

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 May 2012 (03.05.2012)

PCT

(10) International Publication Number
WO 2012/058352 A1

(51) International Patent Classification:

B32B 5/26 (2006.01) **C08L 77/02** (2006.01)
B32B 27/12 (2006.01) **C08L 77/04** (2006.01)
B32B 27/34 (2006.01) **C08L 77/06** (2006.01)
B32B 17/02 (2006.01) **C08L 77/08** (2006.01)
B32B 17/10 (2006.01) **B29C 70/50** (2006.01)
C08J 5/04 (2006.01) **B29C 70/68** (2006.01)
C08L 77/00 (2006.01) **C08J 5/18** (2006.01)

(21) International Application Number:

PCT/US2011/057953

(22) International Filing Date:

27 October 2011 (27.10.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/408,166 29 October 2010 (29.10.2010) US
61/410,108 4 November 2010 (04.11.2010) US
61/410,104 4 November 2010 (04.11.2010) US
61/410,100 4 November 2010 (04.11.2010) US
61/410,093 4 November 2010 (04.11.2010) US

(71) Applicant (for all designated States except US): **E. I. du Pont de Nemours and Company** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ELIA, Andri, E.** [US/US]; 4 Ridgeway Drive, Chadds Ford, PA 19317 (US). **KIRCHNER, Olaf, Norbert** [DE/CH]; Chemin de Tres-Chez-Roget, CH-1272 Genolier (CH). **MESAROS, David, V.** [US/US]; 6395 Terrace Circle, Salida, CO 81201 (US). **WAKEMAN, Martyn, Douglas** [GB/CH];

Rue du Perron 70, CH-1196 Gland (CH). **YUAN, Shengmei** [US/US]; 51 Harris Circle, Newark, DE 19711 (US).

(74) Agent: **SEBREE, Chyrrea, J.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: POLYAMIDE COMPOSITE STRUCTURES AND PROCESSES FOR THEIR PREPARATION

(57) Abstract: The present invention relates to the field of composite structures, overmolded composites structures and processes for their preparation, particularly it relates to the field of polyamide composite structures. The disclosed composite structures have a surface, which surface has at least a portion made of a surface polyamide resin composition, and comprise a fibrous material selected from non-woven structures, textiles, fibrous battings and combinations thereof, said fibrous material being impregnated with a matrix resin composition, wherein the matrix polyamide resin composition and the surface resin composition is selected from polyamide compositions comprising a blend of (A) one or more fully aliphatic polyamides selected from group (I) polyamides, and (B) one or more semiaromatic polyamides selected from group (II) polyamides having a melting point of at least 280°C.



WO 2012/058352 A1

TITLEPOLYAMIDE COMPOSITE STRUCTURES AND PROCESSES FOR THEIR
PREPARATION

5

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

10 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-
15 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
20 lightweight, high strength and temperature resistance.

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
25 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.
30 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.

US 4,255,219 discloses a thermoplastic sheet material useful in forming composites. The disclosed thermoplastic sheet material is made of polyamide 6 and a
5 dibasic carboxylic acid or anhydride or esters thereof and at least one reinforcing mat of long glass fibers encased within said layer.

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
10 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
15 used to overmold the impregnated fibrous material (i.e. the overmolding polymer composition) are desired to have good adhesion one to the other, 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 a reasonable lifetime.

Unfortunately, conventional thermoplastic polyamide resin compositions that are
20 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
25 overmolded composite structures leading to reduced mechanical properties, premature aging and problems related to delamination and deterioration of the article with use and time.

In such case of weak adhesion, the interface between the composite structure and the overmolding resin will break first, rendering the overmolded composite structure
30 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.

There is a need for a thermoplastic polyamide composite structure that exhibits good mechanical properties, especially flexural strength and impact resistance and having at least a portion of its surface leading to good adhesion between the surface and an overmolding resin comprising a polyamide resin.

