Title: PARTICLE-MATRIX COMPOSITION COATED WITH MIXTURE COMPRISING POLYSULFIDE POLYMER

Abstract: The invention pertains to a composition comprising a particle and a matrix, wherein the particle is at least partially coated with a compound or a mixture of compounds comprising at least one of a) a polysulfide polymer and a curing system; and b) a cured polysulfide polymer obtained from a polysulfide polymer having at least two epoxy end groups. Most preferred polysulfide polymers are: formula (I), (II), (III) and formula (IV) wherein n is independently 1-200 and R is formula (V) wherein m is 0 to 10, R₃ is independently H or CH₃, and the end indicated with the double asterisk is bonded to the epoxide group. The invention further relates to particle-elastomers comprising said composition, and skim products, tires, tire treads, and belts comprising these particle-elastomers.
PARTICLE-MATRIX COMPOSITION COATED WITH MIXTURE COMPRISING POLYSULFIDE POLYMER

The invention pertains to a composition comprising a particle and a matrix, wherein the particle is at least partially coated with a mixture of compounds, and to a particle-elastomer composition. The invention further relates to a skim product, a tire, a tire tread, and belt comprising said particle-elastomer composition.

In the tire and belt industry, among others, better mechanical, heat build up and hysteresis properties are being demanded. It has long been known that the mechanical properties of rubber can be improved by using a large amount of sulfur as a cross-linking agent to increase the crosslink density in vulcanized rubbers. However, the use of large amounts of sulfur suffers from the disadvantage of high heat generation that leads to a marked decrease in heat resistance and resistance to flex cracking, among other properties, in the final product. In order to eliminate the foregoing disadvantage, it was proposed to add treated chopped fiber, pellets made thereof or treated pellets, particularly treated with polysulfides, Bunte salt, and sulfur to sulfur-vulcanization systems. These pellets further contain wax to improve processing.

In JP 66008866 it was disclosed to use benzothiazole sulfide as adhesive promoters for polyamide fibers. This method, however, does not provide tires and belts having low crack growth, low loss modulus, and low tangent delta. In JP 56129280, JP 60072928, JP 60072929 and JP 60072972, polysulfide polymers are applied as a part of and adhesive system to adhere fibers such as polyester and aramid fibers to rubber. None of these methods provide tires and belts having low crack growth, low loss modulus, and low tangent delta.

In WO 2006/087161 fibers are treated with polysulfide, sulfur, and Bunte salt and compounded into rubber. This reference describes using polysulfide monomers in combination with sulfur, which composition acts as a curing system for the Bunte
The present invention relates to polysulfide polymers rather than to Bunte salts.

In US 3,673,150 glass fiber is impregnated with Thiokol A, which is a polymer obtained from sodium tetrarsulfide and ethylene dichloride, having the formula \((\text{CH}_2\text{CH}_2\text{S}_4)_n\), and which does not contain epoxide groups. If Thiokol A is considered a polysulfide polymer according to the invention the composition of US 3,673,150 lacks a curing system. If Thiokol A is considered a curing agent, it is a curing agent for cross-linking chains of polyolefins with two or more of its sulfur atoms, but it is unable to cure Thiokol A itself. Thus Thiokol A is not a curing system for polysulfide polymers and dependent on the definition of Thiokol A it is either a polysulfide polymer or a curing system, but not both at the same time.

Waxed pellets as such are known in the art. For instance, in EP 0 889 072 the coating of aramid pellets with a polymeric component, e.g. a wax, was disclosed. These pellets are however not coated with a polysulfide polymer containing wax.

In US 6,068,922 pellets comprising aramid fibers and an extrudable polymer, e.g. polyethylene, polypropylene or polyamides are disclosed. The fibers may be coated by typical sizing agents (RF, epoxy, silicone), but polysulfide polymer coating is not mentioned.

The present invention provides a solution to the above problems by the use of a novel class of treated particles, such as chopped fibers, staple fiber, pulp, or powder, in the sulfur vulcanization of rubbers and provides in a particle and a pellet thereof that solves a long-standing problem of reducing hysteresis and heat generation in rubber compositions.

To this end the invention relates to a composition comprising a particle and a matrix, wherein the particle is at least partially coated with a compound or a mixture of compounds comprising at least one of

a) a polysulfide polymer and a curing system; and
b) a cured polysulfide polymer obtained from a polysulfide polymer having at least two epoxy end groups.

More preferably, the composition comprises a linear or branched polysulfide polymer compound having the formula A-B-C, wherein B is a moiety comprising independently 1-200 repeating units of the formula:

-\[X-R_2\cdot X-R_1\cdot S_x\]^{-}

wherein

X is independently CH₂, S or O;

x is 2, 3, or 4;

R₁ and R₂ are independently selected from substituted or unsubstituted alkylene with 1 to 10 carbon atoms, substituted or unsubstituted arylene with 6 to 10 carbon atoms, alkyleneoxy with 1 to 5 carbon atoms, and alkylenoxyalkylene with 2 to 10 carbon atoms; wherein the substituent is the moiety comprising independently 1-200 repeating units of the formula:

D-[X-R_2\cdot X-R_1\cdot S_x]-E

wherein X, R₁, R₂, and x have the previously given meanings; or X, R₁ and R₂ are independently a bond with the proviso that the moiety X-R₂\cdot X-R₁ contains at least 2 atoms;

A and C are independently selected from hydrogen and groups containing at least one of halogen, epoxy, hydroxy, isocyanate, silyl, and vinyl; and one of D and E is a bond and the other has the same meaning as A.

