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(54) Title: A METHOD FOR MANUFACTURING A SLAB

(57) Abstract: The present invention relates to a method for manufacturing a slab comprising solid fillers and organic binders. More in detail the present method comprises a method for manufacturing a slab having a front layer and a rear layer, said slab comprising fillers, organic binders and additives, said method comprises mixing starting materials comprising fillers, organic binders and additives, heating, shaping, pressing and cooling. The present method furthermore relates to a slab obtained according to the present method.



Title: A method for manufacturing a slab

Description

5 The present invention relates to a method for manufacturing a slab comprising solid fillers and organic binders. More in detail the present method comprises mixing, shaping, pressing and cooling of starting materials comprising solid fillers, organic binders and additives. The present method furthermore relates to a slab obtained according to the present method.

10 Methods for manufacturing slabs are known from the prior art. For example, International application WO 2005/014952 (corresponding to US2006119002) relates to a thin, i.e. a thickness of 3.5 to 6 mm, stratified, reinforced slab consisting of two outer layers and at least one resistant middle layer wherein the outer layers and the at least one middle layer consist of the same permanently hardened mix, comprising inert
15 materials and a binding resin. The mass of the middle layer is a fibrous layer where linear elements or filaments made of glass. The mix forming outer layers and at least one middle layer is a Breton stone mix. The technology according to Breton stone envisages using a mix consisting of inert materials and a cement binder or a binder consisting of a synthetic resin with the addition of fillers, wherein the mix, which is deposited in a suitable thickness
20 inside a forming support, preferably in the form of two rubber sheets with dimensions matching those of the final slab desired, is subjected inside a vacuum chamber to the action of a press, the ram of which is kept vibrating at a redefined frequency. After the vacuum compaction accompanied by a vibratory movement, the resulting slab is transferred to a hot hardening station where, owing to the effect of heat, the resin
25 hardens. The slab is then freed from the rubber sheets so that it can be conveyed away for the normal finishing operations (such as sizing, polishing, etc.).

 US Patent application publication 2012/119414 relates to a process for manufacturing a slab having an average thickness of about 2.5 mm to about 50 mm from a composite material, said process comprising: (a) mixing solid filler and thermoplastic
30 binder in a kneading device at a pressure in the range of about 100 kPa to about 1500 kPa to obtain a composite material; and (b) forming the composite material into a shaped article; wherein the thermoplastic binder comprises about 60 wt.% to about 100 wt.% of a thermoplastic polyester, based on the total weight of the binder, and

wherein the thermoplastic polyester comprises about 90 wt.% to about 100 wt.% of recycled polyethylene terephthalate.

US Patent application publication 2012/049413 relates to a process for manufacturing a shaped article from a composite material, said process comprising mixing
5 solid filler and thermoplastic binder in a mixing device to obtain a composite material, forming the composite material into a shaped article; and cooling the shaped article at a cooling rate of at least about 5 °C./min to about 120 °C./min, wherein the weight ratio of the solid filler to the thermoplastic binder is about 2:1 to about 15:1. shaped article is a slab. The shaped article is a slab having a thickness of about 0.3 cm to about 5 cm,
10 wherein an upper surface and a bottom surface slab are cooled simultaneously by belt cooling.

US Patent application publication US 2013/130009 relates to an isotropic slab of engineered stone, having a thickness of about 2 mm to about 10 mm, the slab comprising a composite material comprising about 50 to about 95 wt.% of solid filler
15 and about 5 to about 50 wt.% of a thermoplastic binder, based on the total weight of the isotropic slab. Such a slab has been manufactured according to a process comprising the following subsequent steps: feeding solid filler and a thermoplastic binder to a mixing device, mixing the solid filler and the thermoplastic binder in the mixing device at a temperature of 230 °C to 350 °C. to obtain a composite material, forming the composite
20 material into a thin slab; and cooling the thin slab to a temperature greater than about 75 °C. by belt cooling.

International application WO02/090288 relates to a process for the preparation of a composition, which comprises a matrix of solid particles, i.e. a combination of aggregate, filler and sand, embedded in a binder, wherein the binder is
25 present in an amount in the range of from 1 to 50 % by weight and comprises a synthetic thermoplastic polymer, i.e. waste or recycled polymer selected from the group of polypropylene, polyethylene terephthalate, polybutylene terephthalate and mixtures thereof, which process comprises mixing heated particles and binder, shaping if desired, and allowing the mixture to solidify, wherein solid particles and binder are heated
30 independently of each other prior to mixing such that on mixing the temperature of the mixture is in the range of from 230 to 300 °C, and wherein the solid particles are heated to a higher temperature than the binder.

US Patent application publication US 2003/122273 relates to a method of manufacturing a building product from a mix including particulate material and a binder, wherein the binder being a thermoplastic binder which binder is an asphaltene-containing binder, which comprises heating the mix including the thermoplastic binder at least to a temperature at which the thermoplastic binder in the mix liquefies, subjecting the heated thermoplastic mix to a pressing action that shapes the heated mix, and cooling the shaped heated thermoplastic mix to solidify the thermoplastic binder and form the building product.

US Patent No. 6,177,179 relates to a process for the production of an Integral, board-like component with a visible side and a rear side which comprises the steps: filling a casting mold with a first hardenable casting mass which contains a first syrup with a first monomer and a first filler for forming the visible side layer, further filling the casting mold with a second hardenable casting mass which contains a second syrup with a second monomer and filling a second inorganic filler into the casting mold, wherein the filler forms the rear side layer together with the second casting mass, closing the casting mold, and initiating the hardening of the first and the second casting masses, beginning on the visible side of the component, wherein the first filler has a greater specific density than the syrup of the first casting mass, wherein the barrier layer is essentially impermeable for the first monomer and can be securely bonded to the visible side layer as well as the rear side layer.