SUMMARY OF THE INVENTION

Described herein is a composite structure 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, unidirectional fiber, fibrous battings and combinations thereof, said fibrous material being impregnated with a matrix resin composition, wherein the matrix polyamide resin composition and the surface polyamide resin composition are selected from polyamide compositions comprising a blend of:

- (A) one or more fully aliphatic polyamides selected from group (I) polyamides, preferably having a melting point of less than 280°C.; and
- (B) one or more semi-aromatic polyamides selected from group (II) polyamides having a melting point of at least 280°C.

Further described herein is a process for making the composite structure of the invention, comprising a step of i) impregnating the fibrous material with the matrix resin composition, wherein at least a portion of the surface of the composite structure is made of the surface resin composition.

DETAILED DESCRIPTION

The composite structure according to the present invention has improved impact resistance and 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 impact resistance and flexural strength of the composite structure and a good adhesion between the composite structure and the overmolding resin leads to structures exhibiting good resistance to deterioration and/or delamination of the structure with use and time.

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

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.

10 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.

15 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
20 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 for Group I or for Group II polyamides in the scope of the current invention, always the peak of the melting endotherm of the first heating scan of
25 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.

30 The present invention relates to composite structures and processes to make them. The composite structure according to the present invention comprises a fibrous material that is impregnated with a matrix resin composition. At least a portion of the surface of the composite structure is made of a surface resin composition. The matrix

resin composition and the surface resin composition may be identical or may be different.

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. Depending on the end-use application of the 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 composite structure according to the present invention 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 composite structure 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.

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.

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.

Preferably, the ratio between the fibrous material and the polymer materials in the composite structure, 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 composite structure.

The matrix resin composition and the surface resin composition are selected from polyamide compositions comprising a blend of:

(A) one or more fully aliphatic polyamides selected from group (I) polyamides, preferably the one or more fully aliphatic polyamides selected from group (I) polyamides have a melting point of less than 280°C.; and

(B) one or more semi-aromatic polyamides selected from group (II) polyamides having a melting point of at least 280°C.

The matrix resin composition and the surface resin composition may be the same or different. When the surface resin composition and the matrix resin composition are different, it means that the component (A), i.e. the one or more group (I) fully aliphatic polyamides, and/or the component (B), i.e. the one or more semi-aromatic polyamides selected from group (II) polyamides, are not the same and/or that the amounts of component (A) and/or (B) are different in the surface resin composition and the matrix resin composition.

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.

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 (B) 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.

Preferably, the one or more semi-aromatic polyamides (B) 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 isophthalic acid, substituted phthalic acid such as for example 2-methylterephthalic acid and unsubstituted or substituted isomers of naphthalenedicarboxylic acid, wherein the carboxylic acid component contains at least 55 mole-% of terephthalic acid (the mole-% being based on the carboxylic acid mixture). 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 (B) contains at least 55 mole-% of terephthalic acid. The one or more semi-aromatic polyamides (B) 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 (B) 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 (B) 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).

Examples of semi-aromatic polyamides (B) 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, Delaware.

The one or more fully aliphatic polyamides (A) are formed from aliphatic and alicyclic monomers such as diamines, dicarboxylic acids, lactams, aminocarboxylic acids, and their reactive equivalents. A suitable aminocarboxylic acid is 11-

aminododecanoic acid. Suitable lactams include caprolactam and laurolactam. In the context of this invention, the term "fully aliphatic polyamide" also refers to copolymers derived from two or more such monomers and blends of two or more fully aliphatic polyamides. Linear, branched, and cyclic monomers may be used.

