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(54) Title: SELF-CURED THERMOPLASTIC VULCANIZATES

(57) Abstract: The invention relates to self-cured thermoplastic vulcanizates comprising a thermoplastic and a vulcanized elastomer, such as butyl rubber. More particularly, the invention relates to cured thermoplastic vulcanizates wherein the elastomer phase is based on self-curing or self-cured azidobutyl rubber. The thermoplastic vulcanizates are useful in the preparation of shaped articles for high purity applications, such as condenser caps, medical components and fuel cell components as well as tire inner liners.



SELF-CURED THERMOPLASTIC VULCANIZATES

Field of the Invention

The invention relates to thermoplastic vulcanizates comprising a thermoplastic and an elastomer, such as butyl rubber. More particularly, the invention relates to cured thermoplastic vulcanizates wherein the elastomer phase is based on self-curing or self-cured azidobutyl rubber.

Background

The development of a novel elastic fibers by Du Pont (US 2,623,031) and thermoplastic polyurethanes by B.F. Goodrich (US 2,871,218) ushered in a new class of materials known as thermoplastic elastomers (TPE's). Below their respective softening temperatures, these materials possess physical characteristics typically observed for compounds which are based on thermoset elastomers with the processability attributes of traditional thermoplastics. Following these seminal discoveries, Gessler et. al. (US 3,037,954) described the preparation of a new category of TPE's known as thermoplastic vulcanizates (TPV's). TPV's are marked by the presence of a dispersed, thermoset, elastomeric phase contained within a thermoplastic continuous phase. This class of TPE is prepared through a dynamic vulcanization process in which the elastomeric phase is being dispersed, under constant shear, throughout a thermoplastic matrix while being vulcanized. This process ensures a uniform distribution of the thermoset within the plastic matrix in addition to minimizing thermoset domain size and domain size distribution. The pioneering work by Gessler et. al. laid the foundation for future TPV developments ultimately leading to the introduction of the most commercially significant class of TPV commercialized by Monsanto under the trade name Santoprene® (US 4,130,535 and US 4,311,628). Santoprene® is based on a dynamically vulcanized EPDM phase dispersed within a continuous matrix of polypropylene (PP).

The random copolymer of isobutylene (IB) and isoprene (IP) is a synthetic elastomer commonly referred to as butyl rubber (IIR). Since the 1940's, IIR has been prepared in a slurry process in which isobutylene is randomly copolymerized with small amounts of isoprene (1-2 mol %). The backbone structure of IIR, which is mostly comprised of polyisobutylene segments, imparts superior air impermeability, oxidative stability and excellent fatigue resistance to this material (*see* Chu, C. Y. and Vukov, R., *Macromolecules*, **18**, 1423-1430, 1985).

The first major application of IIR was in tire inner tubes. Despite the low levels of backbone unsaturation (ca. 0.8 to 1.8 mol %), IIR possesses sufficient vulcanization activity for inner tube

application. With the evolution of the tire inner liner, it became necessary to enhance the cure reactivity of IIR to levels typically found for conventional diene-based elastomers such as butadiene rubber (BR) or styrene-butadiene rubber (SBR). To this end, halogenated grades of butyl rubber were developed. The treatment of organic IIR solutions with elemental chlorine or bromine results in the isolation of halobutyl rubber (HIIR), such as chlorobutyl (CIIR) and bromobutyl (BIIR) rubber. These materials are marked by the presence of reactive allylic halides along the polymer main chain.

In preparing a TPV based on commercially available grades of butyl rubber, one has several cure packages which are compatible with IIR and/or HIIR. Regular butyl rubber can be vulcanized with a traditional sulfur-accelerator cure system or one based on phenolic resins. With halogenated grades of butyl rubber, comes increased cure versatility. In addition to traditional sulfur or phenolic resin based cure systems, halobutyl rubber can be cured with polyfunctional nitrogen or sulfur based nucleophiles, bismaleimides or Lewis acids such as ZnO. In fact, the first example of a TPV as provided by Gessler et. al. was comprised of a ZnO cured chlorobutyl elastomeric phase dispersed within a continuous matrix of polypropylene. In selecting the type of butyl on which to base a TPV, halobutyl possesses a number of disadvantages. Irrespective of the cure system employed, it is well known to those skilled in the art that cured articles based on halobutyl rubber contain small amounts of organic halides arising from vulcanization induced thermal degradation. While the levels of organic halides are quite small, their presence can preclude the use of halobutyl based TPV's in a variety of pharmaceutical and consumer goods applications.

While IIR lacks any organic halide or organic halide precursors, the cure versatility of this material is much more limited than that of halobutyl rubber. For reasons similar to those described above, the use of sulfur-accelerator cure systems may be viewed as problematic for pharmaceutical and consumer goods end uses. In this case, undesirable organic or inorganic sulfides are created as by-products of the vulcanization process. The use of a sulfur based cure system has the added disadvantage of yielding oligo-sulfide crosslinks of limited thermal stability. A low sulfur cure system possesses C-S bonds which have a dissociation energy of 285 kJ/mol. A traditional sulfur cure system possesses oligo-sulfido crosslinks with S-S covalent bond energies ranging from 155 kJ/mol to 270 kJ/mol (Sartomer Cure Concepts Volume 1). Given the high processing temperatures needed to melt and/or soften the thermoplastic component of a given TPV, the use of sulfur-based cure systems is problematic.