From International application WO 2013/011360 is known a method for obtaining a hybrid polymer coating for petrous or ceramic substrates, the coating having a thickness between 0.1 and 2 mm and comprising a mixture of micronized powder, gravels, base resin selected from polyurethane, polyester, epoxy or acrylic and in general pigments and additives for said resin. The method comprises a step of preparing a base mixture comprising at least one first gravel of quartz, silica or silica sand in a mixer, preparing a base resin selected from polyurethane, polyester, epoxy or acrylic, adding the resin to the mentioned mixture and stirring in a mixer, creating a vacuum inside the mixer, applying a layer of the semi-fluid mixture obtained on a substrate and retaining on the same, vibrating the substrate to displace the larger gravels towards the bottom; accelerating the curing of the mixture by providing or generating heat, the mixture being consolidated on the substrate, and mechanical finishing including a mechanical polishing of the coating polymer to obtain the mentioned thickness required and a smooth surface.

Such a vibration process for causing a degree of migration of particles from one layer to another layer is also known from International application WO 2004035502. This document discloses a method of forming a particle mass comprising at least two particle populations arranged in a desired graded relationship, the method comprising: forming in a container a first layer of dry particles constituting a first particle population having a desired particle size distribution, superimposing on the first layer a second layer of dry particles constituting a second particle population having a desired particle size distribution, the second layer being in direct contact with the first layer at a contact interface, and causing the particle mass in the container to vibrate to cause a desired degree of migration of particles from one or both layers across the contact interface under the influence of force experienced by particles in the mass.

JP2006137807 relates to an epoxy resin compact obtained by impregnating epoxy resin into a fiber glass mat as reinforcing material. A mixture (250-350 weight parts) of hydrated aluminum-powder of large particle size group having particle size of 15-100 micrometer and small particle size group with particle size of less than 4 micrometer is mixed with an epoxy resin (100 weight parts) to obtain a varnish. The varnish was impregnated into a fiber glass mat and heated at 120[deg]C for 10 minutes, to obtain a prepreg. The initial and final filler distribution is the same across the final product.

JP2005089648 relates to an insulating plate of electric switch used for motor circuits, prepared by impregnating a fiber glass mat with a mixture containing granular filler for improving arc resistance, a resin binder, and hardener for resin binder to form a prepreg and molding the formed prepreg. Such a mixture contains filler, binder and hardener, wherein the filler, i.e. aluminum hydroxide, contains particles of large size (15-100 micron) and particles of small size (less than 4 micron), in mass ratio of 10:6-10:14. The initial and final filler distribution is the same across the final product.

JPS54-37174 relates to a moulding fibre reinforced plastic material by pulverizing components, forming a slurry, applying the slurry to web, drying and moulding under heat and pressure. This document discloses the pulverization of an epoxy resin and hardener to particles smaller than 50 micrometer and the subsequent preparation of a slurry with silica powder, colloid silica and methanol. The slurry was applied to a glass fibre mat and five sheets of the web were laminated under pressure and heat to obtain a flame retardant sheet. The initial and final filler distribution is the same across the final product.

JPS54162781 relates to insulating boards for tightening rails with slabs, prepared by moulding glass fibre reinforced unsaturated polyester, quartz sand filler and additives mixture at specific temperature and pressure. The mixture as disclosed therein contains unsaturated polyester, calcium carbonate powder and quartz powder containing
5 99.9% of SiO₂, 50% of the particles having a size of 2 - 10 micrometer and is impregnated into a glass mat, and moulded in a mould. The initial and final filler distribution is the same across the final product.

On basis of the above discussion of relevant prior art one must realize that nowadays a wide range of polymer-filler composite products is used in the
10 construction of buildings, cars, aviation etc. These products are manufactured with different technologies that can basically be divided into two categories, namely i) chemical processes employing a liquid thermoset resin that solidifies via chemical reaction (like two component adhesives) and ii) mechanical processes using a thermoplastic resin at high temperature, that subsequently solidifies by cooling.

15 In the technical area of artificial (or engineered) stone products for the building industry require very high levels of fillers, e.g. up to 90% by weight, to mimic the stone like features of natural stone products. A very important technical challenge is how to effectively mix such very highly filled polymer-mineral composites, while at the same time keeping the wear of the mixing devices at an acceptable level.

20 As discussed above, some processes employ thermoset resins, mainly in a batch process. The presence of a liquid resin in the mixture of starting material enables mixing while minimizing erosion or abrasion. However, such a batch process is capital intensive, generates industrial waste; uses (toxic) chemicals and limits plant productivity and the flexibility of product dimensions. The slab produced according to
25 these batch processes has generally a minimum thickness of typically 10 mm (due to process constraints and mechanical properties) and the maximum length is about 3600 mm (due to process equipment constraints, such as batch press dimensions).

It has also been attempted to use thermoplastic or thermoset resins in a continuous (mechanical) process. Such a technology would need less capital investment
30 having higher productivity and would lead to a reduction of waste, avoidance of toxic chemicals and increase of flexibility in product dimensions. However, such attempts have proven to be unsuccessful, because machine wear is too high when high concentration of hard coarse minerals are used for manufacturing high quality end products and degassing

the end product to a final product free of air pores has shown to be unviable at such low binder content in a continuous process.

An aspect of the present invention is to provide a method for manufacturing a slab wherein one or more of the objections as discussed above are overcome.

