

(51) International Patent Classification:
B29C 45/00 (2006.01)(21) International Application Number:
PCT/US20 16/056060(22) International Filing Date:
7 October 2016 (07.10.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/239,461 5 October 2015 (09.10.2015) US

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(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

[Continued on next page]

(54) Title: OVERMOLDED CARBON FIBER STRUCTURES WITH TAILORED VOID CONTENT AND USES THEREOF

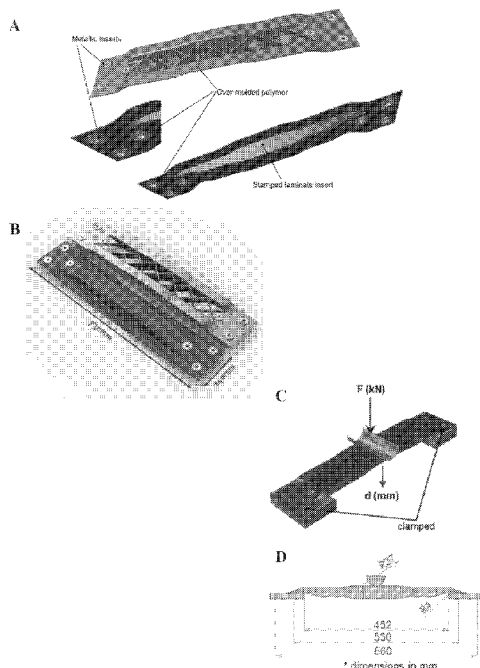


Figure 1

(57) Abstract: The present invention relates to novel carbon composites presenting very high directional properties in the UD carbon layer direction greater with improved failure mode as compared to full carbon fiber and standard composite fibers. The invention further relates to a process of preparation of such carbon composites using a novel overmolding thermoplastic resin composition, to such overmolding thermoplastic resin composition, to methods of preparation thereof and to articles made from such carbon composites.

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OVERMOLDED CARBON FIBER STRUCTURES WITH TAILORED VOID CONTENT AND USES THEREOF

Field of the Invention

5 This invention relates to carbon fiber (CF) composites for use in composite structures, for instance for use in automotive, industrial, consumer, or aerospace applications.

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.

In highly demanding applications, such as for example structural parts in automotive and aerospace applications, composite materials are desired due to a unique
15 combination of light weight, high strength and temperature resistance.

However, glass fiber composites have been found to be limited in stiffness and weight specific stiffness compared with metallic materials such as steel and aluminum. Therefore, in order to achieve the needed part stiffness, when using glass fiber composite, increases in the design space are needed, which
20 unfortunately are often not available, depending on the nature of the part.

On the other hand, carbon composites have excellent weight specific properties due to the high fiber modulus and can be used to replace metal with significant weight savings but use of carbon fiber composites for high volume applications, such as the automotive and consumer electronic sectors, requires a focus upon cost
25 effectiveness.

High performance composite structures can be obtained using thermosetting resins or thermoplastic resins as the polymer matrix. Beyond the cost of the carbon fiber material used in the final part, two issues are important in reducing the production cost of carbon fiber composites.

The first issue is fast part-making cycle times. Thermoplastic-based composite structures present several advantages over thermoset-based composite structures including the ability to be post-formed or reprocessed by the application of heat and pressure. The part-making cycle time is limited by heat transfer in a stamping or injection molding operation where molten thermoplastic materials are molded in cycle times typically below 60s. Additionally, less time is needed to make the thermoplastic composite structures than for thermoset composites since they do not require time for the cross-linking reaction to occur during the curing step, which requires additional processing lines for higher manufacturing volumes, and they have increased potential for recycling.

The second issue is to reduce the ratio of starting material to material used in the final molded part with a ratio of 1:1 being ideal. When textile based carbon fiber architectures are used, such as weaves or multi-axial fabrics, and when the undraped template from the final part to the starting piece of material is not rectilinear but rather curvilinear, waste occurs which is costly even if recycled into different lower performing material derivatives.

Hence a thermoplastic carbon fiber composite system is desired for fast cycle times and high manufacturing volumes while also limiting the waste or trim of broad goods textiles.

A further requirement in many structures found in many industries for example the automotive industry, is for the structure made from carbon fiber thermoplastic to not only be stiff during normal use, but also to absorb significant amounts of energy during a crash or failure incident thus protecting either other parts of the structure or the occupants or merchandise associated.

It is well known that carbon fiber composites can be used to absorb significant amounts of energy in crash, especially in axial crush where delamination of the carbon fibers from the matrix resin and large interfacial areas involved are able to absorb large amounts of energy.

Applications used in crash situations are often required to follow a desired force displacement curve such that intrusion is limited while avoiding a high force peak

and catastrophic failure of the component. Rather, a controlled response is required such that the molded part builds resistance to the applied force to a desired force peak at a given intrusion but without major failure, which is then followed by progressive damage and a significant increase in energy absorption.

- 5 It has been found that fully impregnated carbon fiber nylon beams over-molded with standard glass fiber nylon resins, as an example of structures in automotive, consumer electronic and other such parts, have been seen to build load during test until catastrophic failure occurs.

10 A well-known assumption is that it is desirable in carbon fiber structures to have a low void content, preferably below 2%, for high stiffness and good overall mechanical properties. To achieve this it is known to use fully impregnated carbon tape with voids of less than 2% as a starting material for the structure, or to use partially impregnated carbon tape that is then pre-consolidated in a second step after laydown to reduce the void content to about 2% or less. Both of these
15 processes are quite costly.

Therefore, the challenge is to provide structures with comparable stiffness to that of fully impregnated carbon fiber nylon beams, allowing them to achieve a similar peak load, but at lower costs, and in addition to improve energy absorption properties. Higher energy absorption properties are advantageous in order to maintain high
20 levels of force for greater displacements, in particular to enable load triggering and tailored rip-through in the part.

Summary of the Invention

It is an aim of this invention to provide a carbon fiber based composite material that has a high stiffness yet has a high energy absorption ability and strain to rupture.

- 25 It is another aim of the invention to provide an article made from a carbon fiber based composite material that has a high energy absorption ability and strain to rupture.

It is advantageous to provide a carbon fiber based composite material, and articles made therefrom, that are economical to produce.

It is advantageous to provide a carbon fiber based composite material, and articles made therefrom, with reduced waste or trim.

It is advantageous to provide a carbon fiber based composite material, and articles made therefrom, that have consistent and reliable properties.

- 5 Objects of this invention have been achieved by providing the process according to claim 1, the composite material according to claim 22, the overmolding thermoplastic resin according to claim 35 and the process of preparation thereof according to claim 20.

Disclosed herein is a process for preparing a carbon fiber composite structure
10 comprising:

- (i) providing at least two layers of unidirectional (UD) carbon fiber tape, said UD carbon fiber tape comprising unidirectional carbon fibers impregnated in a thermoplastic resin, the fibre to resin content being in a range from 50% to 70% with an initial void content before stacking higher than 2%,
- 15 (ii) stacking said at least two layers of UD carbon fiber tape in a cross ply arrangement with respect to each other,
- (iii) applying heat at a temperature adapted to melt the thermoplastic resin;
- (iv) cooling under pressure the heated stacked layers to harden the composite structure,
- 20 wherein the heated stacked layers are overmolded with a thermoplastic resin and fiber composition, said thermoplastic resin and fiber composition comprising a glass fibrous material, a carbon fibrous material, and a polyamide resin.

Experimental data supports that, in composites of the invention where the unidirectional CF bundles are already pre-impregnated with the thermoplastic resin
25 in the form of UD CF tape, where the UD CF tape layers are stacked in a cross-ply arrangement according to the invention with respect to each other, and where the resulting stacking of carbon fiber layers has a void content of more than 2%, the overmolding of such a stacking with a resin of the invention surprisingly leads to a composite presenting not only stiffness and peak load comparable to those of pre-
30 consolidated carbon fiber material but also an importantly increased energy to peak

load and energy to major failure as compared to pre-consolidated carbon fiber material.

The invention thus relates to the unexpected findings of novel carbon composites with excellent strain to complete failure and retention of load at strain levels well
5 above the maximum force peak. Such composites with those improved properties have practical applications where high stiffness in addition to high energy absorption are needed such as crash protection in automotive and other applications. It has been unexpectedly found that the use of carbon fiber unidirectional tapes (UD carbon fiber tape), formed of long or continuous strands of
10 unidirectional carbon fiber impregnated with a thermoplastic resin (e.g. in a continuous pultrusion or other such tape production process including single or double sided melt coating, wire coating or encapsulation of fiber by resin, reactive thermoplastic impregnation, and powder impregnation (with the objective being to prefabricate an impregnated UD tape of carbon fiber and polyamide)) in the forming
15 of a carbon fiber composite material, wherein the void content is of more than 2%, in conjunction with an over-molding resin of the invention modified for efficient healing during the overmolding step with the thermoplastic resin of the outside pre-impregnated carbon layers leads to increased energy absorption and equivalent stiffness in comparison to the use of pre-impregnated carbon fiber layers with a
20 lower void content as a starting material in the stacking and heat forming process or other over-molding resin. The stacking of carbon fiber layers to form laminates and the heat forming process after stacking the layers together can use standard procedures (e.g. using laminators, double belt press, continuous molding etc.).

The properties of the composite of the invention are particularly unexpected since it
25 is composed of UD tapes with void contents after tape making of higher than 2%, such as for example a void content of about 4 to 12% or of about 6 to 8%, while still presenting high stiffness and good overall mechanical properties. These properties allow the use of UD tapes that are less costly to produce and suitable for being directly stamp-formed into a shell structure using a heating device, a press, and a
30 shaping tool without the need to use fully impregnated tape or an additional pre-consolidation step.

The stiffness and peak load equivalent to low void content carbon fiber material and the gain in performance at peak force shown by the carbon fiber composite of the invention, while providing a composite at lower cost than with standard carbon fibers, is surprising.

- 5 Further objects and advantageous aspects of the invention will be apparent from the claims, and from the following detailed description and accompanying figures.

Brief Description of the drawings

Figure 1 illustrates beams (A & B) molded from a flat sheet of composite material according to embodiments of the invention and of comparative material which were
10 then over-molded with a short fiber filled resin and the test on mechanical properties (flexural testing bed) of a beam made of a laminate sheet of a composite of the invention as compared to a laminate sheet made of a comparative composite as described in Example 1 (C & D). Specific geometry of the beam prepared with a composite of the invention is further illustrated (E & F & G). The generic beam
15 structure has a length of 730 mm (B), an upper rib thickness of 2 mm, a width of 140 mm (B), a laminate shell thickness of 1.5 mm that is over-molded with 1.5 mm of over-molding polymer (G), with a height of 15 mm, 30 mm, and 50 mm at the different steps (F). The beam has a width to depth to length ratio of 9.3, 4.7, and 2.8 as examples of such structures. Figure 1 also depicts the flexural testing details
20 including span and loading radius (C & D).

Figure 2 illustrates the comparative process which has been used for comparative examples C1 and C2 with a pre-consolidation step. **A**: Provision of a UD tape as made; **B**: UD tape X-plying and spot welding; **C**: Pre-consolidation process of X-plyed tapes; **D**: pre-consolidated X-plyed UD tape; **E**: Stamped X-plyed UD tape; **F**:
25 Over-molded stamped X-plyed UD tape.

Figure 3 illustrates the process of the invention which has been used for the examples without pre-consolidation step. **A**: Provision of a UD tape as made; **B**: UD tape X-plying and spot welding; **C**: Stamped X-plyed UD tape; **D**: Over-molded, stamped X-plyed UD tape.

Figure 4 is a schematic representation of the comparative process which has been used for comparative examples C1 and C2 with a pre-consolidation step (A) and an Example of conditions for a process of the invention (without pre-consolidation step) (B).

5 **Figure 5** is a schematic representation of the conditions used for comparative process used for preparing comparative examples C1 and C2 with a pre-consolidation step (left) and of the process of the invention (without pre-consolidation step) (right).

Figure 6 represents results obtained under Example 1 for a stacking of 10 layers
10 having a thickness of 2 mm and a stacking arrangement of [0/0/90/0/0]_s ; where the preheat profile to 300°C is shown in (A), stamping tool temperature = 140°C, Time at pressure = 38s at a pressure of 40 bar. **A**: preheat conditions and number of steps (each under PID pyrometer control) for B,C,D and void contents **B**: micrograph of the stamped composite part without pre-consolidation **C**: micrograph
15 of the preconsolidated UD tape without stamping **D**: micrograph of the preconsolidated UD tape with stamping.

Figure 7 represents micrograph results and void contents obtained under Example 1 where X-ply UD tape has been stamp-formed either with or without the prior pre-consolidation stage and the resulting stamping has then been over-molded with a
20 comparative resin and the resin composition of the invention **A**: Structure of X-ply UD tape that has been stamp-formed, without prior preconsolidation, and then over-injected with over-molding resin 1; **B**: Structure of X-ply UD tape that has been pre-consolidated into a flat sheet and then stamp-formed, followed by over-injection with over-molding resin 1; **C**: Structure of X-ply UD tape that has been pre-
25 consolidated into a flat sheet and then stamp-formed, followed by over-injection with over-molding resin 2; **D**: Structure of X-ply UD tape that has been stamp-formed, without prior preconsolidation, and then over-injected with over-molding resin 2.

Figure 8 represents micrograph results and void contents results obtained under Example 1 showing the overall structure, a first detailed zoom of an exemplary
30 section and a second further detailed zoom showing the agglomerations of fiber and local resin rich areas and where voids are located in the structure; where X-ply

UD tape has been stamp-formed either with (A) or without (B) the prior pre-consolidation stage and the resulting stamping has then been over-molded with the resin composition of the invention; **A**: Structure of X-ply UD tape that has been stamp-formed, with prior preconsolidation, and then over-injected with over-molding resin 2 where flatter and wider agglomerations of UD fibers are seen with smaller resin rich areas and an overall more homogeneous microstructure; **B**: Structure of X-ply UD tape without prior pre-consolidation that has been stamp-formed, followed by over-injection with over-molding resin 2 where agglomerations of UD fibers contain voids within the center of the agglomeration and the shape of the agglomeration is more square like than A, and where the UD fiber agglomerations are spaced with wider resin rich areas than A and hence have overall a less homogeneous microstructure.

Figure 9 shows micrograph results and void contents results of the UD tape made by pultrusion before any subsequent thermal processes stages (hence before any pre-consolidation, stamping, or over-molding operation as detailed elsewhere in this application); and where the agglomerations of UD fibers contain voids within the center of the agglomeration and the shape of the agglomeration is more square or circular than flat and rectangular like than Figure 8A, and where the as made void content is 6 to 8% across the whole of the tape width (ROI is region of interest).

Figure 10 shows photographs of the exemplary beam structure made of X-ply UD tape that has been stamp-formed (with or without prior preconsolidation) and then over-molded with an over-molding resin and where said beam has been tested in 3 point flexural testing according to Figure 1 C and D with the photograph showing the failure mode of the beam and of the X-ply UD tape; **A**: X-ply UD tape that has been stamp-formed, without prior preconsolidation, and then over-injected with over-molding resin 1 (OM1) and where the UD fibers have fractured with a strand like behavior corresponding to the carbon fiber agglomerations seen in Figure 8B; **B**: X-ply UD tape that has been pre-consolidated into a flat sheet and then stamp-formed, followed by over-injection with over-molding resin 1 (OM1) where the X-ply UD tape has failed in shear without a strand like fracture due to the more homogeneous microstructure as shown in Figure 8A; **C**: X-ply UD tape that has been stamp-formed, without prior preconsolidation, and then over-injected with

over-molding resin 2 (OM2) and where the UD fibers have fractured with a strand like behavior corresponding to the carbon fiber agglomerations seen in Figure 8 B and where the combination of OM2 and no preconsolidation enables rip-through of the three load introduction points; **D**: X-ply UD tape that has been pre-consolidated into a flat sheet and then stamp-formed, followed by over-injection with over-molding resin 2 where the X-ply UD tape has failed in shear without a strand like fracture due to the more homogeneous microstructure as shown in Figure 8 A.

Detailed description of embodiments of the invention

For purposes herein, the term "fiber" is defined as 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 or oval shaped.

Fibrous layer basis weight refers to the weight per unit area of the dry fibrous layer. The filament count in a fiber tow is useful in defining a carbon fiber tow size. Common sizes include 12,000 (12k) filaments per tow, or 50,000 (50k) filaments per tow.

As used herein, the term resin pre-impregnated unidirectional carbon tape is *per se* well known to the skilled person and can be made using melt pultrusion, powder or film impregnation, reactive impregnation, or many other methods. The resin is spread throughout the cross section of the tape rather than an agglomeration or coating at the outside or surrounding the carbon fibers. Any voids present in the structure are randomly distributed rather than a preferential area which has an intended lack of resin or impregnation.