This compound can have an essentially linear molecular structure but may have a partially branched linear structure as well. In the above formula, if R₁ and/or R₂ have the meaning substituted alkylene with 1 to 10 carbon atoms, or substituted arylene with 6 to 10 carbon atoms, the substituent is the moiety comprising independently 1-200 repeating units of the formula D-[X-R_2\cdot X-R_r S_x]-E, and groups R₁ and R₂ in said repeating unit is independently selected from alkylene with 1 to 10 carbon atoms, arylene with 6 to 10 carbon atoms, alkylenoxy with 1 to 5 carbon atoms, and alkylenoxyalkylene with 2 to 10 carbon atoms.
X is preferably selected from S and O. The alkylene group can be exemplified by methylene, ethylene, propylene, isopropylene, butylenes, isobutylene, neopentylene, hexylene, and the like. The arylene group can be exemplified by phenylene, benzylene, or methylbenzylene, and the like, while the moiety X-R₂-X-Rᵣ can be alkyleneoxyalkylene group, such as methyleneoxymethylene, ethyleneoxyethylene, methyleneoxyethylenoxy, ethyleneoxyethyleneoxy, and propenlyoxypropylene, and the like, wherein the oxy group can be replaced by sulfide. Specific examples, for instance, can be represented by the following formulae:

-CH₂OCH₂OCH⁻₂; -C₂H₄OCH₂OC₂H₄⁻; -C₂H₄OC₂H₄OC₂H₄⁻;
-C₃H₆OCH₂OC₃H₆⁻; -C₂H₄OC₂H₄OC₂H₄OC₂H₄⁻; -CH₂SCH₂SCH₂⁻;
-C₂H₄SCH₂SC₂H₄⁻; -C₂H₄SCH₂SC₂H₄⁻; -C₂H₄OC₂H₄SC₂H₄OC₂H₄⁻.

The most preferable divalent organic group X-R₂-X-Rᵣ is the one expressed by the following formula: -C₂H₄OCH₂OC₂H₄⁻.

The aforementioned divalent organic groups can be branched by the substituent comprising independently 1-200 repeating units of the formula:

D-[X-R₂-X-R₁-S₂]-E

wherein X, Rᵢ, R₂, and x have the previously given meanings.

Examples of reactive end groups A and C (and/or D and E) include but are not limited to epichlorohydrin, glycidylether of bisphenol A, vinyl triethoxysilane, and (3-glycidyloxypropyl) trimethoxysilane. Most preferred groups A and C are H, glycidyl and the reaction product of the polysulfide polymer wherein A or C is H and the reactive compound glycidylether of bisphenol A or F. Slightly branched and unbranched polysulfide polymers having 5 to 38 repeating units are commercially available under the tradenames Thioplast™ G, Thiokol® LP, Thioplast™ EPS, and Thiokol® ELP.

Among the most preferred polysulfide polymers are the commercially available polymers of the structure:
wherein \( n \) is independently 1-200 and \( R_1 \) is

\[
\begin{align*}
\text{O} & \quad \text{R'} \quad \text{S} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{SH} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{SH}
\end{align*}
\]

(Formula II)

and

\[
\begin{align*}
\text{O} & \quad \text{R'} \quad \text{S} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{S} \quad \text{R'} \quad \text{O} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{S} \quad \text{R'} \quad \text{O}
\end{align*}
\]

(Formula IV)

wherein \( n \) is independently 1-200 and \( R_1 \) is

\[
\begin{align*}
\text{O} & \quad \text{R'} \quad \text{S} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{SH} \\
\text{O} & \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{n} \quad \text{SH}
\end{align*}
\]

(Formula III)

wherein \( m \) is 0 to 10, \( R_3 \) is independently \( \text{H} \) or \( \text{CH}_3 \), and the end indicated with the double asterisk is bonded to the epoxide group.

For similar compounds many different curing systems have been described e.g. in Journal of Applied Polymer Science, 1959, vol. 2, issue 4, pages 39-45 and in Topics in Sulfur Chemistry, volume 3, page 26. Curing systems include but are
not limited to lead(IV) oxide, Mn(IV) oxide, low molecular weight phenolic resins, di- and polyisocyanates, di- and polyepoxides, dicumyl peroxide, cumene hydroperoxide, calcium peroxide, zinc peroxide, sodium perborate, sodium periodate, iodine, tetrabutylammonium peroxydisulfate, p-quinonedioxime, and combinations of sulfur and a polysulfide. A preferred curing system is a combination of sulfur and a polysulfide (C) of the formula

\[
\begin{array}{c}
\text{R} \\
\text{S} \quad \text{[S]}_n \quad \text{S} \\
\text{R}
\end{array}
\]

wherein \( n = 2-6 \);

R is independently selected from hydrogen, halogen, nitro, hydroxyl, C1-C12 alkyl C1-C12 alkoxy, and C7-C12 aralkyl.

For polysulfide polymer carrying glycidyl functionality a choice can be made from any epoxy curing system known in the art. Examples of curing agents include but are not limited to polyols, such as polyvinylalcohol and polyetherpolyols, polyacid anhydride, polycarboxylic acid, polyisocyanates, and primary amines. In some cases an additional catalyst is required for curing to take place. Furthermore, the polysulfide polymer carrying at least two glycidyl groups can be cured to themselves without adding a curing system. The term "cured" polysulfide polymer having at least two epoxy end groups means that the polysulfide polymer molecule having at least two epoxy end groups is at least partially coupled to another polysulfide polymer molecule having at least two epoxy end groups through their glycidyl groups.

In a preferred embodiment the invention relates to a composition comprising a particle and a matrix having enhanced rubber properties in an elastomer. The matrix may be a wax or a polymer. The composition contains up to 85 wt% of matrix, preferably wax, based on the weight of the composition. Examples of suitable waxes are microcrystalline wax of higher alkyl chains, such as a C22-C38 alkyl chain, paraffin wax or alkyl long chain fatty acid waxes, such as C12-C40 alkanecarboxylic acids. Instead of a wax, the matrix can also be selected from an
extrudable polymer. Particularly useful are, e.g. polyethylene, polypropylene or polyamides, or mixtures of such extrudable polymers and wax. The extrudable polymers may be modified or unmodified polymers and copolymers.