More in detail, an aspect of the present invention is to provide a method for manufacturing a slab wherein a slab having excellent product properties is obtained.

The present invention relates thus to a method for manufacturing a slab having a front layer and a rear layer, said slab comprising fillers, organic binders and additives, said method comprises mixing starting materials comprising fillers, organic binders and additives, heating, shaping, pressing and cooling, characterized in that said method comprises the following steps:

i) providing a mixture comprising organic binders, additives and fillers, wherein said fillers comprise fine particles and a first amount of coarse particles;

ii) providing a porous substrate layer;

iii) contacting the mixture of step i) with the porous substrate layer of step ii);

iv) exerting a force on the construction obtained in step iii) for migrating said organic binder and said fine particles from said mixture of step i) into said porous substrate layer;

v) cooling the construction obtained in step iv) for obtaining a slab, wherein due to said step iv) the concentration of said first amount of coarse particles in said front layer of said slab is higher than in said rear layer of said slab.

The present inventors found that by using such a method for manufacturing a slab one or more of the above identified aspects can be achieved. According to the present method the effect of step iv) is that both binder and fine particles present in the mixture according to step i) will migrate into the porous substrate layer according step ii) resulting in an enrichment of the first amount of coarse particles on one side of the final slab. This enrichment of coarse particles will result in an increase of the surface hardness of the final slab, especially at the side where this enrichment is present. During step iv) the concentration of the first amount of coarse particles in the mixture of step i) will increase due to the migration of binder and fine particles into the porous substrate layer. Thus the concentration of the first amount of coarse particles in the

mixture of step i) at the beginning of the present method will be much lower than the concentration of the first amount of coarse particles at the end of step iv). According to the present method there is a migration of the organic binder and fine particles resulting in a selective filtering of the first amount of coarse particles. The present method will thus result in a change in filler distribution during the manufacturing process, i.e. the formation of a filler concentration profile across the thickness of the final slab after the manufacturing process. The present method thus relates to a selective filler migration of binder and fine particles from the front layer to the rear layer, i.e. binder and fine particles passing through porous substrate layer, while the first amount of coarse particles is retained in the front layer. In practice some parts of organic binder and fine particles will remain in the front layer of the slab. This organic binder will function as a "matrix" for the first amount of coarse particles.

Examples of such a porous substrate layer are a glass fiber matt, voids of a loose particulate material, e.g. dry powder, or a combination thereof. The present method will lead to products, e.g. slabs, that are non isotropic, but also display a non homogeneous distribution of coarse particles, fine particles and binder in the final product. The present inventors found that the final concentration profile of the coarse particles, i.e. in the slab, depends on the initial front and rear layer composition and pore size of the porous substrate layer, i.e. a mat, e.g. a glass fiber mat, a loose particulate material, e.g. dry powder, or a combination thereof. In a specific embodiment of the present method the concentration of coarse particles in the front layer can be lower than the concentration of coarse particles in the rear layer. The present invention specifically relates to an increase of the concentration of coarse particles in the front layer during the pressing process, i.e. step iv), thus raising the Barcol hardness of the final product, i.e. the slab.

The pore size of the porous substrate layer is such that during step iv) the first amount of coarse particles will not migrate into the porous substrate layer. The pore size of the porous substrate layer is chosen such that the porous substrate layer will function as a selective filter or membrane wherein only materials, e.g. fine particles and organic binder, having a size smaller than the pore size of the porous substrate layer can migrate into the pores, interstices or voids of the porous substrate layer. The result of such a selective filtering property of the porous substrate layer is that materials having a size bigger than the pores, interstices or voids of the porous substrate layer will remain in the originally provided mixture.

According to a preferred embodiment of the present method the concentration of the fine particles in the rear layer is higher than the concentration of the fine particles in the front layer.

5 In addition by providing two separate compositions, i.e. the mixture according to step i) and the porous substrate layer according to step ii), the present inventors were able to prepare a composition of coarse particles and organic binder which does not have a high impact on the life time of the mixing equipment, i.e. abrasion of the apparatuses.

10 The porous substrate layer in step ii) is a mat, a loose particulate material, or a combination thereof. The substrate layer as such has pores since binder and fine particles must migrate into the substrate layer, whereas the first amount of coarse particles must stay in the mixture. In an embodiment of a mat, such a mat is a porous mat.

In an embodiment of a loose particulate material, the loose particulate material comprises a second amount of coarse particles.

15 In a preferred embodiment the porous substrate layer in step ii) comprises a porous mat chosen from the group of glass fibers, flax fibers, Abaca fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof. A benefit of using such a porous mat is to increase the impact resistance and flexural strength of the final product.

20 In the present method the organic binder is preferably chosen from the group of thermoset and thermoplast type binders, or a combination thereof.

In case of the application of thermoset type binders in step i) the present method further comprises a step of heating during one or more of step i), step ii), step iii) and step iv).

25 Present step i) may further comprise mixing organic binders, additives and fillers at an elevated temperature.

30 In a preferred embodiment step iii) further comprises applying the mixture comprising organic binders, additives and fillers on a support in a continuous mode and applying the porous substrate layer on top of said mixture laying on the support.

In another preferred embodiment step iii) further comprises applying the porous substrate layer on a support in a continuous mode and applying the mixture

comprising organic binders, additives and fillers on top of the porous substrate layer laying on the support.

An example of such a support is an end less conveyor belt.

For obtaining a high pressure in a continuous mode of the present method step iv) further comprises transferring the support, the support comprising the porous substrate layer and the mixture comprising organic binders, additives and fillers through a slit between rotating rolls. By adjusting the width of the slit between the rotating rolls both the pressure exerted on the feed material and the thickness of pressed feed material can be set at a desired range.