As used herein, the term "impregnated" means the resin composition flows into the cavities and void spaces of the fibrous material. For example, the quality and level of impregnation can be assessed and measured by determining the void content.

Void content can be measured as described in the Examples.

In the preparation of the UD carbon fiber used in the invention, the resin can be applied to the UD carbon fiber for the pre-impregnation process in a form of a conventional resin composition such as a PA66 or a PA66/6 blend (75:25 blend

ratio) and the resin composition can be applied to the fibrous materials by conventional means such as for example powder coating, reactive thermoplastic impregnation, film lamination, extrusion coating or a combination of two or more thereof, provided that the resin composition is applied on at least a portion of the surface of the composite structure. In the case of extrusion coating, polymer may be applied using a pultrusion die where resin is applied on both sides of the fibrous material and where impregnation pins are optionally used, optionally an internal converging die may also be used; alternatively a single sided coating carriage can be used where molten resin is extruded through a die onto the fibrous material, preferably in spread form, where the fibrous material is supported by a curved surface to drive the resin into the fibrous material. A round or flattened wire coating die may also be used. In case of a powder coating process, a polymer powder which has been obtained by conventional grinding methods is applied to the UD carbon fiber. The powder may be applied onto the UD carbon fiber by scattering, sprinkling, spraying, thermal or flame spraying, extruding, printing, or fluidized bed coating methods. Multiple powder coating layers can be applied to the fibrous material. Optionally, the powder coating process may further comprise a step which consists in a post sintering step of the powder on the fibrous material. Subsequently, thermopressing is performed on the powder coated fibrous materials, with an optional preheating of the powder coated fibrous materials outside of the pressurized zone. Rheology modifiers, heat stabilizer and black pigmentation can be used as adjuncts to the thermoplastic resins used for preparing the UD CF layer. Other polymers suitable for the preparation of the UD CF layers used in the context of the invention include, without limitation, polypropylene, thermoplastic polyesters, Polyphenylene sulfide, and different grades and blends of nylons as described below.

Polyamide resins suitable in the manufacture of the UD CF layers used in the context of the invention 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. The polyamide resins are selected from fully aliphatic polyamide resins, semi-aromatic polyamide resins and mixtures thereof. The term "semi-aromatic" describes polyamide resins that comprise at least some aromatic carboxylic acid monomer(s) and aliphatic

diamine monomer(s), in comparison with "fully aliphatic" which describes polyamide resins comprising aliphatic carboxylic acid monomer(s) and aliphatic diamine monomer(s).

5 Fully aliphatic polyamide resins are formed from aliphatic and alicyclic monomers such as diamines, dicarboxylic acids, lactams, aminocarboxylic acids, and their reactive equivalents. A suitable aminocarboxylic acid includes 11-aminoDodecanedioic acid. In the context of this invention, the term "fully aliphatic polyamide resin" refers to copolymers derived from two or more such monomers and blends of two or more fully aliphatic polyamide resins. Linear, branched, and
10 cyclic monomers may be used. Star polymers may also be used.

Carboxylic acid monomers useful in the preparation of fully aliphatic polyamide resins include, but are not limited to, 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). Useful diamines
15 include those 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 and/or mixtures thereof. Suitable examples of fully aliphatic polyamide resins include PA6;
20 PA6,6; PA4,6; PA6,10; PA6,12; PA6,14; PA6,13; PA6,15; PA6,16; PA11; PA12; PA10; PA9,12; PA9,13; PA9,14; PA9,15; PA6,16; PA9,36; PA10,10; PA10,12; PA10,13; PA10,14; PA12,10; PA12,12; PA12,13; PA12,14 and copolymers and blends of the same.

Semi-aromatic polyamide resins are homopolymers, copolymers, terpolymers, or
25 higher polymers wherein at least a portion of the acid monomers are selected from one or more aromatic carboxylic acids. The one or more aromatic carboxylic acids can be terephthalic acid or mixtures of terephthalic acid and one or more other carboxylic acids, like isophthalic acid, substituted phthalic acid such as for example 2-methylterephthalic acid and unsubstituted or substituted isomers of
30 naphthalenedicarboxylic acid, wherein the carboxylic acid component preferably contains at least 55 mole percent of terephthalic acid (the mole percent 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 preferably contains at least 55 mole percent of terephthalic acid. Furthermore, the one or more carboxylic acids can be

5 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 semi-aromatic polyamide resin contains at least 25 mole percent of terephthalic acid. Semi-

10 aromatic polyamide resins comprise one or more diamines that can be chosen among diamines having four or more carbon atoms, including, but not limited to tetramethylene diamine, hexamethylene diamine, octamethylene diamine, nonamethylene diamine, decamethylene diamine, 2-methylpentamethylene diamine, 2-ethyltetramethylene diamine, 2-methyloctamethylene diamine;

15 trimethylhexamethylene diamine, bis(p-aminocyclohexyl)methane; m-xylylene diamine; p-xylylene diamine and/or mixtures thereof. Suitable examples of semi-aromatic polyamide resins include poly(hexamethylene terephthalamide) (polyamide 6,T), poly(nonamethylene terephthalamide) (polyamide 9,T), poly (decamethylene terephthalamide) (polyamide 10,T), poly(dodecamethylene terephthalamide)

20 (polyamide 12,T), hexamethylene adipamide/hexamethylene terephthalamide copolyamide (polyamide 6,T/6,6), hexamethylene terephthalamide/hexamethylene isophthalamide (6,T/6,I), poly(m-xylylene adipamide) (polyamide MXD,6), hexamethylene adipamide/hexamethylene terephthalamide copolyamide (polyamide 6,T/6,6), hexamethylene terephthalamide/2-methylpentamethylene terephthalamide

25 copolyamide (polyamide 6,T/D,T), hexamethylene adipamide/hexamethylene terephthalamide/ hexamethylene isophthalamide copolyamide (polyamide 6,6/6,T/6, 1); poly (caprolactam-hexamethylene terephthalamide) (polyamide 6/6,T) and copolymers and blends of the same, in particular PA6,T; PA6,T/6,6, PA6,T/6,I; PAMXD,6; PA6,T/D,T and copolymers and blends of the same.

30 According to a particular aspect, the fiber to resin mass fraction content in the UD tape used for the preparation of the stacking is in a range from 50% to 70% fiber with an initial void content before stacking higher than 2%. The preparation of the

UD tapes for obtaining such a void content is usually performed by known methods when no preconsolidation step is applied.

As used herein, the term "fibrous material" means a material that is any suitable mat, fabric, or web form known to those skilled in the art. The fibers or strands used to form the fibrous material are interconnected (i.e. at least one fiber or strand is touching at least one other fiber or strand to form a continuous material) or touching each other so that a continuous mat, web or similar structure is formed. The fibrous material may be made up of glass or carbon fibers, mineral fibers such as basalt, Kevlar or aramid, or mixtures of these. Carbon fibers give a particularly good result.

The fibrous material comprising carbon fibers which are used in the thermoplastic resin and fiber composition of the invention, encompass aligned fibrous structures. Examples of aligned fibrous structures include without limitation unidirectional (UD) fiber strands, bidirectional strands, multidirectional strands, multi-axial textiles. Textiles can be selected from woven forms, knits, braids and combinations thereof. The aligned fiber structure may also incorporate elements of non-woven structures (e.g. mats, felts, fabrics, webs, fibrous battings), and combinations thereof.

According to an advantageous embodiment, the stack of fibrous layers prior to the overmolding step comprises between 2 to 26 layers of pre-impregnated UD carbon fiber tape, such as for examples 2 to 20, 2 to 10, 2 to 8. According to exemplary embodiment, a stack of 8 layers of UD carbon tape is used for forming a part, such stacking leading to a thickness of about 1.5 to 1.6 mm which is the thickness of material needed to fill the molding cavity of this part.

In an embodiment, the initial void content of the unidirectional (UD) carbon fiber tape before stacking comprised between about 4 to 12% such as about 6 to 8% (41).

A variety of stacking sequences (ply angles) can be selected according to the needs of the part (42), such as uni-directional stacks, balanced and symmetric stacks with orientations such as balanced biaxial, directionally biased biaxial, quasi-isotropic, and directionally isotropic with off-axis UD plies; such as for example: [90/0/0/0]s, [45/0/-45/0]s, [90/0/90/0]s, [90/45/0/-45]s, and where the 45 degree ply can be replaced by an arbitrary angle such as needed by the part in question. According to

a particular aspect, the angle between fibers of one of two cross ply stacked layers with respect to the other is between 0 and 90°.

According to a particular aspect, an optional step of spot welding the UD tapes within the stacked layers (42) can be carried out by a variety of means for example
5 ultrasonic spot welding, vibration welding, and thermal spot welding since bonding the layers of UD tape together before heating (iii) (optionally with pre-consolidation after spot welding and before heating)) offers increased ease of material handling during the molding operations. The welds formed between two or more plies have the aim of creating a stack of UD plies that can be manipulated manually or via
10 automated means when the stack is below the polymer melt temperature without loss of ply orientations or pieces of UD tape, which are still evident as discrete plies in that re-melt of the whole structure has not occurred to form a homogeneous mass where all plies are merged into a coalesced whole.

According to a further particular embodiment, the stacked UD tape layers (42) are
15 heated above the UD tape polymer melt temperature (43) under step (iii) after which pressure is applied to bond the layers of UD carbon fiber tape into a homogeneous structure followed by crystallization and cooling under pressure (44) and to shape the form of the composite before over-injection molding. The cooled part may optionally be trimmed (46) under step (iv) and prior to the over-molding operation
20 the part is warmed (47) to aid bonding of the said over-molding thermoplastic resin and fiber composition (48a) and cooling again under pressure (iv').

A description of a stamp-forming process (44) is given in Example 1. Typical heating temperatures for a stacking of layers of UD carbon fiber tape comprising PA66-6 as an impregnation resin are 290 to 300°C (heat treatment), and the
25 molding tool used in the stamping press is heated at 120-160°C. The heated material must be transferred quickly and ideally in less than 10s such that it is still sufficiently above the melt temperature when pressure is applied in the molding tool for consolidation to occur across the part. Typical pressures applied during part forming to the layered UD structure are 20 to 200 bars, and preferably 40-100 bars.

According to a particular embodiment, the void content of the stacked layers (42) is advantageously kept higher than 2% before the stamp-forming step (44), typically between about 4 to 8 %.

Alternatively, the stacking of layers of UD carbon fiber tape can be heated above melt temperature using an induction heated tool located inside a molding press where only the surface of the tool is heated, allowing pressure to be applied while molten and then the tool to be cooled while pressure is maintained followed by removal of the shaped UD preform. The stamped structured is then re-heated (47) before subjecting to the overmolding step (48a) with the overmolding resin composition according to the invention.

According to a particular aspect, the heated stacked layers (43) may be overmolded under pressure (e.g. by over compression or over injection) with said thermoplastic resin and fiber composition, either before the 1 step process (48b) cooling step (iv) (45b), or in a 2 step process (48a) after re-heating the hardened composite structure obtained under step (v).

According to a particular aspect, the pressure applied to the stacked layers during the cooling step is of about 10 to about 150 bars.

According to a particular embodiment, the over-injection of the overmolding thermoplastic resin and fiber composition is carried out at a temperature higher than the melting temperature of the over-molding thermoplastic resin composition, typically at 290 to 300°C for PA66, which is adjusted according to the specific polyamide grade in use, as is well known in the art for injection molding polyamide resins and is controlled by the injection molding machine in use, supplied for example by the Engel company, and where the injection molding tool temperature is maintained at a temperature according to the specific polymer grade and is adjusted as part of setting up the specific component being molded, for example at 100 to 120°C for PA66.

More particularly, in the case of a process of the invention where overmolding is carried out after a re-heating step (47) of the hardened composite structure obtained under step (iv), the hardened composite is heated just below its melting

point (47), for example 180-230°C for PA66-6 and then rapidly transferred in an over-molding tool located in a molding press where the over-molding thermoplastic resin and fiber composition of the invention is applied (48a) under pressure to the warmed stacked UD layers (over-molding process).

- 5 According to an advantageous embodiment, the steps of applying heat and pressure to the stacked layers (step (iii)) and over-injecting the thermoplastic resin and fiber composition of the invention onto the heated stacked layers are part of a single thermal forming step where the resin from the UD carbon fiber layers is melted throughout the stacked layers (e.g. in an oven directly in an over-molding
10 tool) and the molten thermoplastic resin and fiber composition of the invention is over-injected on the heated stacked layers: the heated UD carbon fiber tapes layers are pressed together by the pressure of the over-molding resin as it is directly injected onto the stamping, thereby eliminating multiple heating stages and the cost of the associated equipment, specifically eliminating a stamp-forming stage (44).
- 15 According to an alternative aspect for achieving a single thermal forming step as described above, thermal treatment step can be carried-out by pre-heating the UD carbon fiber tape stacked layers in an oven above melt temperature and, in parallel, an extruder is used to compound dry fiber and matrix resin components of the overmolding resin and fiber composition of the invention or pellets of pre-
20 compounded fiber and resin components of the overmolding resin and fiber composition of the invention which are then extruded using a die into a molten mass or charge. The molten mass is then transported with the heated UD carbon fiber tape stacked layers, preferably by robot, into a steel molding tool mounted in a vertically acting hydraulic press, for example as exemplified by equipment supplied
25 by the company Dieffenbacher which is well known in the art, where the UD carbon fiber tape stacked layers are pressed together and where over-molding of the UD occurs (48b) and the part is cooled under pressure (45b).

According to a particular embodiment, the void content of the stacked layers (42) is advantageously kept higher than 2% before the overmolding step (48b), typically
30 between about 4 to 8 % for example from about 6 to about 8%.

According to a further particular aspect, in the process for preparing the composite structure of the present invention, the overmolding step is conducted during a period of time which is a function of the thickness of the over-molding resin, typically during a period of less than 2 minutes.

- 5 According to a further particular aspect, in the process of the present invention, the overmolding step is conducted during a period of time of less than 2 minutes at tool temperatures from about 120 to about 160°C and pressures above between 200 and 1000 bars.

- 10 According to a particular aspect, the overmolded stacked layers (45b and 45a2) are cooled under pressure to harden the composite structure, where an in-mold cooling time is typically of 7-10s per mm of over-mold thickness, and preferably less than 1 minute part cycle time for use in mass production, with a molding tool temperature from 100°C to about 160°C, for example between 100 and 120°C and with injection pressures of 500 bars needed for suitable packing of nylon materials as is well
15 known in the art.

According to one aspect, the UD layers of the composite structure can be used as a material that covers the bulk of the component for an over-all stiffening effect, or for use as strips or local patches where stiffening is needed only in local areas.

- 20 According to another further particular aspect, is provided a composite structure obtainable by a process according to the invention.

In an embodiment, the composite structure may comprise a plurality of UD carbon fiber tape layers.

- 25 In an advantageous embodiment, the composite structure may comprise between 2 to 26 layers, such as for examples 2 to 20, 2 to 10, 2 to 8 of UD carbon fiber tape.

In an advantageous embodiment, the composite structure may comprise between 4 to 8 layers of UD carbon fiber tape.

In an embodiment, a composite material structure according to the invention has a resin to UD carbon fiber content in a range from 0.3 to 0.5 wt%.

In an embodiment, is provided a composite material structure according to the invention wherein the overmolded thermoplastic resin and fiber composition is injection overmolded.

5 In another embodiment, is provided a composite material structure according to the preceding claim wherein the resin composition has a melting temperature comprised between about 220°C and 280°C and more particularly 250-275°C.

In an embodiment, each layer of resin impregnated unidirectional (UD) carbon fiber tape in a composite of the invention or used in a method of the invention has a basis weight greater than 100 g/m² and less than 1000 g/m², in particular between
10 200 g/m² and 500 g/m².

According to another further particular aspect, the resin composition of the invention used for the UD tape (Table 1) is different from the over-molding resin and is selected to have a melt viscosity at 290°C of between 10 Pa.s and 300Pa.s, and more preferably 10 to 75 Pa.s measured at 290°C and over a shear rate range of
15 40 to 5000 reciprocal seconds and also applicable to shear rates of 10-40 reciprocal seconds. Rheology of the blends was measured using a Kayeness capillary rheometer from Dynisco. Dried pellets of samples were melted in the rheometer barrel at the test temperature. A 0.762 mm diameter; 15.24mm long die was used as the capillary. The piston velocity driving the capillary flow was varied during the
20 measurement and a force transducer was used to compute apparent melt viscosity as a function of shear-rate.