The composition comprising the coated particles can be in the form of the particle as such, or may be compressed by conventional means to a pellet. Alternatively, the particles may be contained in a matrix and shaped into a pellet, for instance by cutting the particle-matrix composition to pellets.

The pellet may be composed of any particle according to the invention. Preferred particles are selected from aramid, polyester, polyamide, cellulose, glass, and carbon. The particles may be in any form such as chopped fiber, staple fiber, pulp, fibrils, fibrid, beads, powder, and the like. Aramid fibers (which include chopped fiber, staple fiber, and pulp) and powders have the preference, more specifically particles of poly(p-phenylene-terephthalamide) or co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide. Most preferred are chopped fiber, staple fiber, and powder. Powder and beads have the additional advantage that they do not need a spinning step and can directly be obtained from the polymer.

The term "pellet" includes terms, apart from pellet, that are synonymous or closely related such as tablet, briquette, pastilles, granule and the like.

Pellets can be made from any particle, including short cut fibers, chopped fiber, staple fiber, pulp, fibrils, fibrid, beads, and powder, by mixing these particles with a matrix of a wax and/or an extrudable polymer and the coating chemicals.

For instance, the pellet can be prepared according to the method described in WO 0058064. Alternatively, pellets can be prepared directly using chopped fiber or powder and the like, wax, polysulfide polymer and, if necessary, the polysulfide curing system. The particles and the wax and/or extrudable polymer matrix, and optionally the curing agent, and other chemicals are mixed intensively and optionally heated up to a temperature at or above the melting point of the wax or extruded polymer. Then the mixture is formed into the shape of a pellet or tablet.
at a temperature below the melting point of the wax or extruded polymer. Wax (and/or extrudable polymer) can be used in amounts up to 85 wt% based upon the weight of the composition. Alternatively, pellets can also be made from a mixture of particle and matrix, after which the polysulfide polymer and the curing system; and/or the cured polysulfide polymer is added to at least partially coat the particles contained in the pellet.

The treatment of the composition thereof is based on the above polysulfide polymer and polysulfide curing chemicals, preferably Thiokol LP, 2-mercaptobenzothiazyl disulfide, which chemicals further contain sulfur or a sulfur donor. Compositions of the invention can also contain a wax as a carrier medium to improve processing. Examples of suitable waxes are microcrystalline wax of higher alkyl chains, such as C22-C38 alkyl chains, paraffin wax or alkyl long chain fatty acid waxes, such as C12-C40 alkanecarboxylic acids. After treatment the composition may be used as such or may be comminuted to appropriate size, to be suitably used in rubber compounds. After treatment fibers may be chopped to appropriate length, for use in rubber compounds, or chopped fiber may be treated by the above chemicals, or chopped fibers and the above chemicals including a wax may be mixed, optionally heated and formed into a well dosable shape.

Alternatively, the treatment of particles, including fiber and powder, or pellets made thereof, can be based on glycidyl functional polysulfide polymer where no further curing agents are required.

A suitable coating amounts 0.5-50 wt% based on the weight of composition, preferably 1-30 wt%, more preferably 2-15 wt%.

The treatment of the composition can be carried out using a solution of polysulfide polymer, 2-mercaptobenzothiazyl disulfide (MBTS), and sulfur in a suitable solvent, e.g. toluene or a dispersion of said chemicals in e.g. toluene/water. 2-Mercaptobenzothiazyl disulfide can be replaced by other benzothiazole derivatives.
Pellets prepared according to the method described in WO 0058064 can be treated either using a solution of polysulfide polymer, 2-mercaptobenzothiazyl disulfide (MBTS), and sulfur in a suitable solvent e.g. toluene or a dispersion of said chemicals in e.g. toluene/water or using a mixture of said chemicals in a suitable matrix such as stearic acid. The matrix can be used in amounts up to 85 wt% based upon the weight of the composition.

Pellets can be prepared directly using powder or chopped fiber, wax and polysulfide polymer (A), 2-mercaptobenzothiazyl disulfide (MBTS), and sulfur as described above. Preferably, the wax is stearic acid. The wax can be used in amounts up to 85 wt% based upon the weight of the composition.

Preferred coatings comprise 10-98 wt%, more preferably 50-95 wt% polysulfide polymer, 0.1-20 wt%, more preferably 0.5-10 wt% curing system, and optionally 0.01-10 wt%, more preferably 0.2-2.5 wt% sulfur, based on the weight of the coating. The amount of sulfur is the amount of sulfur as used as such, or the amount of sulfur that is generated if a sulfur donor is used. In the composition, preferably stearic acid can be present in amounts up to 85 wt%, preferably between 45 and 67 wt%.

The meaning of the term "coating" is well known for the skilled man and can be found in any relevant textbook. Thus a coated particle is a particle containing a layer of the coating material (the coating) around its surface. If the particle is partially coated, only part of the particle is covered by said layer. In principle there is no difference whether the particles are coated and made to a pellet, or when the particles are made to a pellet and then coated. The coating composition will completely penetrate the pellet and coat the individual particles therein. It is also possible that the coating material or part of the coating material penetrates between fibers of the particle, or even between filaments and microfilaments, thereby impregnating the particle.
Compositions comprising polysulfide polymer having glycidyl end groups may be given a heat treatment. Preferably, compositions are heated during 1 to 60 minutes at a temperature from 80 to 200 °C. More preferably, compositions are heated during 5 to 25 minutes at a temperature from 120 to 170 °C.

