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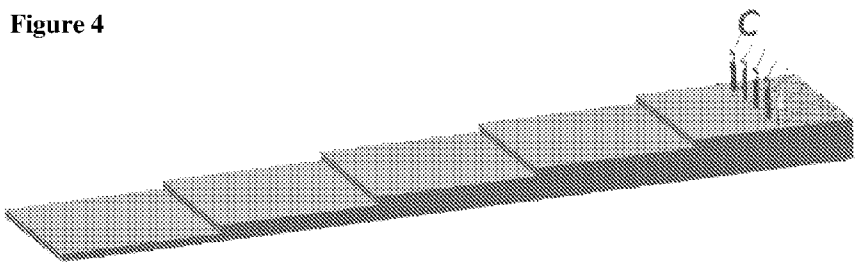
(54) Title: THERMOPLASTIC PREPREG PRODUCTION METHOD

Figure 4



(57) Abstract: The present invention relates to a thermoplastic prepreg production method which is developed in order to be used as structural and visual material in all industrial fields, mainly aviation, defense industry and automotive, and which enables the thermoplastic resin to be impregnated into the stitched fabric formed with a reinforcing yarn (A). The objective of the present invention is to provide a thermoplastic prepreg production method which enables to apply more accurate resin amount to the stitched fabrics comprising reinforcing yarn (A) and thermoplastic yarn (B), and to be processed more easily.

THERMOPLASTIC PREPREG PRODUCTION METHOD

Field of the Invention

The present invention relates to a thermoplastic prepreg production method which is developed in order to be used as structural and visual material in all industrial fields, mainly aviation, defense industry and automotive, and which enables the thermoplastic resin to be impregnated into the stitched fabric formed with a yarn that is manufactured from reinforcing fibers.

Background of the Invention

The prepregs are divided into two main categories, namely thermoset and thermoplastic. The thermoplastic prepreg is a structure comprised of thermoplastic resin impregnated yarns manufactured from reinforcing fibers. The thermoplastic prepregs are very popular today due to their lightweight, recycling potential, and resistance against corrosion properties.

Today, the resin used in thermoplastic prepreg production is applied as powder, film or granule. The thermoplastic prepregs that are obtained are then transformed into composite material which is the final product with production methods such as, thermoforming, compression molding via heat and pressure or overmolding.

In thermoplastic prepreg production, materials such as polyamides (PA) (polyamide 6 (PA6), polyamide 6,6 (PA66), polyphthalamide (PPA)), polyphenylene sulfide (PPS), polysulfone (PSU) polyarylenethersulfone, polyolefines (polyethylene (PE), polypropylene (PP) etc.), polyimide (PI), polyesters, preferably such as polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), polyether ether ketone (PEEK) can be used.

Manual or automatic methods are preferred in feeding the resin in powder, film and granule form to the system. Especially powder and granule applications used

in thermoplastic prepreg production cause homogenization problem in distributing resin, difficulty in using optimum raw material, and high amount of waste occurring during production.

Thermoplastic prepreg production is performed with discontinuous or continuous methods. In both discontinuous and continuous methods, even in case of feeding the resin in powder form is automatic, the thermoplastic resin/reinforcing fiber ratio cannot be applied in the desired accuracy. Variations occur in the powder amounts used in unit area. In case it is supplied in granule form, since resin particles sizes are too big, accumulations occur since homogenous melting cannot be provided on the thermoplastic prepreg. The impregnation of the resin in the fiber structure is not easy due to same reason. In other words, the resin cannot penetrate into the structure comprised of yarn manufactured from reinforcing fiber homogenously.

United States Patent Document no US5445701, an application known in the state of the art, discloses a thermoplastic resin method in form of film. However, this method is expensive, as well as difficulties in supplying the film compatible for the desired thermoplastic material can be experienced.

