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(54) **OVERMOLDED POLYAMIDE COMPOSITE STRUCTURES AND PROCESS FOR THEIR PREPARATION**

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(57) **ABSTRACT**

Disclosed herein are overmolded composite structures and processes for their preparation. The disclosed overmolded composite structures comprise i) a first component having a surface, of which at least a portion made of a surface resin composition, and comprising a fibrous material being impregnated with a matrix resin composition, ii) a second component comprising an overmolding resin composition, wherein said second component is adhered to said first component over at least a portion of the surface of said first component, and wherein the matrix resin composition and the surface resin composition are identical or different polyamide compositions.

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OVERMOLDED POLYAMIDE COMPOSITE STRUCTURES AND PROCESS FOR THEIR PREPARATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Application No. 61/408,166, filed Oct. 29, 2010, which is now pending, the entire disclosure of which is incorporated herein by reference; and U.S. Provisional Application Nos. 61/410,093, filed Nov. 4, 2010; 61/410,100, filed Nov. 4, 2010; 61/410,104, filed Nov. 4, 2010; and 61/410,108, filed Nov. 4, 2010, all of which are now pending, the entire disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to the field of overmolded composite structures and processes for their preparation, particularly it relates to the field of polyamide overmolded composite structures.

BACKGROUND OF THE INVENTION

[0003] With the aim of replacing metal parts for weight saving and cost reduction while having comparable or superior mechanical performance, structures based on composite materials comprising a polymer matrix containing a fibrous material have been developed. With this growing interest, fiber reinforced plastic composite structures have been designed because of their excellent physical properties resulting from the combination of the fibrous material and the polymer matrix and are used in various end-use applications. Manufacturing techniques have been developed for improving the impregnation of the fibrous material with a polymer matrix to optimize the properties of the composite structure. In highly demanding applications, such as for example structural parts in automotive and aerospace applications, composite materials are desired due to a unique combination of lightweight, high strength and temperature resistance.

[0004] High performance composite structures can be obtained using thermosetting resins or thermoplastic resins as the polymer matrix. Thermoplastic-based composite structures present several advantages over thermoset-based composite structures such as, for example, the fact that they can be post-formed or reprocessed by the application of heat and pressure, that a reduced time is needed to make the composite structures because no curing step is required, and their increased potential for recycling. Indeed, the time consuming chemical reaction of cross-linking for thermosetting resins (curing) is not required during the processing of thermoplastics. Among thermoplastic resins, polyamides are particularly well suited for manufacturing composite structures. Thermoplastic polyamide compositions are desirable for use in a wide range of applications including parts used in automobiles, electrical/electronic parts, household appliances and furniture because of their good mechanical properties, heat resistance, impact resistance and chemical resistance and because they may be conveniently and flexibly molded into a variety of articles of varying degrees of complexity and intricacy.

[0005] U.S. Pat. No. 4,255,219 discloses a thermoplastic sheet material useful in forming composites. The disclosed thermoplastic sheet material is made of polyamide 6 and a

dibasic carboxylic acid or anhydride or esters thereof and at least one reinforcing mat of long glass fibers encased within said layer.

[0006] For making integrated composite structures and to increase the performance of polymers, it is often desired to “overmold” one or more parts made of a polymer onto a portion or all of the surfaces of a composite structure so as to surround or encapsulate said surfaces. Overmolding involves shaping, e.g. by injection molding, a second polymer part directly onto at least a portion of one or more surfaces of the composite structure, to form a two-part composite structure, wherein the two parts are adhered one to the other at least at one interface. The polymer compositions used to impregnate the fibrous material (i.e. the matrix polymer composition) and the polymer compositions used to overmold the impregnated fibrous material (i.e. the overmolding polymer composition) are desired to have good adhesion one to the other, extremely good dimensional stability, and to retain their mechanical properties under adverse conditions, including thermal cycling, so that the composite structure is protected under operating conditions and thus has an increased lifetime.

[0007] Unfortunately, conventional thermoplastic polyamide resin compositions that are used to impregnate one or more fibrous layers and to overmold the one or more impregnated fibrous layers may show poor adhesion between the overmolded polymer and the surface of the component comprising the fibrous material, i.e. the composite structure. The poor adhesion may result in the formation of cracks at the interface of the overmolded composite structures leading to reduced mechanical properties, premature aging and problems related to delamination and deterioration of the article with use and time

[0008] In such case of weak adhesion, the interface between the composite structure and the overmolding resin will break first, rendering the overmolded composite structure weaker than either of its components. Therefore, high adhesion strength between the components is highly desirable. However, once the bonding strength is high enough that the interface can sustain the applied load without being the first to break, yet higher mechanical performance of the structure is highly desirable as is needed for the most highly demanding applications. Lower mechanical performance in these most demanding applications may impair the durability and safety of the article upon use and time. Flexural strength, i.e. the maximum flexural stress sustained by the test specimen during a bending test, is commonly used as an indication of a material’s ability to bear (or to sustain, or to support) load when flexed. When overmolding a resin composition onto at least a portion of a composite structure, high mechanical performance such as flexural strength of the structure is desired beyond that realized by good bonding strength between the composite structure and the overmolding resin.

[0009] There is a need for an overmolded polyamide composite structure that exhibits good mechanical properties, especially flexural strength and having at least a portion of its surface allowing a good adhesion between its surface and an overmolding resin comprising a polyamide resin.

