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(54) Title: COMPACT STRUCTURE OF A COMPOSITE NATURE AND METHOD OF PREPARATION THEREOF

(57) Abstract: The compact formation contains a matrix which can be prepared through compaction of a layer or layers of non-woven fabrics and also a component of discrete particles originally situated in this layer or layers of non- woven fabrics retained in the filtering mechanism. That may be a polymer matrix which can be prepared through the compression of the filtration layer or layers of non-woven fabrics with fibers made of polymer materials, fibres made of biopolymer materials, microfibers and/or nanofibers. A used waste filter may also be a layer of the filter. The functional and/or modifying additive aimed to control the resulting properties of composite material (additive showing an activity in the electric or magnetic field, additive to particles of biological material, or additive to particles with bioactive, biocidal, and/or antibacterial effects may then be a component of discrete particles. A component of discrete particles may also be an additive based on cross-linked powder elastomer as well as particles of toxic material encapsulated in the matrix, which enable their very easy and effective disposal. Furthermore, the invention deals with the preparation of compact formation of composite character.

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COMPACT STRUCTURE OF A COMPOSITE NATURE AND METHOD OF PREPARATION THEREOF

The sphere of technology

The invention deals with a compact formation of composite character with the possibility of targeted control of the resulting properties of the composite, also comprising the possibility of processing of waste filtering materials. Furthermore, the invention involves the manner of preparation of the mentioned compact formation, in particular in form of a pressed or rolled product or semi-finished product.

Present state of the art

Composites are heterogeneous systems consisting of no less than two phases, usually of a different chemical composition, which differ from each other in their physical and mechanical properties. Phases separated by an interface are (except for cavities filled with gas) almost always in a solid state. One of the phases has the function of the binding matrix; others are secondary phases called fillers in case of polymer composites. The secondary phases are usually not continuous; they are formed by particles of various shapes (globular, tabular, fibrous). The minimum size of particles in the secondary phases has not been unambiguously determined yet. From a microstructural perspective, such heterogeneous systems can be considered as composites in which the smallest dimension of the secondary phase is higher than 10^{-8} m.

Due to broadening possibilities of mutual combining of components which form the composite, the classification of composites becomes a complicated problem. As regards their composition, composites are classified as follows:

a) According to materials which form the matrix of the composites – organic, inorganic, macromolecular materials or a combination of at least two distinct materials,
b) According to the geometrical shape of the secondary phase – composites with particulate and fibrous fillers. Combined hybrid systems with particulate and fibrous fillers are gaining ever more importance.

In case of polymer composites with particulate fillers, besides the shape of particles (spherical, foliated, needle-shaped, irregular), thermomechanical properties are also important (thermal expansion, stiffness, deformation properties). Inorganic fillers (e.g. calcium carbonate, silicon oxide and aluminium oxide, small glass balls sized from 5 to 500 μm, particularly finely crushed mica, microscopic metal particles) are stiffer and usually tougher than polymer matrices, while being of a low plasticity (except for metal particles), therefore, the composites that are formed by them are also stiffer than matrices and gain certain physical and mechanical properties (a higher electric and thermal conductivity, a lower thermal expansion, better sliding properties, etc.) according to the selected type of filler.

E.g. the composite magnetic material according to the European Patent No. 289628 may be taken as an example of particulate polymer composites with specific properties. The magnetic particles contained in the mentioned material have a core made of magnetic material surrounded by a blend of fibrous material and by a solid binder. The particles may be embedded in a polymer resin, which has places selective for the relevant ions.

Composite materials made of silicon dioxide and titanium silicalite, silicon dioxide and β-zeolite or silicon dioxide, β-zeolite and titanium silicalite according to the patent of the CR No. 291722 are comprised of micro-balls with the average diameter of 20 to 150 μm, contain up to 70 % of gravimetric zeolite compounds and are characterized by values of the specific surface from 300 to 800 m^2/g. The preparation of these materials is carried out by dispersing of submicrometer particles of titanium silicalite, β-zeolite or the blends thereof in a colloidal solution of silicic acid obtained by means of acid hydrolysis of silicon alkoxides, and by putting the hybrid sol obtained in this manner through the emulsification and gelatinization process in organic environments. The invention also refers to the use of ternary mixtures of silicon dioxide, β-zeolite and titanium silicalite as a catalytic agent during the oxidation of aromatic compounds and during the hydroxylation of benzene to phenol, always using hydrogen peroxide.