The present inventors found that the presence of air bubbles in the binder containing mixture will have a negative influence on the final mechanical properties of the final slab. It is thus preferred to further include in step i) a step of de-aeration, preferably during or after mixing said organic binders, additives and fillers. Such a step of de-aeration can be carried out by vibrating the mixture with an under pressure, i.e. vacuum conditions in the mixing unit and or the press. Such a step of de-aeration may also comprise the application of an under pressure without vibration.

In another embodiment of the present method step iii) further comprises the positioning of a porous reinforcement material, such as a porous substrate layer, e.g. a porous mat, on the interface between said mixture comprising organic binders, additives and fillers and a layer of loose particulate material. Such a porous reinforcement material will lead to an improved impact resistance of the final product and may prevent the transfer of the first amount of coarse particles from the mixture to the layer of loose particulate material. However, the porous reinforcement material may not hinder the transfer of the organic binder from the mixture into the layer of loose particulate material. Examples of such a porous reinforcement material are chosen from the group of glass fibers, flax fibers, Abaca fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof. In a specific embodiment the porous reinforcement material is chosen from a nonwoven type mat or a woven type mat, preferably a glass fiber woven mat.

The particle size distribution of the fine particles in the mixture of step i) is preferably chosen from a range below 63 micron.

It is preferred that the first amount of coarse particles differs from the second amount of coarse particles in one or more aspects chosen from the group of

chemical composition, mineral type, particle size, particle shape and particle size distribution.

According to a preferred embodiment the particle size distribution of the first amount of coarse particles is broader than the particle size distribution of the second amount of coarse particles. Such a particle size distribution allows a very high volume fraction of minerals in the final composition of the coarse enriched first layer.

According to another preferred embodiment the particle size distribution of the first amount of coarse particles is chosen from a range between 63-800 micron, wherein the particle size distribution of the second amount of coarse particles is chosen from a range within 200-1200 micron. More specifically, in a preferred embodiment the particle size distribution of the first amount of coarse particles is chosen from a range between 63-500 micron, wherein the particle size distribution of the second amount of coarse particles is chosen from a range within 500-800 micron. This particle size distribution of both the first and second amount of coarse particles will be chosen such that the final volume fraction of coarse minerals in the front layer is very high (> 0.75) yielding high product hardness, while the initial volume fraction of coarse minerals in the rear layer is lower for providing absorption capacity.

The present inventors found that the average particle size of the second amount of coarse particles as said porous substrate layer is chosen so that during step iv) organic binder and fine particles from said mixture of step i) migrate into said porous substrate layer.

The thickness of the slab obtained after step vi) is in a range of 2 to 10 mm.

According to a preferred embodiment the weight percentage of organic binder is in a range of 5 – 30 wt.%, the weight percentage of fillers is in a range of 50 to 95 wt.%, the weight percentage of additives is in a range of 0,1-5 wt.%, all weight percentages being based on the total weight of the slab obtained after step vi).

According to another preferred embodiment organic binder comprises 60 - 100 wt.% of thermoplastic polyester and 0 - 40 wt.% of a polyolefin, based on the total weight of the organic binder.

It is preferred that 90 - 100 wt.% of said thermoplastic polyester is one or more chosen from the group of polybutylene terephthalates, modified polyethylene terephthalates, recycled polyethylene furanoate, polycarbonates, polylactates and

recycled polyethylene terephthalates, based on the total weight of the thermoplastic polyester.

The organic binder is preferably a thermoset type binder chosen from the group of unsaturated polyester resin, acrylic resin, epoxy resin or phenolic resin, or a
5 combination thereof.

The porous reinforcement material is preferably chosen from a nonwoven type mat or a woven type mat, preferably a glass fiber woven mat, and possibly from other materials as discussed above.

Examples of the first amount of coarse particles are chosen from the
10 group of inorganic minerals, such as quartz, glass, silica sand (SiO_2), calcium carbonates, such as marble (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$), aluminum tri-hydrate (ATH), wollastonite (CaSiO_3), coesite, cristobalite, keatite, moganite, seifertite, stishovite and tridymite, especially inorganic minerals having a Mohs hardness of at least 7.

Examples of the second amount of coarse particles are chosen from the
15 group of inorganic minerals, such as quartz, glass, silica sand (SiO_2), calcium carbonates, such as marble (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$), aluminum tri-hydrate (ATH) and wollastonite (CaSiO_3).

The present method is preferably carried out as a continuous process, i.e. steps i) –v) are carried out in a continuous mode.

The present invention furthermore relates to a slab consisting of a front
20 layer and a rear layer obtainable according to the present method as discussed above, wherein the concentration profile of the first amount of coarse particles shows a gradient over the thickness of said slab, wherein the concentration of said first amount of coarse particles in said front layer of the slab is higher than in said rear layer of the slab.

In a preferred embodiment of the present slab the concentration of fine
25 particles in the rear layer of the slab is higher than the concentration of fine particles in the front layer of the slab.

According to another embodiment the rear layer of the slab comprises a mat. Such a mat is preferably chosen from the group of glass fibers, flax fibers, Abaca
30 fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof.

In a preferred embodiment the present slab further comprises a reinforcement material located at the interface of said front layer and said rear layer.

In a slab according to the present invention the particle size distribution of the first amount of coarse particles is chosen from a range between 63-800 micron, wherein the particle size distribution of the second amount of coarse particles is chosen from a range within 200-1200 micron.

5 The present slab is further characterized in that the Barcol Hardness exceeds a value of 65, preferably 75, in case of an organic thermoset type binder (according to ASTM D 2583-07 "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor").