SUMMARY OF THE INVENTION

[0010] Described herein is an overmolded composite structure comprising: i) a first component having a surface, which surface has at least a portion made of a surface resin composition, and comprising a fibrous material selected from non-woven structures, textiles, fibrous battings and combinations

thereof, said fibrous material being impregnated with a matrix resin composition, ii) a second component comprising an overmolding resin composition, wherein said second component is adhered to said first component over at least a portion of the surface of said first component, and wherein the matrix resin composition and the surface resin composition are identical or different and are selected from polyamide compositions comprising a blend of semi-aromatic polyamides. Preferably, the matrix polyamide resin composition and the surface polyamide resin composition are independently selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B).

[0011] Further described herein is a process for making the overmolded composite structure described above. The process for making the overmolding composite structure described above comprises a step of overmolding a second component comprising an overmolding resin composition on the first component described above.

DETAILED DESCRIPTION

[0012] The overmolded composite structure according to the present invention has improved flexural strength and allows a good adhesion when a part made of an overmolding resin composition comprising a thermoplastic polyamide is adhered onto at least a portion of the surface of the composite structure. A good flexural strength of the overmolded composite structure and a good adhesion between the composite structure and the overmolding resin leads to structures exhibiting good resistance to deterioration or delamination of the structure with use and time.

[0013] Several patents and publications are cited in this description. The entire disclosure of each of these patents and publications is incorporated herein by reference.

[0014] As used herein, the term "a" refers to one as well as to at least one and is not an article that necessarily limits its referent noun to the singular.

[0015] As used herein, the terms "about" and "at or about" are intended to mean that the amount or value in question may be the value designated or some other value about the same. The phrase is intended to convey that similar values promote equivalent results or effects according to the invention.

[0016] As used herein, the term "melting point" in reference to a polyamide refers to the melting point of the pure resin as determined with differential scanning calorimetry (DSC) at a scan rate of 10° C./min in the first heating scan, wherein the melting point is taken at the maximum of the endothermic peak. In customary measurements of melting behavior of blends of polymers, more than one heating scans may be performed on a single specimen, and the second and/or later scans may show a different melting behavior from the first scan. This different melting behavior may be observed as a shift in temperature of the maximum of the endothermic peak and/or as a broadening of the melting peak with possibly more than one peaks, which may be an effect of possible transamidation in the case of more than one polyamides. However, when selecting polyamides in the scope of the current invention, always the peak of the melting endotherm of the first heating scan of the single polyamide is used. As used herein, a scan rate is an increase of temperature per unit time. Sufficient energy must be supplied to maintain a constant scan rate of 10° C./min until a temperature of at least 30° C. and preferably at least 50° C. above the melting point is reached.

[0017] The present invention relates to overmolded composite structures and processes to make them. The overmolded composite structure according to the present invention comprises at least two components, i.e. a first component and a second component. The first component consists of a composite structure having a surface, which surface has at least a portion made of a surface resin composition, and comprises a fibrous material selected from non-woven structures, textiles, fibrous battings and combinations thereof, said fibrous material being impregnated with a matrix resin composition.

[0018] The overmolded composite structure may comprise more than one first components, i.e. it may comprise more than one composite structures and may comprise more than one second components.

[0019] The second component is adhered to the first component over at least a portion of the surface of said first component, the portion of the surface being made of the surface resin composition described herein. The first component may be fully or partially encapsulated by the second component, or the second component may be adhered to only a portion of the surface of the first component.

[0020] As used herein, the term "a fibrous material being impregnated with a matrix resin composition" means that the matrix resin composition encapsulates and embeds the fibrous material so as to form an interpenetrating network of fibrous material substantially surrounded by the matrix resin composition. For purposes herein, the term "fiber" refers to a macroscopically homogeneous body having a high ratio of length to width across its cross-sectional area perpendicular to its length. The fiber cross section can be any shape, but is typically round. The fibrous material may be in any suitable form known to those skilled in the art and is preferably selected from non-woven structures, textiles, fibrous battings and combinations thereof. Non-woven structures can be selected from random fiber orientation or aligned fibrous structures. Examples of random fiber orientation include without limitation chopped and continuous material which can be in the form of a mat, a needled mat or a felt. Examples of aligned fibrous structures include without limitation unidirectional fiber strands, bidirectional strands, multidirectional strands, multi-axial textiles. Textiles can be selected from woven forms, knits, braids and combinations thereof. The fibrous material can be continuous or discontinuous in form.

[0021] Depending on the end-use application of the overmolded composite structure and the required mechanical properties, more than one fibrous materials can be used, either by using several same fibrous materials or a combination of different fibrous materials, i.e. the first component described herein may comprise one or more fibrous materials. An example of a combination of different fibrous materials is a combination comprising a non-woven structure such as for example a planar random mat which is placed as a central layer and one or more woven continuous fibrous materials that are placed as outside layers. Such a combination allows an improvement of the processing and thereof of the homogeneity of the first component thus leading to improved mechanical properties. The fibrous material may be made of any suitable material or a mixture of materials provided that the material or the mixture of materials withstand the processing conditions used during impregnation by the matrix resin composition and the surface resin composition.

[0022] Preferably, the fibrous material comprises glass fibers, carbon fibers, aramid fibers, graphite fibers, metal fibers, ceramic fibers, natural fibers or mixtures thereof; more preferably, the fibrous material comprises glass fibers, carbon fibers, aramid fibers, natural fibers or mixtures thereof; and still more preferably, the fibrous material comprises glass fibers, carbon fibers and aramid fibers or mixture mixtures thereof. By natural fiber, it is meant any of material of plant origin or of animal origin. When used, the natural fibers are preferably derived from vegetable sources such as for example from seed hair (e.g. cotton), stem plants (e.g. hemp, flax, bamboo; both bast and core fibers), leaf plants (e.g. sisal and abaca), agricultural fibers (e.g., cereal straw, corn cobs, rice hulls and coconut hair) or lignocellulosic fiber (e.g. wood, wood fibers, wood flour, paper and wood-related materials). As mentioned above, more than one fibrous materials can be used. A combination of fibrous materials made of different fibers can be used such as for example a composite structure comprising one or more central layers made of glass fibers or natural fibers and one or more surface layers made of carbon fibers or glass fibers. Preferably, the fibrous material is selected from woven structures, non-woven structures or combinations thereof, wherein said structures are made of glass fibers and wherein the glass fibers are E-glass filaments with a diameter between 8 and 30 microns and preferably with a diameter between 10 to 24 microns.