In an embodiment of the invention, the overmolding thermoplastic resin composition of the invention comprises between 25 wt% and 70 wt % (typically between 35 and 70% or between 30 and 60%, such as from 30 to 50% %wt or such as from 30 to
25 45% wt) of a blend of polyamide resin PA 66/PA6 wherein the wt ratio between the two polyamides comprises between 40 wt% and 100 wt ratio of PA66. According to a further embodiment, the overmolding thermoplastic resin composition of the invention comprises 42% of a blend of a polyamide resin PA 66/PA6 (60:40).

According to a particular embodiment, the overmolding thermoplastic resin
30 composition is a resin composition comprising a composition of Table 2.

The fibrous material used in the composition of the overmolding thermoplastic resin composition is preferably discontinuous, however in embodiments of the invention the glass and/or carbon fiber material used may also be a woven or non-woven material.

- 5 The amount of overmolding thermoplastic resin provided in the overmolding step may advantageously be selected either for the full part, or by region over the part where different regions have different amounts or thicknesses of over-mold resin on or surrounding the UD tape, for example from no over-molding resin applied locally, to a heavy and thick layer of over-molding resin on both sides of the UD tape, such
10 that in the region of the composite structure considered or over the whole part, the over-molding resin has a weight fraction ratio to total part weight (UD carbon tape plus over-molding resin) of between 0% where the overmolding resin composition is applied to local areas only to 100% where a local over-molding feature is comprised fully of over-molding resin and UD carbon tape is absent in that local area of the
15 part where the UD tape reinforcement is not needed.

In a particular embodiment, the average part based composite structure to over-molding resin weight based ratios is 20-80%. In the exemplary beam structure, the mass ratio of over-mold resin to composite structure resides between 2:1 and 2.6:1, which is a function of the over-molding tool cavity in relation to the thickness of the
20 UD tape composite structure.

The amount of fibrous material made of glass fibers provided in the overmolding thermoplastic resin composition of the invention is preferably selected such that the mass fraction of glass to total mass fraction in the over-molded polymer is between 25 and 70%, and more preferably between 25 and 40 wt %, with a further specific
25 embodiment shown in Table 2.

In an embodiment, the carbon fiber content provided in the overmolding thermoplastic resin composition of the invention is preferably selected such that the mass fraction of carbon to total mass fraction in the over-molded polymer is between 10 and 70% and more preferably between 10 and 25 wt %, with a further
30 specific embodiment shown in Table 2.

The polyamide resin composition may further comprise one or more common additives, including, without limitation, ultraviolet light stabilizers, flame retardant agents, flow enhancing additives, lubricants, antistatic agents, coloring agents (including dyes, pigments, carbon black, and the like), nucleating agents,
5 crystallization promoting agents and other processing aids or mixtures thereof known in the polymer compounding art.

Fillers, modifiers and other ingredients described above may be present 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
10 nm.

Preferably, any additives used in the polyamide resin composition are well-dispersed within the polyamide resin. Any melt-mixing method may be used to combine the polyamide resins and additives of the present invention. For example,
15 the polyamide resins and additives 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 polyamide resins and additional additives in a stepwise fashion, part of the polyamide resin and/or additives are first
20 added and melt-mixed with the remaining polyamide resin(s) and additives being subsequently added and further melt-mixed until a well-mixed or homogeneous composition is obtained.

According to another embodiment, the overmolding thermoplastic resin and fiber composition of the invention comprises: a glass fibrous material, a carbon fibrous
25 material, and a polyamide resin.

According to a particular aspect, overmolding thermoplastic resin and fiber composition of the invention further comprises a viscosity and wettability enhancer such as for example Dodecanedioic acid (DDDA). According to a particular embodiment, the resin composition of the invention contains from about 0.3% to 2
30 % DDDA (e.g. 0.5 to about 1.8%).

According to another embodiment, a viscosity and wettability enhancer can be selected among Lysine, Alanine, Pentaerythritol and H₂O.

According to a particular aspect, overmolding thermoplastic resin and fiber composition of the invention further comprise a toughener for increasing ductility of the overmolding thermoplastic resin composition of the invention. According to a particular embodiment, a toughener comprises ethylene/propylene/hexadiene terpolymer grafted with between 5% and 0.1 % maleic anhydride, such as between 4 and 0.5 % or between 3 and 1% for example between 3 and 4% such as for example 2.1 %.

- 10 According to a further particular aspect, polymeric tougheners may also include: (a) A copolymer of ethylene, glycidyl (meth)acrylate, and optionally one or more (meth)acrylate esters, (b) An ethylene/ α -olefin or ethylene/ α -olefin/diene (EPDM) copolymer grafted with an unsaturated carboxylic anhydride such as maleic anhydride. Fusabond/TRX type, (c) A copolymer of ethylene, 2-isocyanatoethyl (meth)acrylate, and optionally one or more (meth)acrylate esters, (d) a copolymer of ethylene and acrylic acid reacted with a Zn, Li, Mg or Mn compound to form the corresponding ionomer.
- 15

According to a particular embodiment, an impact modifier comprises an Ethylene- α olefin copolymer containing from about 95-50 weight % of polymerised ethylene and from about 5 to 50 wt% of at least one polymerised α olefine containing from 3 to about 20 Carbon atoms.

20

According to a particular embodiment, the impact modifier further comprises a copolymer of ethylene, propylene and a diene grafted (or copolymerised) with 0.1 to 3 weight % of a dicarboxylic acid.

- 25 According to a particular aspect, the content of the glass fiber in the overmolding resin composition of the invention is between 25 and 70 wt%, preferably between 25 and 40 wt %, for example 30 wt %

According to a particular aspect, the content of the carbon fibrous material in the thermoplastic resin and fiber composition of the invention for overmolding is

between 10% and 70 wt% and preferably between 10 and 25%wt %, for example 15 wt %.

According to a particular aspect, is provided a thermoplastic resin and fiber composition comprising 25 to 70 wt% of a blend of PA66/PA6, 0.3 to 2 wt%
5 viscosity and wettability enhancer, 1 to 10 wt% of impact modifier, 1 to 5% of toughener, 25 to 70 wt% of glass fiber and 10 to 70 wt% of carbon fiber.

The resin composition of the invention can be applied to the UD carbon fiber tape stacking in the form of a melt or a film which has been obtained by conventional extrusion methods known in the art such as for example blow film extrusion, cast
10 film extrusion and cast sheet extrusion are applied to one or more layers of the fibrous materials, e.g. by layering.

According to a particular aspect of the invention, the overmolding thermoplastic composition of the invention presents advantageous properties comprising:

- Significantly reduced viscosity compared with comparable toughened over-
15 molding resins (e.g. Zytel 75CG45) under injection molding conditions giving excellent flow behaviour and tool fill;
- Comparable viscosity compared with non-toughened over-molding resins under injection molding conditions giving comparable fill behaviour to standard resins;
- 20 - good wetting capacity on the composite during the injection molding process due to the modified viscosity;
- confers high stiffness, resistance and ductility to the overmolded composite compared with other resins (low stiffness) .

According to a particular embodiment, the article made of the composite of the
25 invention is a beam part.

According to another particular embodiment, the article is a structural component comprising a reinforcing layer made from the composite material of the invention.

Depending on the end-use application, the composite structure may be shaped into a desired geometry or configuration.

One process for shaping the composite structure of the invention comprises a step of shaping the composite structure after the UD tape cross-ply has been made (42) and optionally preconsolidated. Shaping the composite structure 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 composite structure is preheated to a temperature above the melt temperature of the 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 thereafter removed from the press or the mold after cooling to a temperature below the melt temperature of the resin composition. Such a forming operation may also be performed by continuous compression molding.

The composite structures according to the invention are characterized by very high directional properties in the UD carbon fiber direction (greater than a biaxial balanced twill carbon fiber weave for example), while transverse properties of the UD are much lower which hence benefits for a layering of the UD carbon fiber tapes in the UD stack to give suitable properties for an application with a mix of normal and transverse properties. Such layering structures can comprise combinations of layers at 0 degrees, 90 degrees, and at intermediate angles such as 45 degrees, 60 degrees, or 80 degrees or other angle between 0 and 90; to reduce warpage in such structures it is desired that the laminate stack be both balanced and symmetrical about the neutral axis. Specific examples include, for a 2 mm structure made of 0.18-0.2 mm thick tape: a UD stack $[0]_n$, quasi-isotropic stack $[0/90/\pm 45/0]_s$, a directional stack $[0/0/90/0/0]_s$; further examples for a 1.5 mm thick stack made of 8 plies of 0.18-0.2 mm thick as used in the exemplary beam structure are $[90/0/0/0]_s$, $[45/0/-45/0]_s$, $[90/0/90/0]_s$, and $[90/45/0/-45]_s$.

In all cases, it is desired that the void content of the stacked UD tape (42) when incorporated in the final over-molded part through various intermediate processes as described above has a void content higher than 2%, typically of 4 to 12% or of about 6 to 8%.

When sheets of such composite structures are molded into a beam part representative of a plurality of automotive, consumer electronics, industrial, and other such components, the advantages are clearly demonstrated, as illustrated in the examples presented hereafter.

- 5 Due to their advantageous properties, the composite structures according to the present invention may be used in a wide variety of applications such as for example components for automobiles, trucks, commercial airplanes, aerospace, rail, household appliances, computer hardware, portable hand held electronic devices, recreation and sports equipment, structural components for machines, buildings,
10 photovoltaic equipment or 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
15 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
20 vehicle bulkheads, pressure vessels such as refrigerant bottles, 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.

- 25 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
30 such as for example housings for hand held electronic devices, televisions, screens, and computers.

EXAMPLES

Example 1: Example of a finished product made of a composite material of the invention and comparative Examples

In order to compare the performance of a beam made of a composite of the invention with a beam made of a composite of comparative examples, the following tests were made.

Generic beam structures were molded from a composite sheet and used to study the mechanical properties including the force needed to fracture, the beam compliance or stiffness, the displacement needed to reach peak load and subsequent load and displacement evolution after peak load until major failure of the beam structure. A series of beams were prepared as described below with the materials used described in Table 1.

Table 1

Overmolding resin (Glass-carbon hybrid over-molding resin)	
OM1 (comparative)	PA66 GF 50 BK HS resin (Vizilon™) Commercially available 50% wt.% glass reinforced PA66 heat stabilized and black pigmented over-molding resin
OM2 (resin of the invention)	As described in Table 2
Carbon Fiber	
Carbon fiber (CF) Unidirectional (UD) tape	CF UD tape 0.19 mm thick, resin 73.15% PA66 DuPont Zytel® FE310036/24.72% Ultramid B27 PA6/1.5% rheology modifier and heat stabilizer (dipentaerythritol) / 0.63% carbon black (Americhem 31878F1), 48% Vf carbon fiber of type 12k Toray T-700 →void content 6-8% as made by pultrusion

In a further particular aspect, the resin used in the CF UD tape in Table 1 has a melt viscosity of 10 to 75 Pa.s measured at 290°C and over a shear rate range of 40 to 5000 reciprocal seconds and the over-molding resin OM2 used in Table 2 has a melt viscosity of 90 Pa.s at 2000 s⁻¹ to 720 Pa.s at 50 s⁻¹ measured at 290°C.

Manufacturing of cross-ply UD tape

Parts were made using a Fiberforge UD tape deposition cell (US 6,607,626, US 6,939,423, US 8,007,894, US 8,048,253, US 8,168,029) whereby UD tapes were cross-plyed by feeding the end of a coil of tape across a CNC controlled table, with each piece of UD table placed where needed which was then automatically cut and then locally ultrasonically spot welded to the layer of UD tape below, which may be

at the same or a different orientation, such that the layers of UD tape were placed into an 8 layer structure. The stacking sequence was [90/0/90/0]_s, where "90" and "0" are the angles in degrees formed between the fiber axis and the layers of the UD tape within the stack.

5

For the sake of comparison, cross-ply UD tape prepared using the Fiberforge process was considered in two ways for producing the exemplary beam parts.

- First, the cross-ply UD tape with 6-8% void content was used directly without any additional melt bonding pre-consolidation phase, as performed for Examples E1 and E2.
- Secondly, cross-ply UD tape with 6-8% void content was subjected to a pre-consolidation step to melt bond the UD tape layers together and to reduce the void content to below 2% (Figure 6C), as performed for Comparative Examples C1 and C2.

10

15

For comparative examples C1 and C2, the pre-consolidation step comprised melt bonding and additional void reduction to below 2% of the stacked UD tape layers using a hot/cold press after the UD tapes had been placed and locally ultrasonically spot welded together (hot side at 280°C, cold side at 180°C, pressure hot side 1.7 bars, cold side 12 bars, dwell time at temperature under pressure 350-400s hot side, 60s cold side).

20

Figures 2 and 3 illustrate the process of comparative examples (with pre-consolidation step for reducing the void content) and the process of the invention using UD tape layers comprising UD tapes with high void content without pre-consolidation step, respectively.

25

The void content was measured according to ISO7822 1990(en) following method C, Statistical counting. Samples were prepared for optical microscopy by embedding in Struers acrylic cold mount resin and polishing to give clear contrast between fiber, resin, and voids. Images were taken using an Olympus optical microscope with automatic X-Y-Z stage to capture multiple images of the sample.

30

An area of the full thickness and 15-25 mm length was imaged with sufficient resolution to detect both intra-bundular and inter bundular voids. The voids were then counted by segmenting the grey scale image into a binary image, where all

features except voids were removed, and the void area automatically counted using "Analysis" software.

Preparation of exemplary beam structure

5 Beams were molded from the cross-ply UD tape obtained as described above, in either unconsolidated or pre-consolidated forms, with the combinations of over-mold and laminate shown in Table 4. The laminate made was then trimmed to suit the beam tool dimensions using a KMT 6-axis robotic water jet cutter.

Example E2 corresponds to beams made with unconsolidated (un-con) cross-ply
10 CF UD tape layers overmolded with a resin of the invention (OM2), whereas Example E1 corresponds to beams made with unconsolidated (un-con) cross-ply CF UD tape layers overmolded with a comparative resin (OM1). Comparative Examples C1 and C2 correspond to beams made with pre-consolidated (pre-con) cross-ply CF UD tape layers, respectively overmolded with a comparative resin
15 (OM1) or a resin of the invention (OM2).

The generic beam structure is depicted in Figure 1 with the dimensions of a length of 730 mm, an upper rib thickness of 2 mm, a width of 140 mm, a laminate shell thickness of 1.5 mm that is over-molded with 1.5 mm of over-molding polymer, with a height of 15 mm, 30 mm, and 50 mm at the different steps (Figure 1E & F & G).
20 The beam has a width to depth to length ratio of 9.3, 4.7, and 2.8 as examples of such structures.

Figure 4 schematizes the main steps of a process according to an embodiment of the invention (B) as compared to a process with pre-consolidation step used in comparative examples (A). As shown on Figure 4, the process of the invention
25 which was used comprises two molding steps, wherein the thermoplastic resin and fiber composition of the invention is overmolded after re-heating the hardened composite structure obtained under step (iv) (Figure 4B, left).

In this example the process may follow the steps of:

(41) providing a UD tape made from unidirectional carbon fiber and a thermoplastic
30 resin

(42) cross plying UD tape and locally fixing the layers together, for instance by spot welding

(43) heating of non-consolidated UD layers, for instance by infrared radiation, above melt temperature of the thermoplastic resin

5 (44) Stamp-forming of heated UD layers

(45a1) Cooling under pressure

(46) Optional trimming of the heated, stamped formed, and cooled UD layers

(47) Warming of the stamped UD layers to slightly below the melt temperature of the thermoplastic resin

10 (48a) Over-injection of the overmolding resin composition of the invention

(45a2) Cooling under pressure

(49) Isolating the final part.

Alternatively, the process may follow the steps of:

15 (41) providing a UD tape made from unidirectional carbon fiber and a thermoplastic resin

(42) cross plying UD tape and locally fixing the layers together, for instance by spot welding

(43) heating of non-consolidated UD layers, for instance by infrared radiation, above melt temperature of the thermoplastic resin

20 (48b) Over-injection or overinjection of the overmolding resin composition of the invention

(45b) Cooling under pressure

(49) Isolating the final part.