The subject of the published Czech patent application No. 2003-3131 is composite material consisting of a foam polyurethane polymer composite matrix which continuously fills the space in the structure of the particulate composite among solid particles based on inorganic and polymer particles sized from 0.001 to 5 mm and/or particles of fibrous character, formed by at least one substance selected from a group of substances involving inorganic particles, polymer particles, lignocellulosic particles with a range of sizes between 0.01 and 5 mm. Moreover, the construction elements based on this composite and intended for reinforcing constructions are dealt with, for which laminates or wood have been used so far.

The US patent No. 6276214 refers to flat semi-finished products made of polymer composites with electrically conductive particles intended for strain gauges measuring stress in reinforced concrete structures. Polyolefines, polyacrylates, polyesters, polyamides, polyacrylonitrile, polysulfone, polycarbonate, polyvinyl acetate, polyvinyl alcohol as well as rubber homopolymers, silicon polymers and cellulose polymers tend to be mentioned as examples of polymer matrix materials. Conductive particles may be e.g. soot, graphite, fullerenes, carbon nanotubes, metal powder, metal beads.

The Japanese patent application No. 2006008969 also deals with polymer composites with fine metal particles.

The subject of two published Chinese patent applications CN101016399 and CN1834147 are nanocomposites based on inorganic nanoparticles and on a polymer matrix. In the latter case, an addition of reactive compatibilizer is mentioned which is aimed to increase the adhesion at the interface between phases.

Generally, the interface between the phases has an important role in composites. During the interaction of phases which differ from each other in physical and chemical properties, the surface of mutual contact cannot be explicitly considered an interface where different degrees of cohesion in phases of chemical and physical bonds (predominantly van der Waals forces) occur. A thin layer surrounding the contact area can be considered a part of the phase interface, which tends to be locally deformed due to the influence of dissimilar coefficients of thermal expansion and toughness of the phases. The layer matrix at the phase interface has a different morphology than the inner area of the matrix (the chemical composition is, however, the same). That is shown in a reduced mobility of molecular segments in the boundary layer, especially if a solid anchoring of macromolecules of the matrix on the surface of the filler occurs. In such a case we speak of an immobilized layer, which is characterized by a greater stiffness and a lower ability to create an extensive local plastic deformation. In this regard, they differ from the more remote areas of the matrix which are non-affected by secondary phases. It is also assumed that at the phase interface there is an increased level of free enthalpy, which facilitates diffusion (predominantly of water molecules). In order to increase the mutual cohesion of phases and to reduce the diffusion of foreign molecules by a phase interface, the surface of secondary phases (filler) is modified in the so-called sizing process. The modification consists in the applying of a suitable chemical substance on the surface of particles or fibres. If the secondary phases are inorganic, then the finishing substance contains both inorganic functional groups reacting with their surface and organic functional groups reacting with the polymer matrix. The most frequent sizing processes comprise various types of silanes and organic titanium compounds.

However, a higher mutual cohesion between the phases does not necessarily improve all mechanical properties of the composite. In case of inorganic particulate fillers and fibrous reinforcements, it leads to an increase in stiffness and toughness; in case of composites with particulate fillers, it usually causes a decrease in tenacity. At the same time, a dissipation of energy, which is indispensable in order to achieve a good toughness, occurs more easily in case of a lower mutual cohesion between particulate fillers and the matrix.

From the above-mentioned description and the analysis of examples of known composite materials it is obvious that basic problems (in particular occurring in special types of composites with special properties) include achieving an optimum dispersion of secondary phase particles (filler) in the binding matrix on the one hand and achieving an optimum cohesion of both components of the composite at the interface between the phases on the other hand. Currently, these optimizations are often achieved at the expense of a considerably complicated and costly modification of the manner of preparation of the relevant composite.