[0023] The fibrous material may further contain a thermoplastic material and the materials described above, for example the fibrous material may be in the form of commingled or co-woven yarns or a fibrous material impregnated with a powder made of a thermoplastic material that is suited to subsequent processing into woven or non-woven forms, or a mixture for use as a uni-directional material or a fibrous material impregnated with oligomers that will polymerize in situ during impregnation.

[0024] Preferably, the ratio between the fibrous material and the polymer materials in the first component. i.e. the fibrous material in combination with the matrix resin composition and the surface resin composition, is at least 30 volume percent fibrous material and more preferably between 40 and 60 volume percent fibrous material, the percentage being a volume-percentage based on the total volume of the first component.

[0025] The matrix resin composition of the first component is made of a thermoplastic resin that is compatible with the surface resin composition. The matrix resin composition and the surface resin composition are independently selected from polyamide compositions comprising a blend of semi-aromatic polyamides. Preferably, the matrix resin composition and the surface resin composition are independently selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B). The matrix resin composition and the surface resin composition may be identical or different.

[0026] The overmolding resin composition is selected from polyamide compositions.

[0027] Polyamides are condensation products of one or more dicarboxylic acids and one or more diamines, and/or one or more aminocarboxylic acids, and/or ring-opening polymerization products of one or more cyclic lactams. Polyamides may be fully aliphatic or semi-aromatic and are described hereafter.

[0028] The term "semi-aromatic" describes polyamides that comprise at least some monomers containing aromatic groups, in comparison with "fully aliphatic" polyamide which describes polyamides comprising aliphatic carboxylic acid monomer(s) and aliphatic diamine monomer(s). The one or more semi-aromatic polyamides may be derived from one or more aliphatic carboxylic acid components and aromatic diamine components such as for example m-xylylenediamine and p-xylylenediamine, it may be derived from one or more aromatic carboxylic acid components, such as terephthalic acid, and one or more aliphatic diamine components, it may be derived from mixtures of aromatic and aliphatic dicarboxylic acid components and mixtures of aromatic and aliphatic diamine components, it may be derived from mixtures of aromatic and aliphatic carboxylic acids and aliphatic diamines or aromatic diamines, it may be derived from aromatic or aliphatic carboxylic acids with mixtures of aliphatic and aromatic diamines.

[0029] Preferably, the one or more semi-aromatic polyamides are formed from one or more aromatic carboxylic acid components and one or more aliphatic diamine components. The one or more aromatic carboxylic acids can be, for example, terephthalic acid or mixtures of terephthalic acid and one or more other carboxylic acids, such as isophthalic acid, substituted phthalic acid such as for example 2-methylterephthalic acid and unsubstituted or substituted isomers of naphthalenedicarboxylic acid. Preferably, the one or more aromatic carboxylic acids are selected from terephthalic acid, isophthalic acid and mixtures thereof and more preferably, the one or more carboxylic acids are mixtures of terephthalic acid and isophthalic acid, wherein the mixture contains at least 55 mole-% of terephthalic acid. More preferably, the one or more carboxylic acids is 100% terephthalic acid. Furthermore, the one or more carboxylic acids can be mixed with one or more aliphatic carboxylic acids, like adipic acid; pimelic acid; suberic acid; azelaic acid; sebacic acid and dodecanedioic acid, adipic acid being preferred. More preferably the mixture of terephthalic acid and adipic acid comprised in the one or more carboxylic acids mixtures of the one or more semi-aromatic polyamide contains at least 55 mole-% of terephthalic acid. The one or more semi-aromatic polyamides described herein comprises one or more aliphatic diamines that can be chosen among diamines having four or more carbon atoms, including, but not limited to tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, 2-methylpentamethylene diamine, 2-ethyltetramethylene diamine, 2-methyloctamethylene diamine; trimethylhexamethylene diamine, bis(p-aminocyclohexyl)methane; and/or mixtures thereof. Preferably, the one or more diamines of the one or more semi-aromatic polyamides described herein are selected from hexamethylene diamine, 2-methyl pentamethylene diamine and mixtures thereof, and more preferably the one or more diamines of the one or more semi-aromatic polyamides are selected from hexamethylene diamine and mixtures of hexamethylene diamine and 2-methyl pentamethylene diamine wherein the mixture contains at least 50 mole-% of hexamethylene diamine (the mole-% being based on the diamines mixture).

[0030] Examples of semi-aromatic polyamides useful in the polyamide composition described herein are commercially available under the trademark Zytel® HTN from E. I. du Pont de Nemours and Company, Wilmington, Del.

[0031] In a preferred embodiment, the matrix resin composition and the surface resin composition are independently

selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B).

[0032] The term “semi-crystalline” semi-aromatic polyamide refers to those polyamides which are partly crystalline as shown by the presence of an endotherm crystalline melting peak in a Differential Scanning Calorimeter (“DSC”) measurement (ASTM D-3417), 10° C./minute heating rate.

