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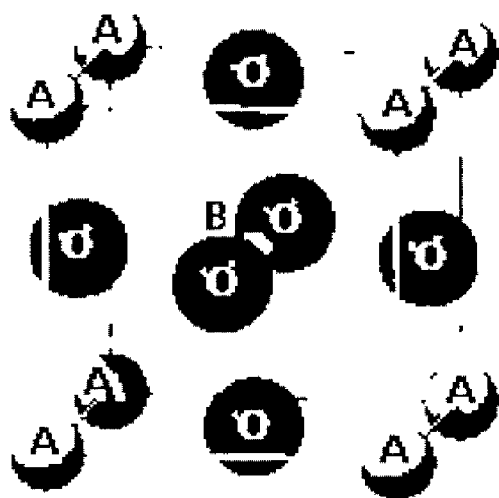
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(54) Title: USE OF A MINERAL HAVING PEROVSKITE STRUCTURE IN VINYL AROMATIC POLYMER FOAM

Fig. 1



(57) Abstract: The invention relates to the use of a mineral having perovskite structure in vinyl aromatic polymer foam, i) for decreasing the thermal conductivity, ii) for increasing the mechanical properties (namely compressive strength and bending strength), or iii) for improving the self-extinguishing properties of the foam. The polymer foam further comprises one or more athermanous additives selected from a) powder inorganic additive selected from powders of silica and calcium phosphate, b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder geopolymer composite.



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Use of a mineral having perovskite structure in vinyl aromatic polymer foam

The present invention relates to the use of mineral having perovskite structure in vinyl aromatic polymer foam, preferably i) for decreasing the thermal conductivity, ii) for increasing the mechanical properties (namely compressive strength and bending strength), or iii) for improving the self-extinguishing properties of the foam. The invention also relates to processes for the preparation of expandable polymer granulate and the expandable polymer granulate. The invention further relates to vinyl aromatic polymer foam and to a masterbatch comprising the mineral having perovskite structure.

Vinyl aromatic polymers are known and are used for the preparation of expanded products that are adopted in a variety of applications, of which the most important one is for thermal insulation. This is why there is a continuously increasing demand for expanded vinyl aromatic polymers with low thermal conductivity as well as good mechanical and self-extinguishing properties.

It is generally known that the addition of athermanous additives from the group of heat absorbers (e.g. carbon black), heat scatterers (e.g. minerals from the group of silicas and titanium oxides) and heat reflectors (e.g. aluminium pigment and graphite) decreases the thermal conductivity of vinyl aromatic polymer foams. Examples for such types of polymers are those obtained by suspension polymerization of vinyl aromatic monomer(s) (in particular of styrene) and optionally comonomers. Other examples for such type of polymers are those ob-

tained by the extrusion of general purpose polystyrene or its copolymers.

Typically, the addition of a combination of athermanous additives that can absorb or scatter heat radiation to prolong the IR rays' pathway results in a significant decrease of thermal conductivity. However, the addition of IR reflectors results in the most advantageous effect. A combination of IR scatterers and IR reflectors can influence the reduction of the concentration of typical IR absorbers (such as carbon black) and leads to an improvement of the self-extinguishing effect of polystyrene foams. However, an addition of carbon black, especially in extrusion processes, requires the addition of a relatively high amount of brominated flame retardant, to maintain acceptable self-extinguishing properties, e.g. suitable performance for passing the flammability test according to the German industry standard DIN 4102 (B1, B2).

Poor thermal stability of foams made of vinyl aromatic polymers filled with carbon-based athermanous additives is also a problem. Such foams, having black or grey colour, absorb a relatively high amount of heat energy, thus the insulation boards made thereof and applied on building walls can shrink or deform significantly. Thus, the insulation performance may deteriorate. Finally, when trying to create an optimum cell structure with a narrow cell size distribution, in order to obtain materials with significantly decreased thermal conductivity, several problems were indentified when using carbon black, graphite or especially mineral athermanous additives, because these additives also act as nucleating agents and have a negative effect on bubble formation.

On the other hand, the presence of small amounts of athermanous fillers of the heat scatterer type does not result in a substantial deterioration of the flame retarded polymer foam's self-extinguishing properties. Rather, these properties are improved, but the decrease of the foam's thermal conductivity is not as pronounced as it would be in foams comprising carbon-based additives, i.e. comprising athermanous additives of the heat absorber or of the heat reflector type (in particular carbon blacks and/or graphites).

WO 2006/058733 A1 teaches expandable styrene polymer granulates containing a) filler selected from the group of inorganic powder materials (such as silicic acid) and b) carbon black or graphite. The amount of a) filler is 5 to 50 wt.%, and the amount of b) carbon black or graphite is 0.1 to 10 wt.%. The filler of WO 2006/058733 A1 has an average particle diameter in a range of from 1 to 100 μm .

EP 0 620 246 A1 teaches the use of athermanous materials in polystyrene hard foam (EPS or XPS). Examples for athermanous materials are metal oxides (such as Fe_2O_3 or Al_2O_3), non-metal oxides (such as SiO_2), metal powder, aluminium powder, carbon (such as carbon black, graphite or even diamond), or organic colorants or colorant pigments.

JP 63183941 teaches the use of aluminium pigment, titanium dioxide and graphite, having specific particle size and heat radiation reflectivity, to decrease the thermal conductivity of polystyrene foams. The silica powder used in Example 6 as

listed in Table 1 of JP 63183941 has an average particle size of 3.2 μm .

EP 0 632 522 A, JPH08311232 and JP2001279014 A teach foams containing powder ceramics and the use of such foams in the preparation of dielectric lenses.

WO2010/128369 A1 teaches thermoinsulating expanded articles comprising an expanded polymeric matrix, obtained by expansion and sintering of beads/granules of a vinyl aromatic (co)polymer, in whose interior a filler is homogeneously dispersed, which comprises at least one athermanous material selected from coke, graphite and carbon black and optionally an active inorganic additive within the wave-lengths ranging from 100 to 20,000 cm^{-1} . The polymeric matrix comprises a copolymer of styrene and at least one vinyl aromatic comonomer substituted in the ring or on the vinyl group and/or a mixture of polystyrene and up to 10% by weight, with respect to the mixture, of a thermoplastic polymer compatible with polystyrene and having a glass transition temperature $> 100^{\circ}\text{C}$.

US 2012/0091388 A1 discloses expanded vinyl aromatic polymers comprising a. graphite, b. optional self-extinguishing brominated additive, c. optional synergist for b., and d. optional inorganic additive. An example for d. inorganic additive is silicon oxide (such as aerosilica). The BET surface of a typical aerosilica is well above 100 m^2/g , and the particle size is well below 10 nm. When using aerosilica for example in an extrusion process for the production of expandable vinyl aromatic polymer granulate, it is impossible to stabilize the process even in the presence of small amounts of aerosilica,

e.g. below 1 wt. %: because of aerosilica's very high BET, the resultant modification of rheology is so strong that pressure increases dramatically and it is not possible to stabilize the process and the granulate.

WO 2012/024709 A1 teaches flame retarded expandable polymers containing solid carbon-based additives containing sulphur, wherein the sulphur content is at least 2000 ppm. Examples for the solid additive are anthracite, coke and carbon dust.

A desired expanded polymer foam should contain athermanous filler(s) of a type and in an amount that maintain the foam's self-extinguishing and mechanical properties in the same range as in an expanded polymer without such fillers, and that at the same time decrease the thermal conductivity of the foam.

It has now surprisingly been found in accordance with the present invention that the use of mineral having perovskite structure decreases the thermal conductivity of vinyl aromatic polymer foam, without adversely affecting the foam's flammability and mechanical properties.

The present invention has the following aspects:

- (I) the use of mineral having perovskite structure in vinyl aromatic polymer foam;
- (II) processes for the preparation of expandable polymer granulate;
- (III) expandable polymer granulate comprising x) mineral having perovskite structure and y) vinyl aromatic polymer;

- (IV) vinyl aromatic polymer foam comprising x) mineral having perovskite structure and y) vinyl aromatic polymer; and
- (V) a masterbatch comprising x) mineral having perovskite structure and y) vinyl aromatic polymer.

Detailed description

In a first aspect, the invention relates to the use of a mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure (in the following "*mineral having perovskite structure*", or "*perovskite*") in vinyl aromatic polymer foam. The foam further comprises one or more athermanous additives selected from a) powder inorganic additive selected from powders of silica and calcium phosphate, b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder geopolymer composite.

According to a first embodiment of the first aspect, the invention relates to the use of mineral having perovskite structure for decreasing the thermal conductivity of the vinyl aromatic polymer foam, the decrease being measured according to ISO 8301.

According to a second embodiment of the first aspect, the present invention relates to the use of mineral having perovskite structure for improving the mechanical properties, specifically for increasing compressive strength and bending strength, of vinyl aromatic polymer foam, the increase in com-

pressive strength and in bending strength being measured in accordance with EN 13163.

According to a third embodiment of the first aspect, the present invention relates to the use of mineral having perovskite structure for improving the self-extinguishing properties of vinyl aromatic polymer foam, the improvement being measured in accordance with EN ISO 11925-2. Perovskite reduces flame development by the creation of char with higher viscosity and thus reduces dripping and flaming. Preferably, the improvement of the self-extinguishing properties is an improvement as measured in accordance with DIN 4102 B1, B2.

