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(54) Title: IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF COMPOSITES

(57) Abstract: Molded composites comprising a rigid epoxy foam between two surface layers are produced from a sandwich of a foamable and curable epoxy resin between the surface layers which is first foamed but not cured and then molded and cured.



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**IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF COMPOSITES**

The present invention relates to a process for the production of laminar composite structures and to the composite structures thus produced. In particular the present invention relates to the manufacture of high strength light weight, rigid, composite materials. The invention further relates to the production of high strength, light weight shaped articles from such composites.

We have found that the light weight, rigid composites that can be produced by the present invention are particularly useful as materials in the transportation industries such as in automotive, aircraft and shipping industries where they may be used to replace metal and glass reinforced plastic articles such as panels. In recent years there has been a trend to replace traditional steel components with lighter materials of comparable strength such as aluminium, fibre reinforced polymeric materials, foam materials and composites particularly composites containing foamed layers. There is however a continuing need for materials of increased strength and reduced weight.

The composites produced according to the present invention have a wide variety of uses in additional applications in which high strength combined with light weight is required. Other uses include as raw materials in the production of sporting goods such as skis and in line skates and in the production of furniture.

The strength required of a material will depend upon the use to which it is to be put. For example the important characteristics can be high tensile strength and high flexural modules as measured by ASTM D790/ISO 178 norm or alternatively it can be resistance to impact compression strength or torsional strength and in certain uses a combination of these properties may be required.

In our PCT Application PCT/EP05/00105 we describe composites that we have found to have particularly desirable properties and in particular the combination of low weight and high strength and stiffness that can be obtained from composites sandwich structures consisting of at least two surface layers enclosing a layer of rigid epoxy foam.

Composite sandwich structures with a foam core are known and have been proposed as materials having significant strength and stiffness together with an advantage derived from weight considerations. For example the abstract of Japanese Patent

publication JP 58049223 A2 discloses sandwich structures comprising epoxy foam sandwiched between two metal plates. Two articles by S. Venkatraman and Kishore, the first in the Journal of Reinforced Plastics and Composites Vol 16 No. 7/1997 and the second in the Journal of Reinforced Plastics and Composites Vol 17 No. 8/1998  
5 disclose composites comprising a thin layer of flexible foam sandwiched between two thick layers of glass-epoxy resin materials. The first of these articles relates to impact studies on the glass/epoxy laminates and the second to Investigations on the role of foam layers in the Failure of Glass-Epoxy composite subjected to repeated impacts. In both articles the layer of flexible epoxy foam is provided as a prefoamed  
10 flexible layer and is adhered to the glass/epoxy layer by means of an adhesive. The later article concludes that the way the sheet layers of flexible foam are arranged with respect to the direction of impact influences the spread of the crack path on repeated impact.

15 United States Patent 3598671 discloses a method of preparing foam plastic laminated structures in which at least one component of a foam forming material is applied as a coating onto the surface of one sheet of a base material. A further component of the foam forming material is applied as a coating onto the surface of a second sheet of the base material. The sheets are then brought together so that the  
20 components of the foam forming materials are brought together so that they foam and produce a foamed core plastic laminated structure. Example 2 of US 3598671 produces such a laminate comprising a layer of epoxy foam  $\frac{1}{4}$  inch thick sandwiched between two layers of fiberglass each approximately  $\frac{1}{8}$  inch thick. Accordingly the combined thickness of the two layers of fiberglass is substantially the same as the  
25 thickness of the foam. The foam is also extremely heavy, having a density of 7.5 lbs per square foot. United States Patent 3598671 does not therefore envisage the high strength light weight materials of the present invention.

30 United States Patent 3914725 produces epoxy foams containing units derived from the tetraglycidyl ester of cyclohexanone or methyl cyclohexanone tetrapropionic acid. Example 26 produces a sandwich construction of the foam between two aluminium sheets from a foamable material that requires 30 minutes to cure to a density of  $0.38 \text{ g/cm}^3$ .