[0033] Preferred semi-crystalline semi-aromatic polyamides (A) are selected from the group consisting of poly(ϵ -caprolactam/tetramethylene terephthalamide) (PA6/4T), poly(ϵ -caprolactam/hexamethylene terephthalamide) (PA6/6T), poly(ϵ -caprolactam/decamethylene terephthalamide) (PA6/10T), poly(ϵ -caprolactam/dodecamethylene terephthalamide) (PA6/12T), poly(hexamethylene decanediamide/hexamethylene terephthalamide) (PA610/6T), poly(hexamethylene dodecanediamide/hexamethylene terephthalamide) (PA612/6T), poly(hexamethylene tetradecanediamide/hexamethylene terephthalamide) (PA614/6T), poly(ϵ -caprolactam/hexamethylene isophthalamide/hexamethylene terephthalamide) (PA6/6I/6T), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/hexamethylene terephthalamide) (PA D6/66/ /6T), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA 6TDT), poly(hexamethylene hexanediamide/hexamethylene terephthalamide) (PA66/6T), poly(hexamethylene terephthalamide/ hexamethylene isophthamide) (PA6T/6I), poly(hexamethylene hexanediamide/hexamethylene terephthalamide/ hexamethylene isophthamide) (PA66/6T/6I), poly (decamethylene decanediamide/decamethylene terephthalamide) (PA1010/10T) poly(decamethylene decanediamide/dodecamethylene decanediamide/decamethylene terephthalamide/dodecamethylene terephthalamide) (PA1010/1210/10T/12T), poly(11-aminoundecanamide/tetramethylene terephthalamide) (PA11/4T), poly(11-aminoundecanamide/hexamethylene terephthalamide) (PA11/ 6T), poly(11-aminoundecanamide/decamethylene terephthalamide) (PA11/10T), poly(11-aminoundecanamide/dodecamethylene terephthalamide) (PA11/12T), poly(12-aminododecanamide/tetramethylene terephthalamide) (PA12/4T), poly (12-aminododecanamide/hexamethylene terephthalamide) (PA12/6T), poly(12-aminododecanamide/decamethylene terephthalamide) (PA12/10T), and poly(dodecamethylene dodecanediamide/dodecamethylene dodecanediamide/dodecamethylene terephthalamide)) (PA1212/12T). Particularly preferred semi-crystalline semi-aromatic polyamides (A) are selected from the group consisting of poly(hexamethylene terephthamide/2-methylpentamethylene terephthamide) (PA 6TDT), poly(hexamethylene hexanediamide/hexamethylene terephthamide) (PA66/6T), poly(hexamethylene terephthamide/ hexamethylene isophthamide) (PA6T/6I), poly(hexamethylene hexanediamide/hexamethylene terephthamide/ hexamethylene isophthamide) (PA66/6T/6I).

[0034] The term “amorphous” semi-aromatic polyamide refers to those polyamides which are lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter (“DSC”) measurement (ASTM D-3417), 10° C./minute heating rate.

[0035] Preferred amorphous semi-aromatic polyamides (B) comprise isophthalic acid as aromatic carboxylic acids, wherein the amount of isophthalic acid in the semi-crystalline semi-aromatic polyamide is at least 60 mole-%.

[0036] Examples of amorphous semiaromatic polyamides (B) that are also known as transparent semiaromatic poly-

amides can be found in M. I. Kohan Nylon plastics handbook, Hanser, Munich (1995), page 377 to 380 the content of which is incorporated herein by reference. Preferred amorphous semiaromatic polyamides (B) are selected from the group consisting of poly(hexamethylene terephthamide/hexamethylene isophthamide) (PA6T/6I), poly(hexamethylene hexanediamide/hexamethylene terephthamide/ hexamethylene isophthamide) (PA66/6T/6I) wherein the amount of isophthalic acid in the semi-crystalline semi-aromatic polyamide is at least 60 mole-%. Particularly preferred amorphous semiaromatic polyamides (B) are poly(hexamethylene terephthamide/ hexamethylene isophthamide) (PA6T/6I) in a molar ratio 6T:6I of approximately 30:70.

[0037] The matrix and the surface polyamide resin composition described herein comprises a blend of semi-aromatic polyamides. Preferably, the matrix resin composition and the surface resin composition are selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B) wherein semi-aromatic semi-crystalline polyamide (A) is preferably selected from the group consisting of PA66/6T, PA6TDT, PA6I/6T PA66/6I/6T wherein the amount of terephthalic acid in the semi-crystalline semi-aromatic polyamide (A) is at least 55 mole-% and their combinations and copolymers thereof, and wherein the semi-aromatic amorphous polyamide (B) is selected from the group consisting of PA6I/6T and PA66/6T/6I wherein the amount of isophthalic acid in the amorphous semi-aromatic polyamide is at least 60 mole-% and their combinations and copolymers thereof.

[0038] The matrix and the surface polyamide resin composition described herein comprises a blend of semi-aromatic polyamides. Preferably, the matrix resin composition and the surface resin composition are selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B) in a weight ratio (A:B) from about 99:1 to about 5:95, more preferably from about 97:3 to about 50:50 and still more preferably from about 95:5 to about 65:35.

[0039] The overmolded composite structure comprises a second component comprising an overmolding resin composition. The second component is adhered to the first component described above over at least a portion of the surface of the first component. The overmolding resin composition is selected from a polyamide composition.

[0040] The surface resin composition described herein and/or the matrix resin composition and/or the overmolding resin composition may further comprise one or more impact modifiers, one or more heat stabilizers, one or more oxidative stabilizers, one or more ultraviolet light stabilizers, one or more flame retardant agents or mixtures thereof.