The preferred concentration of mineral having perovskite structure in the vinyl aromatic polymer foam, for i) the decrease of the thermal conductivity, ii) the improvement of the specified mechanical properties, and iii) the increase of the self-extinguishing properties, is in a range of from 0.01 to 50 wt.%, based on the weight of vinyl aromatic polymer in the granulate including solid and, if any, liquid additives, but exclusive of propellant, more preferably 0.05 to 25 wt.%, most preferably 0.1 to 15 wt.%, in particular 0.5 to 12 wt.%, such as 1 to 8 wt.%.

The mineral having perovskite structure as used in accordance with the invention has a crystalline structure of general formula of ABX_3 , where A and B are two cations of different sizes and X is an anion that bonds to both, the A atoms are larger than the B atoms, and its ionic radii close to that on the anion X thus they can form together a cubic (orthorhombic) close packing with space group Pm3m. In the structure, the B cation

is 6-fold coordinated and A cation 12-fold coordinated with the oxygen anions.

A ideal cubic perovskite structure has cations A at the corners of the cube, and cation B in the centre, with oxygen ions in the face-centered positions, as shown in Fig. 1 (structure of the ideal cubic perovskite (ABO_3), where A represents cation, B represents cation, and O represents oxygen anions forming an octahedron).

For the stoichiometric oxide perovskites, the sum of the oxidation states of cations A and B should be equal to 6.

Preferably, A is selected from the group consisting of Ca, Sr, Ba, Bi, Ce, Fe, and mixtures thereof. Moreover, the A atom can be represented also by hybrid organic-inorganic groups, e.g. $(\text{CH}_3\text{NH}_3)^+$.

Among the most preferred representatives of perovskite structures are dielectric BaTiO_3 , high-temperature semiconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, materials exhibiting magnetoresistance $\text{R}_{1-x}\text{A}_x\text{MnO}_3$, where $\text{R} = \text{La}^{3+}$, Pr^{3+} or other earth ion, $\text{A} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} , Bi^{2+} , Ce^{2+} , and multiferroic materials.

The B atom is preferably represented by Ti, Zr, Ni, Al, Ga, In, Bi, Sc, Cr, Pb as well as ammonium groups. The X atom is preferably represented by oxygen or halide ion, or mixtures thereof.

Perovskites have large reflectance properties in the broad wavelength and a high optical constant, even in the far-infrared region. Hence, perovskites are infrared reflective materials that reflect infrared rays included in sunlight or

the like and reduce the amount of absorbed energy in the infrared range.

A preferred perovskite has a BET surface size in a range of from 0.01 to 100 m²/g, as measured according to the standards ASTM C1069 and ISO 9277, as explained below.

The method to determine the mineral having perovskite structure's BET surface is preferably based on the standards ASTM C1069 and ISO 9277 and is conducted as follows: in the first step, 2 to 5 g of sample are dried at 105°C and placed in a desiccator for cooling and further degassing. Subsequently, 0.3 to 1.0 g of the dry material is weighed into a test tube and placed in the degassing unit for about 30 min. Afterwards, the sample is transferred to the measuring unit and is measured using the Micromeritics Tristar 3000 instrument.

The BET active surface is preferably in a range of from 0.05 to 50 m²/g and more preferable in a range of from 0.1 to 15 m²/g.

Typical perovskites have an average particle size in a range of from 0.01 to 100 µm, as measured according to the standard procedure using a Malvern Mastersizer 2000 apparatus. The average particle size is preferably in a range of from 0.1 to 50 µm, more preferably in a range of from 0.5 to 30 µm.

Average particle size in the description of the present invention means median primary particle size, D(v, 0.5) or d(0.5), and is the size at which 50% of the sample is smaller and 50%

is larger. This value is also known as the Mass Median Diameter (MMD) or the median of the volume distribution.

Furthermore, it is preferred that i) the thermal conductivity, ii) the mechanical and iii) the self-extinguishing properties of the polymer foam are improved by the use of minerals with perovskite structure having:

i) an average particle size, as determined by laser diffraction, in the range of from 0.01 to 600 μm .

In a further preferred embodiment, the mineral having perovskite structure has a thermal conductivity of less than 10 $\text{W/m}\cdot\text{K}$, preferably 5 $\text{W/m}\cdot\text{K}$ or less (300°C).

It is further preferred that the mineral having perovskite structure has a moisture content in a range of from 0.01 to 3.0 wt.%, preferably in a range of from 0.05 to 1.5 wt.%.

The polymer used in accordance with the invention is based on one (or more) vinyl aromatic monomer(s), preferably styrene, and optionally one or more comonomers, i.e. it is a homopolymer or a copolymer.

The polymer used in accordance with all aspects of the invention is based on one (or more) vinyl aromatic monomer(s), preferably styrene, and optionally one or more comonomers, i.e. it is a homopolymer or a copolymer.

The addition of a co-monomer of a specific styrene comonomer possessing steric hindrance, in particular p-tert-

butylstyrene, or alpha-methyl styrene comonomer, or some other sterically hindered styrene comonomer, to styrene, may advantageously increase the glass transition temperature of such a vinyl aromatic copolymer. In such a manner, the addition of a specific styrene comonomer to the styrene monomer improves the thermal stability of vinyl aromatic copolymer, which subsequently leads to better dimensional stability of moulded blocks made thereof.

The vinyl aromatic copolymer as used in the present invention is preferably comprised of 1 to 99 wt.% of styrene monomer and correspondingly 99 to 1 wt.% of p-tert-butylstyrene monomer, as follows (amounts in wt.%, based on the total amount of monomer):

Monomer	Preferred (wt.%)	More preferred (wt.%)	Most preferred (wt.%)
Styrene	1-99	50-99	70-98
p-tert-Butyl styrene	99-1	1-50	30-2

Alternatively, the vinyl aromatic copolymer as used in the present invention is preferably comprised of 1 to 99 wt.% of styrene monomer and correspondingly 99 to 1 wt.% of alpha-methyl styrene monomer, as follows (amounts in wt.%, based on the total amount of monomer):

Monomer	Preferred (wt.%)	More preferred (wt.%)	Most preferred (wt.%)
Styrene	1-99	50-98	75-95
alpha-Methyl styrene	99-1	2-50	25-5

In addition to the mineral having perovskite structure, the materials according to the invention (the polymer composition, the granulate, the foam and the masterbatch) may contain further additives, as is set out below.

The polymer foam further comprises one or more athermanous additives selected from a) powder inorganic additive (other than mineral having perovskite structure), b) powder carbonaceous additive, and c) powder geopolymer or powder geopolymer composite. The powder inorganic additive is selected from powders of silica and powders of calcium phosphate. The powder carbonaceous additive is selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides and graphene.

Silica

The silica as preferably used in accordance with the invention is amorphous and has the following specific properties:

- (i) a BET surface of from 1 to 100 m²/g, and
- (ii) an average particle size in a range of from 3 nm to 1,000 nm.

The method to determine the silica's BET surface is the method for the determination of BET described above. The silica as preferably used according to the invention has a BET surface in a range of from 3 to 80 g/m², more preferably 5 to 70 m²/g, most preferably 8 to 60 m²/g, such as 10 to 50 m²/g, in particular 13 to 40 m²/g, or 15 to 30 m²/g, such as about 20 m²/g.

Moreover, the silica as preferably used according to the present invention is defined by an average particle size, as measured according to the procedure detailed below, of 3 nm to 1000 nm.

The method to determine the average particle size is conducted as follows: in the first step, 45 g of distilled water and 5 g of sample are placed into a beaker and stirred to allow the entire sample to be wetted. Subsequently, the sample is dispersed in an external ultrasonic probe for 5 min at 100% amplitude. The measurement is performed automatically using the primary agglomerate program in a Malvern MasterSizer 2000 device.

It is preferred that the average particle size of the silica as preferably used according to the present invention is within a range of 20 to 800 nm, preferably 30 to 600 nm, such as 40 to 400 nm, in particular from 100 to 200 nm.

According to the present invention, the silica is preferably used in an amount of from 0.01 to less than 2 wt.%, based on the weight of the polymer (inclusive of solid and, if any, liquid additives, but exclusive of propellant). More preferably, the silica is used in an amount of 0.1 to 1.6 wt.%, most preferably 0.5 to 1.5 wt.%, such as about 1.0 wt.%, based on the weight of the vinyl aromatic polymer (inclusive of solid and, if any, liquid additives, but exclusive of propellant).

The silica as preferably used according to the invention is amorphous (i.e. non-crystalline) silicon dioxide, and the silica particles are preferably spherically shaped.

It is most preferred that the silica comprises Sidistar type of material from ELKEM, typically with an average primary particle size of about 150 nm and a low BET surface area of about 20 m²/g, and most preferred is that a) is Sidistar T120.

Calcium phosphate

The calcium phosphate as typically used according to the invention has an average particle size, as measured by laser diffraction, of 0.01 µm to 100 µm. It is preferred that the average particle size is from 0.1 µm to 50 µm, such as 0.5 µm to 30 µm. The calcium phosphate is preferably tricalcium phosphate (specifically a type of hydroxyapatite).