25 In the following example the molding operation comprises two principle steps as further illustrated on Figure 5 (Example of process of the invention on the right and comparative process of the left):

Molding step1:

30 Composite sheets were cut to a size of 890x340 mm to suit the molding tool. The stamp-forming molding tool consisted of a constant 1.5 mm cavity steel tool, tempered by pressurized water heater/chillers such that a desired temperature could be maintained, where 140°C was used in these experiments suited to the specific polymer composition being used. The tool is guided by location pins and

heal blocks, as is well known in the art to ensure accurate guidance of the tool during closure. The molding tool was mounted in a vertical hydraulic press with down-stroking hydraulics and fast acting hydraulic accumulators to ensure rapid closure and pressure build up. The sheet materials were located inside a blank holder frame that was mounted to an electrically driven-servo sled. The sled loaded the materials into a fast acting medium wave infra-red oven where the cross-ply UD tape was heated above the melting temperature of the UD tape (43), i.e. to about 290-300°C, with the temperature controlled by infra-red pyrometers. A 5 to 30s dwell at 290-300°C was used to ensure that the middle of the UD tape stacks was sufficiently melted (illustration of step (iii)). The sled was then programmed to move rapidly from the IR oven to above the steel stamping tool, with a transfer time of typically 8s from leaving the oven to when the press molding tool was closed (44). A force of 1800 kN giving a pressure of 100-150 bars was applied for 30s to ensure consolidation, crystallization and cooling under pressure (45a1) (illustration of step (iv)), before the tool was opened and the stamped part was removed. An alternative to the use of the blankholder and sled is the use of pick-and-place robots, for example 6-axis robots, and needle grippers. The stamped shell structure was then removed from the molding tool and trimmed to the shape of the second stage over-molding tool (46).

Molding step 2:

The stamped shell structure was then taken to an over-injection molding cell comprising conveyors, an ABB 6 axis robot with vacuum gripper, a forced hot air convection warming oven (Reinhardt), an Engel 700T injection molding press, and an injection molding tool. The stamped composite sheet forming the structural insert for the beam tool was warmed to 220-230°C (re-heating step) in the warming oven (47) prior to rapid robotic transfer to the open over-injection tool. Typical transfer times were 13s. Over-molding resin compositions (composition of the invention and comparative composition, respectively) were then used and over-injected (48a) onto the stamped insert such that fusion bonding or autohesion (healing) occurred between the two polyamide compositions such that the molten over-molding polymer melts into a thin distance of the stacked UD tapes and as both materials cool in the injection molding tool the polymer of the stacked UD tapes recrystallizes through the interface with to give an integral part (45a2), as seen in Figure 7A. An

injection pressure of nominally 500 bars was used with an injection tool temperature of 120°C and a hold time of 30s as is typical of the normal range used in the art to injection mold polyamide resins. A delayed injection pattern was used to move the weld line away from the center of the beam using the 4 hot runner injection point control system. The over-molded beam was then removed from the molding tool and packaged in a dry bag to maintain the as molded moisture level prior to test.

Over-molding resin composition

An overmolding resin of the invention was prepared using a Berstorff compounder with 40 mm screw and side feeders with a set barrel temperature of 280°C, a die pressure of 19 bars, a screw speed of 300 RPM, at a throughput of 120 kg/hr as a blend of Nylon PA66/6 with Dodecanedioic acid (DDDA) as a chain scission agent to reduce viscosity and increase wettability. Additionally, a resin toughener was added to the mixture with the side feeder, namely a toughener as described in US 6,756,443 called DuPont Fusabond TRX-301™ copolymer which is polymer composed of maleic anhydride modified ethylene propylene diene monomers (EPDM) available from E.I. DuPont de Nemours and Company, Wilmington, Delaware, USA. Additionally, an impact modifier was also added, Ethylene-octene copolymer (Engage® 8180 consisting of 72 % wt/wt ethylene and 28 % wt/wt from Dow Chemical Co., Midland, MI.). Fibrous material in the form of a blend of carbon fibers and glass fibers was further added with the side feeder and the resulting composition was strand cut into pellets suitable for injection molding. The composition of the resulting overmolding resin of the invention (OM2) is shown in Table 2 below.

Table 2

Nature of the Component	Component	%
Glass fiber	PPG 3660 E glass fiber, PPG	30
Viscosity & wettability enhancer	DDDA	0.5
Polyamide resin	PA66 (DuPont Zytel 101®)	23.02
Polyamide resin	PA66 (DuPont Zytel 101 PWD500, a ground Zytel® 101 with average particle size of 500 µm)	2
Polyamide resin	PA6 (BASF Ultramid B3)	17
Carbon fiber	Zoltek PX33CF333 48	15
Impact modifier	Ethylene-octene copolymer (Engage® 8180 consisting of 72 % wt/wt ethylene and 28 % wt/wt from Dow	5.64

	Chemical Co., Midland, MI.)	
Toughener	Ethylene/propylene/hexadiene terpolymer grafted with 2.1% maleic anhydride (DuPont Fusabond TRX-301®)	3.75
Nature of the Component	Component	%
Carbon black	Carbon black AMER 38395C1	2.44
Heat stabilizer	7:1 :1 HS tri-blend	0.4
Nucleating & lubricant	Calcium salt of long chain linear carboxylic acids Clariant Licomont CaV102®	0.25
		100

The properties of the overmolding resin composition of the invention (OM2) were tested in comparison to Zytel 75CG45 (not containing DDDA) according to the ISO standards detailed in Table 3 at 23°C dry as molded (DAM) and are represented under Table 3 as an average over 5 samples below. It can be seen that the stiffness and strength of OM2 were marginally increased with changes to strain to failure and unnotched charpy within the standard deviation.

Table 3

Tensile			
		OM2	Zytel 75CG45
Tensile Mod. [MPa]	ISO 527	17'396	16'702
St.Dev.		202	288
Tensile Str.at Break [MPa]	ISO 527	192.7	175.3
St.Dev.		1.4	0.9
Elongation at Break [%]	ISO 527	3.2	3.4
St.Dev.		0.1	0.2
Unnotched CHARPY [kJ/m²]	ISO 179/1eU	81.5	83.8
St.Dev.		3.5	6.6
Multi-axial impact			
Strength [N]	ISO 6602-3	892.9	944.8
Energy [J]	ISO 6602-3	0.3	3

By modifying the over-molding resin to reduce viscosity, increased wetting could be achieved at the interface. Table 4 below compares the over-molding resin of the invention (OM2) with the same composition without the DDDA (Zytel 75CG45) and the comparative glass filled over-molding resin of lower stiffness as it contains only glass fiber, (Zytel 70G50HSLA BK039B, OM1).

Table 4

Sample	Shear Rate [1/s]	Viscosity [Pa-s]
OM1 Zytel 70G50HSLA BK039B	50.0	498.3
	100.0	375.9
	250.0	255.6
	500.0	183.6
	750.0	157.6
	1000.0	139.7
	2000.0	103.0
Zytel 75CG45	50.0	2136.0
	100.0	1540.8
	250.0	822.0
	500.0	547.3
	750.0	416.1
	1000.0	350.4
	2000.0	223.2

10

Sample	Shear Rate [1/s]	Viscosity [Pa-s]
OM2	50.0	719.8
	100.0	536.7
	250.0	277.7
	500.0	196.1
	750.0	147.7
	1000.0	129.4
	2000.0	93.6

It can be seen that the strain to failure is above 3% while maintaining a tensile modulus of 17GPa to give a tough and yet stiff molding material while maintaining the lower viscosity of a conventional injection molding resin for example OM 1 Zytel 70G50HSLA BK039B which does not contain DDDA.

Testing of exemplary beam structure

In order to demonstrate the advantages of the composite structures exemplified by the beam structure, the beams were tested in a mechanical laboratory according to the sequence defined below and illustrated in Figures 1C and D.

- 5 Beams were tested using an Instron servo-hydraulic universal testing machine with extended testing bed. Solid steel supports were fabricated and the beams were fixed to the support plates using 6x steel bolts at each end which were tightened with a torque wrench. A force was applied to the center of the beam with a loading nose of radius 37 mm. The test supports had a radius of 4 mm, and the test span
10 was 452 mm. Tests were performed at 23°C and the samples were dry as molded (DAM). The test speed was 0.2 inches per minute. Three repeat tests were made for each of Examples C1, C2, E1, E2, with average results shown under Table 5 below (VC stands for void content measured as described above).

15

20

25

Table 5

Ex.	Cross- plied UD tape treatment	OM resin	Peak Load (kN)	Displa- cement at Peak Load (mm)	Energy to Peak Load (J)	Displace- ment at Major Failure (mm)	Energy to Major Failure (J)	Pre- inflection Complian- ce (kN/mm)
C1	pre-con	OM2	25.9	44.1	593.9	52.4	762.3	1.20
C2	pre-con	OM1	20.9	36.8	401.8	37.3	410.7	1.27
E1	un-con	OM2	23.9	54.7	775.9	87.9	1'469.2	1.22
E2	un-con	OM1	23.1	36.8	434.1	38.1	461.8	1.33

It can be seen that the pre-consolidation step, which reduced the UD tape void content to below 2%, did not increase the beam compliance, which was 1.20 kN/mm for C1 and 1.22 for E1 (both overmolded with resin OM2) and 1.27 kN/mm for C2 and 1.33 for E2 (both overmolded with resin OM1). Peak force was marginally higher for C1 than for E1 whereas between C2 and E2 the peak force for the unconsolidated material was marginally higher. Hence, the unconsolidated UD tape can be considered near equivalent to pre-consolidated UD tape from the perspective of part stiffness and peak load, which is a surprising observation.

Further, it can be seen that combination of unconsolidated UD tape and OM2 led to increases in the energy at peak load, which was determined by integrating the area under the force displacement curve. C1 (pre-consolidated) overmolded with OM2 had an energy to peak load of 594J which was lower than the energy to peak load of non-preconsolidated E1 overmolded with the same resin (776J). Surprisingly, the desired increased in energy at peak load was not observed by using the consolidated UD tape overmolded with OM1 (C2) nor using the unconsolidated UD tape overmolded with OM1 (E1) but requires the use of the OM2 and unconsolidated UD tape.

It is to be noted that the unexpected and significant improvements in the beam properties occur not only in the energy to peak load but especially and desirably in the energy to major failure of the beam. Here, the energy to major failure of the beam increased which is achieved with the novel combination of unconsolidated UD tape and OM2 resin amounts to by a factor of two. Specifically, E1 using unconsolidated UD tape and OM2 had an energy at beam major failure at 1'469J which is almost twice the energy at beam major failure observed for C1 using pre-consolidated UD tape and OM2 resin (762J).

However, the same unconsolidated UD tape material does not show such improvement in the energy absorbed to major beam failure when overmolded with a comparative resin (OM1) as comparative example E2 using unconsolidated UD tape and OM1 resin had an energy at beam major failure of 462J, which is equivalent to comparative example C2 using pre-consolidated UD tape and OM1 resin (411J).

Those results support the advantageous effects of the combination of unconsolidated UD tape and OM2 in achieving the doubling of energy absorbed to major beam failure with an equivalent beam stiffness and peak force.

5 In this test, conventional glass fiber beams typically fracture in the beam center with a catastrophic failure as the glass laminate fails at the beam center. This results in a sudden drop in load. Carbon fiber laminate beams, while stiffer, also show the same failure type with central catastrophic failure.

As opposed, the beams made of laminates of the composite of the invention present equivalent peak load and stiffness to a standard pre-consolidated UD CF
10 tape beam, while exhibiting a significant increase in energy absorption and displacement to major failure than pre-consolidated UD CF tape beams.

Further, the process of the invention leads to materials presenting increased stiffness compared with conventional toughened glass fiber compositions (for instance as known from WO 2004/022652A1).

15 Therefore, the process and materials of the invention are offering the possibility of reducing overall manufacturing cost of carbon fiber parts (due to the avoidance of pre-consolidation step before conversion into the final part), while achieving desired crash performances.

The flexural test results are further exemplified by consideration of the void content
20 in the UD tape area of the over-molded beam (shown in Figures 7 and 8) and the mode of failure of the UD tape area of the beam in Figure 10. It can be seen that the increased energy absorbed with the combination of non-preconsolidation UD tape and OM2 resin overmold can be related to the microstructure of the composite and the resulting failure mode which together surprisingly increase energy absorption.

25 It can be seen in Figure 9 that the as made UD tape has a void content of 6-8% with the voids occurring inside local agglomerations of carbon fibers, and not inside the resin rich areas between the bundles of carbon fiber. This is due to the difficulty of impregnating to the inside of the high local fiber volume fraction bundles (low permeability) and relatively high resin viscosity (compared to other fluids).

30 In the comparative example, preconsolidation aims and achieves a lowering of void

content by an additional thermal and pressure treatment step to make a homogeneous sheet. Figures 6A and C show that a flat sheet of UD tape that has been preconsolidated and not stamped has a void content of below 2%. UD tape that has been stamped into a flat plaque after IR heating but without the preconsolidation stage has a void content of 6-9% (Figures 6A and B). Where a sample that has been preconsolidated and also reheated and stamped (Figures A and D), the void content is also below 2%, i.e. the heating and stamping process as performed does not increase the void content. In the comparative example, preconsolidation to achieve a lower initial void content is well known in the art to increase failure strength for example in tensile testing compared with void filled samples, while it is also desired to eliminate this stage as in this invention to avoid the associated cost.

Figure 7 represents micrograph results and void contents obtained under Example 1 where X-ply UD tape has been stamp-formed either with or without the prior preconsolidation stage and the resulting stamping has then been over-molded with a comparative resin or the resin composition of the invention. The differences are shown in more detail in Figure 8 showing the overall structure, a first detailed zoom of an exemplary section and a second further detailed zoom showing the agglomerations of fiber and local resin rich areas and where voids are located in the structure. In C1, X-ply UD tape has been stamp-formed, with prior preconsolidation, and then over-injected with over-molding resin 2 (C), and flatter and wider agglomerations (0.2 to 1mm) of UD fibers are seen with smaller resin rich areas (0.1-0.2mm) and an overall more homogeneous microstructure (Figure 8A). In contrast, (Figure 8B) shows micrograph taken from E1 where X-ply UD tape that has not been pre-consolidated into a flat sheet and then stamp-formed, followed by over-injection with over-molding resin 2 where agglomerations (0.1 to 0.6mm) of UD fibers contain intra-bundular voids within the center of the agglomeration and the shape of the agglomeration is more square like or circular than rectilinear or ellipsoidal in Figure 8A, and where the UD fiber agglomerations are spaced with wider resin rich areas of much lower fiber volume fraction (0.1 to 0.4 mm) than C1 and hence have overall a less homogeneous microstructure.

Hence, the improved energy absorption during test but without loss of part stiffness is achieved by a less homogeneous microstructure with increased void content inside the middle of local agglomerations of carbon fibers with resin rich areas between these agglomerations when used with the tough and lower viscosity over-molding resin OM2.

It should be noted that the void content after stamp-forming for non-preconsolidated UD was 6-9% (Figure 6B) but that after over-injection this is reduced to less than 3% due to the high pressures applied during over-molding and the warming of the stamped UD tape insert prior to over-molding as shown in Figure 8B.

The microstructure of Figure 8B gives rise to a change in failure mechanism as seen during the beam tests, as given in Figure 10. In beams with both OM1 and OM2 where preconsolidation is used (C2 and C1 seen in Figure 10 B & D), the X-ply UD tape has failed in shear in the side wall, tension in the flange, and compression in the base all without a strand like fracture due to the more homogeneous microstructure. In beams with both OM1 and OM2 without preconsolidation (E2 and E1 seen in Figure 10 A & C), the X-ply UD tapes have fractured with a strand like behavior and delaminations between layers of the UD tape over a much wider fracture surface corresponding to the agglomerations seen in Figure 8 B. When no pre-consolidation stamped UD is then over-injected with OM 2, the UD fibers have again fractured with an even more noticeable strand like behavior corresponding to the agglomerations seen in Figure 8 B with rip-through of the three load introduction points (E1 in Figure 10C).

Hence, the improved energy absorption during test but without loss of part stiffness is achieved by a less homogeneous but controlled microstructure with increased void content inside the middle of local agglomerations of carbon fibers with resin rich areas between these agglomerations when used with the tough and lower viscosity over-molding resin OM2 that gives a strand like failure of the UD tape layers with delaminations between layers of the UD tape with rip-through of the loading areas maintaining force during the flexural test to higher displacements.

Claims

1. **A process for preparing a carbon fiber composite structure** comprising:

5 -(i) providing at least two layers of unidirectional (UD) carbon fiber tape, said UD carbon fiber tape comprising unidirectional carbon fibers impregnated in a thermoplastic resin, the fiber weight fraction to resin weight content being in a range from 50% to 70% with an initial void content before stacking higher than 2%,

10 (ii) stacking said at least two layers of UD carbon fiber tape in a cross ply arrangement with respect to each other,

 (iii) applying heat at a temperature adapted to melt the thermoplastic resin;

 (iv) cooling under pressure the heated stacked layers to harden the composite structure,

wherein the heated stacked layers are overmolded with a thermoplastic resin and

15 fiber composition, said thermoplastic resin and fiber composition comprising a glass fibrous material, a carbon fibrous material, and a polyamide resin.