[0041] The surface resin composition described herein and/or the matrix resin composition and/or the overmolding resin composition may further comprise one or more reinforcing agents such as glass fibers, glass flakes, carbon fibers, carbon nanotubes, mica, wollastonite, calcium carbonate, talc, calcined clay, kaolin, magnesium sulfate, magnesium silicate, boron nitride, barium sulfate, titanium dioxide, sodium aluminum carbonate, barium ferrite, and potassium titanate. When present, the one or more reinforcing agents are present in an amount from at or about 1 to at or about 60 wt-%, preferably from at or about 1 to at or about 40 wt-%, or more preferably from at or about 1 to at or about 35 wt-%, the

weight percentages being based on the total weight of the surface resin composition or the matrix resin composition, as the case may be.

[0042] As mentioned above, the matrix resin composition and the surface resin composition may be identical or different. With the aim of increasing the impregnation rate of the fibrous material, the melt viscosity of the compositions may be reduced and especially the melt viscosity of the matrix resin composition.

[0043] The surface resin composition described herein and/or the matrix resin composition and/or the overmolding resin composition may further comprise modifiers and other ingredients, including, without limitation, flow enhancing additives, lubricants, antistatic agents, coloring agents (including dyes, pigments, carbon black, and the like), nucleating agents, crystallization promoting agents and other processing aids known in the polymer compounding art.

[0044] Fillers, modifiers and other ingredients described above may be present in the composition in amounts and in forms well known in the art, including in the form of so-called nano-materials where at least one of the dimensions of the particles is in the range of 1 to 1000 nm.

[0045] Preferably, the surface resin compositions and the matrix resin compositions and the overmolding resin composition are melt-mixed blends, wherein all of the polymeric components are well-dispersed within each other and all of the non-polymeric ingredients are well-dispersed in and bound by the polymer matrix, such that the blend forms a unified whole. Any melt-mixing method may be used to combine the polymeric components and non-polymeric ingredients of the present invention. For example, the polymeric components and non-polymeric ingredients may be added to a melt mixer, such as, for example, a single or twin-screw extruder; a blender; a single or twin-screw kneader; or a Banbury mixer, either all at once through a single step addition, or in a stepwise fashion, and then melt-mixed. When adding the polymeric components and non-polymeric ingredients in a stepwise fashion, part of the polymeric components and/or non-polymeric ingredients are first added and melt-mixed with the remaining polymeric components and non-polymeric ingredients being subsequently added and further melt-mixed until a well-mixed composition is obtained.

[0046] The overmolded composite structure according to the present invention may be manufactured by a process comprising a step of overmolding the first component described above with the overmolding resin composition. By "overmolding", it is meant that a second component comprising the overmolding resin composition described herein is molded or extruded onto at least one portion of the surface of the first component, which surface is made of a surface resin composition.

[0047] The overmolding process includes a process whereby the second component is molded in a mold already containing the first component, the latter having been manufactured beforehand as described hereafter, so that the first and second components are adhered to each other over at least a portion of the surface of the first component. The first component is positioned in a mold having a cavity defining the outer surface of the final overmolded composite structure. The overmolding resin composition may be overmolded on one side or on both sides of the first component and it may fully or partially encapsulate the first component. After having positioned the first component in mold (optionally after preheating and performing the first component), the over-

molding resin composition is then introduced in a molten form. The first component and the second component are adhered together by overmolding. The at least two parts are preferably adhered together by injection or compression molding as an overmolding step, and more preferably by injection molding.

[0048] Depending on the end-use application, the first component according to the present invention may have any shape. In a preferred embodiment, the first component according to the present invention is in the form of a sheet structure. The first component may be flexible, in which case it can be rolled.

[0049] The first component can be made by a process that comprises a step of impregnating the fibrous material with the matrix resin composition, wherein at least a portion of the surface of the first component, i.e. the composite structure, is made of the surface resin composition. Preferably, the fibrous material is impregnated with the matrix resin by thermopressing. During thermopressing, the fibrous material, the matrix resin composition and the surface resin composition undergo heat and pressure in order to allow the resin compositions to melt and penetrate through the fibrous material and, therefore, to impregnate said fibrous material.

[0050] Typically, thermopressing is made at a pressure between 2 and 100 bars and more preferably between 10 and 40 bars and a temperature which is above the melting point of the matrix resin composition and the surface resin composition, preferably at least about 20° C. above the melting point to enable a proper impregnation. Heating may be done by a variety of means, including contact heating, radiant gas heating, infra red heating, convection or forced convection air heating, induction heating, microwave heating or combinations thereof.

[0051] The impregnation pressure can be applied by a static process or by a continuous process (also known as dynamic process), a continuous process being preferred for reasons of speed. Examples of impregnation processes include without limitation vacuum molding, in-mold coating, cross-die extrusion, pultrusion, wire coating type processes, lamination, stamping, diaphragm forming or press-molding, lamination being preferred. During lamination, heat and pressure are applied to the fibrous material, the matrix resin composition and the surface resin composition through opposing pressured rollers or belts in a heating zone, preferably followed by the continued application of pressure in a cooling zone to finalize consolidation and cool the impregnated fibrous material by pressurized means. Examples of lamination techniques include without limitation calendaring, flatbed lamination and double-belt press lamination. When lamination is used as the impregnating process, preferably a double-belt press is used for lamination.

[0052] Should the matrix resin composition and the surface resin composition be different, the surface resin composition always faces the environment of the first component so as to be accessible when the overmolding resin composition is applied onto the first component.

[0053] The matrix resin composition and the surface resin composition are applied to the fibrous material by conventional means such as for example powder coating, film lamination, extrusion coating or a combination of two or more thereof, provided that the surface resin composition is applied on at least a portion of the surface of the composite structure, which surface is exposed to the environment of the first component.