According to the present invention, the calcium phosphate, if present, is preferably used in an amount of from 0.01 to 50 wt.%, based on the weight of vinyl aromatic polymer including solid and, if any, liquid additives, but exclusive of propellant, more preferably 0.1 to 15 wt.%, most preferably 0.5 to 10 wt.%, in particular 1 to 8 wt.%.

Moreover, b) carbon-based athermanous additives can be present in the foam, such as graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene.

Graphite

The graphite as preferably used in the present invention has the following properties:

- (i) a carbon content in a range of from 50 to 99.99 wt.%
and

- (ii) a particle size in a range of from 0.01 to 100 μm .

Preferably, the graphite's carbon content is in a range of from 95 to 99.9 wt.% and more preferably over 99.5 wt.%. Preferably, the carbon content is measured according to the method L-03-00A of the company GK.

The graphite as preferably used according to the invention has a particle size in a range of from 0.01 to 100 μm , preferably as measured according to method L-03-00 of the company GK, which is a laser diffraction method using a Cilas 930 particle size analyzer equipment. It is preferred that the particle size of the graphite as used according to the invention is from 0.1 to 30 μm . The most preferred particle size range is from 0.5 to 25 μm , in particular from 1 to 10 μm ; specifically, for example, a range of from 3 to 8 μm .

The graphite's mean particle size is preferably in a range of from 5 to 7 μm , D90 in a range of from 7 to 15 μm , and D100 in a range of from 15 to 20 μm .

The sulphur content of the graphite as preferably used according to the invention is in a range of from 10 to 2000 ppm, as measured according to ASTM D1619, more preferably from 100 to 1500 ppm, in particular from 400 to 1000 ppm.

The ash content of the graphite as preferably used according to the invention is in a range of from 0.01 to 2 wt.%, preferably from 0.1 to 1 wt.%, in particular below 0.5 wt.%. The ash content is preferably measured according to method L-02-00 of the company GK.

The moisture content of the graphite as preferably used according to the invention is in a range of from 0.01 to 1 wt.%, preferably from 0.1 to 0.5 wt.%, in particular below 0.4 wt.%. The moisture content is preferably measured according to a method of the company GK (L-01-00).

The graphite is preferably used according to the invention in an amount of 0.01 to 10 wt.%, based on the weight of the vinyl aromatic polymer (inclusive of solid and, if any, liquid additives, but exclusive of propellant), preferably in a range of from 1.0 to 8.0 wt.%, more preferably in a range of from 1.5 to 7.0 wt.%, in particular in a range of from 2.0 to 6.0 wt.%, such as in a range of from 2.5 to 5.0 wt.%, e.g. in a range of from 3 to 4 wt.%. More preferably, a) the silica and b) the graphite are used in a weight ratio a):b) in a range of from 1:1.5 to 1:8, most preferably a) the silica and b) the graphite are used in a weight ratio a):b) in a range of from 1:2 to 1:5, in particular a) the silica and b) the graphite are used in a weight ratio a):b) of about 1:3.

The best performance in foams in terms of i) decrease of thermal conductivity, ii) increase in mechanical properties and iii) improvement in self-extinguishing properties is achieved, accompanied by a reduction in the required content of graphite, when (in addition to the mandatory mineral having perovskite structure as athermanous additive) silica and graphite are present, specifically Sidistar T120 from Elkem is used in combination with the natural graphite CR5995 from GK, in a weight ratio of about 1:3, as further athermanous additives. Then it is possible to reduce the graphite content to

about 3 wt.%, and to maintain the thermal conductivity at the same level as if 5 to 6 % of graphite were used, whilst the mechanical properties are significantly improved, as compared to foam containing from 5 to 6 wt.% of graphite without addition of Sidistar T120 and/or a mineral having perovskite structure.

Carbon Black

The carbon black as preferably used according to the invention has a BET surface, as measured according to ASTM 6556, of more than 40 to 250 m²/g.

It is preferred that the BET surface of the carbon black as used according to the invention is from 41 to 200 m²/g, preferably from 45 to 150 m²/g, in particular from 50 to 100 m²/g.

The sulphur content of the carbon black as preferably used according to the invention is in the range of from 50 to 20,000 ppm, as measured according to ASTM D1619, preferably from 3,000 to 10,000 ppm.

The carbon black is preferably present in an amount of 0.1 to 12 wt.%, based on the weight of the vinyl aromatic polymer including additives, but exclusive of propellant, preferably 0.2 to 12.0 wt.%, more preferred 0.5 to 9.0 wt.%, such as 1.0 to 8.0 wt.%, in particular 2.0 to 7.0 wt.%, such as 3.0 to 6.0 wt.%, e.g. about 5.0 wt.%.

c) Geopolymer and geopolymer composite

It has further been found that it is possible to maintain the foam's self-extinguishing and mechanical properties in the

same range as in an expanded polymer without addition of filler or any other athermanous additive, while at the same time the thermal conductivity can be decreased significantly, namely by addition of c) a geopolymer, or a geopolymer composite prepared from geopolymer and various types of athermanous fillers. This is possible because the geopolymer itself gives fire resistance, and may in the composite encapsulate the particles of athermanous additive, especially those additives based on carbon, and separates them from any interactions with the flame, the polymer or the flame retardant. Geopolymer and geopolymer composite further decrease thermal conductivity, based on a heat radiation scattering effect.

Geopolymer synthesis from aluminosilicate materials takes place by the so-called geopolymerization process, which involves polycondensation phenomena of aluminates and silicate groups with formation of Si-O-Al-type bonds. In a preferred embodiment, geopolymers encapsulate carbon-based athermanous fillers in a matrix and limit the contact (interphase) between carbon-based filler and brominated flame-retardants, including those based on polystyrene-butadiene rubbers. This phenomenon allows a significant decrease of the required concentration of brominated flame retardant in expandable vinyl aromatic polymer composites.

A preferred geopolymer composite is prepared by a process wherein an athermanous additive component is present during the production of geopolymer composite, so that the geopolymer composite incorporates the athermanous additive component. Preferably, this athermanous additive component comprises one

or more athermanous additives selected from the group consisting of

- a. carbon black, petroleum coke, graphitized carbon black, graphite oxides, various types of graphite (especially poor and amorphous forms with a carbon content in the range of from 50 to 90 %) and graphene, and
- b. titanium oxides, ilmenite, rutiles, chamotte, fly ash, fumed silica, hydromagnesite/huntite mineral, barium sulfate and mineral having perovskite structure,

preferably the athermanous additive component of the geopolymer composite comprises one or more carbon-based athermanous additives selected from the group of heat absorbers and heat reflectors,

in particular the athermanous additive component is carbon black, graphite, or a mixture thereof.

Further details of the preparation of geopolymer composite may be found in the international application entitled "Geopolymer and composite thereof and expandable vinyl aromatic polymer granulate and expanded vinyl aromatic polymer foam comprising the same", PCT/EP2016/050594, filed on even date herewith.

In the following, the further athermanous fillers that are present, namely one or more of a) powder inorganic additive selected from powders of silica and calcium phosphate, b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder

geopolymer composite, will be referred to as additional athermanous fillers or additives.

The foam also preferably comprises one or more of nucleating agent, flame retardant, synergist, thermal oxidative stabiliser, flame retardant thermal stabiliser, and dispersion aid.

For instance, the flame retardant system is, especially in an extrusion process, usually a combination of two types of compounds, namely x) a brominated aliphatic, cycloaliphatic, aromatic or polymeric compound containing at least 50 wt.% of bromine, and a second compound (so called synergistic compound, y) which can be bicumyl (i.e. 2,3-dimethyl-2,3-diphenylbutane) or 2-hydroperoxy-2-methylpropane, or dicumyl peroxide, cumene hydroxide, or 3,4-dimethyl-3,4-diphenylbutane.

The total content of flame retardant system, i.e. x) plus y), is typically in a range of from 0.1 to 5.0 wt.% based on the weight of vinyl aromatic polymer including solid and, if any, liquid additives, but exclusive of propellant, preferably between 0.2 and 3 wt.%. The weight-to-weight ratio of bromine compound x) to synergistic compound y) is preferably in a range of from 1:1 to 15:1, usually in a range of from 3:1 to 10:1, in particular from 2:1 to 7:1.

In a further aspect, the invention relates to (II) processes for the preparation of expandable polymer granulate. The granulate according to the invention comprises one or more additional athermanous additives selected from a) powder inorganic additive selected from powders of silica and calcium

phosphate, b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder geopolymer composite.

In a first embodiment (IIa), the process is a process for the preparation of expandable polymer granulates comprising the following steps:

- i) feeding vinyl aromatic polymer into an extruder,
- ii) adding mineral having perovskite structure and optionally thermal stabiliser and flame suppressant,
- iii) injecting blowing agent into the melt of polymer,
- iv) extruding the homogenous blend, and
- v) pelletizing the blend in an underwater pelletizer, so as to obtain the granulate.

