the same as, or lower Tan δ values than Comparator Formula 2 which indicates that formulations of the invention are capable of delivering desirable low rolling resistance performance without the use of silica. Formulation 5 delivered improved (higher) resilience than comparator formula 2 which is a yet further indicator of the desirable rolling resistance performance achievable by formulations according to the invention. All formulations according the invention demonstrated improved ARI values versus Comparator formula 1 and either comparable or improved values, versus Comparator Formula 2 which is an indication of their ability to provide desirable wear performance without the use of a silica reinforcing agent.

TABLE 2

Property	1	2	3	4	5
Elongation at break, EB (%)	569	584	523	523	532
Resilience (%)	58	63	57	61	70
tan δ (°) at 60°C	0.11	0.09	0.09	0.09	0.07
Abrasion Resistance Index, ARI (%)	103.9	108.1	109	114	107
Heat build-up, HBU, at 55°C (minutes)	20.4	16	20.4	20.4	13.5
Blowout time at 100°C (minutes)	11.0	Not tested	24	14.0	60

Resilience is an important property of tread rubber compound since it affects rolling resistance and heat build-up. The higher the resilience, the lower the rolling resistance and heat build-up (HBU). The lower the rolling resiliance the less fuel is required to prop l the vehicle forward. Formulations 4 and 5 demonstrated the highest resilience.

Tan δ is a measure of rolling resistance of a rubber compound. Formulations 5 gave the lowest rolling resistance.

Abrasion resistance (ARI) is a measure of associated with potential wear resistance of tyre treads.

Heat build-up (HBU) is an important property in tyre tread formulations. Failure known as blowout occurs in the shoulder region of the tread if excessive HBU is generated in the shoulder region. Formulation 5 gave the lowest HBU.

Formulations 3, 4 and 5 all took longer time to blowout than the comparator formulation 1. The longer the time it takes for blowout failure to occur, the longer is the service life and the safer is the tyre.

As illustrated in Table 3, formulations of the invention display desirable strength and hardness properties.

TABLE 3

Physical Property	1	2	3	4	5
Density ($Mgcm^{-3}$)	1.1138	1.1206	1.0891	-	1.0807
M100 (MPa)	2.4	2.2	2.93	2.93	2.09
M300 (MPa)	12.6	11.7	12.17	12.2	10.6
Tensile strength (MPa)	29.4	29.0	29.0	28.0	27.0
Elongation at Break (%)	569	584	523	523	532
Hardness (IRHD)	69	64	74	74	64

Whilst specific embodiments of the present invention have been described above, it will be appreciated that departures from the described embodiments may still fall within the scope of the present invention. For example, any suitable type of nanoparticle and carbon black may be used. Moreover, any type of natural rubber may be used.

Claims

1. A rubber composition comprising a mixture of natural rubber.nanocarbon and carbon black reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of 1 : 40 to 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of 1 : 100 to 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component.
2. A rubber composition according to claim 1, wherein the relative ratio of nanocarbon to carbon black in pphr is in the range of any of the following: 1 : 30 to 1 : 3; 1 : 20 to 1 : 5 or 1 : 18 to 1 : 6.
3. A rubber composition according to any of claims 1 or 2, wherein the relative ratio of nanocarbon to natural rubber in pphr isin the range of any of the following: 1 : 100 to 8 : 100; 2 : 100 to 6 : 100 or 2 : 100 to 5 : 100.
4. A rubber composition according to any preceding claim, wherein the rubber component contains from 1 to 10, 1 to 8, 1 to 6 or 2 to 5 pphr nanocarbon.
5. A rubber composition according to any preceding claim, wherein carbon black is present at a level of from 10 to 50 or 20 to 40 pphr.
6. A rubber composition according to any preceding claim, wherein nanocarbon and carbon black are the only reinforcing agents.
7. A rubber composition according to any preceding claim, wherein there is no silica and Si-coupling agent.
8. A rubber composition according to any preceding claim, wherein the natural rubber is selected from any one of or combination of the following: unprocessed and processed latex products such as ammonia containing latex concentrates; RSS, ADS or crepes; TSR, SMR L, SMR CV; speciality rubbers SP, MG, DP NR; or field grade (cup lump) rubber products such as TSR, SMR 10, SMR 20, SMR 10 CV, SMR 20 SV, SMR GP.
9. A rubber composition according to any preceding claim, wherein the natural rubber is selected from chemically modified natural rubber products including: epoxidized natural rubbers (ENRs) such as for example ENR 25 and ENR 50.
10. A rubber composition according to any preceding claim containing a vulcanizing agent.

11. A rubber composition according to any preceding claim containing one or more delaying accelerators.
12. A composition according to any preceding claim containing one or more activating agents.
13. A rubber composition according to any preceding claim containing one or more antioxidants.
14. A tyre comprising at least one component part made from a rubber composition as defined in any of claims 1 to 13.
15. A tyre according to claim 14, wherein the rubber composition as defined in any of claims 1 to 13 is used in the tread of the tyre.
16. A tyre according to claim 14, wherein the rubber composition as defined in any of claims 1 to 13 is used in tyre components such as the inner liner, sidewall and shoulder where the tread makes its transition to the sidewall.
17. A tyre according to any of claims 14 to 16, wherein the tyre is a heavy vehicle tyre such as a truck tyre, a bus tyre, a car tyre, an aircraft tyre or a tyre for an earth moving vehicle.
18. Use of a rubber composition according to any claims 1 to 11 for in the manufacture of component parts for tyres such as the treads, inner liner, sidewall and shoulder where the tread makes its transition to the sidewall.
19. A rubber composition having nanocarbon and carbon black as reinforcing agents wherein the relative amount in parts per hundred rubber (pphr) of nanocarbon to carbon black is in the range of from 1 : 40 to 1 : 2 and the relative amount in parts per hundred rubber (pphr) of nanocarbon to natural rubber is in the range of from 1 : 100 to 10 : 100 and wherein the nanocarbon component is pre-dispersed within the natural rubber component and wherein said rubber component is from a masterbatch produced via:

(a) formation of an aqueous slurry containing a dispersion of nanocarbon, at a level of from 2% to 10%by weight of the aqueous slurry, and a surfactant and optionally a stabiliser;

(b) grinding of the aqueous nanocarbon containing slurry;

(c) combination of the aqueous slurry with a natural rubber latex concentrate or diluted latex solution and mixing until a uniform mixture is obtained;

(d) coagulation of the mixture followed by aqueous washing, and removal of excess surfactant, water and excess optional stabilisers by coagulate squeezing or suitable alternative method;

(e) formation of dried rubber nanocarbon masterbatches by either direct drying of the coagulate from step (d) or by coagulate cutting to granulate size and subsequent drying; wherein the pH of the slurry and latex are similar or equivalent prior to combination, and wherein the pH of the nanocarbon may be adjusted using a suitable base to align it to the pH of the rubber latex.

20. A rubber composition according to claim 19, wherein the formation of the aqueous slurry contains a dispersion of nanocarbon at a level of from 3% to 5% by weight of the aqueous slurry and a surfactant and optionally a stabiliser.
21. A rubber composition according to any of claims 19 and 20, wherein the pH of the slurry and latex are within 2, 1 or 0.5 pH units prior to combination.