35 Heat activatable foamable epoxy materials that are adhesive and both foam and cure are known and are used in the production of structural reinforcement in automobiles. For instance the foamable material may be applied to the surface of a metal or plastic

carrier to produce a component which is inserted into a part of the vehicle structure which requires reinforcement. The heat activatable foamable epoxy materials are typically formulated so that they will foam and cure under the conditions that prevail in the electrocoat (e-coat) process used to provide an anticorrosion coating to the metal surfaces of the vehicle structure or in any other painting operations. This process involves the vehicle body frame being dipped in a bath of anticorrosion fluid and then passed to an oven held at a temperature in the range 150°C to 180°C. The body then passes through the oven where the anticorrosion coating is dried and baked and the foamable material foams and cures to produce a rigid foam. The time taken for the body to pass through the oven is typically between 15 and 30 minutes. Such foamable epoxy materials and their uses are described in United States Patents 4922596; 4978562; 5124186 and 5884960. We have found that these foamable epoxy materials are particularly useful in the present invention. United States Patent Application 09/939152 discloses structurally reinforced panels comprising a metal panel, a woven roving and bonded to one side of a matrix material which may be an epoxy foam.

There remains a need for a process that can be used to provide an epoxy foam sandwich structure more quickly and also which enable the production of moulded articles which preferably have a desirable surface finish.

The present invention there provides a process for the production of a rigid sandwich structure comprising a foamed epoxy resin between two surface layers comprising providing a layer of curable and expandable epoxy material between two surface layers heating the sandwich structure under conditions whereby the curable and expandable epoxy material foams but remains flexible and subjecting the sandwich structure that contains the flexible layer of foamed epoxy material to moulding conditions whereby the structure is moulded and the foamed epoxy material cures to produce a rigid moulded sandwich structure.

In a preferred embodiment the invention provides a process for the production of composites comprising a layer of epoxy foam sandwiched between two surface layers comprising providing a layer of expandable and curable epoxy material between two surface layers to form a three layer structure and subjecting the three layer structure to infra red or radio frequency heating to heat the expandable epoxy material to a temperature in the range 150°C to 220°C for up to 5 minutes and

subsequently subjecting the resulting sandwich to pressure for up to 5 minutes at a temperature of from 40 to 100°C.

We have found that if these conditions are employed the expandable epoxy material will expand due to the heating to a temperature in the range 150°C to 220°C for up to 5 minutes and will also bond to the surface layers. However, we have also found that providing these conditions are employed the epoxy will first soften and melt and will not be cured or will have cured only to a small extent and it remains flexible and thermoplastic. Accordingly, the epoxy resin formulation is selected so that it will expand but remain thermoplastic. The flexible laminate formed may then be finished by the application of pressure which can be a moulding process to shape the laminate or a surface finishing process. We have found that if the ambient temperature is maintained at a temperature of from 40 to 100°C during the application of pressure and the pressure is applied for no more than 5 minutes the laminate will cure to produce a rigid sandwich structure that is light in weight and of great strength.

The nature and quantity of the curing agent is therefore selected so that it will no more than partially cure the resin during the foaming process and will finish the curing of the foamed epoxy resin during the moulding process. The curing reaction is typically an exothermic reaction and once the cure has started the reaction can be self accelerating.

The present invention therefore is particularly useful for the production of a composite comprising a sandwich structure comprising at least two surface layers attached to a central layer of rigid epoxy foam wherein the layer of epoxy foam is at least 1.5 times the combined thickness of the two surface layers and the foam has a density of between 0.4 and 1.5 gram/cc as described in PCT/EP05/00105.

In particular the invention is useful in the production of composites comprising at least two surface layers each layer having a thickness of from 0.2 to 10 millimetres and a core layer of a rigid epoxy foam having a thickness of from 2 to 200 millimetres.

In a further embodiment of the present invention the composites have a density in the range of from 0.1 to 1.0 gram/cc In yet a further embodiment a composite of the present invention which is from 5 to 8 millimeters thick has a flexural modulus of from

100 mPa to 700 mPa preferably 200 mPa more preferably 200 mPa to 700 mPa as measured by ASTM D 790/ISO 178 norm.