Preferably, the extrusion process (IIa) comprises the steps:

- i) feeding a first polymer component comprising vinyl aromatic polymer into a first mixer;
- ii) feeding a first additive component a) into the first mixer, to produce a first mixture from the first polymer component and the first additive component;

- iii) feeding a second polymer component b) comprising vinyl aromatic polymer into a second mixer;
- iv) feeding a second additive component b) into the second mixer, to produce a second mixture from the second polymer component and the second additive component, wherein the processing conditions in the second mixer are more severe than the processing conditions in the first mixer, by providing higher shear force;
- v) combining the first and second mixtures, to produce a third mixture;
- vi) injecting blowing agent c) into the third mixture, to produce a fourth mixture;
- vii) mixing the fourth mixture; and
- viii) pelletizing the fourth mixture, to obtain the granulate.

The first polymer component can be a vinyl aromatic polymer having a melt index from 4 to 20 g/10 min, as measured according to ISO 1133.

The second polymer component can be a vinyl aromatic (e.g. styrene) homopolymer (or preferably copolymer with p-tert butyl styrene or alpha-methyl styrene), having a melt index ranging from 4 to 30 g/10 min, as measured according to ISO 1133.

According to this first and preferred embodiment of the second aspect, the invention allows for the separate addition of first and second additive components into a mixture that is ultimately charged with propellant and is pelletized, so as to obtain the expandable granulate. Because of the separate addition of the first and second additive components, the process is highly flexible and allows for the processing of additives that have very different processing requirements, in particular in view of their stability under those processing conditions that are necessary so that the different additive components can best perform their desired function. Typically, at least a part (and preferably all) of the mineral having perovskite structure is introduced as part of the second additive component in this extrusion process, whereas at least a part (and preferably all) of the flame retardant system is introduced as part of the first additive component in this extrusion process. This is advantageous since the flame retardant system typically requires more moderate processing conditions, in particular as compared to mineral having perovskite structure. Thus, according to the invention, a mixture comprising mineral having perovskite structure can be prepared in a dedicated mixer that provides for the high shearing that is preferred for this type of additive, so that it is properly dispersed.

As a first alternative, the second additive components (e.g. the mineral having perovskite structure and the additional athermanous filler) can be mixed with polymer, in equipment that provides for high shearing and good dispersion, and the obtained mixture is directly, i.e. as a melt, combined with

the mixture containing the first additive components, to give a mixture that is ultimately charged with blowing agent.

As a second alternative, the second additive components (e.g. the mineral having perovskite structure and the additional athermanous filler) can be mixed with polymer and be provided as a masterbatch. Such a masterbatch is advantageous in case the plant design does not allow for the processing conditions that are preferable for the mineral having perovskite structure, e.g. high shearing conditions. The masterbatch can for instance be prepared off-site, in dedicated processing equipment, and having to provide such processing equipment on site can be dispensed with. The masterbatch comprising the mineral having perovskite structure and the additional athermanous filler is subject of the fifth aspect of the present invention, and is described below.

According to a second embodiment of the second aspect (IIb), expandable polymer granulates is prepared in an aqueous suspension polymerization process comprising the steps:

- i) adding a vinyl aromatic monomer and optionally one or more comonomers to the reactor, and subsequently adding
 - i1) optional polymeric suspension aid,
 - i2) athermanous fillers (mineral having perovskite structure and additional athermanous additive),
 - i3) flame retardant,
 - i4) at least one peroxide (or the mixture of two or more peroxides) as reaction initiator,
- ii) adding the demineralised water, and

ii1) at least one suspending agent which is an inorganic acid salt,

ii2) at least one peroxide (or the mixture of two or more peroxides) as reaction initiator,

ii3) at least one suspension stabilizer selected from the group of anionic surface active compounds and/or high molecular weight compounds (e.g. hydrophilic and/or amphiphilic polymers), and

iii) continuing the polymerization (preferably until the concentration of vinyl aromatic monomer(s) is below 1000 ppm by weight, based on the weight of the polymer),

iv) adding the blowing agent during or after the polymerization step,

v) cooling, and then separating the granulate from the water.

The athermanous filler that is mandatory according to the present invention (namely mineral having perovskite structure) may be added in the form of a masterbatch, it may be introduced at the beginning of the suspension polymerization process, or may be dissolved in the monomer and/or a mixture of the monomer and comonomer. The same applies for the additional athermanous fillers, a), b), and c) as mentioned above.

According to the present invention, the mineral having perovskite structure and the additional athermanous filler are introduced as athermanous fillers ii2), and they may also be introduced in step ii) and/or in step iii) of this suspension process.

The polymer granulate is prepared using well known inorganic salts of phosphoric acid, such as types of calcium phosphate, magnesium phosphate, or a combination of salts as suspending agents. These salts may be added to the reaction mixture in a finely divided form, or as a product of an *in situ* reaction (for example, between sodium phosphate and magnesium sulphate).

The salts are supported in their suspending action by anionic surface-active compounds, such as sodium dodecylbenzene sulfonate or sodium poly(naphthalene formaldehyde) sulfonate. Those surface-active compounds can be also being prepared *in situ* using their precursors such as sodium metabisulfite and potassium persulfate. The suspension can be also stabilized by high molecular weight organic polymers, such as polyvinyl alcohol or hydroxyethylcellulose or hydroxypropylmethylcellulose.

To improve the stability of the suspension, up to 30 wt.% of polymer (fresh vinyl aromatic polymer or waste vinyl aromatic polymer from a previous polymerization) may be added as the optional suspension aid, preferably 5 to 15 wt.%, based on the vinyl aromatic monomer amount. It increases the viscosity of the reagent mixture (monomer with all additives), which facilitates the creation of a suspension. The same or similar effect can be achieved by mass pre-polymerization of the monomer or mixture of comonomers and additives until the suitable melt viscosity is obtained (as for 1% to 30% of polymer concentration).

In the most preferred process, before start of the polymerization step iii), athermanous fillers in the form of a concentrated masterbatch are added to the styrene and/or its mixture with comonomer, particularly p-tert-butylstyrene. The masterbatch can contain from 10 to 60 % of athermanous fillers (i.e. the mineral having perovskite structure, and the additional ones, a), b) and c)), pre-silanized or silanized in the masterbatch compounding process by e.g. triethoxy(phenyl)silane, to decrease its hydrophilic properties.

The polymerization is then continued in an aqueous suspension phase, in the presence of the above-mentioned suspending agents, suspension stabilizers, athermanous fillers, flame retardants and flame suppressors, optionally at least in the presence of suspension aid.

The polymerization process is triggered by initiators. Normally, two organic peroxides are used as initiators. The first peroxide, with a half-life of about one hour at 80-95°C, is used to start and run the reaction. The other, with a half-life of about one hour at 105-125°C, is used during the following polymerization process continued at higher temperature, in the so called high temperature cycle (HTC). For the above specific process with the presence of carbon black, a composition of three peroxides was used to achieve suitable average molecular weight despite the negative inhibiting effect caused by the carbon black's presence. Preferably were used: dicumyl peroxide and tert-butylperoxy-2-ethyl hexyl carbonate peroxide as high temperature cycle peroxides (120°C) and tert-butyl 2-ethylperoxyhexanoate as low temperature cycle peroxide (82-90°C).

The end of the process is typically indicated by a concentration of residual vinyl monomer(s) of below 1000 ppm by weight, based on the mass of vinyl aromatic polymer or copolymer. The vinyl aromatic polymer or copolymer which is obtained at the end of the process typically has an average molecular mass (M_w) ranging from 50 to 600 kg/mol, preferably from 150 to 450, most preferably from 100 to 350 kg/mol. The procedure for controlling molecular mass in suspension polymerization is well known and is described in detail in Journal of Macromolecular Science, Review in Macromolecular Chemistry and Physics C31 (263) p. 215-299 (1991).

During the polymerization process, conventional additives can be added directly to the monomer(s), their solution with suspension aid, to the pre-polymer, or to the suspension. Additives such as the flame retardant system, nucleating agents, antistatic agents, blowing agents and colorants stay in the polymer drops during the process and are thus present in the final product. The concentrations of conventional additives are the same as for the extrusion process, as set out above.

The flame retardant systems suitable for the present suspension process are similar to those used in the extrusion process described above. One suitable system is the combination of two types of compounds, namely a brominated aliphatic, cycloaliphatic, aromatic or polymeric compound containing at least 50 wt.% of bromine (such as hexabromocyclododecane, pentabromomonochlorocyclohexane, or a polymeric bromine compound, specifically brominated styrene-butadiene rubber) and a second compound called synergistic compound which can be e.g. an ini-

tiator or peroxide (e.g. dicumyl peroxide, cumene hydroxide, and 3,4-dimethyl-3,4-diphenylbutane). The content of flame retardant system is typically in a range of from 0.1 to 5.0 wt.% with respect to the total weight of vinyl aromatic polymer (weight of monomer(s) plus weight of polymer if added on the start), preferably between 0.2 and 3 wt.%. The ratio between bromine compound and synergistic compound is preferably in a range of from 1:1 to 15:1 weight to weight, usually from 3:1 to 5:1.

The blowing agent or agents are preferably added during the polymerization to the suspension phase and are selected from aliphatic or cyclic hydrocarbons containing from 1 to 6 carbons and their derivatives. Typically are used n-pentane, cyclopentane, i-pentane, combination of two of them or their mixture. In addition, the halogenated aliphatic hydrocarbons or alcohols containing from 1 to 3 carbons are commonly used. The blowing agent or agents can also be added after the end of polymerization.