10 The present slab is further characterized in that the Barcol Hardness exceeds a value of 55, preferably 70, in case of an organic thermoplast type binder (according to ASTM D 2583-07 "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor").

15 The present slab is further characterized in that the impact resistance of said slab is at least 10 J (according to EN 14617-9:2005), when the porous substrate layer used in step ii) comprises a second amount of coarse particles.

 The present slab is further characterized in that the impact resistance of said slab is at least 20 J (according to EN 14617-9:2005), when the porous substrate layer is chosen from the group of glass fibers, flax fibers, Abaca fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof.

20 Various aspects of the present invention are now illustrated by way of examples and comparative examples.

Example 1 [sample IBQ 111]

25 A mixture of 21 wt.% of a thermoset resin (50% Epoxidised Linseed Oil (ELO) + 46% methyl hexahydro phthalic anhydride (MHHPA) + 3% 2-methyl imidazole (Melm)/alcohol mixture + 1% GLYMO) is mixed with 25 wt.% quartz powder 45 (fines) and 19 wt.% quartz 63-200 particles (coarse) and 35 wt.% quartz 200 – 500 particles (coarse) and heated to 60 °C. An amount of 10g hot mixture is transferred into a hot mould (60 °C) and contacted with an aggregate comprising 0,3g woven glass fiber mat (300 g/m²) and 5 g of dry hot (60 °C) quartz 500-800 particles (coarse) is added on top of the glass fiber.
30 The hot product was pressed to ≥ 50 bar) for 4 minutes and cured at 140 °C during one hour and then cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM D2583-07 and found to be 79,8. This example appears in the Table as IBQ 111.

Example 2 [sample IBQ 117]

A mixture of 21 wt.% of a thermoset resin (50% ELO + 46% MHHPA + 3% Melm/alcohol mixture + 1% GLYMO) is mixed with 25 wt.% quartz powder 45 (fines) and 19 wt.% quartz 63-200 particles (coarse) and 35 wt.% quartz 200 – 500 particles (coarse) and heated to 60 °C. An amount of 10g hot mixture is transferred into a hot mould (60 °C) and contacted with an aggregate comprising 0.3 g woven glass fiber mat (300 g/m²) and 7g of dry hot (60 °C) quartz 500-800 particles (coarse) is added on top of the glass fiber. The hot product was pressed to ≥ 50 bar) for 4 minutes and cured at 140 °C during one hour and then cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM D2583-07 and found to be 78. This example appears in the Table as IBQ 117.

Example 3 [sample IBQ 86]

A mixture of 23 wt.% of a thermoset resin (50% ELO + 46% MHHPA + 3% 1,4-diazo-bicyclo-[2,2,2]Octane (DABCO)/alcohol mixture + 1% GLYMO) is mixed with 26 wt.% quartz powder 45 (fines) and 20 wt.% quartz 63-200 particles (coarse) and 31 wt.% quartz 200 – 500 particles (coarse) and heated to 60 °C. An amount of hot mixture is transferred into a hot mould (60 °C) and pressed to ≥ 50 bar) for 4 minutes and cured at 140 °C during one hour and then and cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM D2583-07 and found to be 47,5. This example appears in the Table as IBQ 86.

Example 4 [sample IBQ 87]

A mixture of 23 wt.% of a thermoset resin (50% ELO + 46% MHHPA+ 3% DABCO/alcohol mixture + 1% GLYMO) is mixed with 26 wt.% quartz powder 45 (fines) and 20 wt.% quartz 63-200 particles (coarse) and 31 wt.% quartz 200 – 500 particles (coarse) and heated to 60 °C. An amount of 9 g hot mixture is transferred into a hot mould (60 °C) and contacted with an aggregate comprising 1,5 g of glass fiber (biaxial 300 g/m²) added on top of the mixture. The hot product was pressed to ≥ 50 bar) for 4 minutes and cured at 140 °C during one hour and then cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM D2583-07 and found to be 66,3. This example appears in the Table as IBQ 87.

Example 5 [sample IBQ 88]

A mixture of 23 wt.% of a thermoset resin (50% ELO + 46% MHHPA + 3% DABCO/Alcohol mixture + 1% GLYMO) is mixed with 26 wt.% quartz powder 45

(Fines) and 20 wt.% quartz 63-200 particles (coarse) and 31 wt.% quartz 200 – 500 particles (coarse) and heated to 60 °C. An amount of 10g hot mixture is transferred into a hot mould (60 °C) and contacted with an aggregate comprising 0.6 g woven glass fiber mat (300 g/m²) and 4g of dry hot (60 °C) quartz 500-800 particles (coarse) is added on top
5 of the glass fiber. The hot product was pressed to ≥ 50 bar) for 4 minutes and cured at 140 °C during one hour and then cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM D2583-07 and found to be 65,3. This example appears in the Table as IBQ 88.

Example 6 [sample IPQ 17]

10 20 wt.% of modified polyethylene terephthalate (PET-G) thermoplastic resin flakes and 21 wt.% quartz powder 45 (fines) and 27 wt.% quartz 63-200 particles (coarse) and 32 wt.% quartz 200 – 500 particles (coarse) are heated for 20 minutes at 240 °C and then mixed at 260 °C using a Hobart N50 mixer until the flakes are molten and a homogeneous mix is obtained. An amount of 17 g hot mixture is transferred into a hot
15 mould (240 °C) and contacted with an aggregate comprising 2 g of dry hot (240 °C) quartz 500-800 particles (coarse) added on top of the mix. The hot product was pressed to ≥ 50 bar) for 4 minutes and cooled to ambient temperature. The hardness was measured after at least 1 hour cooling, according to ASTM2583-07 and found to be 56.