5 The surface layers of the composites of the present invention may be of any suitable material. Examples of suitable material include plastic film or sheeting such as polypropylene or polyethylene film or polyethylene terephthalate film. It is preferred however that the material be a fibrous material. It is particularly preferred that the surface layers be porous so that the epoxy material can penetrate the pores in the surface layers so that the surface layers become embedded in the epoxy foam. A  
10 preferred material is the product available from Saint-Gobain under the trade name "Twindex" which consists of glass fibre/polypropylene or glass fibre/polyethylene terephthalate matt and is described at [www.twintex.com](http://www.twintex.com).

15 The fibrous material may be of any suitable material and its selection will depend upon the use to which the composite material is to be put. Examples of fibrous materials that may be used include woven and non woven textile webs such as webs derived from polyester, polyamide, polyolefin, paper, carbon and kevlar fibre. These webs may be woven or obtained by non woven web manufacturing techniques such as needle punching and point bonding. We prefer to use glass fibre which may also  
20 be woven or non-woven. In particular we prefer to use glass fibre web having the following properties having a weight of from 40 gram/sq metre to 400 gram/sq metre. Other preferred fibrous materials include carbon fibre and Kevlar.

25 The term embedded is used to describe a composite in which the surface layer, although at the surfaces of the composite is largely enveloped by epoxy material. This may be determined from electron micrograph photographs of a cross section of the material layer. It will be appreciated that in order to be embedded it is not essential that all of the surface material be encased with the epoxy material. The epoxy material that extends into and sometimes through the surface layer may be the  
30 same as the epoxy foam although in a preferred embodiment of the present invention it is a separate unfoamed epoxy material that is compatible with the foamable epoxy material and forms a substantially continuous matrix with the foamable material, taking into account the voids formed due to the foaming of the epoxy material. The surface layer material is therefore embedded in this epoxy matrix.

35 In a preferred embodiment of the processes of the present invention the surface layers are porous preferably of fibrous material and in a further preferred

embodiment they are coated and/or impregnated with an epoxy material prior to heating. Preferably when such an epoxy material is used it is compatible with the heat activatable foamable epoxy material, so as to form a substantially continuous matrix therewith, as hereinbefore described. In this way the porous surface layers  
5 can become embedded in the epoxy material. Preferably the epoxy material also cures under the same conditions as the heat activatable material cures. In this embodiment the heating step of the process of the present invention will cure both epoxy resins. Conveniently the epoxy material with which the porous layers are coated and/or impregnated is the same epoxy material as is used as the basis for the  
10 heat activated foamable material although it need not be foamable.

The various embodiments of the present invention envisage in addition, sandwich composites containing four or more layers, their production and materials made therefrom. For example in addition to three layer sandwich structures the composite  
15 may comprise five layers consisting of two outer layers and an inner layer of unfoamed material with two layers of epoxy foam or heat activatable epoxy foam forming material interposed between the fibrous layers. Composites containing a greater number of layers are also envisaged and the non foamed layers may be the same or different according to the needs of the article to be produced.

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Foamable epoxy materials typically contain an epoxy resin, a blowing agent and a curing agent and frequently also contain a filler. The blowing agent and the curing agent are selected so that foaming and curing (hardening) occur at the required speed and within the desired temperature ranges. The materials should therefore be  
25 chosen so that the temperature required for foaming and curing does not damage the surface layers. The epoxy resin may be chosen according to the degree of stiffness that is required in the product. Amine curing agents are frequently used in which case curing temperatures of at least 100°C are generally required. It is preferred that the blowing agent and curing agent be chosen so that foaming starts at a  
30 temperature slightly below the curing temperature. The foamable epoxy resin may be supplied as a liquid typically through use of a solvent such as an alcohol. In this embodiment the epoxy resin may be sprayed or painted onto one or both of the surface layers. The solvent may then be removed by evaporation to provide a continuous or discontinuous layer of foamable epoxy material. The foamable epoxy  
35 resin is however preferably supplied as a solid which may be a die cut sheet or an extrusion, alternatively it may be provided from a mine-applicator.