In another aspect the invention relates to a rubber composition which is the vulcanization reaction product of a rubber, sulfur and optionally sulfur donor, and the composition according to the invention. The composition of the invention acts as a modulus enhancer, strength improver, as well lowers hysteresis. Also disclosed is a vulcanization process carried out in the presence of the composition and the use of these compositions in the sulfur-vulcanization of rubbers. In addition, the present invention relates to a vulcanization process carried out in the presence of the compositions and the use of these compositions in the sulfur-vulcanization of rubbers. Further, the invention also encompasses rubber products which comprise at least some rubber which has been vulcanized, preferably vulcanized with sulfur, in the presence of said compositions. The present invention provides excellent hysteresis behavior as well as improvements in several rubber properties without having a significant adverse effect on the remaining properties, when compared with similar sulfur-vulcanization systems without any of the composition.

The present invention is applicable to all natural and synthetic rubbers. Examples of such rubbers include, but are not limited to, natural rubber, styrene-butadiene rubber, butadiene rubber, isoprene rubber, acrylonitrile-butadiene rubber, chloroprene rubber, isopreneisobutylene rubber, brominated isoprene-isobutylene rubber, chlorinated isoprene-isobutylene rubber, ethylene-propylene-diene terpolymers, as well as combinations of two or more of these rubbers and combinations of one or more of these rubbers with other rubbers and/or thermoplastics.

Sulfur, optionally together with sulfur donors, provides the required level of sulfur during the vulcanization process. Examples of sulfur which may be used in the vulcanization process include various types of sulfur such as powdered sulfur,
precipitated sulfur and insoluble sulfur. Examples of sulfur donors include, but are not limited to, tetramethylthiuram disulfide, tetraethylthiuram disulfide, tetrabutylthiuram disulfide, dipentamethylene thiuram hexasulfide, dipentamethylene thiuram tetrasulfide, dithiodimorpholine, and mixtures thereof.

Sulfur donors may be used instead or in addition to the sulfur. Herein the term "sulfur" shall further also include the mixture of sulfur and sulfur donor(s). Further, references to the quantity of sulfur employed in the vulcanization process, when applied to sulfur donors, mean a quantity of sulfur donor which is required to provide the equivalent amount of sulfur that is specified.

More particularly, the present invention relates to a sulfur-vulcanized rubber composition which comprises the vulcanization reaction product of: (a) 100 parts by weight of at least one natural or synthetic rubber; (b) 0.1 to 25 parts by weight of an amount of sulfur, or sulfur and/or a sulfur donor, to provide the equivalent of 0.1 to 25 parts by weight of sulfur; and (c) 0.1 to 20 parts by weight of the composition of the invention, preferably comprising powder, chopped fiber, staple fiber, or pellets made thereof.

The particle of the present invention is based on natural and synthetic polymers. Examples of such polymers include, but not limited to, aramid, such as para-aramid, polamide, polyester, cellulose, such as rayon, glass, and carbon as well as combinations of two or more of these yarns.

Most preferably the particle is poly(para-phenylene-terephthalamide) fiber, which is commercially available under the trade name Twaron®, or co-poly-(para-phenylene/3,4'-oxydiphenylene terephthalamide), which is commercially available under the trade name Technora®.

The amount of sulfur to be compounded with the rubber is, based on 100 parts of rubber, usually 0.1 to 25 parts by weight, and more preferably 0.2 to 8 parts by weight. The amount of sulfur donor to be compounded with the rubber is an amount to provide an equivalent amount of sulfur, i.e. an amount which gives the same amount of sulfur, as if sulfur itself were used. The amount of composition to
be compounded with the rubber is, based on 100 parts of rubber, 0.1 to 25 parts by weight, and more preferably 0.2 to 10.0 parts by weight, and most preferably 0.5 to 5 parts by weight. These ingredients may be employed as a pre-mix, or added simultaneously or separately, and they may be added together with other rubber compounding ingredients as well. In most circumstances it is also desirable to have a vulcanization accelerator in the rubber compound. Conventional, known vulcanization accelerators may be employed. The preferred vulcanization accelerators include mercaptobenzothiazole, 2,2'-mercaptobenzothiazole disulfide, sulfenamide accelerators including N-cyclohexyl-2-benzothiazole sulenamide, N-tert-butyl-2-benzothiazole sulenamide, N,N-dicyclohexyl-2-benzothiazole sulenamide, and 2-(morpholinothio)benzothiazole; thiophosphoric acid derivative accelerators, thiurams, dithiocarbamates, diphenyl guanidine, diorthotolyl guanidine, dithiocarbamylsulfenamides, xanthates, triazine accelerators and mixtures thereof.

If the vulcanization accelerator is employed, quantities of from 0.1 to 8 parts by weight, based on 100 parts by weight of rubber composition, are used. More preferably, the vulcanization accelerator comprises 0.3 to 4.0 parts by weight, based on 100 parts by weight of rubber. Other conventional rubber additives may also be employed in their usual amounts. For example, reinforcing agent such as carbon black, silica, clay, whiting, and other mineral fillers, as well as mixtures of fillers, may be included in the rubber composition. Other additives such as process oils, tackifiers, waxes, antioxidants, antiozonants, pigments, resins, plasticizers, process aids, factice, compounding agents and activators such as stearic acid and zinc oxide may be included in conventional, known amounts. For a more complete listing of rubber additives which may be used in combination with the present invention see, W. Hofmann, "Rubber Technology Handbook, Chapter 4, Rubber Chemicals and Additives, pp. 217-353, Hanser Publishers, Munich 1989.

Further, scorch retarders such as phthalic anhydride, pyromellitic anhydride, benzene hexacarboxylic trianhydride, 4-methylphthalic anhydride, trimellitic anhydride, 4-chlorophthalic anhydride, N-cyclohexyl-thiophthalimide, salicylic
acid, benzoic acid, maleic anhydride and N-nitrosodiphenylamine may also be included in the rubber composition in conventional, known amounts. Finally, in specific applications it may also be desirable to include steel-cord adhesion promoters such as cobalt salts and dithiosulfates in conventional, known quantities.