2. The process according to claim 1, wherein the thermoplastic resin and fiber composition for overmolding comprises a viscosity and wettability enhancer.

3. The process according to the preceding claim wherein the viscosity and wettability enhancer comprises Dodecanedioic acid (DDDA).

4. The process according to any preceding claim, wherein the thermoplastic resin and fiber composition for overmolding comprise a toughener and/or an impact modifier.

5. The process according to the preceding claim wherein the toughener comprises an ethylene/propylene/hexadiene terpolymer grafted with between 5% and 0.1 % maleic anhydride.

6. The process according to any preceding claim, wherein the content of the glass fibrous material in the thermoplastic resin and fiber composition for overmolding is between 25 and 70 wt.

7. The process according to any preceding claim, wherein the carbon fibrous material in the thermoplastic resin and fiber composition for overmolding is between 10% and 70 wt%.

5 8. The process according to any preceding claim, wherein the thermoplastic resin in the thermoplastic resin and fiber composition for overmolding is a blend of polyamide resin PA 66/PA6 between 35 and 70 wt%.

9. The process according to the preceding claim wherein the blend comprises a
10 proportion of PA 66/PA6 between 90 and 10 wt%.

10. **A process for preparing a carbon fiber composite structure** comprising:

- providing at least two layers of unidirectional (UD) carbon fiber tape and stacking said layers in a cross-ply arrangement;
- over-injecting a molten overmolding thermoplastic resin composition onto
15 the heated stacked layers to ensure healing between the two thermoplastic resins and subsequently cooling under pressure the stacked layers to harden the thermoplastic resin to form said composite structure, wherein the said unidirectional (UD) carbon fiber tapes comprise unidirectional carbon fibers pre-impregnated with a thermoplastic resin with an initial void content before
20 stacking higher than 2%;

and wherein the overmolding thermoplastic resin composition comprises:

- glass fibrous material between 25 and 70 wt %;
- carbon fibrous material between 10% and 70 wt%;
- a blend of polyamide resin PA 66/PA6 between 25 and 70 wt%;
- 25 - a viscosity and wettability enhancer such as Dodecanedioic acid between 0.3 and 2 wt%;
- a toughener such as an ethylene/propylene/hexadiene terpolymer grafted with 3 to 4% maleic anhydride.

30 11. The process according to any preceding claim wherein the stack of layers prior to the overmolding step comprises between 2 to 26 layers of UD carbon fiber tape.

12. The process according to any preceding claim wherein the angle between fibers of one of said two cross ply stacked layers with respect to the other is between 0 and 90°.

13. The process according to any preceding claim wherein the void content is
5 between 4% and 8%.

14. The process according to the preceding claim wherein the void content is between 6% and 8%.

15. The process according to any preceding claim wherein the heat treatment applied to the stacked layers is conducted at a temperature from about 290 to about
10 300°C.

16. The process according to any preceding claim wherein the pressure applied to the stacked layers during the cooling step is of about 10 to about 150 bars.

17. The process according to any preceding claim wherein the overmolding step is conducted during a period of time of less than 2 minutes at temperatures from
15 about 120 to about 160°C and pressures above between 200 and 1000 bars.

18. The process according to any preceding claim wherein each layer of resin impregnated unidirectional (UD) carbon fiber tape has a basis weight greater than 200 g/m² and less than 500 g/m².

19. **A process for the preparation of a thermoplastic resin composition**
20 comprising the following steps:

(a) providing a blend by melt mixing polyamide resins PA66/PA6 wherein the wt ratio between the two polyamides comprises between 40 and 100 %wt of PA66 combined with a viscosity and wettability enhancer selected from the group consisting of Dodecanedioic acid Lysine, Alanine, Pentaerythritol and H₂O;

25 (b) adding an ethylene/propylene/hexadiene terpolymer grafted with 3 to 4% maleic anhydride as a toughener to the blend provided under step (a)

(c) adding a blend of carbon fibrous material and glass fibrous material to the mixture obtained under step (b), such as the resulting mixture contains 25 to 70

wt% PA66/PA6, 0.3 to 2 wt % viscosity and wettability enhancer, 1 to 5 wt% of toughener, 25 to 70 wt% of glass fiber and 10 to 70 wt% of carbon fiber.

20. A composite material structure obtained by a process according to any one of the preceding claims.

5 21. **A carbon fiber composite material structure** comprising at least two stacked layers of unidirectional (UD) carbon fiber in a cross ply arrangement impregnated with a thermoplastic resin, and an overmolded thermoplastic resin and fiber composition, said thermoplastic resin and fiber composition comprising a glass fibrous material, a carbon fibrous material, and a polyamide resin, wherein void
10 content in the stacked layers of unidirectional (UD) carbon fiber is between 3% and 10%.

22. The composite material structure according to any preceding claim wherein the resin to UD carbon fiber content is in a range from 0.3 to 0.5 wt%.

15 23. The composite material structure according to any preceding claim wherein the overmolded thermoplastic resin and fiber composition is injection overmolded.

24. The composite material structure according to any preceding claim wherein the void content is between 4% and 8%.

20 25. The composite material structure according to any preceding claim wherein the overmolding thermoplastic resin and fiber composition comprises glass fibrous material.

26. The composite material structure according to any preceding claim wherein the overmolding thermoplastic resin and fiber composition comprises carbon fibrous material.

25 27. The composite material structure according to any preceding claim wherein the overmolding thermoplastic resin and fiber composition comprises a blend of polyamide resin PA 66/PA6.

28. The composite material structure according to any preceding claim wherein the overmolding thermoplastic resin and fiber composition comprises a viscosity

and wettability enhancer selected from a group consisting of Dodecanedioic acid Lysine, Alanine, Pentaerythritol and H₂O.

29. The composite material structure according to any preceding claim wherein the overmolding thermoplastic resin and fiber composition comprises a toughener
5 such as an ethylene/propylene/hexadiene terpolymer grafted with 3 to 4% maleic anhydride.

30. The composite material structure according to any of the preceding claims wherein the resin composition has a melt viscosity at 290°C of between 10 Pa.s and 400 Pa.s, more particularly of between 10Pa.s and 75Pa.s.

10 31. The composite material structure according to the preceding claim wherein the resin composition has a melting temperature comprised between about 220°C and 280°C and more particularly 250-275°C.

32. The composite material structure according to any preceding claim comprising 2 to 26 layers of UD carbon fiber tape.

15 33. The composite material structure according to any preceding claim wherein each carbon fiber layer has a basis weight between 200 g/m² and 500 g/m².

34. A **thermoplastic resin composition** comprising 25 to 70 wt% of a blend of PA66/PA6, 0.3 to 2 wt% viscosity and wettability enhancer, 1 to 5 wt% of toughener, 25 to 70 wt% of glass fiber and 10 to 70 wt% of carbon fiber.

20 35. An article made of or incorporating the composite material structure according to any preceding claim.

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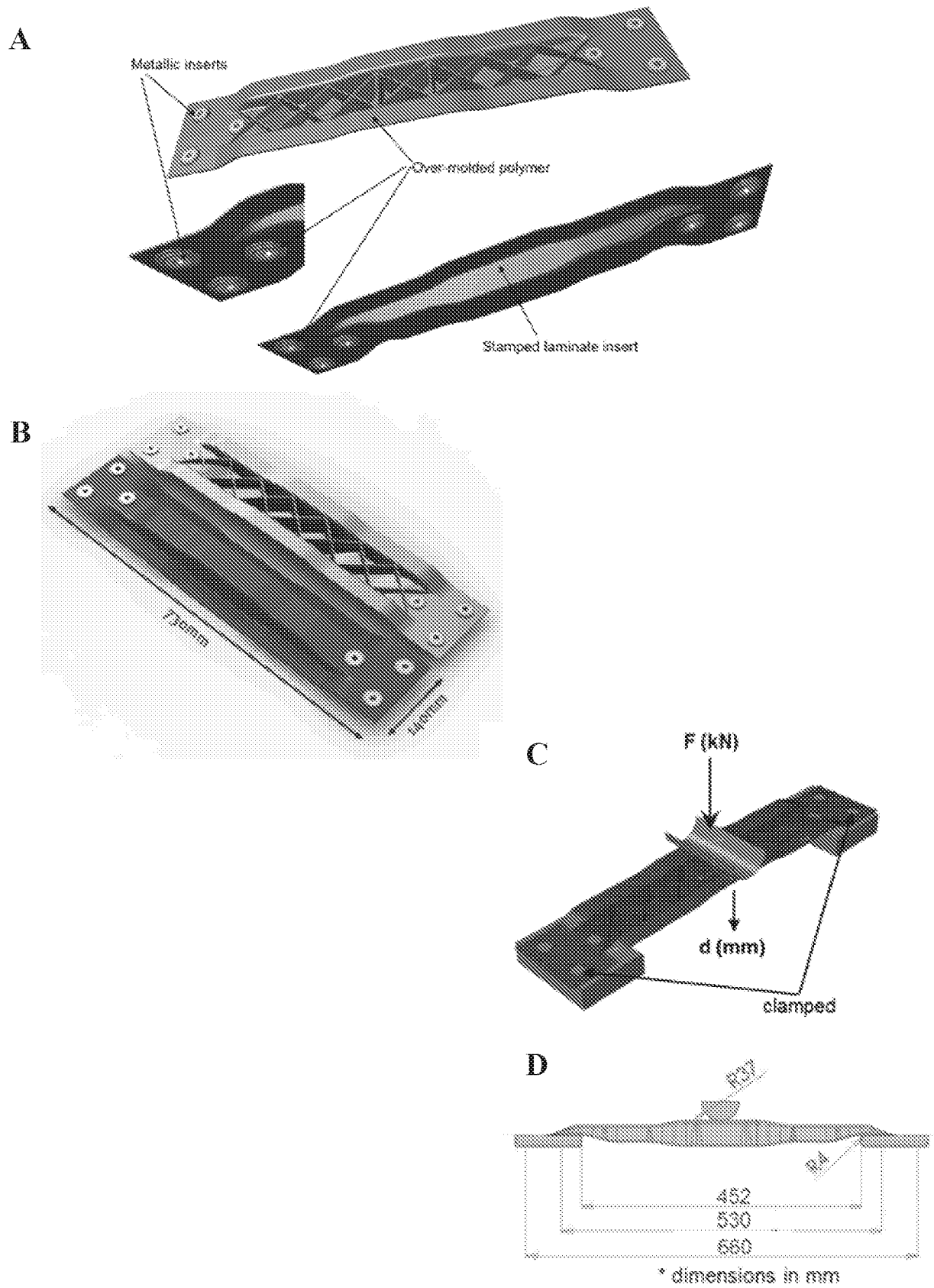
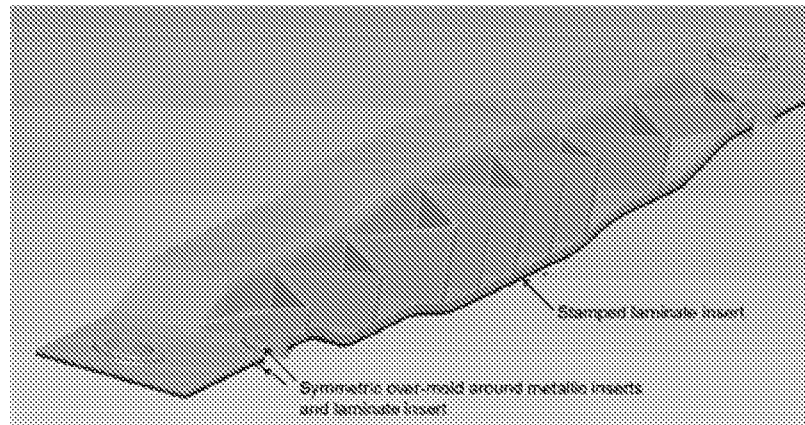


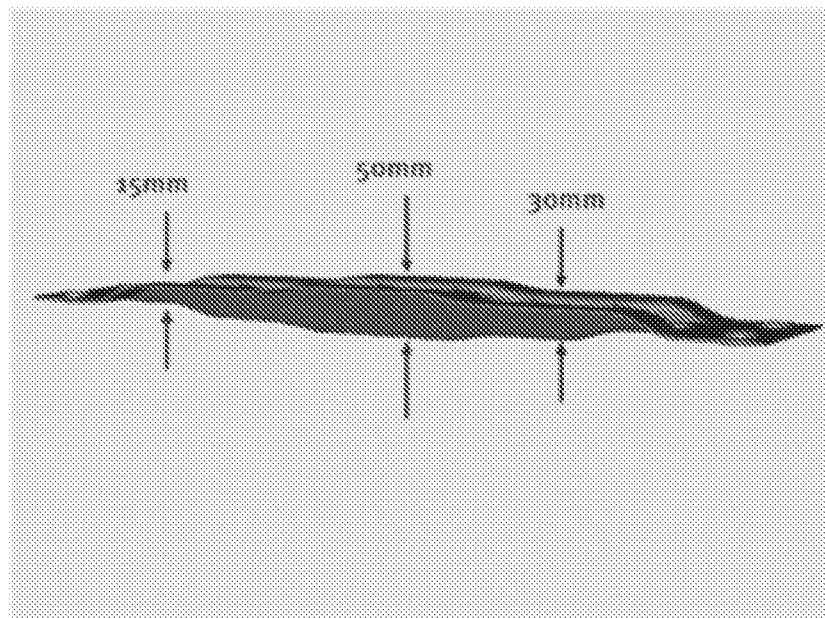
Figure 1

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E



F



G

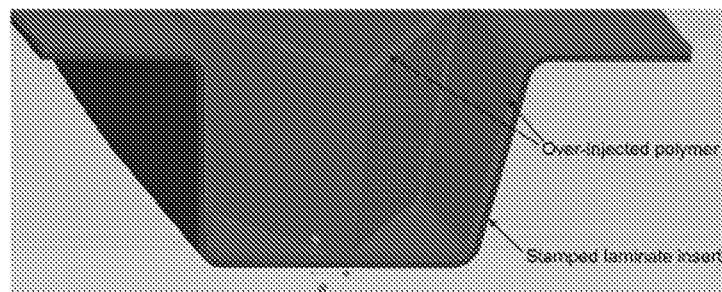


Figure 1 (continued)

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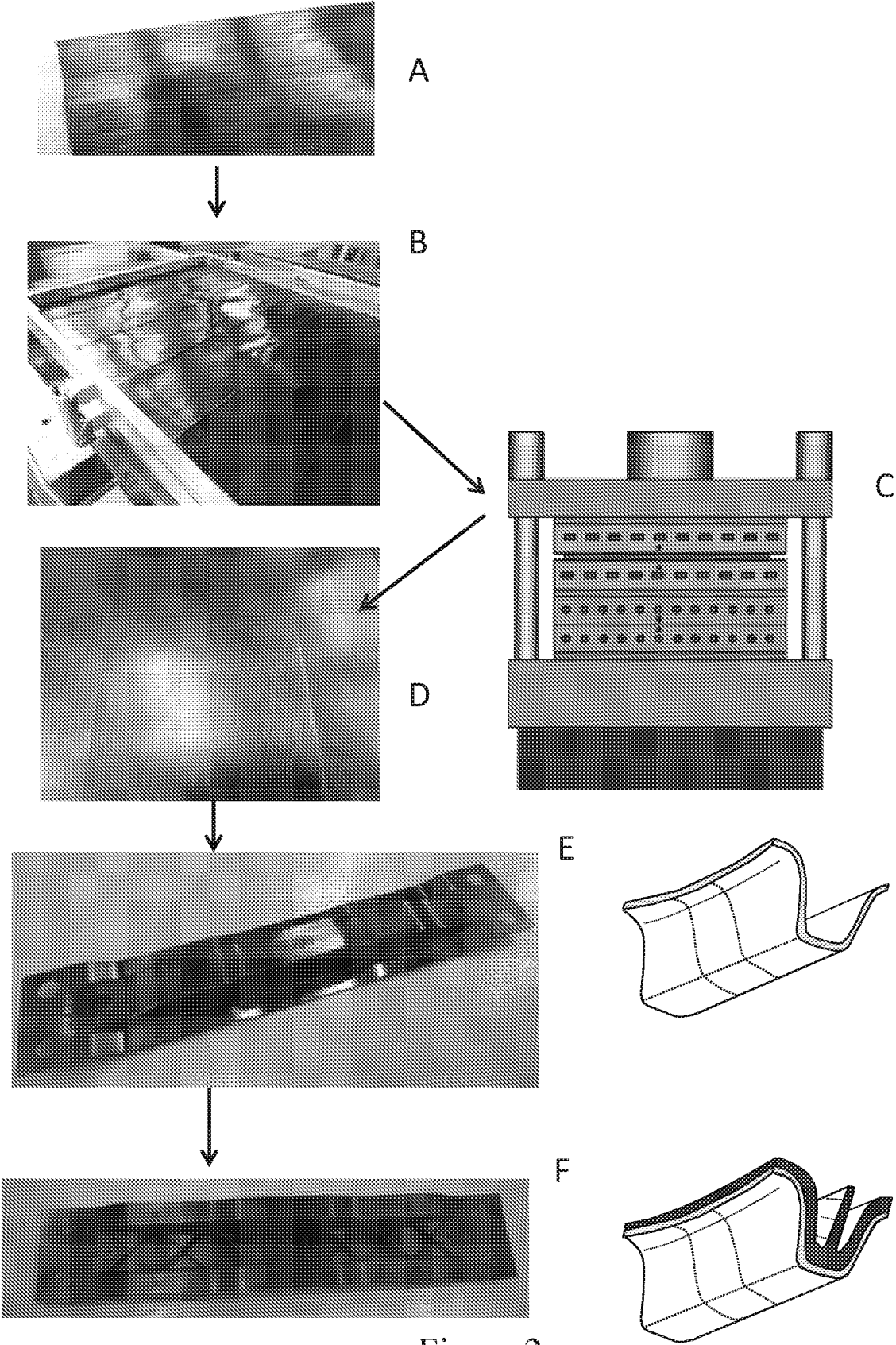