The use of a phenolic resin based cure system with IIR gives rise to cured articles which possess excellent heat resistance, flex to fatigue resistance and low levels of compression set. For IIR-based TPV's, the phenolic resin cure system is superior to traditional sulfur cure packages (stronger C-C crosslinks versus thermally labile C-S and S-S crosslinks). In fact, a TPV based on

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resin cured IIR is available from AES under the trade name Trefsin®. Trefsin® is used in applications where high levels of both gas and moisture impermeability are required.

While the use of resin cure systems avoid the stability limitations normally encountered with sulfur-based curatives, other limitations do exist. Specifically, resin cured TPV's are more hygroscopic and can discolor. In order to minimize the appearance of defects, excess absorbed moisture must be removed through a lengthy, high temperature, drying process prior to article fabrication. The tendency of these materials to discolor necessitates higher loadings of pigments or the use of additional types of pigments (K. Naskar, J. W. M. Noordermeer, Novel Peroxides as Crosslinking Agents in Dynamically Vulcanized Thermoplastic Elastomers, Paper given at 2006 IRC, Lyon, France).

Recently, the preparation of azide-functionalized butyl rubber (referred to as azidobutyl in the following) and self-cured azidobutyl vulcanizates has been described.

Self-curing azidobutyl offers several advantages over the cure systems discussed above. Self-cured azidobutyl formulations can be considered "clean" in that they do not contain any extractable organic or inorganic impurities resulting as unconverted starting material or side products from the cure chemistry. The clean rubber articles can therefore be used, for example, in condenser caps, biomedical devices, pharmaceutical closures and devices such as stoppers in medicine-containing vials, plungers in syringes and seals, such as seals for fuel cells. Where high levels of gas and moisture impermeability are required, an azidobutyl-based self-cured TPV would be desirable. Specifically, by avoiding the use of halobutyl rubber or regular butyl rubber with sulfur-based curatives one also removes the possibility of having the finished article contaminated with extractable organic and/or inorganic halides or sulfides. When compared to a butyl-based TPV which has been resin cured, a self-cured butyl TPV may not possess elevated levels of hygroscopicity nor the tendency to discolor. These enhancements would be of particular benefit for pharmaceutical and consumer goods applications.

There remains a need for a self-cured butyl TPV.

Summary of the Invention

Described herein is the preparation of a novel class of butyl-based TPVs in which the elastomeric phase is, for example, dynamically vulcanized, self-cured azidobutyl rubber.

According to an aspect of the present invention, there is provided a self-cured thermoplastic vulcanizate comprising: a thermoplastic; and, a vulcanized elastomeric material derived from an elastomer comprising repeating units derived from at least one isoolefin monomer and repeating

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units derived from at least one copolymerizable monomer, a plurality of the repeating units derived from the at least one copolymerizable monomer having one or more azide groups attached thereto.

According to another aspect of the present, there is provided a shaped article comprising a thermoplastic vulcanizate of the present invention.

- 5 According to another aspect of the present invention, there is provided a process for preparing a thermoplastic vulcanizate, the process comprising mixing a thermoplastic with an elastomer at a temperature of at least 100°C, the elastomer comprising repeating units derived from at least one isoolefin monomer and repeating units derived from at least one copolymerizable monomer, a plurality of the repeating units derived from the at least one copolymerizable monomer having one
10 or more azide groups attached thereto.

Detailed Description

The present invention relates to thermoplastic vulcanisates comprising azide group functionalized copolymers of at least one isoolefin monomer and at least one copolymerizable monomer, particularly olefinic monomers, and methods of preparing same.

- 15 The azidated copolymers of the present invention comprise repeating units derived from at least one isoolefin monomer and repeating units derived from at least one copolymerizable monomer, wherein a plurality of the repeating units derived from the at least one copolymerizable monomer have one or more azide groups attached thereto.

- 20 In one embodiment, an azide group is linked to a carbon atom of the repeating units through a C-N bond. The link between the azide group and the repeating unit of the copolymer is preferably through a direct bond, an aliphatic moiety (e.g. an alkylene moiety) or a *p*-methyl styrene moiety. Alkylene linkages, especially methylene linkages, and direct bonds are especially preferable. As indicated above, the azide is linked to the copolymer on the repeating units derived from the at least one copolymerizable monomer, not on the repeating units derived from the at least one isoolefin
25 monomer.

- The one or more repeating units comprising the azide group in the azidated copolymers may be on an end unit, or on a unit anywhere else in the polymer. In one embodiment, at least one of the one or more repeating units comprising the azide group is not at the end of the copolymer chain. The average number of azide groups per copolymer chain is preferably equal or greater than 2, or equal
30 or greater than 3, or equal or greater than 4, or equal or greater than 5, or equal or greater than 6, or equal or greater than 7, or equal or greater than 8, or equal or greater than 9, or equal or greater than 10. In one embodiment, about 20% to about 100% of the repeating units derived from the at least one copolymerizable monomer may be linked to azide groups.