[0054] During a powder coating process, a polymer powder which has been obtained by conventional grinding methods is applied to the fibrous material. The powder may be applied onto the fibrous material by scattering, sprinkling, spraying, thermal or flame spraying, or fluidized bed coating methods. Optionally, the powder coating process may further comprise a step which consists in a post sintering step of the powder on the fibrous material. The matrix resin composition and the surface resin composition are applied to the fibrous material such that at least a portion of the surface of the first component is made of the surface resin composition. Subsequently, thermopressing is performed on the powder coated fibrous material, with an optional preheating of the powder coated fibrous material outside of the pressurized zone.

[0055] During film lamination, one or more films made of the matrix resin composition and one or more films made of the surface resin composition which have been obtained by conventional extrusion methods known in the art such as for example blow film extrusion, cast film extrusion and cast sheet extrusion are applied to the fibrous material, e.g. by layering. Subsequently, thermopressing is performed on the assembly comprising the one or more films made of the matrix resin composition and the one or more films made of the surface resin composition and the one or more fibrous materials. In the resulting first component, the films melt and penetrate around the fibrous material as a polymer continuum surrounding the fibrous material.

[0056] During extrusion coating, pellets and/or granulates made of the matrix resin composition and pellets and/or granulates made of the surface resin composition are melted and extruded through one or more flat dies so as to form one or more melt curtains which are then applied onto the fibrous material by laying down the one or more melt curtains. Subsequently, thermopressing is performed on the assembly comprising the matrix resin composition, the surface resin composition and the one or more fibrous materials.

[0057] In some situations it may be desired to preheat the first component at a temperature close to but below the melt temperature of the matrix resin composition prior to the overmolding step so as to improve the adhesion between the surface of the first component and the overmolding resin and then to rapidly transfer the heated composite structure for overmolding; such a step can be improved or even eliminated by using the overmolding resin composition and the surface resin composition. Due to the high adhesion and high bond strength between the overmolding resin and the surface resin composition of the overmolded composite structure according to the present invention, the need for a preheating step is strongly reduced or even eliminated. Should a preheating step be used, the transfer time may not be as critical as for conventional composite structures, meaning that the transfer time may be increased thereby increasing the processing window and reducing molding equipment and automation costs. Such a preheating step may be done by a variety of means, including contact heating, radiant gas heating, infra red heating, convection or forced convection air heating, induction heating, microwave heating or combinations thereof.

[0058] Depending on the end-use application, the first component may be shaped into a desired geometry or configuration, or used in sheet form prior to the step of overmolding the overmolding resin composition. The first component may be flexible, in which case it can be rolled.

[0059] The process for making a shaped first component further comprises a step of shaping the first component, said

step arising after the impregnating step. The step of shaping the first component may be done by compression molding, stamping or any technique using heat and/or pressure, compression molding and stamping being preferred. Preferably, pressure is applied by using a hydraulic molding press. During compression molding or stamping, the first component is preheated to a temperature above the melt temperature of the surface resin composition and preferably above the melt temperature of the matrix resin composition by heated means and is transferred to a forming or shaping means such as a molding press containing a mold having a cavity of the shape of the final desired geometry whereby it is shaped into a desired configuration and is thereafter removed from the press or the mold after cooling to a temperature below the melt temperature of the surface resin composition and preferably below the melt temperature of the matrix resin composition. With the aim of further improving the adhesion between the overmolding resin and the surface resin composition, the surface of the first component may be a textured surface so as to increase the relative surface available for overmolding, such textured surface may be obtained during the step of shaping by using a press or a mold having for example porosities or indentations on its surface.

[0060] Alternatively, a one step process comprising the steps of shaping and overmolding the first component in a single molding station may be used. This one step process avoids the step of compression molding or stamping the first component in a mold or a press, avoids the optional preheating step and the transfer of the preheated first component to the molding station. During this one step process, the first component, i.e. the composite structure, is heated outside, adjacent to or within the molding station, to a temperature at which the first component is conformable or shapable during the overmolding step. In such a one step process, the molding station comprises a mold having a cavity of the shape of the final desired geometry. The shape of the first component is thereby obtained during overmolding.

[0061] The overmolded composite structures according to the present invention may be used in a wide variety of applications such as for example as components for automobiles, trucks, commercial airplanes, aerospace, rail, household appliances, computer hardware, hand held devices, recreation and sports, structural component for machines, structural components for buildings, structural components for photovoltaic equipments or structural components for mechanical devices.

Examples of automotive applications include without limitation seating components and seating frames, engine cover brackets, engine cradles, suspension arms and cradles, spare tire wells, chassis reinforcement, floor pans, front-end modules, steering column frames, instrument panels, door systems, body panels (such as horizontal body panels and door panels), tailgates, hardtop frame structures, convertible top frame structures, roofing structures, engine covers, housings for transmission and power delivery components, oil pans, airbag housing canisters, automotive interior impact structures, engine support brackets, cross car beams, bumper beams, pedestrian safety beams, firewalls, rear parcel shelves, cross vehicle bulkheads, pressure vessels such as refrigerant bottles and fire extinguishers and truck compressed air brake system vessels, hybrid internal combustion/electric or electric vehicle battery trays, automotive suspension wishbone and control arms, suspension stabilizer links, leaf springs, vehicle wheels, recreational vehicle and motorcycle swing

arms, fenders, roofing frames and tank flaps. Examples of household appliances include without limitation washers, dryers, refrigerators, air conditioning and heating. Examples of recreation and sports include without limitation inline-skate components, baseball bats, hockey sticks, ski and snowboard bindings, rucksack backs and frames, and bicycle frames. Examples of structural components for machines include electrical/electronic parts such as for example housings for hand held electronic devices, computers.

EXAMPLES

[0062] The following materials were used for preparing the composites structures according to the present invention and comparative examples.

Materials

[0063] The materials below are comprised in the compositions used in the Examples and Comparative Examples.