Figure 2

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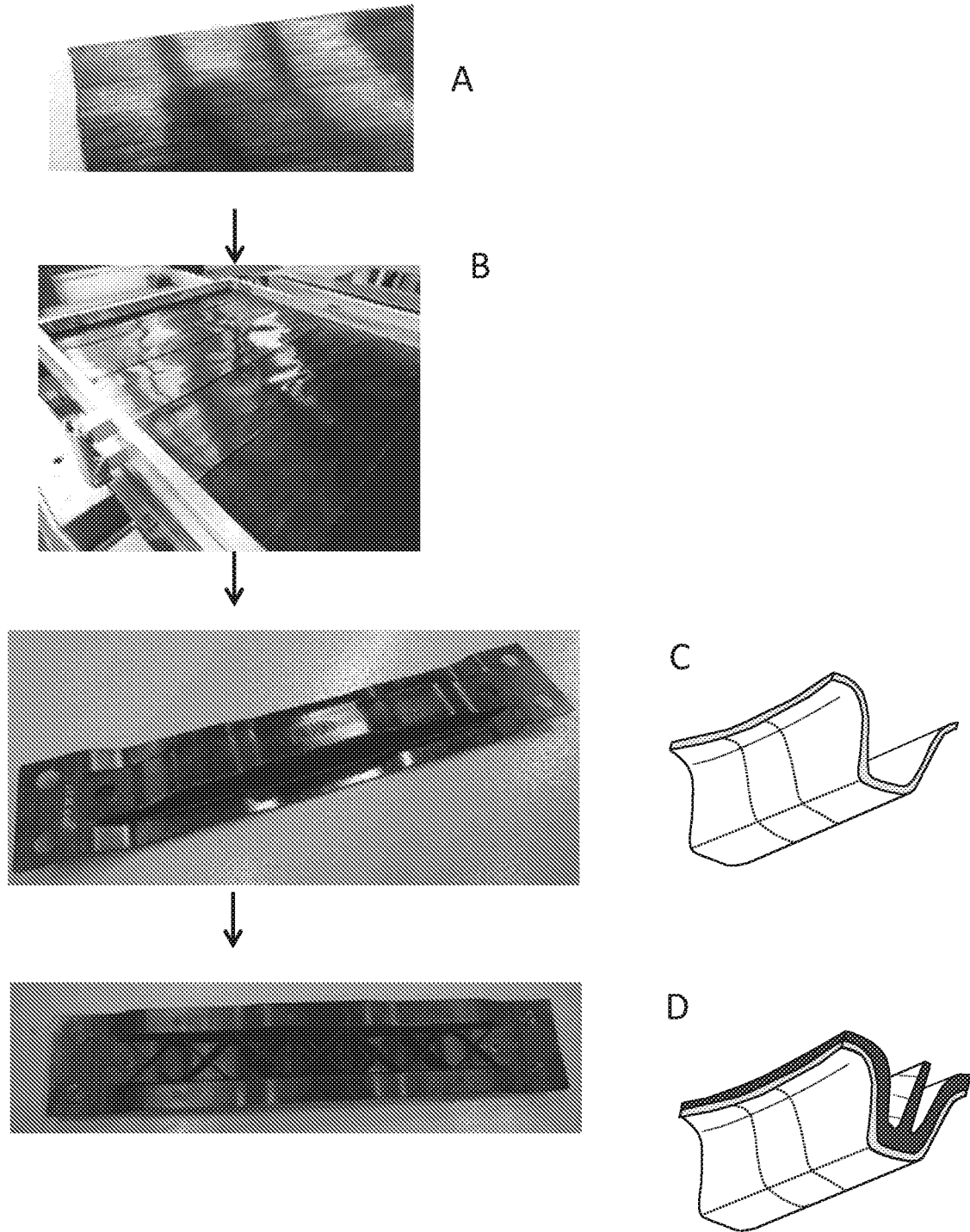


Figure 3

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A

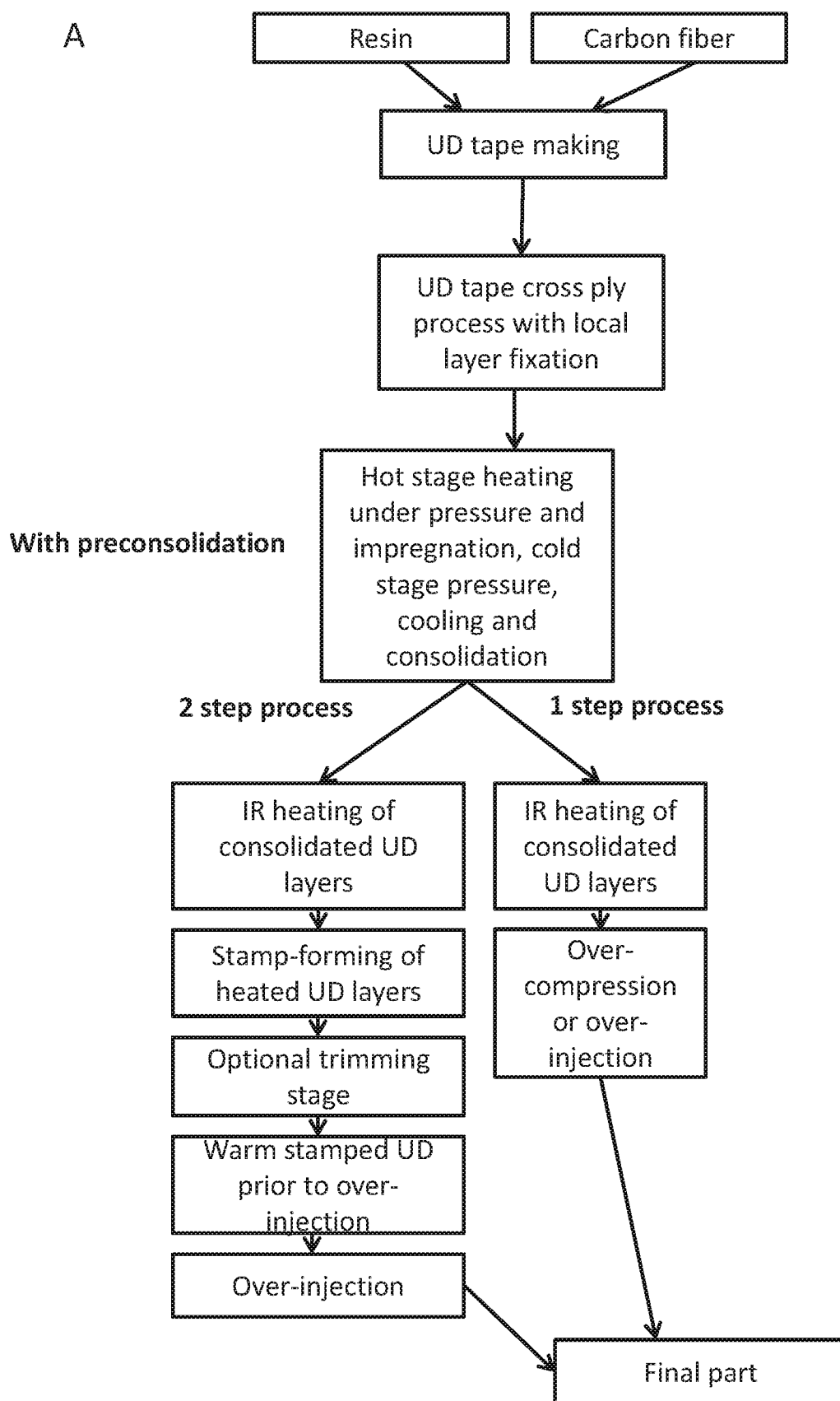


Figure 4

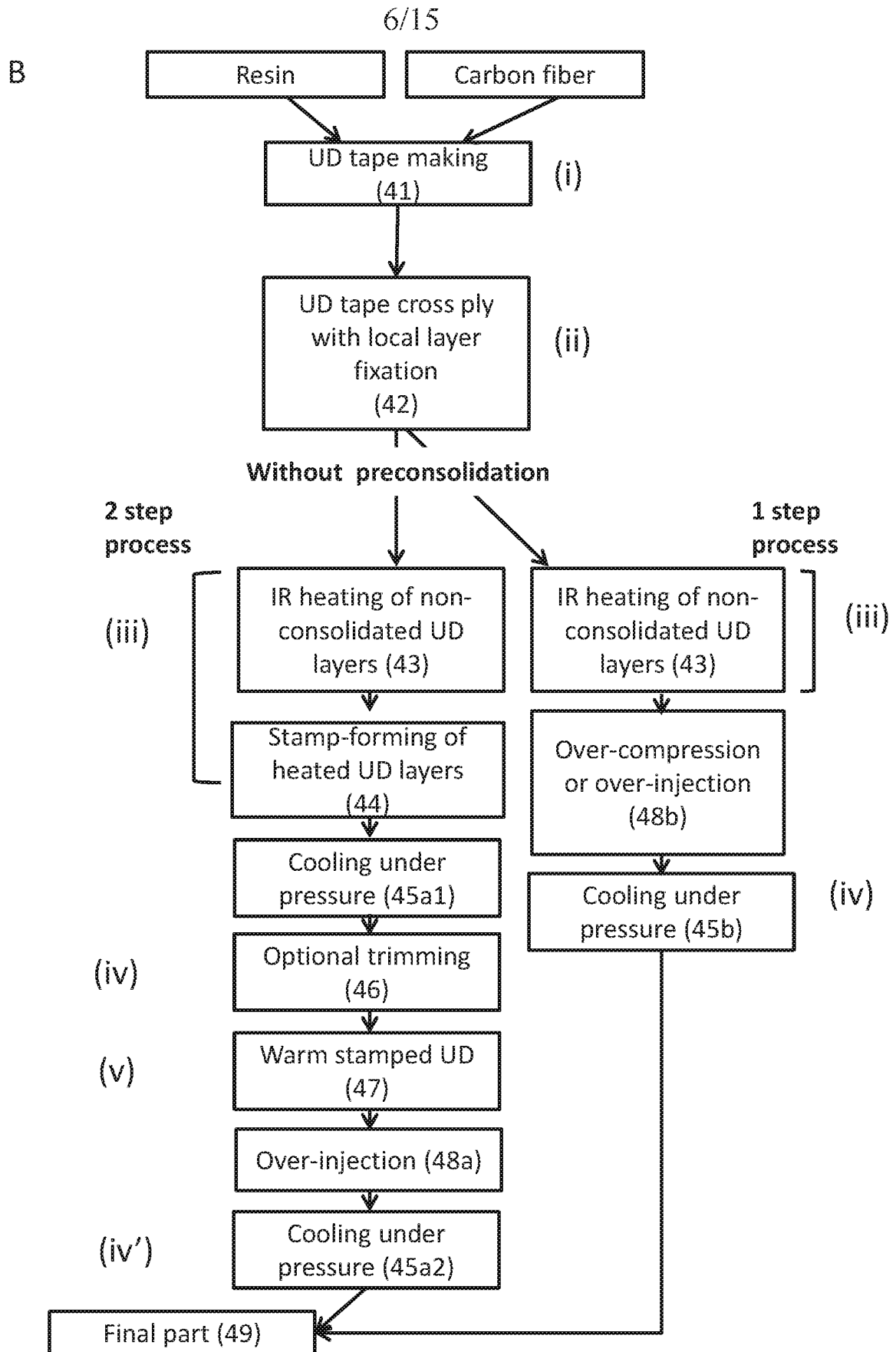


Figure 4 (continued)

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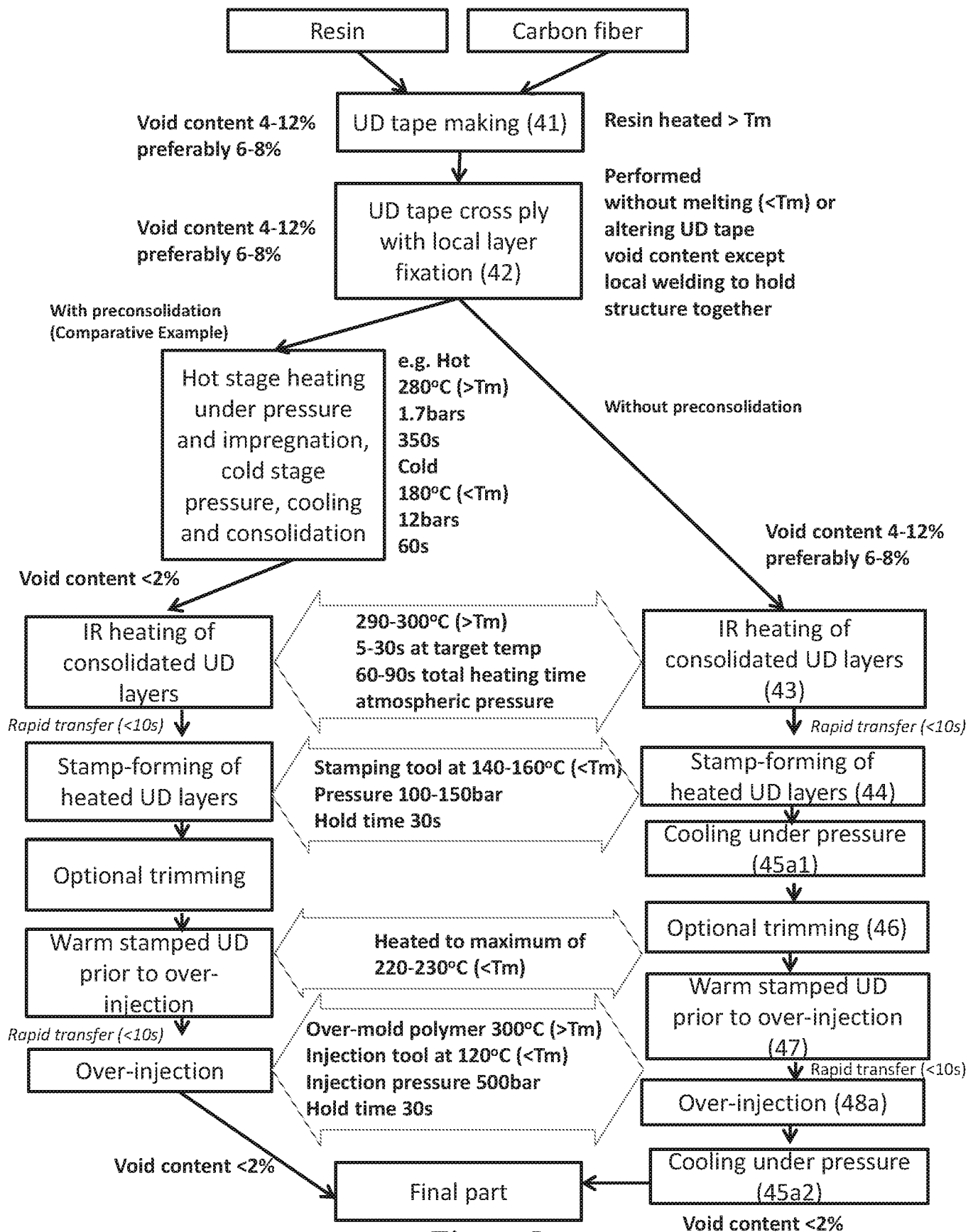