5 Carboxylic acid monomers comprised in the fully aliphatic polyamides are aliphatic carboxylic acids, such as for example adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), sebacic acid (C10), dodecanedioic acid (C12) and tetradecanedioic acid (C14). Preferably, the aliphatic dicarboxylic acids of the one or more fully aliphatic polyamides (A) are selected from adipic acid and dodecanedioic
10 acid. The one or more fully aliphatic polyamides (A) described herein comprise an aliphatic diamine as previously described. Preferably, the one or more diamine monomers of the one or more fully aliphatic polyamide copolymer (A) according to the present invention are selected from tetramethylene diamine and hexamethylene diamine. Suitable examples fully aliphatic polyamides include polyamide 6; polyamide
15 6,6; polyamide 4,6; polyamide 6,10; polyamide 6,12; polyamide 6,14; polyamide 6,13; polyamide 6,15; polyamide 6,16; polyamide 11; polyamide 12; polyamide 9,10; polyamide 9,12; polyamide 9,13; polyamide 9,14; polyamide 9,15; polyamide 6,16; polyamide 9,36; polyamide 10,10; polyamide 10,12; polyamide 10,13; polyamide 10,14; polyamide 12,10; polyamide 12,12; polyamide 12,13; polyamide 12,14. Preferred
20 examples of fully aliphatic polyamides (A) useful in the polyamide composition of the present invention are poly(hexamethylene adipamide) (polyamide 66, PA66, also called nylon 66), poly(hexamethylene dodecanoamide) (polyamide 612, PA612, also called nylon 612), poly(tetramethylene hexanediamide) (polyamide 46, PA46) and are commercially available.

25 Preferred group (I) Polyamides (A) having a melting point of less than 280°C comprise a fully aliphatic polyamide selected from the group consisting of poly(ϵ -caprolactam) (PA 6), and poly(hexamethylene hexanediamide) (PA 66), poly(pentamethylene decanediamide) (PA510), poly(pentamethylene dodecanediamide) (PA512), poly(ϵ -caprolactam/hexamethylene hexanediamide) (PA6/66), poly(ϵ -
30 caprolactam/hexamethylene decanediamide) (PA6/610), poly(ϵ -caprolactam/hexamethylene dodecanediamide) (PA6/612), poly(hexamethylene tridecanediamide) (PA613), poly(hexamethylene pentadecanediamide) (PA615), poly(ϵ -

caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide)
(PA6/66/610), poly(ϵ -caprolactam/hexamethylene hexanediamide/hexamethylene
dodecanediamide) (PA6/66/612), poly(ϵ -caprolactam/hexamethylene
hexanediamide/hexamethylene decanediamide/hexamethylene dodecanediamide)
5 (PA6/66/610/612), poly(2-methylpentamethylene hexanediamide/hexamethylene
hexanediamide/) (PA D6/66), poly(decamethylene decanediamide) (PA1010),
poly(decamethylene dodecanediamide) (PA1012), poly(11-aminoundecanamide)
(PA11), poly(12-aminododecanamide) (PA12), PA6,12, PA12,12 and their copolymers
and combinations.

10 Preferred group (II) polyamides (B) having a melting point of at least 280°C,
comprise a semiaromatic polyamide selected from the group poly(ϵ -
caprolactam/tetramethylene terephthalamide) (PA6/4T), poly(ϵ -
caprolactam/hexamethylene terephthalamide) (PA6/6T), poly(ϵ -
caprolactam/decamethylene terephthalamide) (PA6/10T), poly(ϵ -
15 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-
20 methylpentamethylene hexanediamide/hexamethylene hexanediamide/hexamethylene
terephthamide) (PA D6/66/6T), poly(hexamethylene terephthamide/2-
methylpentamethylene terephthamide) (PA 6TDT), poly(hexamethylene
hexanediamide/hexamethylene terephthamide) (PA66/6T), poly(hexamethylene
terephthamide/ hexamethylene isophthamide) (PA6T/6I), poly(hexamethylene
25 hexanediamide/hexamethylene terephthamide/ 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)
30 (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), and their copolymers and combinations.

The matrix and the surface polyamide resin composition described herein comprises a blend of (A) the one or more group (I) polyamides and (B) one or more polyamides selected from group (II) polyamides wherein the one or more group (I) polyamides are preferably selected from the group consisting of PA6, PA46 and PA66 and their combinations and copolymers, and wherein the one or more polyamides selected from group (II) polyamides are selected from the group consisting of PA66/6T, PA6TDT, PA6T/6I, and their combinations and copolymers.

The matrix and the surface polyamide resin composition described herein comprises a blend of (A) the one or more group (I) polyamides and (B) one or more polyamides selected from group (II) polyamides 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.

The surface resin composition described herein and/or the matrix 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.