The heat activated epoxy foam forming material should be chosen according to the application to which the composite is to be put. However the heat-activated epoxy-based resin should have foamable characteristics upon activation through the use of heat whereby it expands, and bonds to the surface layers. The material should also cross-link under the influence of heat to produce a rigid foam. An example of a preferred formulation is an epoxy-based material that may include polymer modifiers such as an ethylene copolymer or terpolymer that is commercially available from L & L Products, Inc of Romeo, Michigan, under the designations L-5204, L-5206, L-5207, L-5208, L-5209, L-5214 and L-5222 and from Core Products as Core 5207, 5214, 5234 and 5231. These products may also include fillers such as glass, microspheres, calcium carbonate and talc which can reduce the density of the foam. One advantage of these preferred heat activated foamable materials is that they can be processed in several ways to produce the heat activatable foamable layer of the present invention. The layer of foamable activatable epoxy material may be continuous or discontinuous. Possible techniques for the provision of the layer of foamable activatable material include the provision of sheet material, injection moulding, blow moulding, thermoforming, direct deposition of palletized materials, extrusion or extrusion with a mini-applicator extruder. The flexibility of the epoxy material prior to curing enables the creation of designs that allow the production of complex shapes and which exceed the design flexibility capability of most prior art materials.

The heat activatable foamable epoxy resin whether it be as strips or spots is thermally expandable. That is, upon the application of heat they will expand, typically by a foaming reaction and preferably to at least 150% the volume of the unexpanded state, but more preferably to at least twice the volume of the expanded state. The material also cures to provide a rigid epoxy foam, the density of the foam is preferably from 0.4 g/cm<sup>3</sup> to 0.8 g/cm<sup>3</sup>.

Epoxy resin preferably forms about 5% to about 75% by weight and more preferably from about 15% to 65% by weight of the activatable foamable and curable epoxy material composition. Filler preferably forms from about 0% to about 70% by weight and more preferably from about 20% to about 50% by weight of the composition. A blowing agent preferably forms from about 0.5% to about 10% by weight and more preferably from about 0.2% to 5% by weight of the composition. The blowing agent is chosen to cause foaming at the desired temperature and azodicarbonamide is a particularly preferred blowing agent. Blowing agent accelerators or kickers such as



zinc oxide may also be included to ensure foaming at the desired temperature. A curing agent preferably forms from about 0% to about 10% by weight and more preferably from about 0.5% to 5% by weight of the composition. An accelerator preferably forms from about 0% to about 10% by weight and more preferably from about 0.3% to 5% by weight of the composition. A preferred formulation is set out in the following table.

<b>Ingredient</b>	<b>% by weight</b>
Epoxy Resin	15% to 65%
Ethylene Copolymer	0% to 20%
Blowing Agent	0.2% to 5%
Curing Agent	0.5% to 5
Accelerator	0.3% to 5%
Filler	20% to 50%

In the preferred embodiment of the process of the present invention one or more of the surface layers is coated and/or impregnated with an epoxy material prior to heating to foam and cure the heat activatable epoxy material. In this embodiment it is preferred that the epoxy material used to coat and/or impregnate the surface layer cure under the same conditions as those under which the heat activatable foamable material cures. In a particularly preferred embodiment the epoxy material is the same as the epoxy material upon which the heat activated foamable material is based. This embodiment is particularly preferred when the surface layers are porous so that they may be impregnated with epoxy material. Alternatively the impregnation may be accomplished through the application of the foamable epoxy material in liquid form.

Accordingly in a preferred embodiment the surface layers are fibrous layers, which are preferably carbon fibre or glass fibre layers as previously described and are coated and/or impregnated with an epoxy material comprising epoxy resin preferably from about 5% to about 75% by weight and more preferably from about 15% to 65% by weight of the composition. Filler preferably forms from about 0% to about 70% by weight and more preferably from about 20% to about 50% by weight of the composition. Curing agent preferably forms from about 0% to about 10% by weight and more preferably from about 0.5% to 5% by weight of the composition. Accelerator preferably forms from about 0% to about 10% by weight and more

preferably from about 0.3% to 5% by weight of the composition. A preferred coating formulation is set out in the following table.