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Azidated copolymers used by a process of the present invention preferably have a number average molecular weight (M_n) of about 20,000 g mol⁻¹ or greater, or about 30,000 g mol⁻¹ or greater, or about 40,000 g mol⁻¹ or greater, or about 50,000 g mol⁻¹ or greater, or about 60,000 g mol⁻¹ or greater. The number average molecular weight is preferably up to about 500,000 g mol⁻¹, or up to about 1,000,000 g mol⁻¹, or up to about 2,000,000 g mol⁻¹.

In embodiments, the Mooney viscosity (ML 1+8 at 125°C, ASTM 1646) of the azidated copolymer is greater than 5, or greater than 10, or greater than 15, or greater than 20.

In embodiments, when subjected to characterization with a Moving Die Rheometer and conforming to ASTM D5289, 1° arc, 1.7 Hz, 200°C, 30 min test time, the azidated copolymer may show an increase in torque ($M_h - M_l$) in a range of about 0.1 to 30 dNm, or about 0.2 to 20 dNm, or about 1 to 20 dNm, or about 0.5 to 15 dNm, or about 2 to 15 dNm, or about 2 to 10 dNm. Minimum torque (M_l) may be in a range of 0.5 to 5 dNm, or 0.6 to 4 dNm, or 0.7 to 3 dNm.

In embodiments, the azidated copolymer may be derived from a halobutyl rubber, wherein a compound prepared according to ASTM D3985 containing 100 phr of said bromobutyl rubber, 40 phr of IRB #7 black (carbon black), 1 phr of stearic acid and 5 phr of zinc oxide shows M_L in the range of about 1 to 10 dNm and M_H in a range of about 8 to 25 dNm, wherein M_L and M_H are determined according to ASTM D5289 at 160°C, 1° arc, 1.7 Hz die oscillation, 30 min running time, without preheat.

In embodiments, the azidated copolymer may be derived from a brominated polymer from isobutylene and paramethylstyrene (BIMS), wherein a compound prepared according to ASTM D3985 containing 100 phr of said BIMS, 40 phr of IRB #7 black (carbon black), 1 phr of stearic acid and 5 phr of zinc oxide shows M_L in the range of 1 to 10 dNm, M_H in the range of 8 to 25 dNm wherein M_L and M_H are determined according to ASTM D5289 at 160°C, 1° arc, 1.7 Hz die oscillation, 30 min running time, without preheat.

The at least one isoolefin monomer used in preparing the azidated copolymer is not limited to a particular isoolefin. In one embodiment, the suitable isoolefins have from 4 to 14 or from 4 to 7 carbon atoms. Preferred examples include isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene and mixtures thereof. Particularly preferred is isobutylene.

The at least one copolymerizable monomer used in preparing the azidated copolymer of the present invention may be olefinic monomers. In one embodiment the at least one copolymerizable monomer is a multiolefin monomer, divinyl aromatic monomer, alkyl substituted vinyl aromatic monomer, or mixtures thereof.

The multiolefin monomers used in preparing the azidated copolymers of the present invention are not limited to a particular multiolefin monomer. Suitable multiolefins have from 4 to 14 carbon atoms. Examples of such multiolefins include isoprene, butadiene, 2-methylbutadiene, 2,4-dimethylbutadiene, piperylene, 3-methyl-1,3-pentadiene, 2,4-hexadiene, 2-neopentylbutadiene, 2-methyl-1,5-hexadiene, 2,5-dimethyl-2,4-hexadiene, 2-methyl-1,4-pentadiene, 4-butyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2,3-dibutyl-1,3-pentadiene, 2-ethyl-1,3-pentadiene, 2-ethyl-1,3-butadiene, 2-methyl-1,6-heptadiene, cyclopentadiene, methylcyclopentadiene, cyclohexadiene, 1-vinyl-cyclohexadiene and mixtures thereof. In one embodiment, the conjugated diene is isoprene.

Alkyl substituted vinyl aromatic monomers and divinyl aromatic monomers useful in the present invention can have an aromatic core such as benzene, naphthalene, anthracene, phenanthrene or biphenyl. In one embodiment, the divinyl aromatic monomer used in the present invention is vinyl styrene. In one embodiment, the alkyl-substituted vinyl aromatic monomer is a C₁-C₄ alkyl substituted styrene. In one embodiment, C₁-C₄ alkyl substituted styrene includes, for example, *o*-methyl styrene, *p*-methyl styrene, or *m*-methyl styrene.

In one embodiment the azidated copolymer of the present invention comprises copolymers of isoolefin and a multiolefin (hereinafter referred to as isoolefin-multiolefin copolymers). In such an embodiment, one or more of the repeating units derived from the multiolefin monomers comprise an azide moiety. In one embodiment one or more of the repeating units derived from the multiolefin monomers comprise an allylic azide moiety.