[0064] Polyamide 1 (PA1): a polyamide made of terephthalic acid and 1,6-hexamethylenediamine (HMD) and 2-methylpentamethylenediamine (MPMD) (HMD:MPMD=50:50). PA1 has a melting point of about 297° C. to about 303° C. and a glass transition temperature of about 130° C. to about 145° C. This semi-aromatic polyamide is called PA 6TDT and is commercially available from E. I. du Pont de Nemours and Company, Wilmington, Del.

[0065] Polyamide 2 (PA2): a polyamide made of terephthalic acid, isophthalic acid, and 1,6-hexamethylenediamine. This semi-aromatic polyamide has a glass transition temperature of about 120° C. to about 130° C. PA2 is called PA6I6T and is commercially available from E. I. du Pont de Nemours and Company.

[0066] Overmolding resin: a composition comprising semiaromatic polyamide (PA1) made of terephthalic acid and 1,6-hexamethylenediamine (HMD) and 2-methylpentamethylenediamine (MPMD) (HMD:MPMD=50:50), and 50% glass fibers by weight of the total resin composition. The Overmolding resin is commercially available from E. I. du Pont de Nemours and Company.

Preparation of Films

[0067] The resin compositions used in the Examples (abbreviated as "E" in Tables 1 and 2), and Comparative Examples (abbreviated as "C" in Tables 1 and 2) were prepared by melting or melt-blending the ingredients in a twin-screw extruder. Upon exiting the extruder, the compositions listed in Tables 1 and 2 were cast into films by exiting the extruder through an adaptor and a film die at about 325° C. and cast onto a casting drum oil-heated at 120° C., then drawn in air and wound around a core at room temperature. The matrix and surface resin compositions were made into about 102 micron thick films. The thickness of the films was controlled by the rate of drawing.

Preparation of the Composite Structures

[0068] The composite structures E1, C1, and C2 were made by laminating multiple layers of film of compositions shown in Tables 1 and 2, and woven continuous glass fiber textile (prepared from E-glass fibers having a diameter of 17 microns, sized with 0.4% of a silane-based sizing agent and a nominal roving tex of 1200 g/km that have been woven into a 2/2 twill (balanced weave) with an areal weight of 600 g/m²). The lamination sequence for the composite structures E1 and

C1 was as follows: 4 layers of film of surface resin composition, one layer of woven continuous glass fiber textile, 6 layers of film of matrix resin composition, one layer of woven continuous glass fiber textile, 4 layers of film of surface resin composition. The lamination sequence for the composite structure C2 was as follows: 2 layers of film of surface resin composition, 2 layers of film of matrix resin composition, one layer of woven continuous glass fiber textile, 6 layers of film of matrix resin composition, one layer of woven continuous glass fiber textile, 2 layers of film of matrix resin composition, 2 layers of film of surface resin composition.

[0069] The composite structures were compression molded by a Dake Press (Grand Haven, Mich.) Model 44-225, Pressure range 0-25K, with an 8 inch platten. A 6×6" specimen of film and glass textile layers as described above was placed in the mold and heated to a temperature of about 340° C. Once at temperature, the composite structures were held at the temperature for 2 minutes without pressure, then pressed at the 340° C. temperature with the following pressures: about 4 bar for about 2 minutes, then with about 23 bar pressure for about 2 additional minutes, and then with about 46 bar pressure for about 2 additional minutes, and subsequently cooled to ambient temperature. All the composite structures had an overall thickness of about 1.5 mm.

Preparation of the Overmolded Composite Structures

[0070] The overmolded composite structures listed in Table 1 were made by over injection molding about 1.7 mm of the overmolding resin composition onto the composite structures E1 and C1 obtained as described above. The overall thickness of the overmolded composite structure was about 3.2 mm. The composite structure was cut into 3×5" (about 76 mm×127 mm) specimens and placed into a heating chamber (a Hot-pack oven Model 273601) at 150° C. for about 10 minutes. The composite structure was then transferred manually into a mold cavity and was over injection molded with the overmolding resin by a molding machine (made by Nissei Corp., Model FN4000, 1752 KN, 148 cc (6 oz.)). The mold was electric heated at 150° C. and fitted with a 1/8"×3"×5" plaque cavity with a bar gate. The injection machine was set at 320° C.

Flex Strength of Overmolded Composite Structures of Table 1

[0071] The overmolded composite structures obtained as described above were cut into 1/2" (about 12.7 mm) by 3" (about 76 mm) long test specimens (bars) using a MK-377 Tile Saw with a diamond edged blade and water as a lubricant. Flexural Strength was tested on the test specimens via a 3-point bend test. The apparatus and geometry were according to ISO method 178, bending the specimen with a 2.0" support width with the loading edge at the center of the span. The composite structure component of the overmolded specimen was on the tensile side (outer span, down) resting on the two side supports (at 2" apart), while indenting with the single support (the load) on the compression side (inner span, up) on the overmolding resin component of the specimen. The tests were conducted with 1 KN load at 2 mm/min until fracture. The results are shown in Table 1.

[0072] It is seen in Table 1 that overmolded composite structure E1 exhibits higher flexural strength than overmolded composite structure C1, demonstrating the higher strength of the overmolded composite structure comprising a

composite structure made of a combination of at least 2 semi-aromatic polyamides in the matrix resin composition and in the surface resin composition than the overmolded composite structure comprising a composite structure made of a single semiaromatic polyamide in the matrix resin composition and in the surface resin composition.