The process is carried out at a temperature of 110-220° C over a period of up to 24 hours. More preferably, the process is carried out at a temperature of 120-190 °C over a period of up to 8 hours in the presence of 0.1 to 20 parts by weight of the composition, more specifically, compositions comprising chopped fiber, staple fiber or pellet. Even more preferable is the use of 0.2-5 parts by weight of coated chopped fiber, coated staple fiber or fiber pellet made thereof. All of the additives mentioned above with respect to the rubber composition may also be present during the vulcanization process of the invention.

In a more preferred embodiment of the vulcanization process, the vulcanization is carried out at a temperature of 120-190 °C over a period of up to 8 hours and in the presence of 0.1 to 8 parts by weight, based on 100 parts by weight of rubber, of at least one vulcanization accelerator.

The present invention also includes articles of manufacture, such as skim products, tires, tire treads, tire undertreads, or belts, which comprise sulfur-vulcanized rubber which is vulcanized in the presence of the composition of the present invention. The invention is further illustrated by the following examples which are not to be construed as limiting the invention in any way.
Experimental Methods

In the following examples, rubber compounding, vulcanization and testing was carried out according to standard methods except as otherwise stated: Base compounds were mixed in a Farrel Bridge™ BR 1.6 liter Banbury type internal mixer (preheating at 50 °C, rotor speed 77 rpm, mixing time 6 min with full cooling).

Vulcanization ingredients were added to the compounds on a Schwabenthan Polymix™ 150L two-roll mill (friction 1:1.22, temperature 70 °C, 3 min).

Cure characteristics were determined using a Monsanto™ rheometer MDR 2000E (arc 0.5°) according to ISO 6502/1999. Delta S is defined as extent of crosslinking and is derived from subtraction of lowest torque (ML) from highest torque (MH).

Sheets and test specimens were vulcanized by compression molding in a Fontyne™ TP-400 press.

Tensile measurements were carried out using a Zwick™ 1445 tensile tester (ISO-2 dumbbells, tensile properties according to ASTM D 412-87, tear strength according to ASTM D 624-86).

Abrasion was determined using a Zwick abrasion tester as volume loss per 40 m path traveled (DIN 53516).

Heat build-up and compression set after dynamic loading were determined using a Goodrich™ Flexometer (load 1 MPa, stroke 0.445 cm, frequency 30 Hz, start temperature 100 °C, running time 120 min or till blow out; ASTM D 623-78).

Dynamic mechanical analyses, for example loss modulus and tangent delta (Table 5) were carried out using an Eplexor™ Dynamic Mechanical Analyzer (pre-strain 10%, frequency 15 Hz, ASTM D 2231).
Example 1

Aramid staple pellets were prepared according to WO 0058064 and contained 80 wt% Twaron and 20 wt% polyamide resin. The treatment of these pellets was done in the following way:

Thioplast™ EPS 25 and Thioplast™ EPS 70 are commercially available from Akzo Nobel Thioplast. Thioplast™ EPS 25 is a blend of polysulfide polymers of formula I and IV, wherein R' is -CH₂⁻ and n is smaller than 7 with a viscosity of 2 to 3 Pa.s and a degree of branching of 2 mole%. Thioplast™ EPS 70 is a slightly branched polysulfide polymer having the above formula wherein R' - epoxide is the group that is obtained by reacting diglycidylether of bisphenol A or F with the polysulfide polymer precursor having the same formula but wherein R' is replaced by H, and n is smaller than 7 with a viscosity of 5 to 10 Pa.s at 20 °C and a braching of 0.57. Thioplast™ EPS was dissolved in toluene in the presence of a small amount of isohexadecane resulting in a solution of 66 wt% Thioplast™ EPS and 2.6 wt% isohexadecane in toluene. A 2.3 wt% solution of surfactant Elfapur™ LM 75 S in water was prepared. Under vigorous stirring the Thioplast™ solution was added to the aqueous solution followed by the application of an ultraturrax resulting in a stable dispersion comprising approximately 8 wt% Thioplast™ EPS. About 25 g of para-aramid pellets were dipped in 110 ml of the above dispersion for about 5 minutes, after which the treated pellets were filtered off and dried. After being dried, pellets were heat treated at 150 °C for 15 minutes.

The p-aramid fiber pellet compositions are summarized in Table 1.

Table 1. Aramid fiber compositions and treatments.

<table>
<thead>
<tr>
<th>Particle : matrix : polysulfide polymer (wt% : wt% : wt%)</th>
<th>Treatment</th>
<th>Remark</th>
<th>Entry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twaron : PA : EPS 25 = 71.4 : 17.9 : 10.7</td>
<td>none</td>
<td>comparison</td>
<td>T1</td>
</tr>
<tr>
<td>Twaron : PA : EPS 70 = 69.0 : 17.2 : 13.8</td>
<td>none</td>
<td>comparison</td>
<td>T2</td>
</tr>
<tr>
<td>Twaron : PA : EPS 25 = 73.1 : 18.3 : 8.6</td>
<td>15', 150 °C</td>
<td>invention</td>
<td>T3</td>
</tr>
<tr>
<td>Twaron : PA : EPS 70 = 75.5 : 18.9 : 5.6</td>
<td>15', 150 °C</td>
<td>invention</td>
<td>T4</td>
</tr>
</tbody>
</table>

PA= polyamide resin; EPS 25 = Thioplast EPS 25; EPS 70 = Thioplast EPS 70.

The accelerator employed was N-cyclohexyl-2-benzothiazole sulfenamide (CBS). Details of the formulations are listed in Table 2.