In one embodiment the azidated copolymer of the present invention comprises copolymers of isobutylene and isoprene. In one such embodiment the repeating units derived from isoprene comprise allylic azide moiety.

In one embodiment, the monomer mixture used in preparing the isoolefin-multiolefin copolymer comprises from about 80% to about 99.5% by weight of at least one isoolefin monomer and from about 0.5% to about 20% by weight of at least one multiolefin monomer. In one embodiment, the monomer mixture comprises from about 83% to about 98% by weight of at least one isoolefin monomer and from about 2.0% to about 17% by weight of a multiolefin monomer.

In one embodiment, the isoolefin-multiolefin copolymer comprises at least 0.5 mol% repeating units derived from the multiolefin monomers. In one embodiment, the repeating units derived from the multiolefin monomers are at least 0.75 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are at least 1.0 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are at least 1.5 mol%. In one embodiment, the repeating

units derived from the multiolefin monomers are at least 2.0 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are at least 2.5 mol%.

In one embodiment, the isoolefin-multiolefin copolymer comprises at least 3.0 mol% repeating units derived from the multiolefin monomers. In one embodiment, the repeating units derived from the multiolefin monomers are at least 4.0 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are at least 5.0 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are at least 6.0 mol%. In one embodiment, the repeating units derived from the multiolefin monomers at least 7.0 mol%.

In one embodiment, the repeating units derived from the multiolefin monomers are from about 0.5 mol% to about 20 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are from about 0.5 mol% to about 8 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are from about 0.5 mol% to about 4 mol%. In one embodiment, the repeating units derived from the multiolefin monomers are from about 0.5 mol% to about 2.5 mol%.

The preparation of a isoolefin-multiolefin copolymer having at least about 2.0 mol% repeating units derived from at least one multiolefin monomer is described, for example, in Canadian Patent No. 2,418,884, which is incorporated herein by reference in its entirety.

In one embodiment, the azidated copolymers of the present invention comprise copolymers of at least one isoolefin and one or more alkyl substituted aromatic vinyl monomers. In such an embodiment, one or more of the repeating units derived from the aromatic vinyl monomers comprise the azide moiety.

In one embodiment, the azidated copolymers of the present invention comprise repeating units derived from isobutylene and *p*-methyl styrene, wherein one or more repeating units derived from the *p*-methyl styrene have a benzylic azido group, as described in U.S. Patent. No. 5,013,793, which is incorporated herein by reference in its entirety.

In one embodiment, the copolymers of isoolefins monomers and alkyl aromatic vinyl monomers comprise repeating units derived from the alkyl aromatic vinyl moieties from about 0.5 weight percent to about 25 weight percent of the copolymer. In one embodiment, the alkyl aromatic repeating units are from about 1 to about 20 weight percent. In one embodiment, the alkyl aromatic repeating units are from about 2 to about 10 weight percent.

In one embodiment, the azidated copolymer of the present invention comprises a terpolymer of isobutylene, isoprene and alkyl substituted styrene, wherein one or more repeating units derived

from the isoprene have an allylic azido moiety and/or one or more repeating units derived from said *p*-methyl styrene have a benzylic azido group.

In one embodiment, the azidated copolymer comprises terpolymers of isobutylene, isoprene, and *p*-methyl styrene as described in U.S. Patent. No. 6,960,632, which is incorporated herein by
5 reference in its entirety.

In one embodiment, the monomer mixture used in preparing the copolymer of isoolefin, the multiolefin and the alkyl substituted aromatic vinyl monomers comprise from about 80% to about 99% by weight of isoolefin monomers, from about 0.5% to about 5% by weight the multiolefin monomers, and from about 0.5% to about 15% by weight of the alkyl substituted aromatic vinyl
10 monomers. In one embodiment, the monomer mixture comprises from about 85% to about 99% by weight of isoolefin monomer, from about 0.5% to about 5% by weight the multiolefin monomer and from about 0.5% to about 10% by weight alkyl substituted aromatic vinyl monomer.

In one embodiment, the azidated copolymer of the present invention comprises terpolymers of isobutylene, isoprene, and divinyl styrene, as described in U.S. Patent. No. 4,916,180, which is
15 incorporated herein by reference in its entirety.

The mixture used to produce multiolefin butyl rubber polymer may further comprise a multiolefin cross-linking agent. The term cross-linking agent is a term known to persons skilled in the art and is understood to denote a compound that causes chemical cross-linking between the polymer chains as opposed to a monomer that will add to the chain. Examples of suitable cross-linking agents
20 include norbornadiene, 2-isopropenylnorbornene, 2-vinyl-norbornene, 1,3,5-hexatriene, 2-phenyl-1,3-butadiene, divinylbenzene, diisopropenylbenzene, divinyltoluene, divinylxylene and C₁₋₂₀ alkyl substituted derivatives thereof. More preferably, the multiolefin cross-linking agent is divinylbenzene, diiso-propenylbenzene, divinyltoluene, divinyl-xylene and C₁₋₂₀ alkyl substituted derivatives thereof, and/or mixtures of the compounds given. Most preferably, the multiolefin
25 cross-linking agent comprises divinyl-benzene and diiso-propenylbenzene.