The surface resin composition described herein and/or the matrix 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.

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.

5 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), flame retardants, nucleating agents, crystallization promoting agents and other
10 processing aids known in the polymer compounding art.

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.

15 Preferably, the surface resin compositions and the matrix resin compositions 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
20 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
25 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.

Depending on the end-use application, the composite structure according to the
30 present invention may have any shape. In a preferred embodiment, the composite structure 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.

In another aspect, the present invention relates to a process for making the composite structures described above and the composite structures obtained thereof. The process for making a composite structure having a surface comprises a step of i) impregnating the fibrous material with the matrix resin composition, wherein at least a portion of the surface of 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.

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.

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.

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 composite structure.

5 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
10 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 composite structure 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
15 pressurized zone.

 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
20 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 composite structure, the films melt and penetrate around the fibrous material as a polymer continuum surrounding the fibrous material.

25 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
30 comprising the matrix resin composition, the surface resin composition and the one or more fibrous materials.

Depending on the end-use application, the composite structure obtained under step i) may be shaped into a desired geometry or configuration, or used in sheet form. The process for making a composite structure according to the present invention may further comprise a step ii) of shaping the composite structure, said step arising after the impregnating step i). The step of shaping the composite structure obtained under step i) may be done by compression molding, stamping or any technique using heat and/or pressure. Preferably, pressure is applied by using a hydraulic molding press. During compression molding or stamping, the composite structure is preheated to a temperature above the melt temperature of the surface resin composition 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 the matrix resin composition.

The composite structures of the invention are particularly suited to overmoulding with an overmoulding resin composition that is selected from polyamide compositions comprising a blend of:

- (A) one or more fully aliphatic polyamides selected from group (I) polyamides, wherein the one or more fully aliphatic polyamides selected from group (I) polyamides have a melting point of less than 280°C; and
- (B) one or more semi-aromatic polyamides selected from group (II) polyamides having a melting point of at least 280°C.

The 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

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

Materials

The following materials were used for preparing examples (abbreviated as "E" in the tables) of composites structures according to the present invention and comparative examples (abbreviated as "C" in the tables) of composite structures.

Polyamide 1 (P1): a group II polyamide made of terephthalic acid and 1,6-hexamethylenediamine (HMD) and 2-methylpentamethylenediamine (MPMD) (HMD:MPMD = 50:50). P1 has a melting point of about 297°C to about 303°C. This semi-aromatic polyamide is called PA6T/DT and is commercially available from E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Polyamide 2 (P2): a group I polyamide made of adipic acid and 1,6-hexamethylenediamine with a weight average molecular weight of around 32000 Daltons. P2 has a melting point of about 260°C to about 265°C. This aliphatic

polyamide is called PA6,6 and is commercially available, for example, from E. I. du Pont de Nemours and Company.

Polyamide 3 (P3): a group I polyamide. This cyclic aliphatic polyamide is commercially available from Arizona Chemical under the Tradename Unirez® and has a melting point of 133 to 143 °C.

Polyamide 4 (P4): a group I polyamide terpolymer made of polyamides 6, 66, and 610. P4 has a melting point of about 255°C. This aliphatic polyamide is commercially available, from E. I. du Pont de Nemours and Company.

Polyamide 5 (P5): a group I polyamide made of ε-caprolactam. This aliphatic polyamide is called PA6 and has a melting point of about 220°C. P5 is commercially available, for example, from BASF corporation.

Polyamide 6 (P6): a group I polyamide, poly(tetramethylene hexanediamide. This aliphatic polyamide is called PA46 and is commercially available, for example, from DSM corporation. P6 has a melting point of about 275°C to about 290°C.

Preparation of films

The resin compositions used in the Examples (abbreviated as “E” in the Tables), and Comparative Examples (abbreviated as “C” in the Tables) were prepared by melting or melt-blending the ingredients in a twin-screw extruder. Upon exiting the extruder, the compositions listed in Tables 1 to 3 were cast into films by exiting the extruder through an adaptor and a film die at about 310°C and cast onto a casting drum oil-heated at about 120°C, then drawn in air and wound around a core at room temperature. The matrix and surface resin compositions were made into about 150 micron thick films. The thickness of the films was controlled by the rate of drawing.