At the end of the polymerization, spherical particles of expandable styrenic polymer are obtained as granulate, with an average diameter range of 0.3 to 2.3 mm, preferably from 0.8 to 1.6 mm. The particles can have different average molecular mass distribution, depending on their size, but all contain used additives dispersed homogenously in the polymer matrix.

In the final step after the HTC step, the mass is cooled down to e.g. 35°C, and the polymer granulate is separated from the water, preferably in a centrifuging process. The particles are

then dried and preferably coated with a mixture of mono- and triglycerides of fatty acids and stearic acid salts.

After discharging the particles from the reactor, they are typically washed: first with water, then with non-ionic surfactant in aqueous solution, and finally again with water; they are then desiccated and dried with hot air having a temperature in the range 35-65°C.

The final product is typically pre-treated by applying a coating (the same as for the extruded granulate) and can be expanded by the same method as the extrusion product.

According to a third embodiment of the second aspect (IIc), expandable polymer granulate is prepared in a continuous mass process comprising the following steps:

i) providing continuously to a mass prepolymerization reactor (or the first from a cascade reactor) a stream of:

i1) vinyl aromatic monomer and optionally at least one comonomer (preferably p-tert-butylstyrene),

i2) at least one additive solution, and

i3) optionally recycled monomer,

ii) continuing polymerization in the prepolymerization reactor or the sequence of cascade reactors,

iii) adding athermanous fillers (mineral having perovskite structure and additional athermanous additive),

- iv) degassing the polymer,
- v) feeding the polymer in molten state into the extruder, preferably directly from the polymerization plant,
- vi) optionally adding a flame retardant system including synergist and thermal stabilisers,
- vii) injecting the blowing agent,
- viii) extruding the homogenous polymer mixture, and
- ix) pelletizing in an underwater pelletizer, so as to obtain the granulate.

The reactor or cascade reactor is preferably arranged horizontally. If a cascade reactor is used, then there are preferably up to 5 reactors, in particular up to 4, such as three reactors.

The continuous mass polymerization is process congruous to the extrusion process, but the vinyl aromatic polymer or copolymer together with athermanous fillers is used in a molten state and the extruder is fed directly by the polymerization plant.

The mass polymerization reactor (or first from cascade reactors) is fed continuously by vinyl aromatic monomer, particularly styrene, and optionally by its vinyl aromatic comonomer, for instance p-tert-butylstyrene.

At this stage, athermanous fillers in the form of a masterbatch or in the form of powders are fed into the mass polymerisation reactor, one or more additives and optionally recycled monomer recovered from the process.

The athermanous additives (e.g. masterbatches) are preferably dissolved in the vinyl aromatic monomer or before feed to the polymerization reactor.

The polymerisation reaction is initiated thermally, without addition of initiators. In order to facilitate heat collection, polymerisation is generally carried out in the presence of for instance monocyclic aromatic hydrocarbon.

The prepolymerised mass from the pre-polymerisation reactor is pumped through the sequence of several horizontal reactors, and the polymerisation reaction is subsequently continued.

At the end of the mass polymerization stage, the rest of unpolymerized monomer is removed by degassing of the melt.

A vinyl polymer in the molten state, produced in mass polymerization and containing athermanous fillers, is fed into an extruder at a temperature in a range of from 100 to 250 °C, preferably from 150 to 230°C. In the next stage, the flame retardant system and the nucleating agent are fed to the polymer melt. Again, a combination of two types of flame retarding compounds can be used, namely a brominated aliphatic, cycloaliphatic, aromatic or polymeric compound containing at least 50 wt.% of bromine, and a second compound called synergistic compound, which can be bicumyl (2,3-dimethyl-2,3-

diphenylbutane) or 2-hydroperoxy-2-methylpropane. The concentrations of additives are typically the same as for the extrusion process, as set out above.

In the following step, the blowing agent is injected into the molten polymer mixture and mixed. The blowing agent or agents are the same as for the suspension process, i.e. selected from aliphatic or cyclic hydrocarbons containing from 1 to 6 carbons and their derivatives. The polymer with all additives and blowing agent is subsequently extruded to give expandable beads.

The homogenous polymer mixture comprising additives and blowing agent is pumped to the die, where it is extruded through a number of cylindrical die holes with 0.5-0.8 mm of diameter, immediately cooled by a water stream and cut with a set of rotating knives in a pressurized underwater pelletizer, to obtain micropellets (granulate).

The micropellets are transported by water, washed, drained off and fractioned. The final product is pre-treated in the same way as it is in the suspension and extrusion processes.

In a further aspect, the invention relates to (III) expandable polymer granulate comprising one or more propellants, x) mineral having perovskite structure and y) polymer of vinyl aromatic monomer and optionally one or more comonomers.

Preferably, the expandable polymer granulate is obtainable (and is more preferably obtained) by the process according to the second aspect.

The expandable polymer granulate further comprises one or more of the additional athermanous additives a), b) and c) above. Specifically, the expandable polymer granulate further comprises one or more additional athermanous additives selected from a) powders of silica and calcium phosphate, b) powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder geopolymer composite.

In a further aspect, the invention relates to (IV) expanded vinyl aromatic polymer foam comprising x) mineral having perovskite structure and y) polymer of vinyl aromatic monomer and optionally one or more comonomers. The expanded polymer foam has

- a density of 8 to 30 kg/m³, and
- a thermal conductivity of 25 - 35 mW/K·m.

The foam further comprises one or more athermanous additives selected from a) powder inorganic additive selected from powders of silica and calcium phosphate, b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) powder geopolymer and powder geopolymer composite.

Preferably, the expanded polymer foam is obtainable and is more preferably obtained by expansion of the expandable polymer granulate according to the third aspect.

According to the fifth aspect, the invention relates to (V) a masterbatch. The masterbatch comprises x) mineral having perovskite structure and y) vinyl aromatic polymer, and the amount of x) is in a range of from 10 to 70 wt.%, based on the weight of the masterbatch.

Preferably, the amount of mineral having perovskite structure x) is in a range of from 10 to 65 wt.%, based on the weight of the masterbatch, more preferably from 20 to 60 wt.%, in particular from 25 to 55 wt.%.

In a preferred embodiment, y) is a vinyl aromatic polymer having a melt index in a range of from 4 to 30 g/10 min, as measured according to ISO 1133, and the vinyl aromatic polymer is preferably a homopolymer or copolymer with p-tert butyl styrene or alpha-methyl styrene.

The masterbatch, in addition to components x) mineral having perovskite structure and y) vinyl aromatic polymer, further comprises one or more of the additional athermanous additives a) to c). Additional athermanous fillers that are present in the masterbatch are one or more powders of a) silica and calcium phosphate, b) graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and c) geopolymer and geopolymer composite. These additional powder athermanous fillers very often require processing conditions that are similar to the conditions required by the mineral having perovskite structure.

Moreover, the masterbatch preferably comprises one or more silanes. Preferred silanes are for example aminopropyl-

triethoxysilane (e.g. Dynasylan AMEO from Evonik), aminopropyltrimethoxysilane (e.g. Dynasylan AMMO from Evonik), and phenyltriethoxysilane (e.g. Dynasylan 9265 from Evonik).

Preferably, the amount of silane is in a range of from 0.01 to 1 wt.%, based on the weight of the athermanous additive in the masterbatch.

It is noted that, unlike the properties of the additives as starting materials, the properties of additives as contained in granulate or foam are notoriously difficult to determine. It is often considered more appropriate in the art to characterize the additives in granulate and foam with reference to the properties of the additives as initially used.

The advantages of the present invention become apparent from the following examples. Unless indicated otherwise, all percentages are given by weight.

Moreover, whenever reference is made in the present description of the invention to an amount of additive "by weight of vinyl aromatic polymer", this refers to the amount of the additive by weight of polymer component inclusive of (solid and, if any, liquid) additives, but exclusive of propellant.

Examples

Expandable polymer granulate was prepared in an extrusion process, with addition of athermanous fillers in powder form (Examples 1 to 11):

Example 1 (comparative)

A mixture of vinyl aromatic polymer in the form of granules, and containing 2.5 wt.% of polymeric brominated flame retardant (Emerald 3000), 0.5 wt.% of bicumyl, Irganox 1010 in an amount of 0.125 wt.%, Irgafos 126 in an amount of 0.125 wt.%, Epon 164 in an amount of 0.250 wt.%, XIRAN SZ15170 in an amount of 1 wt.% and F-2200 HM in an amount of 1 wt.% were dosed to the main hopper of the main 32D/40 mm twin-screw co-rotating extruder. The melt temperature in the main extruder was 180°C.

The powder of carbon black (Regal 350 from Cabot Corporation with a BET surface of 55.0 m²/g) was dosed to the side arm (54D/25 mm) twin-screw co-rotating extruder via one side feeder, in an amount of 3 wt.%, based on the total weight of granulate, excluding propellant, and the vinyl aromatic polymer (in the form of granules) was dosed to the main hopper of this extruder. The melt, then containing 40 wt.% of concentrated carbon black, was transported to the main extruder. The melt temperature inside the extruder was 190°C.

The blowing agent (n-pentane/isopentane mixture 80/20 %) was injected to the main 32D/40 mm extruder, downstream from the injection of the melt from the side twin-screw extruder. The concentration of blowing agent was 5.5 wt.%, calculated on total mass of product.