In one aspect of the present invention, the azidated copolymer of the present invention is a star branched copolymer linked to a branching moiety. In one embodiment, the branching moiety is a polymeric branching moiety. The polymeric branching moiety useful in the formation of the star branched polymer of the present invention includes polymers and copolymers comprising
30 functional groups capable of copolymerizing or forming a covalent bond with the active chain end of a growing polymeric chain of the copolymer used in the formation of the halogenated polymer. The functional group comprises cationically active unsaturation. Non-limiting examples of such polymeric moieties include polydienes, partially hydrogenated polydienes, such as polybutadiene,

polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene monomer rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. Star branched polymers of the present invention can be prepared by first linking the polymeric chains with the branching moiety followed by halogenations of the polymeric chains. Preparation of starch branch polymers is described in U.S. Patent No. 5,182,333 and European Publication No., 0 320 263, which are incorporated herein by reference in their entirety.

Any thermoplastic known to those skilled in the art as being suitable for use in the formation of thermoplastic vulcanizates can be used. The selected thermoplastic or thermoplastics preferably melt at temperatures in the range of 60 to 250°C. Examples of suitable thermoplastics include polypropylene, polyethylene, polystyrene, acrylonitrile-butadiene-styrene (ABS), allyl resins, ethylene vinyl alcohol, fluoroplastics, polyacetals, polyacrylates, polyacrylonitriles, polyamides, polyimides, polycarbonates, polyesters, polyethylene oxide, polypropylene oxide, polyethylene glycol, polypropylene glycol, polyvinylidene chloride or mixtures thereof.

The elastomer is preferably provided in an amount of from about 20 to 80 wt% of the thermoplastic, more preferably from about 30 to 70 wt%, yet more preferably from about 40 to 60 wt%. The elastomer is mixed with the thermoplastic and preferably uniformly dispersed throughout the thermoplastic in order that the thermoplastic vulcanizate formed upon self-curing of the mixture has substantially consistent properties throughout. Any suitable mixing method or equipment may be used that achieves uniform dispersion of the elastomer in the thermoplastic; for example, an internal mixer, a mill, or an extruder may be used. In a preferred method, the thermoplastic and elastomer are provided as pellets or beads and mixed using an extruder that produces conditions sufficient to melt at least the thermoplastic and preferably both the thermoplastic and the elastomer. The thermoplastic and the elastomer may be provided to the extruder either together or sequentially. The temperature of the thermoplastic and elastomer in the extruder during mixing is preferably at least about 100°C, more preferably at least about 130°C, yet more preferably at least about 150°C, even more preferably at least about 160°C.

During the melt blending of the thermoplastic and elastomer the self-cure of the azidobutyl brings about the formation of the thermoplastic vulcanizate. Curing is usually performed at a temperature in the range of from about 100°C to 250°C, preferably about 110°C to 220°C, more preferably about 130°C to 200°C.

The thermoplastic vulcanizate may be used to create a variety of shaped articles that are particularly suitable for high-purity applications. The shaped articles may be formed by any suitable method, for example extrusion molding, injection molding, blow molding or the like. The shaped articles may comprise, for example, condenser caps, medical components, such as

components of biomedical devices or pharmaceutical devices such as stoppers in medicine-containing vials, plungers in syringes, etc., in fuel cell components, such as seals, and as material for tanks and cylinders for compressed liquids and gases.

5 The vulcanizates according to the present invention are useful in tire inner liners, pharmaceutical closures, pharmastoppers, components of medical devices including syringe plungers, Noise Vibration and Harshness damping materials, lightweight gas barrier materials, for grips, handles, handle bars, sports rackets, consumer goods, shopping cart handles, steering bars, steering wheels, weather stripping, condenser caps, golf balls, shoe soles, fuel cell components, seals and gaskets including but not limited to in-place gaskets, orthopedic devices, extruded profiles, and hoses such
10 as hoses for air conditioning coolant.

The thermoplastic vulcanizates of the present invention may comprise mineral or non-mineral fillers of the type known to persons skilled in the art to be suitable for use with butyl rubber or butyl rubber compounds. The amounts are conventionally from 1 to 50% by weight of the thermoplastic vulcanizate. The fillers may be added to the extruder during mixing of the
15 thermoplastic with the elastomer and/or with the elastomer itself during formation thereof. Examples of suitable fillers include carbon black, talc, silica, titanium dioxide, etc. The thermoplastic vulcanizates of the present invention can also contain further auxiliary products for rubbers, such as reaction accelerators, vulcanizing accelerators, vulcanizing acceleration auxiliaries, antioxidants, foaming agents, anti-aging agents, heat stabilizers, light stabilizers, ozone
20 stabilizers, processing aids, plasticizers, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, inhibitors, metal oxides, and activators such as triethanolamine, polyethylene glycol, hexanetriol, etc., which are known to the rubber industry. For “clean” applications, non-toxic and/or non-leachable fillers and/or auxiliary products are preferably used. Fillers such as plasticizers are preferably not used in such “clean” applications.