Table 2. Rubber formulations incorporating aramid fiber compositions
NR is natural rubber; BR is polybutadiene; 6PPD is N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, TMQ is polymerized 2,2,4-trimethyl-1,2-dihydoquinoline antioxidant, CBS is N-cyclohexyl benzothiazyl sulfenamide.

The vulcanized rubbers listed in Table 2 were tested according to ASTM/ISO norms. A and B are control experiments (rubber only), C and D are comparison experiments (uncured) and 1 and 2 are experiments according to the invention. The results are given in Tables 3-6.

Table 3. Effect of the mixes at 100 °C on processing characteristics (Mooney viscosity).

<table>
<thead>
<tr>
<th>Experiment →</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML(1+4), MU</td>
<td>54</td>
<td>55</td>
<td>57</td>
<td>55</td>
<td>59</td>
<td>59</td>
</tr>
</tbody>
</table>
The data of Table 3 show that the fiber compositions according to the invention show low viscosity as evidenced from the ML (1+4) values.

Table 4. Effect of the mixes at 150 °C on delta torque.

<table>
<thead>
<tr>
<th>Experiment→</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta S, Nm</td>
<td>1.75</td>
<td>1.79</td>
<td>1.83</td>
<td>1.78</td>
<td>1.82</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The data in Table 4 show that the compositions according to the invention (mix 1 and 2) do not influence the extent of crosslinking as demonstrated by delta S values.

Table 5. Evaluation of fibers compositions for improvement in mechanical properties

<table>
<thead>
<tr>
<th>Experiment→</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus, 300%, MPa</td>
<td>13.1</td>
<td>14.8</td>
<td>14.8</td>
<td>14.5</td>
<td>15.6</td>
<td>15.4</td>
</tr>
<tr>
<td>Tear strength, kN/m</td>
<td>135</td>
<td>120</td>
<td>130</td>
<td>130</td>
<td>145</td>
<td>145</td>
</tr>
</tbody>
</table>

It is clear from the data depicted in Table 5 that the compositions of the invention containing polysulfide polymer (mix 1 and 2) have better modulus and tear strength.

Table 6. Evaluation of improvement in dynamic mechanical properties

<table>
<thead>
<tr>
<th>Experiment→</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature rise, °C</td>
<td>32</td>
<td>37</td>
<td>28</td>
<td>28</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Blow out time, min</td>
<td>25</td>
<td>18</td>
<td>29</td>
<td>35</td>
<td>42</td>
<td>45</td>
</tr>
<tr>
<td>Loss modulus, MPa</td>
<td>1.2</td>
<td>1.33</td>
<td>1.21</td>
<td>1.25</td>
<td>1.05</td>
<td>1.09</td>
</tr>
<tr>
<td>Tangent delta</td>
<td>0.158</td>
<td>0.167</td>
<td>0.159</td>
<td>0.156</td>
<td>0.136</td>
<td>0.138</td>
</tr>
</tbody>
</table>

It is noted that the compositions containing polysulfide polymer (mix 1 and 2) showed improved dynamic mechanical properties.
Example 2.
Aramid staple pellets were prepared according to WO 0058064 and contained 80 wt% Twaron and 20 wt% polyethylene resin. The treatment of the pellets was done in the following way:

Thiokol® LP 32 is commercially available from Toray Fine Chemicals Co., Ltd. Thiokol® LP 32 is a slightly branched polysulfide polymer blend of polysulfides having formula I and III, and n is 24 on average with a viscosity of 45 Pa·s and a degree of branching of 0.5 mole%.

Thiokol® LP 32 was dissolved in toluene resulting in a 66 wt% Thiokol® LP 32 solution. A 1.7 wt% solution of surfactant Elfapur™ LM 75 S in water was prepared. Under vigorous stirring the Thiokol® LP 32 solution was added to the aqueous solution followed by the application of an ultraturrax resulting in a stable dispersion containing approximately 10 wt% Thiokol® LP 32.

About 25 g of para-aramid pellets, comprising 80 wt% Twaron® and 20 wt% polyethylene, were dipped in approximately 150 mL of dispersion for about 5 minutes, after which the treated pellets were filtered off and dried.

Sulfur and 2-mercaptobenzothiazyl disulfide were dissolved in toluene resulting in a solution containing 0.4 wt% of sulfur and 0.8 wt% of 2-mercaptobenzothiazyl disulfide. Thiokol® LP 32 was dissolved in toluene and the toluene solution containing sulfur and 2-mercaptobenzothiazyl disulfide was added resulting in a solution containing 8 wt% Thiokol® LP 32, 0.4 wt% 2-mercaptobenzothiazyl disulfide and 0.2 wt% sulfur.

A second batch of about 25 g of para-aramid pellets, comprising 80 wt% Twaron® and 20 wt% polyethylene, was dipped in approximately 100 mL of the above solution for about 5 minutes, after which the treated pellets were filtered off and dried.

A third and fourth batch of about 25 g of para-aramid pellets, comprising 80 wt% Twaron® and 20 wt% polyethylene, was mixed with molten stearic acid containing Thiokol® LP 32 and molten stearic acid containing Thiokol® LP 32, 2-mercaptobenzothiazyl disulfide and sulfur, respectively. Subsequently, pellets were cooled and a small excess of solidified stearic acid possibly containing small
amounts of Thiokol® LP 32, 2-mercaptobenzothiazyl disulfide and sulfur, was removed by sieving. The p-aramid fiber compositions are summarized in Table 7.