Example 7 [sample IPQ 16]

20 20 wt.% of modified polyethylene terephthalate (PET-G) thermoplastic resin flakes and 21 wt.% quartz powder 45 (fines) and 27 wt.% quartz 63-200 particles (coarse) and 32 wt.% quartz 200 – 500 particles (coarse) are heated for 20 minutes at 240 °C and then mixed at 260 °C using a Hobart N50 mixer until the flakes are molten and a homogeneous mix is obtained. An amount of hot mixture is transferred into a hot mould
25 (240 °C) without adding dry aggregate. The hot mix was pressed to ≥ 50 bar) for 4 minutes and cooled to ambient temperature. The Barcol hardness was measured after at least 1 hour cooling according to test method ASTM D 2583-07 and found to be 43,3.

The test results have been summarized in Table 1. From Table 1 one can learn that high Barcol Hardness values have been obtained for 111 and 117. For
30 compositions not according to the invention, i.e. 86 and 16, the Barcol Hardness is low.

Table 1: Test results

Sample	IBQ 111	IBQ 117	IBQ 86	IBQ 87	IBQ 88	IPQ 17	IPQ16
Mixture Quantity, g	10	10		9	10	17	
Thermoset Resin, %wt of Mix	21	21	23	23	23		
5 Thermoplast Resin, %wt of Mix						20	20
Quartz Powder 45 micron, %wt of Mix	25	25	26	26	26	21	21
Coarse Quartz 63 -200 micron, %wt of Mix	19	19	20	20	20	27	27
Coarse Quartz 200-500 micron, %wt of Mi	35	35	31	31	31	32	32
Aggregate							
Glass Fiber, g	0,3	0,3		1,5	0,6		
10 Coarse Quartz 500 - 800 micron, g	5	7			4	2	
Pressure	>50 Bar	>50 Bar	>50 Bar	>50 Bar	>50 Bar	>50 Bar	>50 Bar
Barcol Hardness (ASTM D2583-07)	79,8	78	47,5	66,3	65,3	56	43,3

The present inventors have carried out additional experiments. The methods used in these additional experiments are in agreement with the detailed method steps and conditions as shown in Examples 1-7 as discussed above.

15 Table 2 relates to thermoset resins, Table 3 to thermoplastic resins.

In Table 2 (thermoset resins) the reference value (IBQ86) is an example not according to the invention. The Barcol Hardness is about 47. IBQ87 shows that the use of a glass fiber mat as the porous substrate layer will result in an increase in Barcol Hardness of about 20 points. The use of even more glass fiber matts (IBQ103) will result
20 in an even higher Barcol Hardness of 74.

IBQ82 relates to the use of a loose particulate material (particle size: 500-800 micrometer) as a porous substrate layer. The Barcol Hardness is 61, about 14 points higher than the reference value (IBQ86).

IBQ7 is an experiment not according to the present invention. This
25 experiment failed since there was no penetration into the porous substrate layer, i.e. dry quartz identified as aggregate. The wet mix, i.e. the mixture of organic binders, additives and fillers, leaks away and does not wet the dry quartz. The hardness could not be measured. The particle size of the dry quartz is preferably > 200 microns, more preferably > 500 microns.

30 IBQ88, IBQ111 and IBQ117 relate to the use of both a glass fiber mat and a loose particulate material (particle size: 500-800 micrometer) as a porous substrate layer. The effect is an increase of Barcol Hardness to 65, 80 and 78 for IBQ88, IBQ111 and IBQ117, respectively.

IBQ142, IBQ170 and IBQ169 show the effect of the use of another mat on the Barcol Hardness.

IBQ121 and IBQ122 show the effect of the use of another type of organic binder on the Barcol Hardness.

5 IBQ104, IBQ107, IBQ110, IBQ112, IBQ113, IBQ116 show the effect of the concentration of fine particles in the mixture of step i).

In Table 3 (thermoplastic resins) the reference values (IPQ78, IPQ76, and IPQ82) are examples not according to the invention. The Barcol Hardness of these reference values is about 58, 61 and 62, respectively.

10 IPQ77, IPQ75 and IPQ81 are examples according to the present invention. These examples show that the use of a glass fiber mat as the porous substrate layer will result in an increase in Barcol Hardness of a value of 71, 69 and 70, respectively.

15 IPQ104, IPQ39 and IPQ149 show the effect of the use of a fiber mat as the porous substrate layer resulting in an increase in Barcol Hardness of a value of 67, 66 and 70, respectively.

IPQ16 is a reference value not according to the invention. The Barcol Hardness is about 43. IPQ17 shows the effect of a loose particulate material (particle size: 500-800 micrometer) as a porous substrate layer resulting in a Barcol Hardness of 56.