Preparation of the composite structures

The composite structures E1 to E6, and C1 to C4 were made by laminating multiple layers of film of compositions shown in Tables 1 to 3, 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 to E5 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. The lamination sequence form the composite structures E6, C3, and C4 was as follows: 4 layers of film of surface resin composition, one layer of woven continuous glass fiber textile, 4 layers of film of matrix resin composition, one layer of woven continuous glass fiber textile, four layers of film of matrix resin composition, one layer of woven continuous glass fiber textile, and four layers of film of surface resin composition.

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 6x6" specimen of film and glass textile layers as described above was placed in the mold and heated to a temperature of about 340°C, held at the temperature for 2 minutes without pressure, then pressed at the 340°C temperature with the following pressures in the case of E1 to E4 and C1: about 4 bar for about 2 minutes, then with about 12 bar pressure for about 2 additional minutes, and then with about 23 bar pressure for about 2 additional minutes; in the case of E5 and C2 with about 6 bar for about 2 minutes, then with about 22 bar pressure for about 2 additional minutes, and then with about 45 bar pressure for about 2 additional minutes; and in the case of E6, C3, and C4 with about 4 bar for about 2 minutes, then with about 12 bar for about 2 additional minutes, and then with about 20 bar for about 2 additional minutes; the composite structures were subsequently cooled to ambient temperature. The composite structures had an overall thickness of about 1.5 mm in the case of E1 to E5, C1, and C2, and about 1.6 mm in the case of E6, C3, and C4 .

Multiaxial (Dynatup) Impact Total Energy Table 1

High Speed Puncture Multiaxial Impact test measures the total energy that a test specimen can absorb before breaking when struck by a load dropped onto the specimen at high speed. One such typical test speed used is 2.2 mm/sec, which is equal to 5 mph. This test can differentiate specimens based on their impact resistance.

The composite structures of Examples E1 to E4 and Comparative Example C1

obtained as described above were cut into about 3" (about 76 mm) by about 3" (about 76 mm) square test specimens using a MK-377 Tile Saw with a diamond edged blade and water as a lubricant. High Speed Puncture Multiaxial Impact (Dynatup Impact) was tested on the test specimens via the apparatus and geometry of ASTM method D 3763, which provides a testing platform onto which the specimen is clamped ("support ring") exposing a testing surface, and a "tup" which contains the impact head and the load cell. In the test, the specimens were tested with an 1 1/4 inch ring and a 1/2 " hemispherical tup and a 10,000 lb load. With the specimen clamped onto the testing platform, the tup was raised to the appropriate height and was released so it impacted at about the center of the specimen at 2.2 mm/sec. A load-deflection curve was produced and the total energy absorbed by the specimen before failure (before it was caused to break by the impact) was recorded. The results are shown in Table 1.

It is seen in Table 1 that the examples E1 to E4 exhibit higher total energy to failure than comparative example C1, demonstrating the higher impact resistance of the composite structure made of a Group I aliphatic polyamide (polyamide A) + a group II semiaromatic polyamide (polyamide B) in both the matrix resin composition and in the surface resin composition, than a composite structure made only of a group II semiaromatic polyamide (polyamide B) in both the matrix resin composition and in the surface resin composition.

Flexural Strength of Composite Structures of Tables 2 and 3

Composite structures of Examples E5 and E6, and Comparative Examples C2 to C4 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 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 and 3.

It is seen in Table 2 that the example E5 exhibits higher flexural strength than comparative example C2, demonstrating that the composite structure made of a Group I aliphatic polyamide (polyamide A) + a group II semiaromatic polyamide (polyamide B) in

both the matrix resin composition and in the surface resin composition is stronger (e.g. it can support more load before breaking) than a composite structure that has the Group I aliphatic polyamide (polyamide A) + the group II semiaromatic polyamide (polyamide B) only in the surface resin composition.