Flex Strength of Composite Structures of Table 2

[0073] The composite structures E1, C1, and C2 in Table 2, obtained as described above, were cut into ½" (about 12.7 mm) by 3" (about 76 mm) long test specimens (bars) using a MK-377 Tile Saw with a diamond edged blade and water as a lubricant. Flexural Strength was tested on the test specimens via a 3-point bend test. The apparatus and geometry were according to ISO method 178, bending the specimen with a 2.0" support width with the loading edge at the center of the span. The composite structure was resting on the two side supports (at 2" apart), while indenting with the single support (the load). The tests were conducted with 1 KN load at 2 mm/min until fracture. The results are shown in Tables 2.

[0074] It is seen in Table 2 that the composite structure E1 exhibits higher flexural strength than composite structures C2 and C3, demonstrating the higher strength of the composite structure made of a combination of at least 2 semi-aromatic polyamides in both the matrix resin composition and in the surface resin composition, than a composite structure made of at least 2 semi-aromatic polyamides only in the surface resin composition, or a composite structure made of a single semi-aromatic polyamide in both the matrix resin composition and in the surface resin composition.

TABLE 1

	C1	E1
Matrix Resin Composition		
PA1	100	70
PA2		30
Surface Resin Composition		
PA1	100	70
PA2		30
Overmolding resin	PA1 + 50% glass fibers	PA1 + 50% glass fibers
ISO-178 3 Point Flex		
Flexural Strength at Break (Mpa), laminated down (in tension)	271	288
Number of specimens delaminated	4 out of 8	0 out of 8

TABLE 2

	Composite structure C1	Composite structure C2	Composite structure E1
Matrix Resin Composition			
PA1	100	100	70
PA2			30
Surface Resin Composition			
PA1	100	70	70
PA2		30	30
ISO-178 3 Point Flex			
Flex Strength at break (Mpa)	386	393	441

What is claimed is:

1. An overmolded composite structure comprising:

i) a first component having a surface, which surface has at least a portion made of a surface resin composition, and comprising a fibrous material selected from the group consisting of non-woven structures, textiles, fibrous battings and combinations thereof, said fibrous material being impregnated with a matrix resin composition,

ii) a second component comprising an overmolding resin composition,

wherein said second component is adhered to said first component over at least a portion of the surface of said first component, and

wherein the matrix resin composition and the surface resin composition are identical or different and are selected from polyamide compositions comprising a blend of semi-aromatic polyamides.

2. The overmolded composite structure according to claim 1 wherein the matrix resin composition and the surface resin composition are selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B).

3. The overmolded composite structure according to claim 1 wherein the fibrous material is made of glass fibers, carbon fibers, aramid fibers, natural fibers or mixtures thereof.

4. The overmolded composite structure according to claim 1 wherein the fibrous material is made of glass fibers.

5. The overmolded composite structure according to claim 1 wherein the fibrous material is from 30 volume percent to 60 volume percent of the first component.

6. The overmolded composite structure according to claim 1 wherein the weight ratio (A:B) of the polyamides selected from polyamides (A) and the polyamides selected from polyamides (B) of the polyamide composition is between from about 99:1 to about 5:95.

7. The overmolded composite structure according to claim 1 further comprising one or more additives selected from the group consisting of heat stabilizers, oxidative stabilizers, reinforcing agents and flame retardants or combination thereof.

8. The overmolded composite structure according to claim 1 wherein the one or more semi-aromatic polyamides are selected from the group consisting of PA6/4T, PA6/6T, PA6/10T, PA6/12T, PA610/6T, PA612/6T, PA614/6T, PA6/6I/6T, PA D6/66//6T, PA 6TDT, PA1010/10T, PA1010/1210/10T/12T, PA11/4T, PA11/6T, PA11/10T, PA11/12T, PA12/4T, PA12/6T, PA12/10T PA1212/12T, PA66/6T, PA6I/6T, PA66/6I/6T, PA6T/6I.

9. The overmolded composite structure according to claim 1 wherein the one or more semi-aromatic semi-crystalline polyamides are selected from the group consisting of PA66/6T, PA6TDT, PA6I/6T PA66/6I/6T and their combinations and copolymers thereof, and wherein the semi-aromatic amorphous polyamide (B) is selected from the group consisting of PA6I/6T and PA66/6T/6I wherein the amount of isophthalic acid in the amorphous semi-aromatic polyamide is at least 60 mole-% and their combinations and copolymers thereof.

10. The overmolded composite structure according to claim 1 in the form of a component for automobiles, trucks, commercial airplanes, aerospace, rail, household appliances, computer hardware, hand held devices, recreation and sports, structural component for machines, structural components for buildings, structural components for photovoltaic equipments or structural components for mechanical devices.

11. A process for making the overmolded composite structure of claim **1** comprising a step of overmolding a second component comprising an overmolding resin composition on a first component,

wherein the first component comprises a fibrous material and has a surface, said surface having at least a portion made of a surface resin composition, said fibrous material is selected from the group consisting of non-woven structures, textiles, fibrous battings and combinations thereof and said fibrous material being impregnated with a matrix resin composition,

wherein the matrix resin composition, and the surface resin composition are identical or different and are selected from polyamide compositions comprising a blend of semi-aromatic polyamides.

12. The process according to claim **11** wherein the matrix resin composition and the surface resin composition are

selected from polyamide compositions comprising a blend of a semi-aromatic semi-crystalline polyamide (A) with a semi-aromatic amorphous polyamide (B).

13. The process according to claim **11** further comprising a step of shaping the first component before the step of overmolding.

14. The process according to claim **11** wherein the step of overmolding involves completely encapsulating the first component in the overmolding resin composition.

15. The process according to claim **11**, wherein the first component is heated before the step of overmolding to soften and partially melt a surface which will form an interface with the overmolding resin composition.

16. The process according to claim **11**, wherein the first component is not heated before the step of overmolding.

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