The melt of vinyl aromatic polymer containing flame retardant, bicumyl, carbon black and blowing agent was transported to the 30D/90 mm cooling extruder and pumped through a static mixer, melt pump, screen changer, diverter valve, was then and extruded through the die head with 0.75 mm diameter holes, and was finally underwater pelletized by the rotating knives. Downstream, the rounded product (a granulate with a particle

size distribution of 99.9 % of the fraction 0.8-1.6 mm) was centrifuged to remove the water, and was finally coated by the suitable mixture of magnesium stearate with glycerine monostearate and tristearate. The melt temperature in the cooling extruder was 170°C.

The coated beads were expanded, and the final general properties of the expanded foam composite were then determined:

- thermal conductivity according to standard ISO 8301.
- mechanical properties (compressive and bending strength) according to standard EN 13163.
- flammability according to tests methods: EN ISO 11925-2 and DIN 4102 B1, B2.

Example 2 (comparative)

The components according to Example 1 were used. Regal 350 carbon black was replaced with the CSX910 from Cabot Corporation, having a BET surface area of 71.8 m²/g.

Example 3 (according to the invention)

The components according to Example 1 were used. 1 wt.% of calcium titanate was added, premixed with 3 wt.% of Regal 350, and dosed to the side arm extruder. The concentration of the two additives in the melt in side arm extruder was 40 wt.%.

Example 4 (according to the invention)

The components according to Example 3 were used, and the calcium titanate content was increased to 3 wt.%. The flame retardant concentration was reduced to 2.0 wt.%, bicumyl to 0.4 wt.% and thermal stabilizers subsequently were reduced too. XIRAN SZ15170 and F-2200 HM were absent from the composition.

Example 5 (according to the invention)

Again, the components according to Example 4 were used. The calcium titanate content was increased to 5 wt.%.

Example 6 (according to the invention)

The components according to Example 5 were used. The Regal 350 was replaced with CSX910.

Example 7 (according to the invention)

The components according to Example 6 were used. The calcium titanate was replaced with barium titanate.

Example 8 (according to the invention)

The process and components according to Example 1 were used. The flame retardant was added in an amount of 1 wt.%. The thermo-oxidative and thermal stabilizers were excluded, as was XIRAN SZ15170. The calcium titanate was used in an amount of 5 wt.%.

Example 9 (according to the invention)

The process and components according to Example 8 were used, and calcium titanate was replaced with barium titanate.

Example 10 (according to the invention)

The process and components according to Example 8 were used, and calcium titanate was replaced with strontium titanate.

Example 11 (according to the invention)

The process and components according to Example 8 were used, and calcium titanate was replaced with magnesium titanate.

Table 1. Summary of Examples 1 to 11.

Components (wt.%)	Examples*										
	1	2	3	4	5	6	7	8	9	10	11
GP585X	+	+	+	+	+	+	+	+	+	+	+
Regal 350	3	-	3	3	3	-	-	-	-	-	-
CSX 910	-	3	-	-	-	3	3	-	-	-	-
Calcium titanate	-	-	1	3	5	5	-	5	-	-	-
Barium titanate	-	-	-	-	-	-	5	-	5	-	-
Strontium titanate	-	-	-	-	-	-	-	-	-	5	-
Magnesium titanate	-	-	-	-	-	-	-	-	-	-	5
Emerald 3000	2.5	2.5	2.5	2.0	2.0	2.0	2.0	1.0	1.0	1.0	1.0
Bicumyl	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.2	0.2	0.2	0.2
Irganox 1010	0.125	0.125	0.125	0.1	0.1	0.1	0.1	-	-	-	-
Irgafos 126	0.125	0.125	0.125	0.1	0.1	0.1	0.1	-	-	-	-
Epon 164	0.250	0.250	0.250	0.2	0.2	0.2	0.2	-	-	-	-
Polywax 2000	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
XIRAN SZ15170	1	1	1	-	-	-	-	-	-	-	-
F-2200 HM	1	1	1	-	-	-	-	-	-	-	-
Pentane/Isopentane 80/20	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5

* Examples 1 and 2 are comparative, examples 3 to 11 are according to the invention.

Table 2. Examples 1 to 11.
Final product parameters at a foam density of ca. 19.0 g/l.

Examples*	1	2	3	4	5	6	7	8	9	10	11
Thermal conductivity (mW/m·K) /ISO 8301/	32.5	31.6	32.0	31.0	30.7	30.1	30.0	32.8	31.4	31.2	30.9
Flammability /EN ISO 11925-2/	+	+	+	+	+	+	+	+	+	+	+
Flammability /DIN 4102 B1/B2/	+/+	-/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+
Compressive strength at 10% def. (kPa) /EN 13163/	92	98	100	115	122	126	123	125	126	127	128
Bending strength (kPa) /EN 13163/	179	185	186	198	206	212	210	220	222	219	221
Passed (+ or B2 or B1); Not passed (-)											

* Examples 1 and 2 are comparative, examples 3 to 11 are according to the invention.

Expandable polymer granulate was prepared in an extrusion process, with addition of athermanous fillers in the form of a masterbatch (Examples 12 to 22):

Examples from 1 to 11 were repeated. The masterbatch was prepared on the same extruder as side arm co-rotating twin-screw extruder - 54D/25 mm. Synthos PS 585X was used as the masterbatch's polymer carrier. The results were very similar to those obtained from Examples 1 to 11 (where the athermanous fillers in powder form were used in an extrusion process and were (directly) dosed via the side extruder).

Expandable polymer granulate was prepared in a suspension process (Examples 23 to 33):

Example 23 (comparative)

20 000 kg of styrene was dosed to the 60 m³ reactor. In the next step, the following components (calculated per styrene) were added: 3.0 wt.% of Regal 350 in the form of a 40 wt.% concentrated masterbatch (based on Synthos PS 585X), 0.002 wt.% of divinylbenzene, 2.0 wt.% of Emerald 3000, 0.3 wt.% of Polywax 1000, and 1.0 wt.% of dicumyl peroxide.

The mixture was heated relatively quickly to a temperature of 70°C and mixed at this temperature for 30 min with 275 rpm. Then, the temperature was increased to 90°C and 30 000 kg of demineralised water (temperature of 60°C) were added. The mixing force immediately created a suspension of prepolymer and the suspension was heated to 82°C. Immediately, 0.3 wt.% of Peroxan PO and 0.5 wt.% of TBPEHC were added. The radical polymerization was started and the following surfactant composition was introduced:

- potassium persulfate - 0.0001 wt. %
- Poval 205 - 0.18 wt. % of 5 % concentrated water solution
- Poval 217 (alternatively Poval 224) - 0.09 wt. % of a 5 % concentrated water solution
- DCloud 45 - 0.1 wt. %
- Arbocel CE 2910HE50LV - 0.1 wt. % (hydroxypropylmethyl-cellulose supplied by J. RETTENMAIER & SÖHNE GMBH)

The polymerization was then continued for 120 min. at a temperature of 82°C, and the temperature was then increased to 90°C. The suspension was kept at this temperature for 120 min., to achieve particle identity point of suspension. A further portion of Poval 217 (in a concentration of 0.3 wt. % of a 5 wt. % concentrated solution in water) was introduced. In this step, sodium chloride can be added (in an amount of 0.5 wt. % per water phase) to reduce the water content in the polymer. Alternatively, the surfactant (sodium dodecylbenzenesulfonate, SDBS) can be used (in an amount of 0.2 wt. %).

The reactor was closed and the n-pentane/isopentane 80/20% mixture was added in an amount of 5.5 wt. % over 60 min. Simultaneously, the temperature was increased to 125°C. Then the polymerization was continued for 120 min. and after that time the suspension slurry was cooled down to 25°C.

The product was removed from the reactor and water was removed in a basket centrifuge. The particles were then dried in a fluid bed drier at a temperature of 40°C for 30 min. and fractionated on 80 % of particles fraction 0.8-1.6 mm, 15 % of 0.3-1.3, 4 % of 1.0-2.5 mm and 1 % of higher and lower size. Fractions were then coated the same way as the product as obtained in the extrusion process, and then expanded to foam at 35°C. Then the polymer was centrifuged from water and dried in

the fluid bed dryer. Finally, after sieving, the granulate was coated with a mixture of glycerol monostearate and glycerol tristearate.

Example 24 (comparative)

The components according to Example 23 were used. Regal 350 carbon black was replaced with CSX910 from Cabot Corporation, having a BET surface area of 71.8 m²/g.

Example 25 (according to the invention)

The components according to Example 1 were used. 1 wt.% of calcium titanate (silanized with 0.1 wt.% of Dynasylan 9265), premixed with 3 wt.% of Regal 350, was dosed in the form of a 40 wt.% concentrate to the side arm extruder.

Example 26 (according to the invention)

The components according to Example 25 were dosed and the calcium titanate content was increased to 3 wt.%. The flame retardant concentration was reduced to 1.5 wt.%, dicumyl peroxide content to 0.8 wt.%.

Example 27 (according to the invention)

Again, the components according to Example 26 were dosed. The calcium titanate content was increased to 5 wt.%.

Example 28 (according to the invention)

The components according to Example 27 were used. The Regal 350 was replaced with CSX910.