25 Further features of the invention will now be described with reference to the following Examples.

Examples

Materials

LANXESS Butyl 301, a isobutylene-isoprene copolymer having an unsaturation of 1.85 ± 0.2 mol-% was used in comparative examples. Polypropylene (Pro-fax 6823, Basell), and two polyamides
30 were used as thermoplastic. The polyamides were LANXESS Durethan CI 31 F, a partial aromatic, amorphous polyamide (PA6I), and Grilon CF 6 S, a PA612 supplied by EMS Grivory. N-Butyl benzenesulfonamide (BBSA, Unitex) was used as plasticizer for polyamide-containing mixes, Irganox 1010 and Irganox 1098 (BASF) was used as antioxidant, if applicable.

Bromobutyl 2030 is a brominated isobutylene–isoprene rubber having a bromine content of $1,8 \pm 0,2$ wt-% and a Mooney viscosity of 32 ± 4 MU.

Bromobutyl X2 is a brominated isobutylene–isoprene rubber having a bromine content of $1,8 \pm 0,2$ wt-% and a Mooney viscosity of 46 ± 4 MU.

5 *Example 1a.* LANXESS Bromobutyl 2030 (241 g) was dissolved in tetrahydrofuran (1914 g) and tetrabutylammonium azide (11.2 g) was added to the solution. The mixture was then shaken at room temperature for 1 day. Then acetone was added and the precipitated elastomer was separated from the solvent and dried. The conversion of allylic bromide to allylic azide units was quantitative according to ^1H NMR.

10 *Example 1b.* LANXESS Bromobutyl X2 (250 g) was dissolved in tetrahydrofuran (1333 g) and tetrabutylammonium azide (10.9 g) was added to the solution. The mixture was then shaken at room temperature for 5 hours. Then acetone was added and the precipitated elastomer was separated from the solvent and dried. The conversion of allylic bromide to allylic azide units was 85% according to ^1H NMR.

15 **Blending procedure**

The thermoplastic and the elastomer blends were prepared and injection molded using a DSM Xplore Microcompounder (DSM, 15 mL mixing volume) to form test specimen for tensile testing. The barrel was heated to temperature between 190 and 210 °C, the rotor speed was 100 rpm. For the studies containing polyamide as thermoplastic BBSA plasticizer was added using a syringe.

20 The order of addition of the different materials was as follows: (i) Thermoplastic, (ii) optionally BBSA, (iii) rubber and antioxidant. After a specific mixing time the blend was injection molded into a S2 Microdumbbell mold. The dumbbells were used for tensile testing and extraction experiments. Data in examples present the average and standard deviation of runs performed in triplicate.

25 **Soxhlet Extraction**

Approximately 3.0 g of selected samples were pressed in a 46x46 cm, 0-100 Ton 4 Post Self Contained Press by inserting the sample in Teflon sheets between two metal plates. The sheets were then cut into smaller pieces.

For polyamide-containing blends Soxhlet extractions were performed as described below. The pressed pieces were inserted into thimbles for extraction. The masses of the compounds and thimbles were recorded before beginning extraction. For the PA containing samples, glass microfibre thimbles were used, added to the Soxhlet apparatus and extracted with refluxing toluene

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for 4 h, formic acid for 4 h, toluene for 4 h, and formic acid for 4 h. For the PP containing samples, cellulose thimbles were used added to the Soxhlet apparatus and extracted with refluxing xylene for 12 hours.

After the final extraction, the thimbles were dried under vacuum %mass remaining was calculated.

5 A residual mass is indicative of crosslinked elastomer.

Blends with polypropylene

Table 1 summarizes Examples 2 to 7. Examples 2 to 7 contain polypropylene as thermoplastic. The mix temperatures ranged from 190 to 210°C, at 2.5 to 7 min mixing time. The mold temperature was 25°C, tensile tests were performed at 100 mm per min.

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Table 1.

Example	Elastomer type at 100 phr	Polypropylene [phr]	Mix temperature [°C]	Break stress [MPa]	Elongation at break [%]	Extraction residue
2	LANXESS Butyl 301	100	190	27.6 ± 1.7	59 ± 8	0%
3	LANXESS Butyl 301	100	200	23.9 ± 0.4	79 ± 14	0%
4	LANXESS Butyl 301	100	210	19.3 ± 1.4	112 ± 26	Not determined
5	Example 1a	100	190	23.3 ± 3.1	208 ± 48	58%
6	Example 1a	100	200	25.3 ± 1.0	350 ± 11	42%
7	Example 1a	100	210	25.0 ± 1.4	364 ± 16	Not determined

15 Examples 2 to 4 are comparative, blending according to these conditions gave a material with an elongation at break of 59% to 112% and a break stress of 27.6 to 19.3 MPa, respectively. Upon Soxhlet extraction of Example 2 and 3 no material remained in the Soxhlet thimble, thus no crosslinking had taken place during the blending process.

20 Examples 5 to 7 are inventive examples, blending according to the same conditions as in Examples 2 to 4, but using Azidobutyl 2030 gave a material with an elongation at break of 208% to 364 %. This is significantly higher than those of Examples 2 to 4. Examples 5 to 7 also showed a break stress of 25.3 and 25.0 MPa, respectively. This is on par or higher than those of comparative Examples 3 and 4.