### Table 7. Fiber pellet compositions.

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition (wt%:wt%:wt%)</th>
<th>Remark</th>
<th>Entry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twaron : PE : LP 32 : Elfa</td>
<td>67.8 : 17.0 : 13.6 : 1.6</td>
<td>comparison</td>
<td>T5</td>
</tr>
<tr>
<td>Twaron : PE : SA : LP 32</td>
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<td>comparison</td>
<td>T6</td>
</tr>
<tr>
<td>Twaron : PE : LP 32 : MBTS : S</td>
<td>71.5 : 17.9 : 9.9 : 0.5 : 0.2</td>
<td>invention</td>
<td>T7</td>
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<tr>
<td>Twaron : PE : SA : LP 32 : MBTS : S</td>
<td>30.6 : 7.7 : 56.9 : 4.5 : 0.2 : 0.1</td>
<td>invention</td>
<td>T8</td>
</tr>
</tbody>
</table>

PE= polyethylene; LP 32 = Thiokol® LP 32; Elfa = Elfapur™ LM 75 S; MBTS = 2-mercaptobenzothiazyl disulfide; SA = stearic acid

The accelerator employed was N-cyclohexyl-2-benzothiazole sulfenamide (CBS). Details of the formulations are listed in Table 8.
Table 8. Rubber formulations incorporating aramid pellets

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<tr>
<th>Ingredients ↓</th>
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<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
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<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>BR Buna CB 24</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Carbon Black N-339</td>
<td>55</td>
<td>57</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
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<tr>
<td>Antidegradant 6PPD</td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Antioxidant TMQ</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Accelerator CBS</td>
<td>1.5</td>
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<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
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<tr>
<td>sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>T5</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
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<tr>
<td>T8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

NR is natural rubber; BR is polybutadiene; 6PPD is N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine, TMQ is polymerized 2,2,4-trimethyl-1,2-dihydroquinoline antioxidant.

The vulcanized rubbers listed in Table 8 were tested according to ASTM/ISO norms. E and F are control experiments (rubber only), G and H are comparison experiments (without curing system) and 3 and 4 are experiments according to the invention. The results are given in Tables 9-12.

Table 9. Effect of the mixes at 100 °C on processing characteristics (Mooney viscosity).

<table>
<thead>
<tr>
<th>Experiment→ ML(1+4), MU</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML(1+4), MU</td>
<td>53</td>
<td>55</td>
<td>53</td>
<td>53</td>
<td>54</td>
<td>51</td>
</tr>
</tbody>
</table>
The data of Table 9 show that the fiber composition according to the invention show low viscosity as evidenced from the ML (1+4) values.

Table 10. Effect of the mixes; at 150 °C on delta torque.

<table>
<thead>
<tr>
<th>Experiment—*</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta S, Nm</td>
<td>1.72</td>
<td>1.75</td>
<td>1.76</td>
<td>1.79</td>
<td>1.97</td>
<td>1.92</td>
</tr>
</tbody>
</table>

The data in Table 10 show that the fiber composition according to the invention (herein both polysulfide polymer and curing system are present, mixes 3 and 4) show the highest reinforcement as demonstrated by delta torque values.

Table 11. Evaluation of treated fibers for improvement in mechanical properties

<table>
<thead>
<tr>
<th>Experiment—→</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus, 300%, MPa</td>
<td>13.2</td>
<td>14.8</td>
<td>13.9</td>
<td>14.7</td>
<td>15.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Hardness (IRHD)</td>
<td>71</td>
<td>71</td>
<td>73</td>
<td>72</td>
<td>75</td>
<td>75</td>
</tr>
</tbody>
</table>

It is clear from the data depicted in Table 11 that the polysulfide polymer and curing agent containing fiber composition (mix 3 and 4) of the invention have better modulus and hardness.

Table 12. Evaluation of improvement in dynamic mechanical properties

<table>
<thead>
<tr>
<th>Experiment—→</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature rise, °C</td>
<td>24</td>
<td>26</td>
<td>24</td>
<td>24</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Loss modulus, MPa</td>
<td>1.12</td>
<td>1.07</td>
<td>1.11</td>
<td>0.96</td>
<td>0.89</td>
<td>0.87</td>
</tr>
<tr>
<td>Tangent delta</td>
<td>0.157</td>
<td>0.148</td>
<td>0.146</td>
<td>0.136</td>
<td>0.120</td>
<td>0.122</td>
</tr>
</tbody>
</table>

It is noted that both polysulfide polymer and curing system containing fiber compositions (mixes 3 and 4) show improved dynamic mechanical properties.
PARTICLE-MATRIX COMPOSITION COATED WITH MIXTURE COMPRISING POLYSULFIDE POLYMER

Claims:

1. A composition comprising a particle and a matrix, wherein the particle is at least partially coated with a compound or a mixture of compounds comprising at least one of
   a) a polysulfide polymer and a curing system; and
   b) a cured polysulfide polymer obtained from a polysulfide polymer having at least two epoxy end groups.

2. The composition of claim 1 wherein the particle is a fiber, fibrild, fibril, powder or bead.

3. The composition of claims 1 or 2 wherein the polysulfide polymer is a linear or branched compound having the formula A-B-C, wherein B is a moiety comprising independently 1-200 repeating units of the formula:

\[ \text{D-}[X-R_2-X-R_1-S_x]-E \]

wherein

- X is independently CH₂, S or O;
- x is 2, 3, or 4;
- R₁ and R₂ are independently selected from substituted or unsubstituted alkylene with 1 to 10 carbon atoms, substituted or unsubstituted arylene with 6 to 10 carbon atoms, alkylenoxy with 1 to 5 carbon atoms, and alkylenoxyalkylene with 2 to 10 carbon atoms; wherein the substituent is the moiety comprising independently 1-200 repeating units of the formula:

\[ \text{D-}[X-R_2-X-R_1-S_x]-E \]

wherein X, R₁, R₂, and x have the previously given meanings;

or X, R₁ and R₂ are independently a bond with the proviso that the moiety X-R₂-X-R₁ contains at least 2 atoms;

A and C are independently selected from hydrogen and groups containing at...
least one of halogen, epoxy, hydroxy, isocyanate, silyl, and vinyl; and
one of D and E is a bond and the other has the same meaning as A.