5 It is seen in Table 3 that Example E6 exhibits higher flexural strength than comparative examples C3 and C4, demonstrating that the composite structure made of a Group I aliphatic polyamide (polyamide A) + a group II semiaromatic polyamide (polyamide B) in both the matrix resin composition and in the surface resin composition is stronger than a composite structure made solely from either the Group I aliphatic
10 polyamide (polyamide A) or from the group II semiaromatic polyamide (polyamide B) in both the surface resin composition and the matrix resin composition.

Table 1

	E1	E2	E3	E4	C1
Matrix Resin Composition					
P1	90	90	90	90	100
P2	10				
P3		10			
P4			10		
P5				10	
Surface Resin Composition					
P1	90	90	90	90	100
P2	10				
P3		10			
P4			10		
P5				10	
Dynatup - ASTM D 3763 1 1/4 inch ring, 1/2 " tup, 2.2 mm/sec					
Total Energy (J)	15.7	14.2	14.6	15.7	12.7

Table 2

	E5	C2
Matrix Resin Composition		
P1	90	100
P2	10	
Surface Resin Composition		
P1	90	90
P2	10	10
ISO-178 3 Point Flex		
Flexural Strength at Break (Mpa), τ	392	294

Table 3

	E6	C3	C4
Matrix Resin Composition			
P6	50	100	
P1	50		100
Surface Resin Composition			
P6	50	100	
P1	50		100
ISO-178 3 Point Flex			
Flexural Strength at Break (Mpa)	612	408	495

CLAIMS

What is claimed is:

1. A composite structure 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, wherein the matrix polyamide resin composition and the surface polyamide resin composition are selected from polyamide compositions comprising a blend of:
 - (A) one or more fully aliphatic polyamides selected from group (I) polyamides;
 - and
 - (B) one or more semiaromatic polyamides selected from group (II) polyamides having a melting point of at least 280°C.
2. The composite structure of claim 1 wherein the one or more fully aliphatic polyamides selected from group (I) polyamides have a melting point of less than 280°C.
3. The composite structure according to claims 1 or 2, wherein the fibrous material is made of glass fibers, carbon fibers, aramid fibers, natural fibers or mixtures thereof.
4. The composite structure according to any of the preceding claims wherein the fibrous material is made of glass fibers.
5. The composite structure according to any of the preceding claims wherein the fibrous material is from 30 volume percent to 60 volume percent of the composite structure.
6. The composite structure according to any preceding claim, wherein the weight ratio of the one or more polyamides selected from group (I) polyamides (A) and the one or more polyamides selected from group (II) polyamides (B) (A:B) of the polyamide composition is between from about 99:1 to about 5:95.
7. The composite structure according to any of the preceding claims 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 composite structure according to any of the preceding claims wherein the one or more fully aliphatic polyamides selected from group (I) polyamides is selected from the group consisting of PA46, PA 6, PA 66; PA510, PA512, PA6/66, PA6/610,

PA6/612, PA613, PA615, PA6/66/610, PA6/66/612, PA6/66/610/612, PA D6/66, PA1010, PA1012, PA11, PA12, PA612, PA1212, and their copolymers and combinations.

- 5 9. The composite structure according to any of the preceding claims wherein the one or more fully semi-aromatic polyamides selected from group (II) polyamides is 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, and their copolymers and combinations.
- 10 10. The composite structure according to any of the preceding claims wherein the one or more fully aliphatic polyamides selected from group (I) polyamides is selected from the group consisting of PA66, PA46 and PA6 and wherein the one or more fully semi-aromatic polyamides selected from group (II) polyamides is selected from the group consisting of PA66/6T, PA6TDT, PA6I/6T, PA66/6I/6T, PA6T/6I and their copolymers and combinations thereof.
- 15 11. The composite structure according to any preceding claim in the form of a sheet structure.
- 20 12. The composite structure according to any preceding claim 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.
- 25 13. A process for making a composite structure having a surface, said process comprises a step of:
- 30 i) impregnating with a matrix resin composition a fibrous material selected from non-woven structures, textiles, fibrous battings and combinations thereof, said fibrous material being impregnated with a matrix resin composition, wherein at least a portion of the surface of the composite structure is made of a surface resin composition, and

wherein the matrix polyamide resin composition and the surface resin composition is selected from polyamide compositions comprising a blend of (A) one or more polyamides selected from group (I) polyamides; and (B) one or more polyamides selected from group (II) polyamides having a melting point of
5 at least 280°C.