Ingredient	% by weight
Epoxy Resin	15% to 65%
Ethylene Copolymer	0% to 20%
Curing Agent	0.5% to 5
Accelerator	0.3% to 5%
Filler	20% to 50%

5 The composites of the present invention may be of any required shape and may be formed after foaming and while still flexible. They are preferably formed in a mould designed to provide the required shape. The surface layers and the heat activatable foamable material (prior to foaming) are generally flexible materials. Accordingly the composites may be produced by laying down the first surface layer, optionally coating and/or impregnating said first layer with an epoxy material, then providing a layer of the heat activatable foamable epoxy material against the first surface layer, providing a second surface layer against the layer of heat activatable material. This second layer may optionally be precoated and/or impregnated with an epoxy material or, optionally, coated and/or impregnated after it is provided against the layer of heat

10 acctivatable material. The sandwich may then be heated to the temperature required to cause the heat activatable foamable epoxy material to foam and optionally to cause any epoxy material used to coat and/or impregnate the surface layers to cure. The flexible sandwich may then be moulded under conditions which cause the foamed epoxy material to cure. Where composites having more than three layers are to be produced additional layers may be provided prior to closing the mould and heating to cause foaming and curing. The additional layers may be of any suitable material such as continuous sheet or fibrous layers.

The conditions that are used in the first stage of the process of the present invention are such that the epoxy resin will foam but remain flexible. The conditions required will depend upon the nature of the materials and particularly the nature of the epoxy material. However, we prefer that the conditions are heating employing infra red or radio frequency heating and we prefer that the heating be such that the temperature of the foamable epoxy material is raised to a temperature in the range from 150°C to

30 210°C. The temperature is not and need not be precise since there will be variations

in temperature throughout the layer of the foamable and curable epoxy material. The conditions are however preferably such that a temperature probe inserted within the foamable epoxy material registers a temperature from 150°C to 210°C. The required heating time will also depend upon the nature of the epoxy resin and the heating  
5 temperature. The time should however be sufficient to cause the epoxy resin to foam but it should not be so long that the epoxy material cures to the extent that it is no longer flexible. We have found that when the heating employs a temperature in the range 150°C to 210°C a heating time of up to 5 minutes and preferably from 1 to 3 minutes is suitable.

10 Having been heated to the foaming temperature the epoxy resin will begin to cure and will continue to cure when it is removed from the heating area. It is therefore important that the sandwich of the foamed and flexible epoxy resin and the surface layers be transferred to the moulding stage of the process of the present invention  
15 before the curing process results in a foam that is too rigid to be moulded. The moulding technique will be selected according to the nature of the article required. It may be a simple pressing operation to ensure the adhesion of the surface layers to the epoxy foam and also to provide any desired surface finish. Alternatively the moulding may be compression moulding, vacuum moulding or any other suitable  
20 technique to provide an article of the required shape. The conditions used for the moulding should be such that allow the desired article to be produced and also complete the curing of the foamed epoxy material. We have found that this can be accomplished if the moulding is performed at elevated temperature such as a temperature in the range 40°C to 100°C preferably 50°C to 80°C. We have also  
25 found that if the moulding is performed at a temperature in this range the epoxy resin will cure to yield a rigid foam providing a lightweight article of high strength.

The process of the present invention may be a batch process or a continuous process depending upon the nature of the article to be produced. For example if the  
30 process is to be used to produce panels or sheeting the three layer sandwich containing the foamable and curable epoxy resin may be fed continuously to the heating area, it may pass through the heating area and into the moulding area where it may pass through two plates which exert pressure onto the moving sandwich containing the foamed epoxy resin. Alternatively a process may be employed in  
35 which separate pieces of the sandwich containing the unfoamed material are fed individually to the heating area and then transferred to the moulding area where they are moulded into any desired shape.

Following the moulding process the mould may be opened and the desired composite obtained. If necessary the mould surface may be provided with release lining material to ensure the composite does not adhere to the mould.

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We have found that composites produced according to the present invention have high flexural strength combined with low weight. Typically a composite having a thickness of from 5 millimetres to 8 millimetres has a flexural strength of from 100 mPa to 700 mPa typically 300 mPa to 700 mPa at a density of from 0.1 to 1.0 grams/cc, preferably 0.4 to 0.8 grams/cc which compares favourably with current light weight aluminium, based materials of similar weight per unit area which have a flexural modulus of about 10% that of the composite of the present invention products of comparable weight per unit area. We have also found that the composites of the present invention can sustain considerably greater maximum load than the current light weight aluminium based materials.