Subject matter of the invention

The compact formation of composite character as specified in the invention contributes to a solution of such problems to a significant extent. The subject matter of the invention consists in the fact that the compact formation contains a matrix which can be prepared through the compaction of a layer or layers of non-woven fabrics and also a component of discrete particles originally occurring in this layer or layers of non-woven fabrics retained in the filtration mechanism.

That means that the compact formation of composite character can preferably contain a polymer matrix which can be prepared through the compression of the filtration layer or layers of non-woven fabrics based on fibres made of polymer materials such as polyolefines, polystyrenes, polyesters, polyamides, polyaramids, polyurethane, polyethersulfon, polyvinylalcohol, polyacrylonitril, polyethylenoxide, polyvinylpyrolidon, epoxides or spinnable polymer blends as well as a component of discrete particles formed by particles of the filtration layer or layers of the retained part of the filtered material.

In another version, the compact formation of composite character may contain a biopolymer matrix which can be prepared through the compression of the filtration layer or layers of non-woven fabrics based on fibres made of biopolymer materials such as gelatine, chitosan, collagen or cellulose as well as a component of discrete particles formed by particles of the filtration layer or layers of the retained part of the filtered material.

Microfibers and/or nanofibres may preferably be fibres of non-woven fabrics.

The layer or layers of the used waste filter may also be the layer or layers of the filter.

A functional and/or modifying additive aimed to control the resulting properties of the composite material may preferably be a component of discrete particles. To be precise, the additive in question may be an additive showing an activity or a permanent effect in the electric field, an additive showing an activity or a permanent effect in the magnetic field, an additive to particles based on biological material such as cellulose powder or wood flour, or an additive to particles with bioactive, biocidal, and/or antibacterial effects.

An additive based on cross-linked powder elastomer may also be a component of discrete particles, in particular waste rubber creating a system highly filled with elastomer together with the matrix which can be prepared through the compression of a layer or layers of non-woven fabrics.

However, particles of toxic material encapsulated in the matrix, which enables their very easy and effective disposal, may also be components of discrete particles.

The manner of preparation of the compact formation of composite character specified in the invention is based on the fact that first, i.e. in the first step, a composite matrix is prepared in the form of at least one layer of non-woven fabrics based on spinnable thermoplastic or thermoreactive polymer material, which has the character of a filter, membrane or a porous structure. Afterwards, in the second step, the filtration mechanism is used to fill this structure with particular or fibrous fillers and, in the third step, it is pressed or rolled to a product or semi-finished product formed by a compact composite formation. This processing takes place at a temperature higher than the melting temperature of the thermoplastic polymer material of the matrix, or under conditions typical for the creation of a cross-linked structure of the thermoreactive polymer material of the matrix.

It is obvious that the main contribution of the compact formation of composite character specified in the invention is, in particular, considerable variability and flexibility of its application – starting from composite materials with controlled resulting properties up to an effective processing of waste filters and to the disposal of toxic waste materials. At the same time, an optimum dispersion of particles in the secondary phase (filler) in the binding matrix, and an optimum cohesion of both component of the composite at the interface between the phases is achieved in an relatively easy and effective manner.

Implementation examples of the invention

Example 1

In case of polymer composite containing rubber powder, the filtering structure of the polymer matrix was formed based on non-woven fabrics made of spinnable polypropylene. This structure with a porosity of 0.78 was filled with rubber powder in order to achieve a predominantly uniform arrangement of rubber particles in the structure. Air was used as the carrier medium and induced by depression or driven by overpressure into the filtering structure. The filling was carried out in such a manner so as to ensure that the structure was filled to the maximum without a filter cake. The latter was removed if it occurred.

In the following step, the filled filtering structure was then transferred to the compression mould and compressed at the temperature of 190 °C, which was sufficient to make the fibrous structure melt and to create a compact elastic flat product of composite character with a high content of rubber powder.