Example 29 (according to the invention)

The components according to Example 28 were used. The calcium titanate was replaced with barium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Example 30 (according to the invention)

The process and components according to Example 23 were used. The flame retardant (in an amount of 0.6 wt.%) and dicumyl peroxide (in an amount of 0.4 wt.%) were dosed. Calcium titanate was used in an amount of 5 wt.%.

Example 31 (according to the invention)

The process and components according to Example 30 were used, and calcium titanate was replaced with barium titanate.

Example 32 (according to the invention)

The process and components according to Example 31 were used, and calcium titanate was replaced with strontium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Example 33 (according to the invention)

The process and components according to Example 32 were used, and calcium titanate was replaced with magnesium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Table 3. Summary of Examples 23 to 33.

Components (wt.%)		Examples*										
		23	24	25	26	27	28	29	30	31	32	33
GP585X		+	+	+	+	+	+	+	+	+	+	+
Regal 350		3	-	3	3	3	-	-	-	-	-	-
CSX 910		-	3	-	-	-	3	3	-	-	-	-
Calcium titanate*		-	-	1	3	5	5	-	5	-	-	-
Barium titanate*		-	-	-	-	-	-	5	5	-	-	-
Strontium titanate*		-	-	-	-	-	-	-	-	5	-	-
Magnesium titanate*		-	-	-	-	-	-	-	-	-	-	5
Emerald 3000		2.0	2.0	2.0	1.5	1.5	1.5	1.5	0.6	0.6	0.6	0.6
Dicumyl peroxide		1.0	1.0	1.0	0.8	0.8	0.8	0.8	0.4	0.4	0.4	0.4
Polywax 1000		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pentane/Isopentane 80/20 %		5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5

*silanized with 0.1 wt.% of Dynasylan 9265

* Examples 23 and 24 are comparative, examples 25 to 33 are according to the invention.

Table 4. Examples 23 to 33.
Final product parameters at a foam density of ca. 19.0 g/l.

Examples*	23	24	25	26	27	28	29	30	31	32	33
Thermal conductivity (mW/m·K) /ISO 8301/	33.0	32.1	32.3	31.3	31.0	30.4	30.3	33.1	32.0	31.3	31.0
Flammability /EN ISO 11925-2/	+	+	+	+	+	+	+	+	+	+	+
Flammability /DIN 4102 B1/B2/	+/+	-/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+
Compressive strength at 10% def. (kPa) /EN 13163/	88	90	94	110	119	121	120	124	124	126	129
Bending strength (kPa) /EN 13163/	168	177	181	191	201	205	208	217	220	215	223

Passed (+ or B2 or B1); Not passed (-)

* Examples 23 and 24 are comparative, examples 25 to 33 are according to the invention.

Expandable polymer granulate was prepared in a continuous mass polymerization process (Examples 34 to 44):

Example 34 (comparative)

In this set of experiments, continuous mass polymerization was carried out in a three reactor cascade. The polymerization of styrene was initiated by heating. The powder form of carbon black (Regal 350 from Cabot Corporation with a BET surface of 55.0 m²/g) was added to the first reactor in an amount of 3 wt.% based on the total weight of granulate. After polymerization and degassing of the polymer melt, the flame retardant was added, directly to the extruding raw polystyrene and in an amount of 2.5 wt.%, together with: bicumyl in an amount of 0.5 wt.%, Irganox 1010 in an amount of 0.125 wt.%, Irgafos 126 in an amount of 0.125 wt.%, Epon 164 in an amount of 0.250 wt.% and nucleating agent (Polywax 2000) in an amount 0.3 wt.%. An extrusion was performed in similar like extruder 32D/40 mm attached to the degassing unit. Pentane in admixture with isopentane (80/20 %) was dosed into the extruder during the process (in a concentration of 5.5 wt.%). The granulate form was obtained by means of underwater pelletizing.

Example 35 (comparative)

The components according to Example 34 were used. Regal 350 carbon black was replaced with the CSX910 from Cabot Corporation, having a BET surface area of 71.8 m²/g.

Example 36 (according to the invention)

The components according to Example 34 were used. 1 wt.% of calcium titanate was added (silanized with 0.1 wt.% of Dynasylan 9265), premixed with 3 wt.% of Regal 350 and dosed to the

side arm extruder. The concentration in the melt in the side arm extruder was 40 wt.%.

Example 37 (according to the invention)

The components according to Example 36 were dosed, and the calcium titanate content was increased to 3 wt.%. The flame retardant concentration was reduced to 2.0 wt.%, bicumyl to 0.4 wt.% and thermal stabilizers subsequently were reduced too. XIRAN SZ15170 and F-2200 HM were absent from the composition.

Example 38 (according to the invention)

Again, the components according to Example 36 were dosed. The calcium titanate content was increased to 5 wt.%.

Example 39 (according to the invention)

The components according to Example 38 were used. The Regal 350 was replaced with CSX910.

Example 40 (according to the invention)

The components according to Example 39 were used. The calcium titanate was replaced with barium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Example 41 (according to the invention)

The process and components according to Example 34 were used. The flame retardant was used in an amount of 1 wt.%. The thermo-oxidative and thermal stabilizers were absent, as was XIRAN SZ15170. Calcium titanate was used in an amount of 5 wt.%.

Example 42 (according to the invention)

The process and components according to Example 41 were used and calcium titanate was replaced with barium titanate.

Example 43 (according to the invention)

The process and components according to Example 42 were used and calcium titanate was replaced with strontium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Example 44 (according to the invention)

The process and components according to Example 43 were used and calcium titanate was replaced with magnesium titanate (silanized with 0.1 wt.% of Dynasylan 9265).

Table 5. Summary of Examples 34 to 44.

Components (wt.%)	Examples*											
	34	35	36	37	38	39	40	41	42	43	44	
GP585X	+	+	+	+	+	+	+	+	+	+	+	
Regal 350	3	-	3	3	3	-	-	-	-	-	-	
CSX 910	-	3	-	-	-	3	3	-	-	-	-	
Calcium titanate*	-	-	1	3	5	5	-	5	-	-	-	
Barium titanate*	-	-	-	-	-	-	5	-	5	-	-	
Strontium titanate*	-	-	-	-	-	-	-	-	-	5	-	
Magnesium titanate*	-	-	-	-	-	-	-	-	-	-	5	
Emerald 3000	2.5	2.5	2.5	2.0	2.0	2.0	2.0	1.0	1.0	1.0	1.0	
Bicumyl	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.2	0.2	0.2	0.2	
Irganox 1010	0.125	0.125	0.125	0.1	0.1	0.1	0.1	-	-	-	-	
Irgafos 126	0.125	0.125	0.125	0.1	0.1	0.1	0.1	-	-	-	-	
Epon 164	0.250	0.250	0.250	0.2	0.2	0.2	0.2	-	-	-	-	
Polywax 2000	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	
XIRAN SZ15170	1	1	1	-	-	-	-	-	-	-	-	
F-2200 HM	1	1	1	-	-	-	-	-	-	-	-	
Pentane/Isopentane 80/20	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	

*silanized with 0.1 wt.% of Dynasylan 9265

* Examples 34 and 35 are comparative, examples 36 to 44 are according to the invention.

Table 6. Examples 34 to 44.
Final product parameters at a foam density of ca. 19.0 g/l.

Examples*	34	35	36	37	38	39	40	41	42	43	44
Thermal conductivity (mW/m·K) /ISO 8301/	32.7	31.5	32.2	31.1	30.6	30.2	30.1	32.5	31.7	31.2	30.8
Flammability /EN ISO 11925-2/	+	+	+	+	+	+	+	+	+	+	+
Flammability /DIN 4102 B1/B2/	+ / +	- / +	+ / +	+ / +	+ / +	+ / +	+ / +	+ / +	+ / +	+ / +	+ / +
Compressive strength at 10% def. (kPa) /EN 13163/	90	96	101	114	120	125	124	120	126	128	130
Bending strength (kPa) /EN 13163/	175	181	183	199	205	211	205	215	218	220	222
Passed (+ or B2 or B1); Not passed (-)											

* Examples 34 and 35 are comparative, examples 36 to 44 are according to the invention.

Claims

1. Use of a mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure, in vinyl aromatic polymer foam, wherein the polymer foam further comprises one or more athermanous additives selected from
 - a) powder inorganic additive selected from powders of silica and calcium phosphate,
 - b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and
 - c) powder geopolymer and powder geopolymer composite.
2. The use according to claim 1, wherein the mineral having perovskite structure is used
 - i) for decreasing the thermal conductivity of the vinyl aromatic polymer foam, the decrease being measured in accordance with ISO 8301,
 - ii) for increasing the compressive and bending strengths of the vinyl aromatic polymer foam, the increase being measured in accordance with EN 13163, or
 - iii) for improving the self-extinguishing properties of the vinyl aromatic polymer foam, the improvement being measured in accordance with EN ISO 11925-2,

preferably wherein the improvement of the self-extinguishing properties of the vinyl aromatic polymer foam is measured in accordance with DIN 4102 B1, B2.