Blends with Polyamides

Table 2 summarizes Examples 8 to 19. Examples 8 to 19 contain two different polyamides as thermoplastic. The mix temperatures ranged from 200°C to 210°C, at 2.5 to 7 min mixing time. Different levels of BBSA were employed as plasticizer for the polyamide phase. All blends furthermore contained 0.3 phr Irganox 1010 and 0.22 phr Irganox 1098. Mix and mold temperatures were dependant on the type of polyamide used (refer to T_{Mix} and T_{Mold} in Table 2).

Table 2.

Ex.	Elastomer type (Amount 100 phr)	BBSA phr	T_{mix} [°C]	T_{mold} [°C]	Break stress [MPa]	Elongation at break [%]	Extraction [% residual mass]
8	LANXESS Butyl 301	0	210	100	9.3 ± 2.0	23 ± 3	0
9	LANXESS Butyl 301	17	210	100	5.7 ± 0.7	89 ± 4	n.d.
10	LANXESS Butyl 301	22	210	100	4.9 ± 0.5	95 ± 7	n.d.
11	LANXESS Butyl 301	27	210	100	4.4 ± 0.2	81 ± 15	n.d.
12	Example 1b	0	210	100	8.6 ± 0.8	50 ± 5	23
13	Example 1b	17	210	100	12.2 ± 0.4	205 ± 20	n.d.
14	Example 1b	22	210	100	10.1 ± 0.7	201 ± 13	n.d.
15	Example 1b	27	210	100	10.7 ± 1.5	202 ± 60	19
16	LANXESS Butyl 301	0	200	70	6.0 ± 1.7	178 ± 23	n.d.
17	LANXESS Butyl 301	27	200	70	5.8 ± 1.1	233 ± 25	n.d.
18	Example 1b	0	200	70	10.5 ± 0.8	299 ± 14	n.d.
19	Example 1b	27	200	70	10.7 ± 2.3	383 ± 7	n.d.

In each of examples 8 to 15 63 phr of Durethan CI 31 F was used, for examples 16 to 19 63 phr of Grilon CF 6 S.

Examples 8 to 11 are comparative examples based on Durethan CI 31 F as thermoplastic; blending according to these conditions gave a material with an elongation at break of 23% to 95 % and a break stress in the range of 4.4 MPa to 9.3 MPa. Upon Soxhlet extraction of Example 8 no material remained in the Soxhlet thimble, thus no crosslinking had taken place during the blending process.

Examples 12 – 15 are inventive examples are comparative examples based on Durethan CI 31 F as thermoplastic; blending according to the same conditions as in Examples 8 to 11, but using Azidobutyl X2 gave a material with an elongation at break of 50% to 205 %. This is significantly

- higher than those of respective Examples 8 to 11. Examples 13 to 15 also showed a break stress in the range of 10.1 MPa to 12.2 MPa. This is higher than those of comparative Examples 9 to 11. Examples 12 and 15 show a mass residue upon extensive extraction. Thus, crosslinking has taken place during blending. Furthermore, the extraction residue of Example 12 and 15 was characterized by infrared spectroscopy. Respective spectra showed absorption bands characteristic for butyl rubber (i.e. at 1360 cm^{-1} and 1390 cm^{-1}) as well as absorption bands characteristic for the polyamide (i.e. at 1550 cm^{-1} and 1650 cm^{-1}). Without wishing to be bound by theory, this result suggests that covalent grafting between Example 1b and the polyamide has occurred during the reactive blending process.
- 10 Examples 16 to 17 are comparative examples based on Grilon CF 6 S, blending according to these conditions gave a material with an elongation at break of 178% to 233 % and a break stress in the range of 6.0 MPa to 5.8 MPa.
- 15 Examples 18 to 19 are inventive examples based on Grilon CF 6 S, blending according to the same conditions as in Examples 16 to 17, but using Azidobutyl X2 gave a material with an elongation at break of 299% to 383%. This is significantly higher than those of respective Examples 16 to 17. Examples 18 to 19 also showed a break stress in the range of 10.5 to 10.7 MPa. This is higher than those of comparative Examples 16 to 17.

Claims:

1. A self-cured thermoplastic vulcanizate comprising: a thermoplastic; and, a vulcanized elastomeric material derived from an elastomer comprising repeating units derived from at least one isoolefin monomer and repeating units derived from at least one copolymerizable monomer comprising a multiolefin monomer, divinyl aromatic monomer, alkyl substituted vinyl aromatic monomer or any mixture thereof, a plurality of the repeating units derived from the at least one copolymerizable monomer having one or more azide groups attached thereto.
2. The vulcanizate according to claim 1, wherein the azide group is linked to a carbon atom of the repeating units of the at least one copolymerizable monomer through a C-N bond.
3. The vulcanizate according to claim 1, wherein the azide group is linked to a carbon atom of the repeating units of the at least one copolymerizable monomer through an alkylene moiety.
4. the vulcanizate according to claim , wherein the azide group is linked to a carbon atom of the repeating units of the at least one copolymerizable monomer through an allylic moiety.¹
5. The vulcanizate according to any one of claims 1 to 4, wherein at least one of the plurality of repeating units comprising the azide group is not at an end of the copolymer.
6. The vulcanizate according to any one of claims 1 to 5, wherein average number of azide groups per copolymer is greater than 3.
7. The vulcanizate according to any one of claims 1 to 6, wherein number average molecular weight (M_n) of the copolymer is about 20,000 g mol⁻¹ or greater.
8. The vulcanizate according to any one of claims 1 to 7, wherein from about 20% to about 100% of the repeating units derived from the at least one copolymerizable monomer are linked to azide groups.
9. The vulcanizate according to any one of claims 1 to 8, wherein the thermoplastic comprises polypropylene, polyethylene, polystyrene, acrylonitrile-butadiene-styrene (ABS), allyl resins, ethylene vinyl alcohol, fluoroplastics, polyacetals, polyacrylates, polyacrylonitriles, polyamides, polyimides, polycarbonates, polyesters, polyethylene oxide, polypropylene

oxide, polyethylene glycol, polypropylene glycol, polyvinylidene chloride or mixtures thereof.

10. The vulcanizate according to any one of claims 1 to 9, wherein the thermoplastic the elastomer is present in an amount of from about 20 to 80 wt% of the thermoplastic.
- 5 11. The vulcanizate according to any one of claims 1 to 9, consisting essentially of the thermoplastic, the elastomer and one or more non-toxic and/or non-leachable fillers and/or auxiliary products selected from the group consisting of carbon black, talc, silica, titanium dioxide, reaction accelerators, vulcanizing accelerators, vulcanizing acceleration auxiliaries, antioxidants, foaming agents, anti-aging agents, heat stabilizers, light
10 stabilizers, ozone stabilizers, processing aids, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, inhibitors, metal oxides and activators.
12. A process for preparing a thermoplastic vulcanizate, the process comprising mixing a thermoplastic with an elastomer at a temperature of at least 100°C, the elastomer comprising repeating units derived from at least one isoolefin monomer and repeating units
15 derived from at least one copolymerizable monomer comprising a multiolefin monomer, divinyl aromatic monomer, alkyl substituted vinyl aromatic monomer or any mixture thereof, a plurality of the repeating units derived from the at least one copolymerizable monomer having one or more azide groups attached thereto.
13. The process according to claim 12, wherein the vulcanizate is self-cured at a temperature in
20 a range of about 100°C to 250°C.
14. The process according to any one of claims 12 to 13, wherein the mixing is performed in an extruder that produces conditions sufficient to melt at least the thermoplastic.
15. A shaped article comprising a thermoplastic vulcanizate as defined in any one of claims 1 to 11.
- 25 16. The shaped article according to claim 15, which is a pharmaceutical closure, a pharmastopper or a component of a medical device.
17. A self-curable composition comprising: a thermoplastic; and an elastomer comprising repeating units derived from at least one isoolefin monomer and repeating units derived from at least one copolymerizable monomer comprising a multiolefin monomer, divinyl
30 aromatic monomer, alkyl substituted vinyl aromatic monomer or any mixture thereof, a

plurality of the repeating units derived from the at least one copolymerizable monomer having one or more azide groups attached thereto.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2014/050602

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C08J 3/24** (2006.01), **C08L 101/12** (2006.01), **C08L 23/36** (2006.01), **C08F 8/30** (2006.01)

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)

IPC: **C08J 3/24** (2006.01), **C08L 101/12** (2006.01), **C08L 23/36** (2006.01), **C08F 8/30** (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Google, Total Patent, Intellect, Canadian Patent Database, USPTO, CAPlus [thermoplastic, vulcanizate, elastomer, isooolefin, divinyl, aromatic, azide]

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Zhao, Yi-bo, Huozhayao Xuebao (2012), 35(2), 58-61 English abstract	1-17
A	Jiu, Yongbin, Gaofenzi Cailiao Kexue Yu Gongcheng (2011), 27(6), 34-37 English abstract	1-17
A	US2003082364A1, 01 May 2003 (01-05-2003) Abstract, [0003], [0013], [0016]	1-17
A	US5310795A, 10 May 1994 (10-05-1994) abstract	1-17

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 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 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 document member of the same patent family
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25 August 2014 (25-08-2014)Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US2003082364A1	01 May 2003 (01-05-2003)	None	
US5310795A	10 May 1994 (10-05-1994)	US5310795A DE69419794D1 DE69419794T2 EP0616009A2 EP0616009A3 EP0616009B1 ES2133486T3 JPH06298944A JP3069487B2 US5334659A	10 May 1994 (10-05-1994) 09 September 1999 (09-09-1999) 23 March 2000 (23-03-2000) 21 September 1994 (21-09-1994) 04 January 1995 (04-01-1995) 04 August 1999 (04-08-1999) 16 September 1999 (16-09-1999) 25 October 1994 (25-10-1994) 24 July 2000 (24-07-2000) 02 August 1994 (02-08-1994)