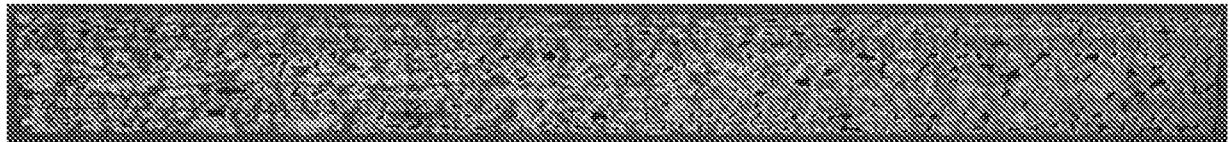
Figure 5

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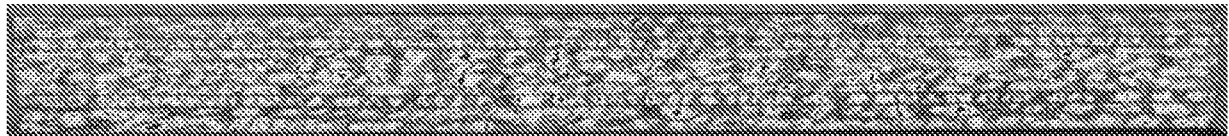
A

Part Number	Number of Heating Stage	T(°C) 1st Heating Stage	Time 1 (sec)	T(°C) 2nd Heating Stage	Time 2 (sec)	T(°C) 3rd Heating Stage	Time 3 (sec)	UD layers	Void content sample 1 (%)	Void content sample 2 (%)	Average void content (%)
B	3	200	60	250	40	300	15	uc	6.1	8.9	7.5
C	Not stamped	-	-	-	-	-	-	pc	0.4	1.5	0.9
D	1	300	5	-	-	-	-	pc	0.3	0.9	0.6

B



C



D

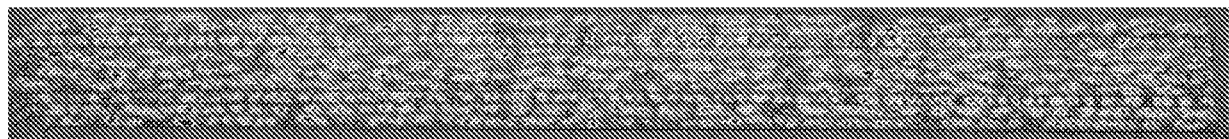


Figure 6

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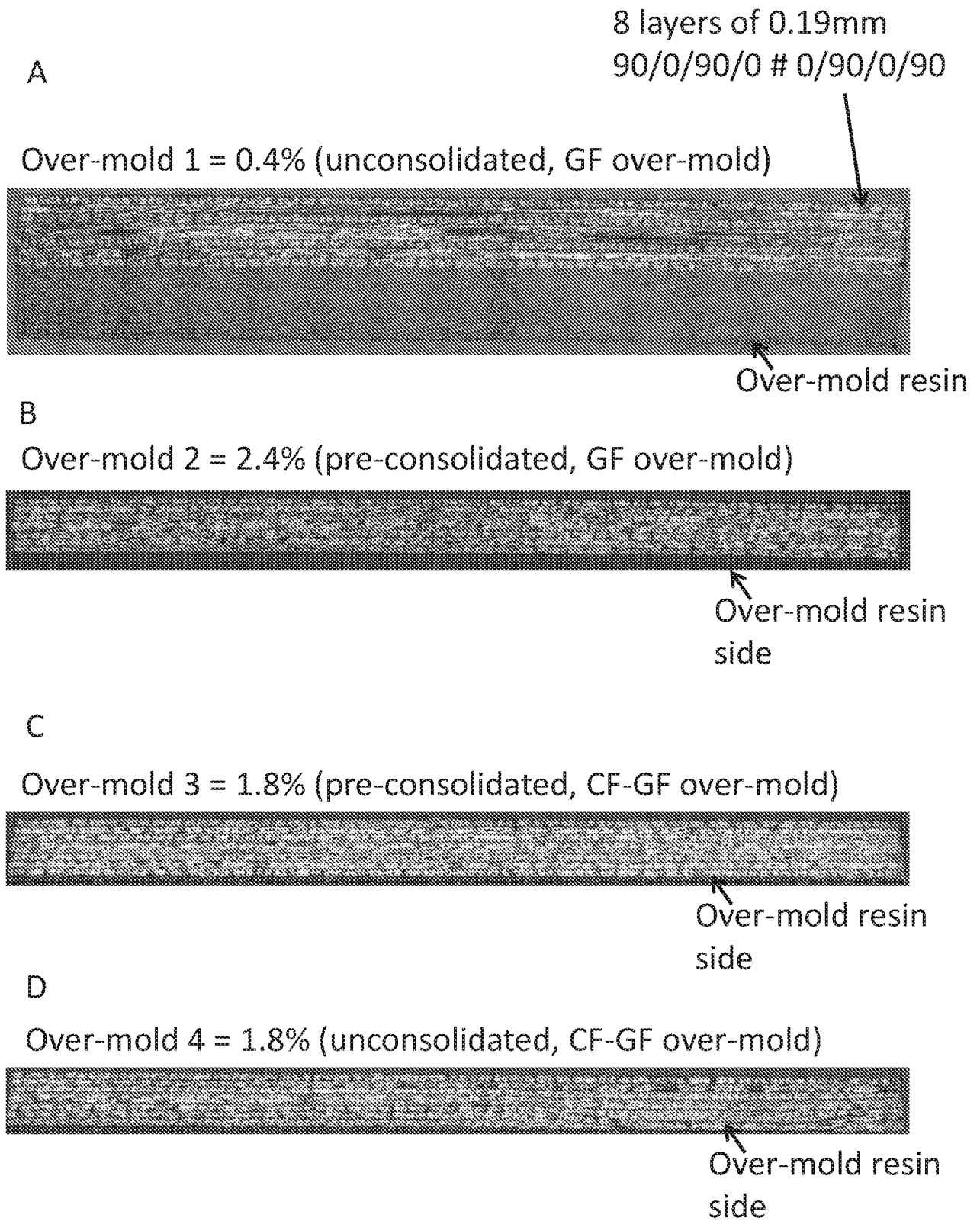
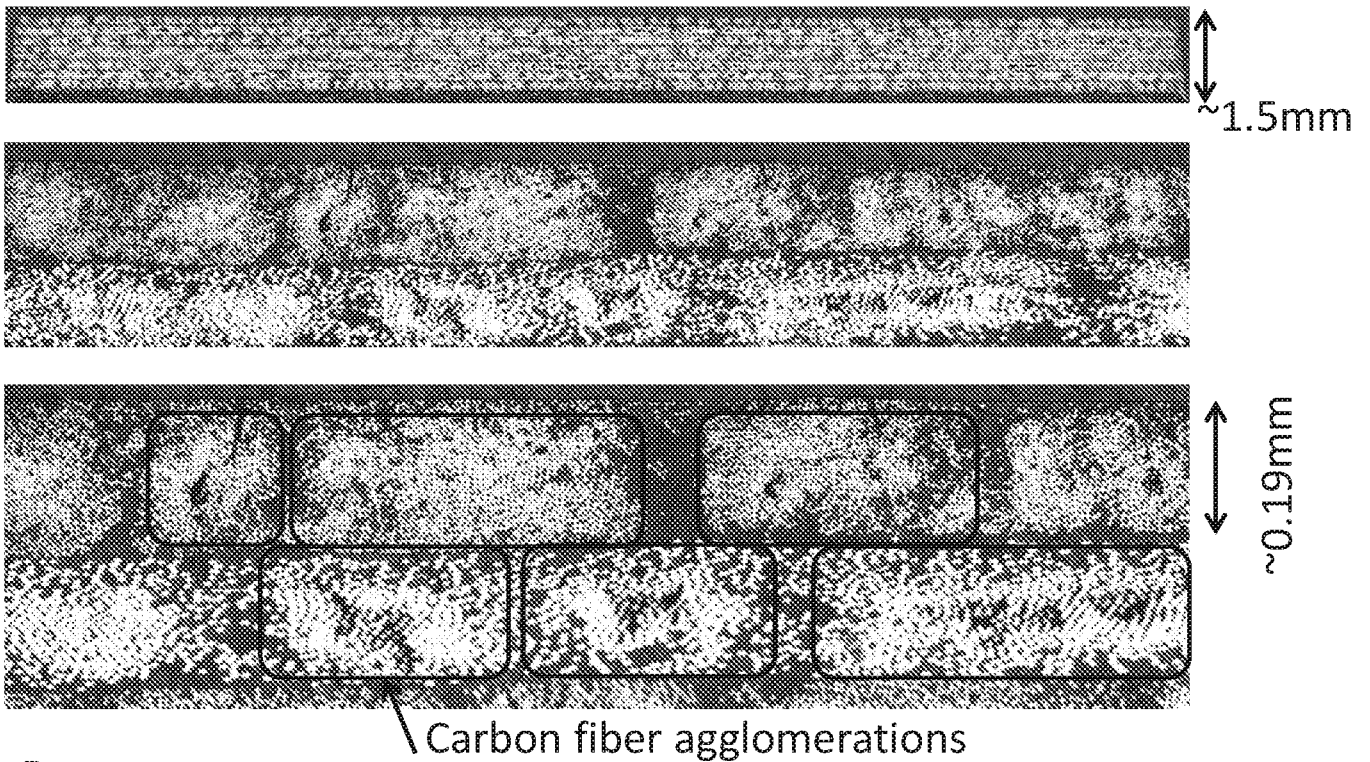


Figure 7

A

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Over-mold 3 = 1.8% (C1, pre-consolidated, CF-GF over-mold)



B

Over-mold 4 = 1.8% (E1 unconsolidated, CF-GF over-mold)

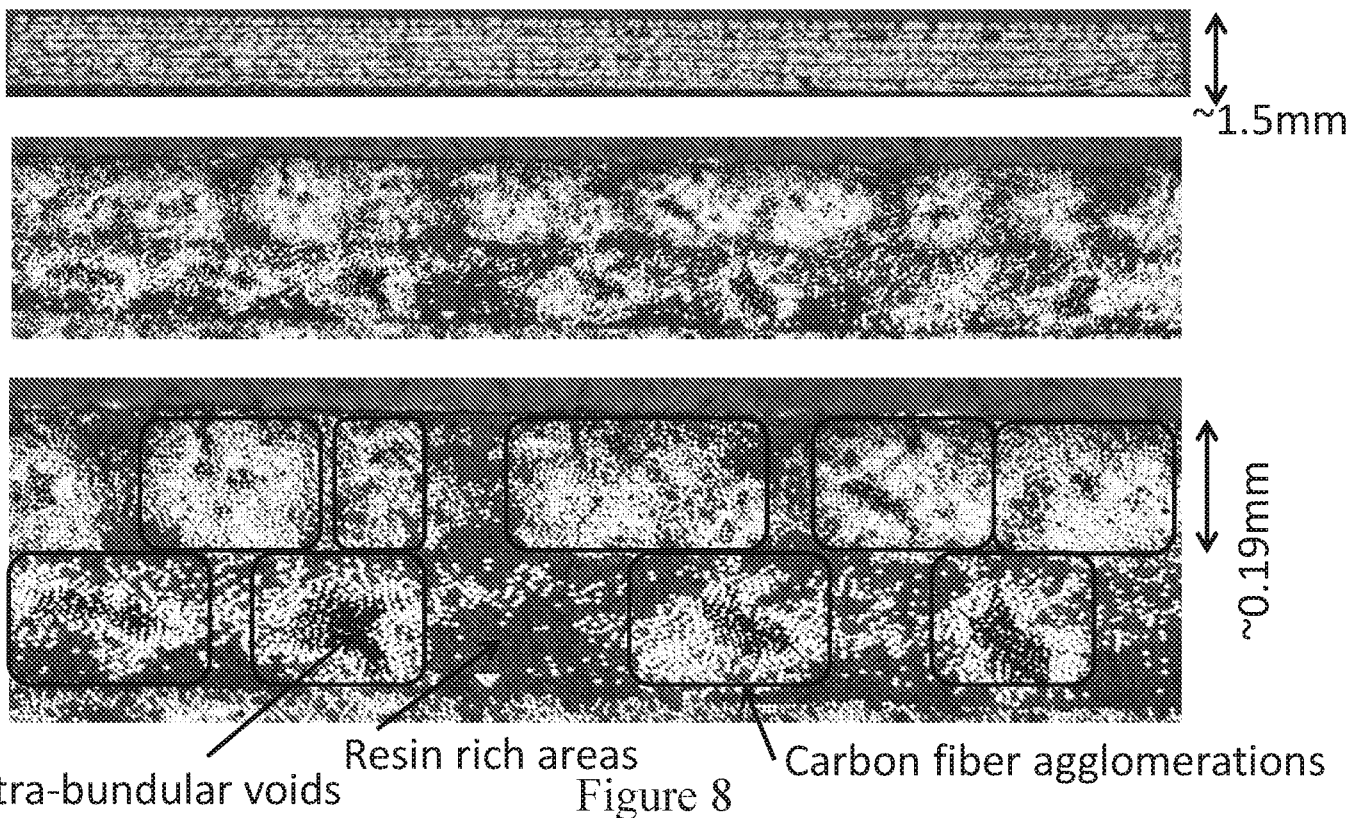
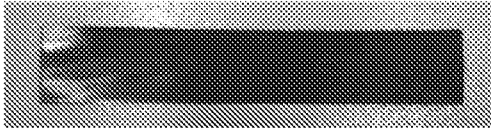


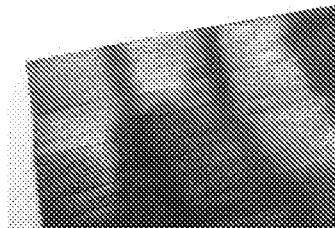
Figure 8

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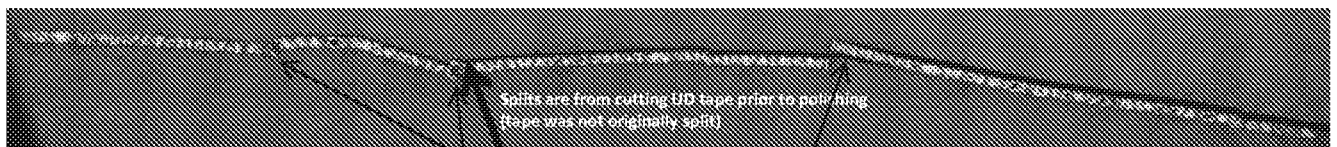
Top view of UD tape



Detail of top view of UD tape



Cross-section of UD tape



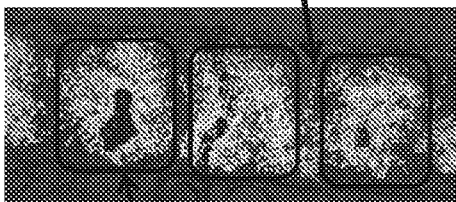
Splits are from cutting UD tape prior to polishing
(tape was not originally split)

**Void content of this ROI (the
whole tape width shown)
6 to 8 % of voids**

Detailed local cross-sections of UD tape

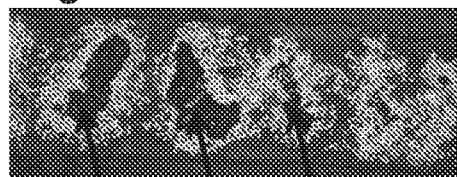
Resin rich areas

Medium voids



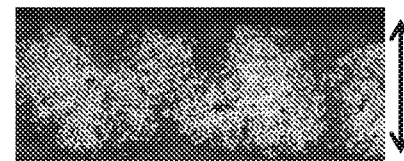
Carbon fiber agglomerations

High voids



Intra-bundular voids

Low voids



~0.19mm

Figure 9

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A

Over-molded beam: unconsolidated UD, OM1 GF over-mold (E2)