14. The process according to claim 13 wherein the one or more fully aliphatic polyamides selected from group (I) polyamides have a melting point of less than 280°C.

15. The process according to claims 13 or 14 further comprising a step ii) of shaping the
10 composite structure, said step arising after step i).

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/057953

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B32B5/26	B32B27/12	B32B27/34	B32B17/02	B32B17/10
	C08J5/04	C08L77/00	C08L77/02	C08L77/04	C08L77/06
	C08L77/08	B29C70/50	B29C70/68	C08J5/18	

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)
B32B C08J C08L 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,P	WO 2010/132335 A1 (DU PONT [US]; KIRCHNER OLAF NORBERT [CH]; WAKEMAN MARTYN DOUGLAS [GB]) 18 November 2010 (2010-11-18) page 22, line 8 - line 14; claims 1-14; examples page 11, line 5 - page 12, line 12 page 4, line 5 - line 9 page 14, line 26 - line 31 -----	1-15
X	WO 2007/149300 A1 (DU PONT [US]; ELIA ANDRI E [US]; MESAROS DAVID V [US]; RENKEN ANDREAS) 27 December 2007 (2007-12-27) page 5, line 26 - line 31; claims 1-5,7-14,16-24; examples page 6, line 18 - page 7, line 19 page 3, line 13 - page 4, line 19 ----- -/--	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 28 March 2012	Date of mailing of the international search report 11/04/2012
--	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kanetakis, Ioannis
--	--

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/057953

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/066763 A1 (DU PONT [US]; TOPOULOS GEORGIOS [CH]) 5 June 2008 (2008-06-05) page 5, line 5 - line 29; claims 1-7,17; example 2 -----	1-9,11,12
X	US 2003/125440 A1 (TAMURA TUTOMU [JP] ET AL) 3 July 2003 (2003-07-03) paragraphs [0010], [0012], [0033], [0035], [0036], [0080] - [0082], [0088], [0089]; claims 1-3; examples 1-4,5-9; tables 1,3 -----	1-12
X	US 2007/117910 A1 (REXIN ORNULF [CH] ET AL) 24 May 2007 (2007-05-24) paragraphs [0048], [0061], [0110]; claims 1,2,6-8,10,13,14,16-18; examples; tables 1,2,4 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/057953

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010132335 A1	18-11-2010	CA 2757522 A1	18-11-2010
		CA 2757525 A1	18-11-2010
		EP 2430079 A1	21-03-2012
		EP 2430080 A1	21-03-2012
		US 2010291819 A1	18-11-2010
		US 2010291821 A1	18-11-2010
		WO 2010132335 A1	18-11-2010
		WO 2010132339 A1	18-11-2010

WO 2007149300 A1	27-12-2007	EP 2029358 A1	04-03-2009
		JP 2009539659 A	19-11-2009
		US 2008008879 A1	10-01-2008
		US 2011272854 A1	10-11-2011
		WO 2007149300 A1	27-12-2007

WO 2008066763 A1	05-06-2008	EP 2089475 A1	19-08-2009
		JP 2010510375 A	02-04-2010
		US 2009005502 A1	01-01-2009
		WO 2008066763 A1	05-06-2008

US 2003125440 A1	03-07-2003	US 2003125440 A1	03-07-2003
		US 2003125481 A1	03-07-2003

US 2007117910 A1	24-05-2007	AT 367420 T	15-08-2007
		AT 387476 T	15-03-2008
		BR PI0604794 A	04-09-2007
		CN 1974665 A	06-06-2007
		EP 1788026 A1	23-05-2007
		EP 1788029 A1	23-05-2007
		ES 2301129 T3	16-06-2008
		JP 2007138178 A	07-06-2007
		KR 20070053116 A	23-05-2007
		US 2007117910 A1	24-05-2007