3. The use according to claim 1 or claim 2, wherein the mineral having perovskite structure is of the general formula ABX_3 , A and B being cations and X being anions, and A is selected from the group consisting of Ca, Sr, Ba, Bi, Ce, Fe, and mixtures thereof.
4. The use according to any one of the preceding claims, wherein the mineral having perovskite structure is of the general formula ABX_3 , A and B being cations and X being anions, and B is selected from the group consisting of Ti, Zr, Ni, Al, Ga, In, Bi, Sc, Cr, Pb, ammonium groups, and mixtures thereof.
5. The use according to any one of the preceding claims, wherein the mineral having perovskite structure is of the general formula ABX_3 , A and B being cations and X being anions, and X is selected from oxygen, halide, and mixtures thereof.
6. The use according to any one of the preceding claims, wherein the mineral having perovskite structure has
 - (i) a BET surface area in a range of from 0.01 to 100 m²/g, as measured according to the standards ASTM C1069 and ISO 9277,

preferably wherein the BET surface is in a range of from 0.05 to 50 m²/g,

more preferably wherein the BET surface is in a range of from 0.1 to 15 m²/g.

7. The use according to any one of the preceding claims, wherein the mineral having perovskite structure further has

(ii) an average particle size in a range of 0.01 to 100 µm, as measured using a Malvern Mastersizer 2000 apparatus,

preferably wherein the average particle size is in a range of from 0.1 to 50 µm,

more preferably wherein the average particle size is in a range of from 0.5 to 30 µm.

8. The use according to any one of the preceding claims, wherein the mineral having perovskite structure further has

(iii) a moisture content in a range of from 0.01 to 3.0 wt.%,

preferably wherein the moisture content is in a range of from 0.05 to 1.5 wt.%.

9. The use according to any one of the preceding claims, wherein the amount of mineral having perovskite structure is in a range of from 0.01 to 50 wt.%, based on the vinyl aromatic polymer inclusive of (solid and, if any, liquid) additives, but exclusive of propellant,

preferably wherein the amount of mineral having perovskite structure is in a range of from 0.05 to 25 wt.%,

more preferably wherein the amount of mineral having perovskite structure is in a range of from 0.1 to 15 wt.%,

most preferably wherein the amount of mineral having perovskite structure is in a range of from 0.5 to 12 wt.%.

10. The use according to any one of the preceding claims, wherein the polymer is a styrene homopolymer or styrene copolymer.

11. The use according to claim 10, wherein the polymer is a styrene copolymer and the comonomer is p-tert-butylstyrene.

12. Process for the preparation of expandable polymer granulates comprising the following steps:

i) feeding vinyl aromatic polymer into an extruder,

ii) adding mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure, and optionally thermal stabiliser and flame suppressant,

iii) injecting blowing agent into the melt of polymer,

iv) extruding the homogenous blend, and

v) pelletizing the blend in an underwater pelletizer, so as to obtain the granulate,

wherein the granulate further comprises one or more athermanous additives selected from

a) powder inorganic additive selected from powders of silica and calcium phosphate,

b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and

c) powder geopolymer and powder geopolymer composite.

13. Process for the preparation of expandable polymer granulates comprising the following steps:

i) adding a vinyl aromatic monomer and optionally one or more comonomers to the reactor, and subsequently adding

i1) optional polymeric suspension aid,

i2) athermanous additives (mineral of the general formula ABX_3 , A and B being cations and X being ani-

- ons, wherein the mineral has perovskite crystal structure, and additional athermanous additive),
- i3) flame retardant,
- i4) at least one peroxide (or the mixture of two or more peroxides) as reaction initiator,
- ii) adding the demineralised water, and
- ii1) at least one suspending agent which is an inorganic acid salt,
- ii2) at least one peroxide (or the mixture of two or more peroxides) as reaction initiator,
- ii3) at least one suspension stabilizer selected from the group of anionic surface active compounds and/or high molecular weight compounds (e.g. hydrophilic and/or amphiphilic polymers), and
- iii) continuing the polymerization (preferably until the concentration of vinyl aromatic monomer(s) is below 1000 ppm by weight, based on the weight of the polymer),
- iv) adding the blowing agent during or after the polymerization step,
- v) cooling, and then separating the granulate from the water,

wherein the mineral having perovskite crystal structure and the additional athermanous additive are introduced as athermanous additives i2), and may also be introduced in step ii) and/or step iii), and

wherein the additional athermanous additive is selected from one or more of

- a) powder inorganic additive selected from powders of silica and calcium phosphate,
- b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and
- c) powder geopolymer and powder geopolymer composite.

14. Process for the preparation of expandable polymer granulate comprising the following steps:

i) providing continuously to a mass prepolymerization reactor (or the first from a cascade of reactors) a stream of:

- i1) vinyl aromatic monomer and optionally at least one comonomer (preferably p-tert-butylstyrene),
- i2) at least one additive solution, and
- i3) optionally recycled monomer,

ii) continuing polymerization in the prepolymerization reactor or the sequence of cascade reactors,

iii) addition of athermanous fillers (mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure, and additional athermanous additive) and optionally further additives (preferably flame suppressant),

iv) degassing the polymer,

v) feeding the polymer in molten state into the extruder, preferably directly from the polymerization plant,

vi) optionally adding a flame retardant system including synergist and thermal stabilisers,

vii) injecting blowing agent,

viii) extruding the homogenous polymer blend, and

ix) pelletizing in an underwater pelletizer, so as to obtain the granulate,

wherein the additional athermanous additive is selected from one or more of

a) powder inorganic additive selected from powders of silica and calcium phosphate,

b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and

c) powder geopolymer and powder geopolymer composite.

15. Expandable polymer granulate, comprising one or more propellants, x) mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure, and y) polymer of

vinyl aromatic monomer and optionally one or more comonomers,

wherein the expandable polymer granulate further comprises one or more athermanous additives selected from

- a) powder inorganic additive selected from powders of silica and calcium phosphate,
- b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and
- c) powder geopolymer and powder geopolymer composite.

16. The expandable polymer granulate of claim 15, wherein the granulate is obtainable by the process according to any one of claims 12 to 14.

17. Expanded polymer foam comprising x) mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure, and y) polymer of vinyl aromatic monomer and optionally one or more comonomers,

the foam having

- a density of 8 to 30 kg/m³, and
- a thermal conductivity of 25 to 35 mW/K·m as measured according to ISO 8301,

wherein the polymer foam further comprises one or more athermanous additives selected from

- a) powder inorganic additive selected from powders of silica and calcium phosphate,
 - b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and
 - c) powder geopolymer and powder geopolymer composite.
18. The expanded polymer foam of claim 17, wherein the foam is obtainable by expansion of the expandable polymer granulate according to claim 15 or claim 16.
19. Masterbatch comprising x) mineral of the general formula ABX_3 , A and B being cations and X being anions, wherein the mineral has perovskite crystal structure and y) vinyl aromatic polymer,
- wherein the amount of mineral having perovskite structure is in a range of from 10 to 70 wt.%, based on the weight of the masterbatch, and
- wherein the masterbatch further comprises one or more athermanous additives selected from
- a) powder inorganic additive selected from powders of silica and calcium phosphate,
 - b) powder carbonaceous additive selected from powders of graphite, carbon black, petroleum coke, graphitized carbon black, graphite oxides, and graphene, and
 - c) powder geopolymer and powder geopolymer composite.

20. The masterbatch according to claim 19 wherein the amount of mineral having perovskite structure is in a range of from 10 to 65 wt.%, based on the weight of the masterbatch,

preferably wherein the amount is in a range of from 20 to 60 wt.%,

more preferably wherein the amount is in a range of from 25 to 55 wt.%.

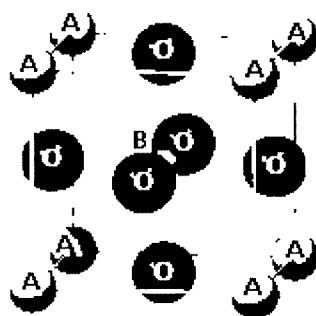
21. The masterbatch according to claim 19 or claim 20 wherein y) is a vinyl aromatic polymer having a melt index in a range of from 4 to 30 g/10 min, as measured according to ISO 1133,

preferably wherein the vinyl aromatic polymer is a homopolymer or copolymer with p-tert butyl styrene or alpha-methyl styrene.

22. The masterbatch according to any of claims 19 to 21, further comprising one or more silanes (preferably selected from aminopropyltriethoxysilane, aminopropyltrimethoxysilane, and phenyltriethoxysilane),

preferably wherein the amount of silane is in a range of from 0.01 to 1 wt.%, based on the weight of the athermanous additive in the masterbatch.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/050616

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J3/22 C08J9/04 C08J9/16 C08K3/04 C08K3/10
C08K3/16 C08K3/22 C08K3/24 C08K3/34 C08K3/36
ADD. C08K3/32

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)

C08J C08K

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 practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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Date of the actual completion of the international search

22 March 2016

Date of mailing of the international search report

30/03/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/050616

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 10 October 2001 (2001-10-10), NAKAYAMA, NAOKI: "Dielectric cellular moldings with improved dimensional stability for spherical Luneburg lenses", XP002741017, retrieved from STN Database accession no. 2001:736936 abstract -& JP 2001 279014 A (ACHILLES CORP) 10 October 2001 (2001-10-10) -----	1-22
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/050616

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