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The composites produced according to the present invention find a wide range of uses where high strength and light weight are required. For example they may be used in the construction industry, in the automobile aircraft and shipping vessel industries. Furthermore they may be used in the production of sporting goods such as skis, roller skates, roller blades and the like.

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The composites may be used as components in buildings, vehicles, sporting goods and furniture. If the composites are to be attached to other components within the finished article attachment means may be provided within the composite to enable assembly. In this embodiment of the invention the attachment may be located within the activatable foamable material prior to heating to foam and cure. In this way the foamable material can expand around the attachment to hold it firmly in place as the epoxy material cures. Typical attachment means comprise clips, studs, bolts and the like which may be of any material providing they retain their strength under the conditions used for activation and foaming.

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Panels were prepared by providing a layer of the foamable and curable epoxy material available from Core Products as between two layers of Twintex (registered Trade Mark) both of which were 0.6 mm thick.

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Three samples were prepared, one in which the layer of epoxy material was Core 5214 and was 1.5 mm thick, another in which the epoxy material was Core 5215 and was 3 mm thick and the third in which the epoxy material was Core 5216 and was 5 mm thick. The samples were heated with infra red heating to a temperature of 200°C for 2 to 3 minutes to provide a sandwich containing flexible foamed epoxy material. The sandwich was flexible with a consistency somewhat similar to chewing gum. The sandwich containing 1.5 mm of foamable epoxy material was expanded to provide a three layer laminate 5 mm thick, the sandwich containing 3 mm of the foamable epoxy material expanded to provide an 8 mm thick sandwich and the 5 mm thick layer was expanded to produce a 12 mm thick sandwich.

While the sandwiches remained flexible they were subjected to pressure from between a pair of plates under an environment where the ambient temperature was from 50-60°C although the temperature of the foamed material could be higher. The two thinner sandwiches were subjected to the pressure for 90 seconds and the thicker sandwich for 2 minutes. The panels had high rigidity and flexural strength.

**CLAIMS**

1. A process for the production of a rigid sandwich structure comprising a foamed epoxy resin between two surface layers comprising providing a layer of curable and expandable epoxy material between two surface layers heating the sandwich structure under conditions whereby the curable and expandable epoxy material foams but remains flexible and subjecting the sandwich structure that contains the flexible layer of foamed epoxy material to moulding conditions whereby the structure is moulded and the foamed epoxy material cures to produce a rigid moulded sandwich structure.
2. A process according to Claim 1 comprising providing a layer of expandable and curable epoxy material between two surface layers to form a three layer structure and subjecting the three layer structure to infra red or radio frequency heating to heat the expandable epoxy material to a temperature in the range 150°C to 220°C for up to 5 minutes and subsequently subjecting the resulting sandwich to pressure for up to 5 minutes at a temperature of from 40 to 100°C.
3. A process according to Claim 1 or Claim 2 wherein the ambient temperature is maintained at a temperature of from 40 to 100°C during the application of pressure and the pressure is applied for no more than 5 minutes.
4. A process according to any of the preceding claims for the production of a composite comprising a sandwich structure comprising at least two surface layers attached to a central layer of rigid epoxy foam wherein the layer of epoxy foam is at least 1.5 times the combined thickness of the two surface layers and the foam has a density of between 0.4 and 1.5 gram/cc.
5. A process according to Claim 4 in which the composite comprises at least two surface layers each layer having a thickness of from 0.2 to 10 millimetres and a core layer of a rigid epoxy foam having a thickness of from 2 to 200 millimetres.
6. A process according to any of the preceding claims in which the composites have a density in the range of from 0.1 to 1.0 gram/cc.