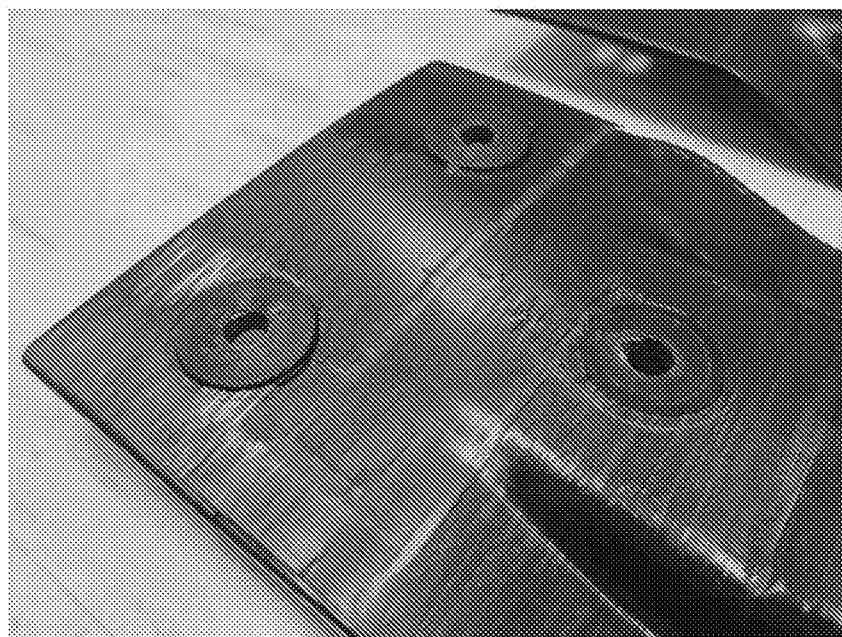


Figure 10

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B

Over-molded beam: Pre-consolidated UD, OM1 GF over-mold (C2)

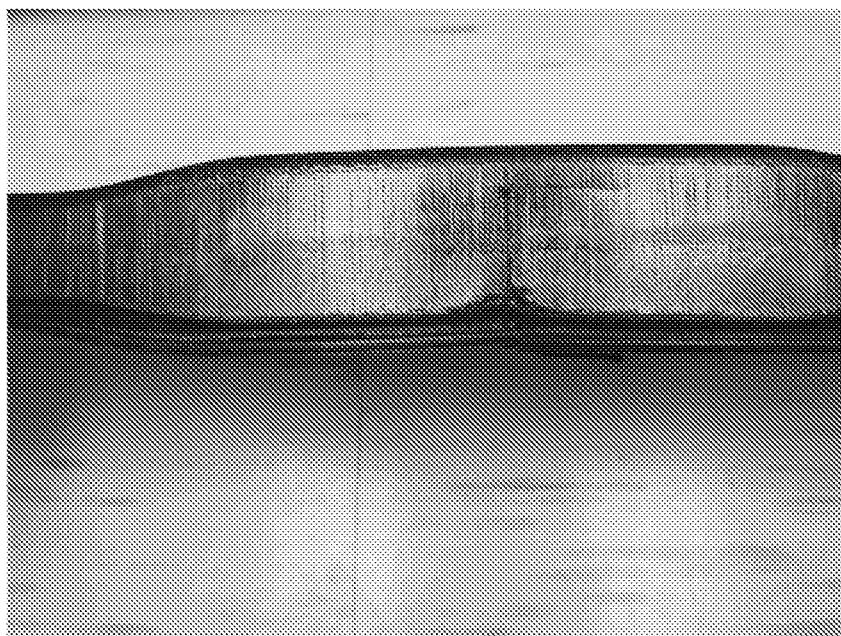
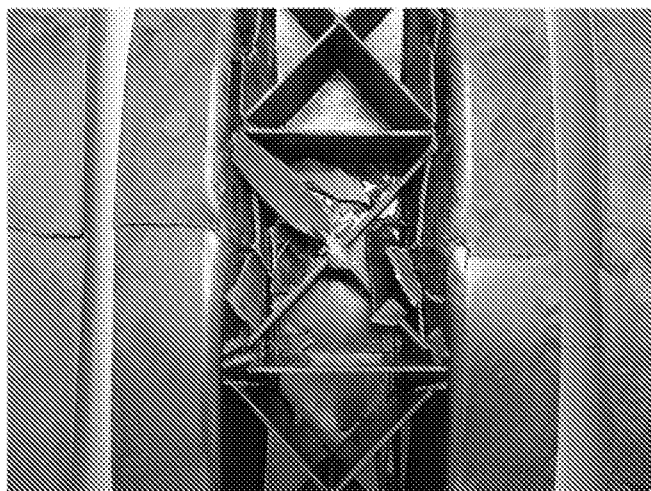


Figure 10 (continued)

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C

Over-molded beam: unconsolidated UD, OM 2 CF-GF over-mold (E1)

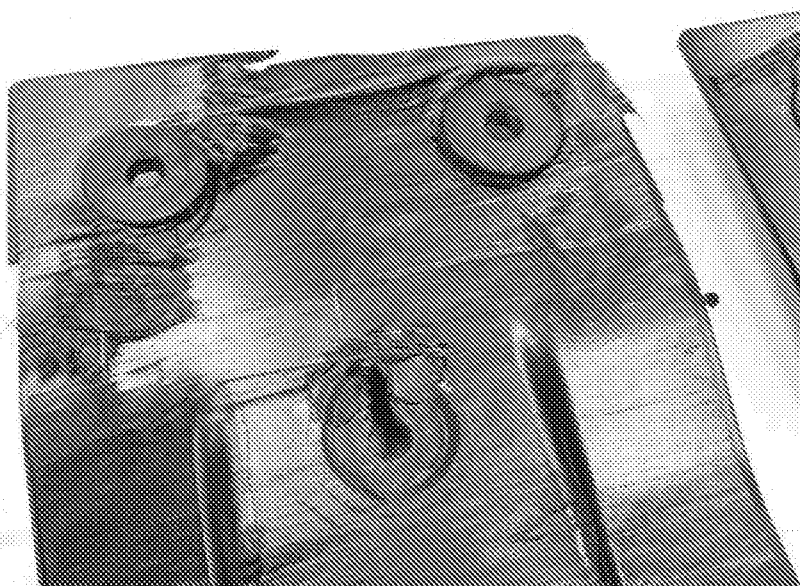
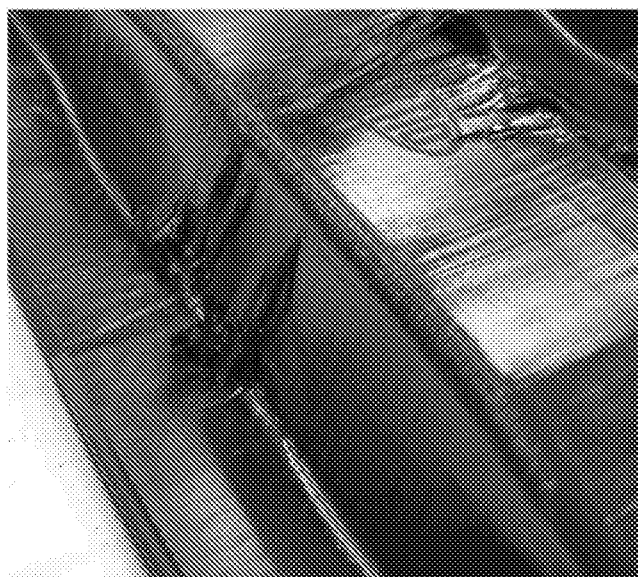


Figure 10 (continued)

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D

Over-molded beam: pre-consolidated UD, OM2 CF-GF over-mold (C1)

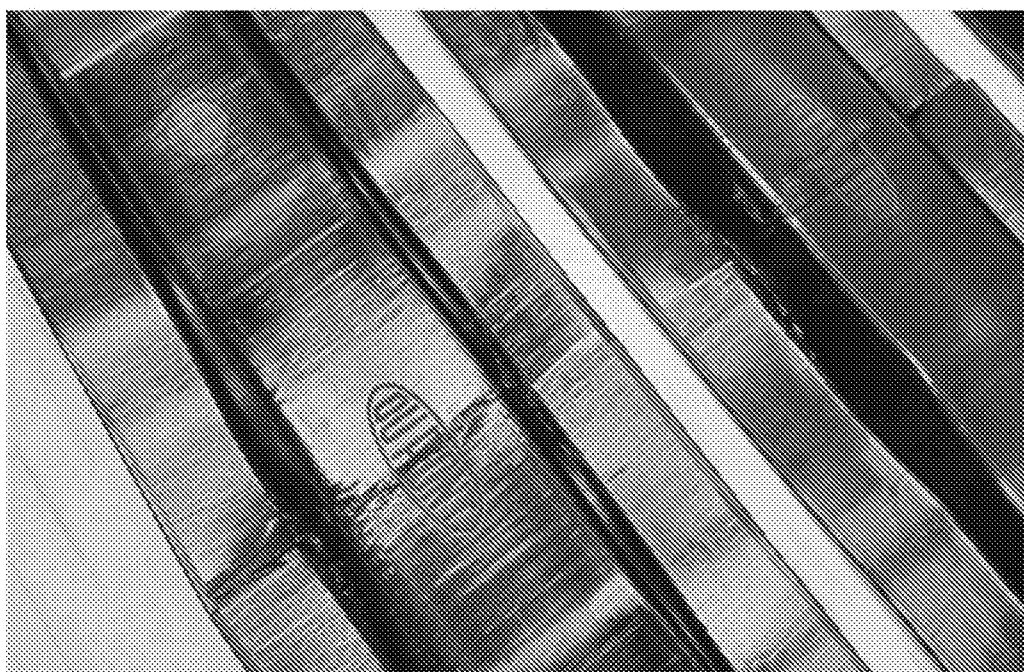
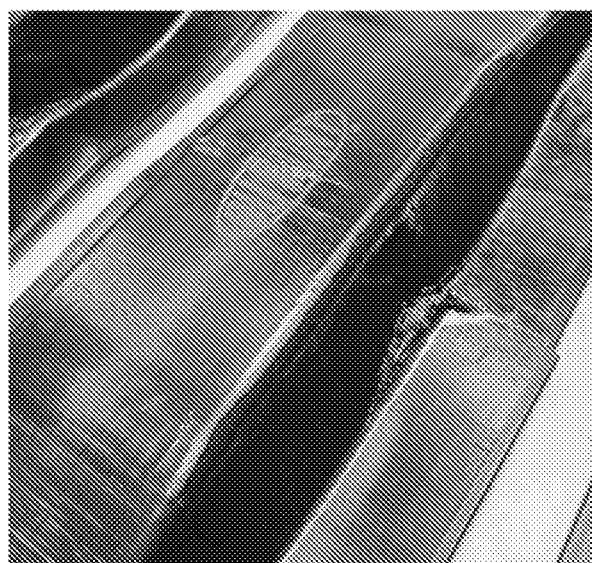
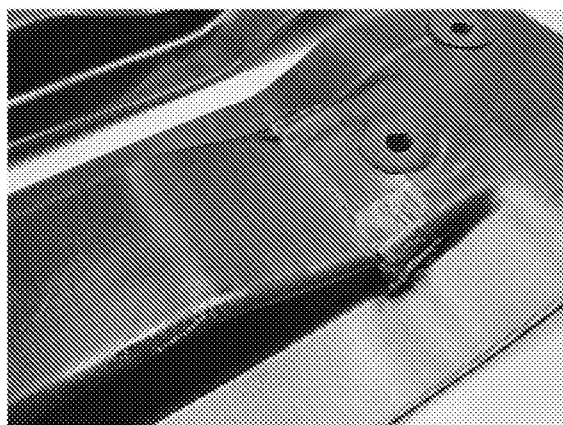


Figure 10 (continued)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/056060

A. CLASSIFICATION OF SUBJECT MATTER INV. B29C45/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B29C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal , WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	wo 2012/058379 A2 (DU PONT [US] ; ELIA ANDRI E [US] ; KI RCHNER OLAF NORBERT [CH] ; WAKEMAN M) 3 May 2012 (2012-05-03)	1
Y	page 8, paragraph 2 - paragraph 6	21,23 ,
A	page 10, paragraph 2 page 16, paragraphs 3,4 -----	25,26 19
X	wo 2014/204522 A1 (DU PONT [US]) 24 December 2014 (2014-12-24)	1
Y	cl aims 1,5,15 -----	21,23 , 25,26
A	CN 104 448 802 A (WUXING MATERIAL TECHNOLOGY JIANGSU CO LTD) 25 March 2015 (2015-03-25) abstract ----- -/- .	34
☒ 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 "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "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 "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 "&" document member of the same patent family		
Date of the actual completion of the international search 8 February 2017		Date of mailing of the international search report 16/02/2017
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 Boone, John

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/056060

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	wo 98/11398 AI (DU PONT CANADA [CA]) 19 March 1998 (1998-03-19) page 7, paragraph 2 -----	34
A	EP 2 816 073 AI (DAINI PPON INK & CHEMICALS [JP]) 24 December 2014 (2014-12-24) Has all ingredi ents but not in the same proporti on, see exampl es; exampl es -----	34

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/056060

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W0 2012058379	A2	03-05-2012	
		BR 112013007232 A2	14-06-2016
		BR 112013010222 A2	13-09-2016
		BR 112013010224 A2	13-09-2016
		BR 112013010227 A2	13-09-2016
		BR 112013010463 A2	02-08-2016
		BR 112013010466 A2	02-08-2016
		BR 112013010473 A2	02-08-2016
		CN 103180133 A	26-06-2013
		CN 103180134 A	26-06-2013
		CN 103189200 A	03-07-2013
		CN 103201100 A	10-07-2013
		CN 103201101 A	10-07-2013
		CN 103209831 A	17-07-2013
		CN 103221208 A	24-07-2013
		CN 103221209 A	24-07-2013
		CN 103237654 A	07-08-2013
		CN 103237655 A	07-08-2013
		CN 103328203 A	25-09-2013
		EP 2632709 A1	04-09-2013
		EP 2632710 A1	04-09-2013
		EP 2632711 A2	04-09-2013
		EP 2632712 A1	04-09-2013
		EP 2632713 A1	04-09-2013
		EP 2632714 A1	04-09-2013
		EP 2632715 A1	04-09-2013
		EP 2632716 A1	04-09-2013
		EP 2632717 A1	04-09-2013
		EP 2632718 A1	04-09-2013
		EP 2632719 A2	04-09-2013
		JP 5878544 B2	08-03-2016
		JP 5911877 B2	27-04-2016
		JP 5931890 B2	08-06-2016
		JP 5932816 B2	08-06-2016
		JP 5972891 B2	17-08-2016
		JP 6027012 B2	16-11-2016
		JP 2013540883 A	07-11-2013
		JP 2013540884 A	07-11-2013
		JP 2013542104 A	21-11-2013
		JP 2013542295 A	21-11-2013
		JP 2013542341 A	21-11-2013
		JP 2013543802 A	09-12-2013
		JP 2013543803 A	09-12-2013
		JP 2013543906 A	09-12-2013
		JP 2013545636 A	26-12-2013
		JP 2013545637 A	26-12-2013
		JP 2014502222 A	30-01-2014
		JP 2016117914 A	30-06-2016
		US 2012108122 A1	03-05-2012
		US 2012108123 A1	03-05-2012
		us 2012108124 A1	03-05-2012
		us 2012108125 A1	03-05-2012
		us 2012108126 A1	03-05-2012
		us 2012108127 A1	03-05-2012
		us 2012108128 A1	03-05-2012
		us 2012108129 A1	03-05-2012
		us 2012108130 A1	03-05-2012
		us 2012108131 A1	03-05-2012
		us 2012108136 A1	03-05-2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/056060

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2016214359 AI	28-07 -2016
		WO 2012058345 AI	03-05 -2012
		WO 2012058346 AI	03-05 -2012
		WO 2012058348 AI	03-05 -2012
		WO 2012058350 A2	03-05 -2012
		WO 2012058351 AI	03-05 -2012
		WO 2012058352 AI	03-05 -2012
		WO 2012058359 AI	03-05 -2012
		WO 2012058366 AI	03-05 -2012
		WO 2012058368 AI	03-05 -2012
		WO 2012058374 AI	03-05 -2012
		WO 2012058379 A2	03-05 -2012

WO 2014204522 AI	24-12 -2014	CN 105555520 A	04-05 -2016
		EP 3010713 AI	27-04 -2016
		JP 2016522305 A	28-07 -2016
		US 2016101592 AI	14-04 -2016
		WO 2014204522 AI	24-12 -2014

CN 104448802 A	25-03 -2015	NONE	

WO 9811398 AI	19-03-1998	CA 2263607 AI	19-03-1998
		DE 69719770 DI	17-04-2003
		DE 69719770 T2	20-11-2003
		EP 0928406 AI	14-07-1999
		US 6094816 A	01-08-2000
		WO 9811398 AI	19-03-1998

EP 2816073 AI	24-12-2014	CN 104114619 A	22-10-2014
		EP 2816073 AI	24-12-2014
		JP 5392590 BI	22-01-2014
		JP W02013122209 AI	18-05-2015
		KR 20140105528 A	01-09-2014
		TW 201343732 A	01-11-2013
		US 2015005413 AI	01-01-2015
		US 2017015799 AI	19-01-2017
		WO 2013122209 AI	22-08-2013