20

Table 2: Test results

	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
			23	quartz	26	quartz	63-500	51	0	none	0	none	23	47
5	9		23	quartz	26	quartz	63-500	51	1,5	3*ref2	0	none	20	66
	8		21	quartz	22	quartz	63-500	59	2,2	6*ref2	0	none	16	74
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
			23	quartz	26	quartz	63-500	51	0	none	0	none	23	47
	10		23	quartz	26	quartz	63-500	51	0	none	6	500-800	15	61
	320		23	quartz	33	quartz	63-500	44	0	none	80	63-500	17,2	N.M.
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
10			23	quartz	26	quartz	63-500	51	0	none	0	none	23	47
	10		23	quartz	26	quartz	63-500	51	0,6	1*ref2	4	500-800	16	65
	10		21	quartz	25	quartz	63-500	54	0,3	1*ref2	5	500-800	13	80
	10		21	quartz	25	quartz	63-500	54	0,3	1*ref2	7	500-800	13	78
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
	200		21	quartz	23	quartz	63-500	56	18	3*ref2	0	none	19	71
	200		21	quartz	27	quartz	63-500	52	22	2*ref6	0	none	19	69
	200		21	quartz	27	quartz	63-500	52	24	3*ref7	0	none	19	69
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
15	50	E2590	23	quartz	26	quartz	63-500		7	3*ref2	0	none	20	71
	50	P345	23	quartz	26	quartz	63-500		7	3*ref2	0	none	20	64
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
	10		21	quartz	21	quartz	63-500	56	0,3	1*ref2	4	500-800	14	72
	10		23	quartz	26	quartz	63-500	51	0,5	1*ref2	7	500-800	13	75
	10		21	quartz	25	quartz	63-500	54	0,3	1*ref2	4	500-800	15	75
20	8		21	quartz	25	quartz	63-500	54	2	6*ref2	0	none	17	75
	10		22	quartz	27	quartz	63-500	51	0,3	1*ref2	4	500-800	15	76
	10		23	quartz	23	quartz	63-500	51	0,3	1*ref2	6	500-800	14	77

Table 3: Test results

	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
	57	rPET IV=0,74	17	quartz	22	quartz	63-500	61	0	none	0	none	17	58
	55	rPET IV=0,74	27	quartz	23	quartz	63-500	61	6	3*ref2	0	none	25	71
		rPET IV=0,74	20	quartz	21	quartz	63-500	59	0	none	0	none	20	61
	75	rPET IV=0,74	20	quartz	21	quartz	63-500	59	6	3*ref2	0	none	22,5	69
		rPET IV=0,74	20	quartz	19	quartz	63-500	52	0	none	0	none	20	62
	55	rPET IV=0,74	21	quartz	23	quartz	63-500	52	0	4*ref2	0	none	20	70
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
	50	rPET IV=0,74	20	quartz	21	quartz	63-500	56	4	2*ref1	0	none	18,6	67
	55	rPET IV=0,74	20	quartz	21	quartz	63-500	59	3	2*ref2	0	none	18	66
	522	rPET IV=0,74	21	quartz	22	quartz	63-500	57	19	1*ref4	0	none	20	70
	Quantity g	Resin type	Resin level,%wt	Fines type	Fines level,%wt	Coarse type	Coarse psd,micron	Coarse level,%wt	Quantity g	Fiber type	Quantity	Aggregate particle size	Resin level,%wt	Barcol Hardness
		PET-G	20	quartz	21	quartz	63-500	51	0	none	0	none	20	62
	17	PET-G	20	quartz	21	quartz	63-500	51	0	none	2	500-800	18	56

CLAIMS

1. A method for manufacturing a slab having a front layer and a rear layer, said slab comprising fillers, organic binders and additives, said method comprises mixing starting materials comprising fillers, organic binders and additives, heating, shaping, pressing and cooling, characterized in that said method comprises the following steps:
- i) providing a mixture comprising organic binders, additives and fillers, wherein said fillers comprise fine particles and a first amount of coarse particles;
 - ii) providing a porous substrate layer;
 - iii) contacting the mixture of step i) with the porous substrate layer of step ii);
 - iv) exerting a force on the construction obtained in step iii) for migrating said organic binder and said fine particles from said mixture of step i) into said porous substrate layer;
 - v) cooling the construction obtained in step iv) for obtaining a slab, wherein due to said step iv) the concentration of said first amount of coarse particles in said front layer of said slab is higher than in said rear layer of said slab,
2. A method according to claim 1, wherein said porous substrate layer in step ii) is a mat, a loose particulate material, or a combination thereof.
3. A method according to claim 2, wherein said mat comprises a material chosen from the group of glass fibers, flax fibers, Abaca fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof.
4. A method according to claim 2, wherein said loose particulate material comprises a second amount of coarse particles.
5. A method according to any one of claims 1-4, wherein the particle size distribution of the fine particles in the mixture of step i) is chosen from a range below 63 micron.
6. A method according to any one of claims 4-5, wherein the first amount of coarse particles differs from the second amount of coarse particles in one or more aspects chosen from the group of chemical composition, mineral type, particle size, particle shape and particle size distribution.

7. A method according to claim 6, wherein the particle size distribution of the first amount of coarse particles is broader than the particle size distribution of the second amount of coarse particles.

8. A method according to any one of claims 6-7, wherein the particle size distribution of the first amount of coarse particles is chosen from a range between 63 - 800 micron, wherein the particle size distribution of the second amount of coarse particles is chosen from a range within 200-1200 micron.

9. A method according to any one of claims 4-8, wherein the average particle size of the second amount of coarse particles as said porous substrate layer is chosen so that during step iv) organic binder and fine particles from said mixture of step i) migrate into said porous substrate layer.

10. A method according to any one of claims 1-9, wherein said organic binder is chosen from the group of thermoset and thermoplast type binders, or a combination thereof.

11. A method according to any one of claims 1-10, wherein in case of thermoset type binders in step i) said method further comprises a step of heating during one or more of step i), step ii), step iii) and step iv).

12. A method according to any one of claims 1-11, wherein step i) further comprises mixing organic binders, additives and fillers at an elevated temperature.

13. A method according to any one of claims 1-12, wherein step iii) further comprises applying said mixture comprising organic binders, additives and fillers on a support in a continuous mode and applying said porous substrate layer on top of said mixture laying on said support.