The prepared composite contained 40 % of gravimetric rubber powder in the polypropylene matrix with a distribution of particles sized from 100 nm to 1 mm.

Example 2

In case of the polymer composite containing wood flour, the filtering structure of the polymer matrix was formed by three layers of non-woven fabrics made of polylactate with dissimilar porosity values, with the input layer having the highest porosity value and the output layer having the lowest porosity value.

Wood flour was stirred in a water solution which contained antibacterial additives, e.g. nisin or thyme extract and also anti-agglomerating additives. Afterwards, the obtained suspension was filtered through the above-mentioned polylactate filtering structure during 1 min.; the produced filter cake was removed with a spatula if it occurred. The full filter (semi-finished composite product) was dried, placed in the compression mould and pressed at a pressing temperature of 180 °C (higher than the melting temperature of polylactate) during 60 s.

The prepared composite contained 80 % of gravimetric functional particles of wood flour with the distribution of particles sized from 10 nm to 0.1 mm in the biocompatible polylactate matrix.

Example 3

The filtering structure of the polymer matrix was created on the basis of non-woven fabrics made of spinnable low-molecular polyethylene and filled magnetic powder particles. The filtration mechanism used vacuum as the suction force, where the suction was carried out on both sides (from one, and subsequently, also from the other side), always during 20 s. Afterwards, compression at a pressing temperature of 120 °C followed.

The prepared composite contained 90 % of gravimetric magnetic particles with the distribution of particles sized from 800 nm to 0.5 mm in the polyethylene matrix.

In a similar manner, composites with metal, glass and ceramic particles were prepared.

Example 4

In case of polymer composite containing electrically conductive particles based on polyaniline powder, the filtering structure of the polymer matrix was created on the basis of non-woven fabrics made of spinnable low-melting polymer. This structure was filled with particles of polyaniline powder. The filtration mechanism used vacuum as the suction force, where the suction was carried out on both sides (from one, and subsequently, also from the other side). The surface filter cake was removed with a spatula if it occurred. The filled system was placed in the compression mould and compressed at a pressing temperature of 90 °C during 2 min.

The prepared composite contained 70 % of gravimetric electrically conductive particles with the distribution of particles sized from 800 nm to 0.5 mm and was, therefore, still electrically conductive.

Example 5

In case of antibacterial biocomposite, the filtration structure of the polymer matrix was made of non-woven nanofabrics based on biopolymer, in the implementation example based on collagen. The filtration mechanism was used to fill this structure with antibacterial particles, and also, if required, to cover the surface of fibres with a coating of a liquid antibacterial substance. The filled filtering structure was placed in the compression mould and compressed in order to transform the biopolymer into a compact formation of composite character.

Example 6

During the preparation of ionic composite, the non-woven filtering nanostructure on the basis of polyurethane nanofibers was placed between electrodes. During the electrochemical process, ions were retained in this filtering structure. After filling up, the filtering structure was dried, placed in the compression mould and compressed into the form of a compact formation of composite character.

Example 7

During the preparation of the biologically active polymer composite, the filtration mechanism was used to transport a bioactive substance or substances into the non-woven polymer nanostructure. After filling up, the filtering structure was compressed into the form of a compact formation of composite character.

Example 8

In order to produce a compact polymer composite, a waste filter was processed through compression on the basis of laminated material, where a layer of nanofibres with a lower melting temperature (70 to 170 °C) is applied on the bottom non-woven material (with the melting temperature of 90 up to 200 °C) from one or on both sides by electrospinning. The fibrous structures produced in this manner were then used for the microfiltration of liquids, such as e.g. a highly effective filtration of bacteria and other microorganisms from water. In this manner, a multi-layer fibrous structure containing the retained toxic substances was produced. Through the compression thereof, a compact composite was produced containing particles of toxic material encapsulated in the polymer matrix.