7. A process according to any of the preceding claims in which the composite is from 5 to 8 millimeters thick has a flexural modulus of from 100 mPa to 700 mPa, preferably 200 mPa to 700 mPa as measured by ASTM D 790/ISO 178 norm.
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8. A process according to any of the preceding claims in which the surface layers of the composites include plastic film or sheeting such as polypropylene or polyethylene film or polyethylene terephthalate film.
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9. A process according to any of Claims 1 to 7 in which the surface layers are of a fibrous material.
10. A process according to Claim 9 in which the fibrous material is selected from woven and non woven textile webs such as webs derived from polyester, polyamide, polyolefin, paper, glass, carbon and kevlar fibre.
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11. A process according to any of the preceding claims in which the foamable epoxy material contains an epoxy resin, a blowing agent and a curing agent and a filler.
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12. A process according to Claim 11 in which the heat activatable foamable epoxy resin is thermally expandable.
13. A process according to Claim 12 in which upon the application of heat the epoxy resin will expand to at least 150% the volume of the unexpanded state.
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14. A process according to any of preceding Claims wherein the epoxy material cures to provide a rigid epoxy foam, the density of the foam is preferably from 0.4 g/cm<sup>3</sup> to 0.8 g/cm<sup>3</sup>.
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15. A process according to any of the preceding claims in which the epoxy foam comprises from 5% to 75% by weight of the activatable foamable and curable epoxy material 0% to 70% by weight of a filler from 0.5% to 10% of a blowing agent from 0,5% to 5% by weight of the composition of a curing agent.
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16. A process according to Claim 15 in which the composition contains from 0.3% to 5% by weight of an accelerator.

17. A process according to any of the preceding claims in which the epoxy resin formulation has the following composition.

Ingredient	% by weight
Epoxy Resin	15% to 65%
Ethylene Copolymer	0% to 20%
Blowing Agent	0.2% to 5%
Curing Agent	0.5% to 5
Accelerator	0.3% to 5%
Filler	20% to 50%

- 5 18. A process according to any of the preceding claims wherein the epoxy resin is foamed by employing infra red or radio frequency heating.

19. A process according to Claim 18 in which the heating is such that the temperature of the foamable epoxy material is raised to a temperature in the  
10 range from 150°C to 210°C.

20. A process according to Claim 18 or Claim 19 wherein the heating employs a temperature in the range 150°C to 210°C a heating time of from 1 to 3 minutes is suitable.

- 15 21. A process according to any of the preceding claims for the production of panels or sheeting wherein the three layer sandwich containing the foamable and curable epoxy resin is fed continuously to a heating area, and passes through the heating area and into the moulding area where it may passes  
20 between two plates which exert pressure onto the moving sandwich.

22. A process according to any of Claim 1 to 20 in which separate pieces of the sandwich containing the unfoamed material are fed individually to the heating area where the epoxy composition is foamed and then transferred to the  
25 moulding area where the composite is moulded and the epoxy resin is cured.

23. A composite obtained by a process according to any of the preceding claims and having a thickness of from 5 millimetres to 8 millimetres has a flexural strength of from 100 mPa to 700 mPa typically 300 mPa to 700 mPa at a  
30 density of from 0.1 to 1.0 grams/cc, preferably 0.4 to 0.8 grams/cc.



24. The use of a composite according to Claim 23 as a component in buildings, vehicles, sporting goods and furniture.

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/007643

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. B29C44/12 B29C44/08

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)  
 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 practical, 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	DE 42 26 988 A1 (SCHMUCKER WULFRAM JOHN [DE]) 17 February 1994 (1994-02-17) column 3, line 34 - column 4, line 33 column 4, lines 13-23	1-20, 23, 24
A	US 6 117 376 A (MERKEL MICHAEL [US]) 12 September 2000 (2000-09-12) column 5, line 43 - column 6, line 22	1, 22
A	US 6 030 559 A (BARRY LEON F [US] ET AL) 29 February 2000 (2000-02-29) claims	1, 21
A	US 5 849 227 A (CHIKUGO RYOJI [JP] ET AL) 15 December 1998 (1998-12-15) claims 1, 2	1

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

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- \*&\* document member of the same patent family

Date of the actual completion of the international search

27 October 2006

Date of mailing of the international search report

06/11/2006

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2006/007643
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Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
DE 4226988	A1	17-02-1994	NONE	
US 6117376	A	12-09-2000	NONE	
US 6030559	A	29-02-2000	AT 243101 T	15-07-2003
			CA 2227073 A1	14-08-1998
			DE 69815561 D1	24-07-2003
			DE 69815561 T2	29-04-2004
			DK 858877 T3	06-10-2003
			EP 0858877 A2	19-08-1998
			ES 2202739 T3	01-04-2004
US 5849227	A	15-12-1998	NONE	