14. A method according to any one of claims 1-12, wherein step iii) further comprises applying said porous substrate layer on a support in a continuous mode and applying said mixture comprising organic binders, additives and fillers on top of said porous substrate layer laying on said support.

15. A method according to any one of claims 13-14, wherein step iv) further comprises transferring said support comprising said mixture comprising organic binders, additives and fillers and said porous substrate layer through a slit between rotating rolls.

16. A method according to any one of claims 1-15, wherein step i) further comprises a step of de-aeration, preferably after mixing said organic binders, additives and fillers.

17. A method according to any one of claims 1-16, wherein the construction obtained in step iii) comprises, in sequence, said mixture of step i), a mat and a layer of loose particulate material.

18. A method according to any one of claims 1-17, wherein the thickness of the slab obtained after step v) is in a range of 2 to 10 mm.

19. A method according to any one of claims 1-18, wherein the weight percentage of organic binder is in a range of 5 – 30 wt.%, the weight percentage of fillers is in a range of 50 to 95 wt.%, the weight percentage of additives is in a range of 0,1-5 wt.%, all weight percentages being based on the total weight of the slab obtained after step v).

20. A method according to claim 19, wherein said organic binder comprises 60 - 100 wt.% of thermoplastic polyester and 0 - 40 wt.% of a polyolefin, based on the total weight of the organic binder.

21. A method according to claim 20, wherein 90 - 100 wt.% of said thermoplastic polyester is one or more chosen from the group of polybutylene terephthalates, modified polyethylene terephthalates, recycled polyethylene furanoate, polycarbonates, polylactates and recycled polyethylene terephthalates, based on the total weight of the thermoplastic polyester.

22. A method according to claim 19, wherein said organic binder is a thermoset type binder chosen from the group of unsaturated polyester resin, acrylic resin, epoxy resin or phenolic resin, or a combination thereof.

23. A method according to any one of claims 1-22, wherein said first amount of coarse particles is chosen from the group of inorganic minerals, such as quartz, glass, silica sand (SiO_2), calcium carbonates, such as marble (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$), aluminum tri-hydrate (ATH), wollastonite (CaSiO_3), coesite, cristobalite, keatite, moganite, seifertite, stishovite and tridymite, especially inorganic minerals having a Mohs hardness of at least 7.

24. A method according to any one of claims 4-23, wherein said second amount of coarse particles is chosen from the group of inorganic minerals, such as quartz, glass, silica sand (SiO_2), calcium carbonates, such as marble (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$), aluminum tri-hydrate (ATH) and wollastonite (CaSiO_3).

25. A method according to any one of claims 1-24, wherein steps i) –v) are carried out in a continuous mode.

26. A method according to any one of claims 1-25, wherein the concentration of said fine particles in said rear layer is higher than the concentration of said fine particles in said front layer.

27. A slab consisting of a front layer and a rear layer and obtained according to the method as disclosed in any one or more of the preceding claims, wherein the concentration profile of the first amount of coarse particles shows a gradient over the thickness of said slab, wherein the concentration of said first amount of coarse particles in said front layer of the slab is higher than in said rear layer of the slab.

28. A slab according to claim 27, wherein said rear layer of the slab comprises a mat.

29. A slab according to claim 28, wherein said mat comprises a material chosen from the group of glass fibers, flax fibers, Abaca fibers, coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof.

30. A slab according to any one of claims 27-29, further comprising a mat located at the interface of said front layer and said rear layer.

31. A slab according to any one of claims 27-30, wherein the particle size distribution of the first amount of coarse particles is chosen from a range between 63-800 micron, wherein the particle size distribution of the second amount of coarse particles is chosen from a range within 200-1200 micron.

32. A slab according to any one of claims 27-31, wherein the Barcol Hardness of said slab exceeds a value of 65, preferably 75, in case of an organic thermoset type binder (according to ASTM D 2583-07 "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor").

33. A slab according to any one of claims 27-31, wherein the Barcol Hardness of said slab exceeds a value of 55, preferably 70, in case of an organic thermoplast type binder (according to ASTM D 2583-07 "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor").

34. A slab according to any one of claims 27-33, wherein the impact resistance of said slab is at least 10 J (according to EN 14617-9:2005), when the porous substrate layer as used in step ii) comprises a second amount of coarse particles.

35. A slab according to any one of claim 27-33, wherein the impact resistance of said slab is at least 20 J (according to EN 14617-9:2005), when the porous substrate layer comprises a material chosen from the group of glass fibers, flax fibers, Abaca fibers,

coir fibers, hemp fibers, jute fibers, carbon fibers and basalt fibers, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2016/050497

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C04B40/02	C04B26/06	C04B26/10	C04B20/00	C04B20/0096
ADD.	C04B111/00	C04B14/04	C04B14/06	C04B14/22	C04B14/28
	C04B14/30	C04B26/18	C04B26/14	B29C67/24	B29L31/10
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)
C04B B29C B29L B28B

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

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X	US 2014/335325 A1 (HUMPHRIES EDWARD [AU] ET AL) 13 November 2014 (2014-11-13) paragraphs [0064], [0065], [0079] - [0084], [0094] - [0099], [0125], [0163]; figures	1-35
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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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Date of the actual completion of the international search 20 December 2016	Date of mailing of the international search report 05/01/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Topalidis, Anestis
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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2016/050497

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	US 2008/006957 A1 (TONCELLI LUCA [IT]) 10 January 2008 (2008-01-10) paragraphs [0022] - [0037] -----	1,20-24, 27
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Information on patent family members

International application No

PCT/NL2016/050497

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