PATENT CLAIMS

1. Compact formation of composite character, in particular in the form of a compressed or rolled product or semi-finished product, characterized by the fact that it contains a matrix which can be prepared through a compaction of a layer or layers of non-woven fabrics and, furthermore, a component of discrete particles originally situated in the same layer or layers of non-woven fabrics retained in the filtration mechanism.

2. Compact formation of composite character according to claim 1, characterized by the fact that it contains a polymer matrix which can be prepared through the compression of the filtration layer or layers of non-woven fabrics based on fibres made of polymer materials such as polyolefines, polystyrenes, polyesters, polyamides, polyaramids, polyurethane, polyetersulfon, polyvinylalcohol, polyacrylonitril, polyethylenoxide, polyvinylpyrolidon, epoxides or spinnable polymer blends and, furthermore, a component of discrete particles formed by particles, a filtration layer or layers of the retained part of the filtered material.

3. Compact formation of composite character according to claim 1, characterized by the fact that it contains a biopolymer matrix which can be prepared through the compression of the filtration layer or layers of non-woven fabrics based on fibres made of biopolymer materials such as gelatine, chitosan, collagen or cellulose and also a component of discrete particles formed by particles, a filtration layer or layers of the retained part of the filtered material.

4. Compact formation of composite character according to claim 2 or 3, characterized by the fact that microfibers and/or nanofibers are the fibres of non-woven fabrics.

5. Compact formation of composite character according to claims 1 to 4, characterized by the fact that the layer or layers of the used waste filter are the layer or layers of the filter.

6. Compact formation of composite character according to claim 5, characterized by the fact that particles of toxic material encapsulated in the matrix are a component of discrete particles.

7. Compact formation of composite character according to claim 1, characterized by the fact that a functional and/or modifying additive aimed to control the resulting

properties of the composite material is a component of discrete particles.

8. Compact formation of composite character according to claim 7, characterized by the fact that an additive based on cross-linked elastomer powder, in particular waste rubber, creating a system highly filled with elastomer together with the matrix which can be prepared through the compression of a layer or layers of a non-woven system, is a component of discrete particles.

9. Compact formation of composite character according to claim 7, characterized by the fact that an additive showing an activity or a permanent effect in the electric field is a component of discrete particles.

10. Compact formation of composite character according to claim 7, characterized by the fact that an additive showing an activity or a permanent effect in the magnetic field is a component of discrete particles.

11. Compact formation of composite character according to claim 7, characterized by the fact that an additive to particles based on biological material such as cellulose powder or wood flour is a component of discrete particles.

12. Compact formation of composite character according to claim 7, characterized by the fact that an additive to particles with bioactive, biocidal, and/or with antibacterial effects is a component of discrete particles.

13. The manner of preparation of the compact formation of composite character, characterized by the fact that first, i.e. in the first step, a composite matrix is prepared in the form of at least one layer of non-woven fabrics based on spinnable thermoplastic or thermoreactive polymer material, which has the character of a filter, membrane or a porous structure. Afterwards, in the second step, the filtration mechanism is used to fill this structure with particular or fibrous fillers and, in the third step, it is pressed or rolled to a product or semi-finished product formed by a compact composite formation at a temperature higher than the melting temperature of the thermoplastic polymer material of the matrix or under conditions typical for creation of a cross-linked structure of the thermoreactive polymer material of the matrix.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. D04H1/407 B29C70/58 B29C43/00 D04H1/413 D04H1/542
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D04H B29C

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 786 059 A (FRANK DIERK [DE] ET AL) 28 July 1998 (1998-07-28) claims 1,13	1,7,13 2-6,8-12
X	US 5 614 312 A (TUCKER KENNETH W [US] ET AL) 25 March 1997 (1997-03-25) column 5, lines 17-35; claims 1,8	1,4,7
X	DE 197 08 694 A1 (BLUECHER GMBH [DE]) 10 September 1998 (1998-09-10) claims 1,9	1,4,7
X	EP 0 607 185 A1 (MINNESOTA MINING & MFG [US]) 27 July 1994 (1994-07-27) page 4, lines 46-49; claim 1	1,4,7,13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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