4. The composition of claim 3 wherein if \( R_i \) and/or \( R_2 \) have the meaning
substituted alkylene with 1 to 10 carbon atoms, or substituted arylene with 6 to
10 carbon atoms, wherein the substituent is the moiety comprising
independently 1-200 repeating units of the formula \( D-[X-R_2-X-R_i-S_x]-E \), groups
\( R_i \) and \( R_2 \) in said repeating unit are independently selected from alkylene with
1 to 10 carbon atoms, arylene with 6 to 10 carbon atoms, alkylenedioxy with 1 to
5 carbon atoms, and alkylenedioxyalkylene with 2 to 10 carbon atoms.

5. The composition of claim 3 or 4, wherein groups A, C, D, and/or E of
polysulfide polymer A-B-C are glycidyl or a group obtained by reaction of the
diglycidylether of bisphenol A or the diglycidylether of bisphenol F, or a resin
thereof, with the proviso that one of D and E is a bond and the other is H, and
both A and C are H.

6. The composition of any one of claims 1-5 wherein the polysulfide polymer is at
least one of

\[
\text{HS} - \left[ \begin{array}{c} \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \end{array} \right]_n \text{O} \text{O} \text{SH}
\]

\[
\text{R'} - \left[ \begin{array}{c} \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \end{array} \right]_n \text{O} \text{O} \text{SH}
\]

\[
\text{HS} - \left[ \begin{array}{c} \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \\ \text{O} \text{O} \text{S} \text{S} \end{array} \right]_n \text{O} \text{O} \text{SH}
\]

and
wherein $n$ is independently 1-200 and $R'$ is

## \begin{align*}
\text{OH} & \quad \text{O} \\
\text{R} & \quad \text{O} \\
\text{R}_3 & \quad \text{O} \quad \text{R}_3
\end{align*}

wherein $m$ is 0 to 10, $R_3$ is independently H or CH$_3$, and the end indicated with the double asterisk is bonded to the epoxide group.

7. The composition of any one of claims 1-6 wherein the coating comprises a polysulfide polymer and a curing system, wherein the curing system is selected from lead(IV)oxide, manganese(IV)oxide, low molecular weight phenolic resin, di- or polyisocyanates, di- or polyepoxides, cumene hydroperoxide, dicumyl peroxide, calcium peroxide, zinc peroxide, sodium periodate, sodium perborate, tetrabutylammonium peroxydisulfate, p-quinonedioxime, iodine, and a mixture of sulfur and a polysulfide.

8. The composition of claim 7 wherein the curing system is a mixture of sulfur and a polysulfide of formula

\[
\text{R} \quad \text{S} \quad \text{N} \quad \text{S} \quad \text{R}
\]

wherein $n = 2-6$;

$R$ is independently selected from hydrogen, halogen, nitro, hydroxy, C1-C12 alkyl, C1-C12 alkoxy, and C7-C12 aralkyl.
9. The composition of any one of the previous claims wherein the coating comprises 10-98 wt% of the polysulfide polymer and 0.1-20 wt% of the curing system, based on the weight of the coating.

10. The composition of any one of the previous claims wherein the matrix is a wax.

11. The composition of claim 10 wherein the wax is a saturated alkanecarboxylic acid having 12-40 carbon atoms.

12. The composition of claim 11 comprising up to 85 wt% based on the weight of the composition of an aliphatic fatty acid wax, or a synthetic microcrystalline wax having a C22-C38 alkyl chain.

13. The composition of any one of the previous claims wherein the particle is selected from aramide, polyester, polyamide, cellulose, glass, and carbon.

14. The composition of any one of the previous claims wherein the particle is selected from chopped fiber, staple fiber, pulp, and powder.

15. The composition of any one of the previous claims wherein the particle is a poly(p-phenylene-terephthalamide) or a co-poly-(paraphenylene/3,4´-oxydiphenylene terephthalamide) fiber.

16. The composition of any one of the previous claims wherein the particle is a fiber which is pre-treated with a sizing.

17. The composition of any one of the previous claims wherein the coating amounts 0.5-50 wt% based on the weight of composition, preferably 1-30 wt%, more preferably 2-15 wt%.

18. A particle-elastomer composition comprising:
   (a) 100 parts by weight of at least one natural or synthetic rubber;
(b) 0.1 to 25 parts by weight of an amount of sulfur and/or a sulfur donor, to provide the equivalent of 0.1 to 25 parts by weight of sulfur; and
(c) 0.1 to 20 parts by weight of the composition of any one of claims 1-17.

19. A skim product comprising the particle-elastomer composition of claim 18 and a skim additive.

20. A tire comprising the composition of claim 18 and/or the skim product of claim 19.

21. A tire tread, undertread, or belt comprising the particle-elastomer composition of claim 18 and/or the skim product of claim 19.
## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC.

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

- C08K
- C08L
- B60C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

- EPO-Internal
- CHEM ABS Data
- WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 3 673 150 A (MARZOCCHI ALFRED) 27 June 1972 (1972-06-27) claims 1,6; examples 4-10</td>
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<td>X</td>
<td>WO 2006/087161 A (TEIJIN TWARON B V (NL); DATTA RABINDRA NATH (NL); DE LANGE PIETER JAN) 24 August 2006 (2006-08-24) abstract; claims 1-12</td>
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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents

- **A** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier document but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- **O** document referring to an oral disclosure, use exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

- **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **X** document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- **Y** document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- **M** document member of the same patent family

Date of the actual completion of the international search: 22 November 2007

Date of mailing of the international search report: 06/12/2007

Name and mailing address of the ISA/Authorized officer

European Patent Office, P B 5818 Patentlaan 2
NL- 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31 651 epc nl,
Fax (+31-70) 340-3016

Schüte, Maya
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