In United States Patent Document no US20140030582, an application known in the state of the art, the wall thickness of the thermoplastic prepregs of the present invention can be produced in range of 0.3 and 6.0 mm. The said invention can function in a limited field since it is not for thermoplastic prepregs with bigger wall thickness.

United States Patent Document no US5464684, an application known in the state of the art, discloses a production method of the polyamide based hybrid yarn. In this method, thermoplastic yarn and reinforcing yarn are produced by mixing with each other by air application. Depending on the complexity of the yarn mixing

process and application of twisting process on carbon fiber which is very brittle, causes decrease of the linear strength of the carbon fiber.

Summary of the Invention

The objective of the present invention is to provide a thermoplastic prepreg production method which enables the resin used in prepreg application to penetrate more into the stitched fabric relative to the conventional applications, in other words which enables the wettability of the fabric formed with a yarn that is manufactured from reinforcing fiber.

Another objective of the present invention is to provide a thermoplastic prepreg production method which enables to apply more accurate amount of resin to the stitched fabrics comprising reinforcing yarn and thermoplastic yarn and also to provide more easily processing of them.

Detailed Description of the Invention

The "Thermoplastic prepreg application method" developed to fulfill the objectives of the present invention is illustrated in the accompanying figures, in which:

Figure 1 is the view of the stitched fabric used for unidirectional thermoplastic prepreg manufactured with the inventive thermoplastic prepreg application method.

Figure 2 is the view of the stitched fabric used for triaxial thermoplastic prepreg manufactured with the inventive thermoplastic prepreg application method.

Figure 3 is the view of the stitched fabric used for biaxial thermoplastic prepreg manufactured with the inventive thermoplastic prepreg application method.

Figure 4 is the view of the stitching yarn (C) used in the inventive thermoplastic prepreg application method.

The components shown in the figures are each given reference numbers as follows:

A. Reinforcing yarn

B. Thermoplastic yarn

C: Stitching yarn

Unidirectional thermoplastic prepreg is obtained in a way disclosed in the invention, for example, after stitching the fabrics with stitching yarn in order to hold the unidirectional fabrics manufactured from thermoplastic yarn used in first and last layer of the stitched fabric and the fabric manufactured from unidirectional reinforcing yarn used in middle layer of the same stitched fabric shown in figure 1.

The stitching types used in production of stitched fabric may be pillar, tricot and the like.

The inventive uni-directional, biaxial, triaxial or multiaxial thermoplastic prepreg production method, which enables the resin to penetrate into the fabric homogenously and deeply in resin impregnation process realized in order to reinforce the stitched fabric which is manufactured, and comprises the steps of

- Stitching with the stitching yarn in order to combine the thermoplastic yarns and reinforcing yarns determined in thermoplastic prepreg design during fabric production phase,
- Placing each one of the unidirectional layers manufactured with reinforcing yarn comprising thermoplastic yarn on its lower and/or upper surface,
- Being comprised of at least two layers such that at least one of the layers will comprise a layer including “unidirectional reinforcing fiber”,
- Increasing the temperature of the stitched fabric above the softening point or melting point of the thermoplastic yarn,

- Applying pressure (0-100 bar) on the stitched fabric at this temperature,
- Applying pre-tensioning (0-5 g/tex) on the stitched fabric at this temperature,
- Enabling the thermoplastic resin in yarn form to penetrate between the fibers of the reinforcing yarn inside the fabric by melting,
- Applying temperature and pressure for a time in range of 2-120 minutes,
- Obtaining the ready to use final product by cooling until it reaches a temperature below glass transition temperature (T_g) of the resin without pressure or under pressure.

In the said invention, the thermoplastic yarns used in forming the stitched fabric is used in form of a thermoplastic yarn (B) selected from a group comprising polyamides (such as polyamide 6 (PA6), polyamide 6,6 (PA66), polyphthalamide (PPA)), polyphenylene sulfide (PPS), polysulfone (PSU) (such as polyethersulfone (PES), polyarylenethersulfone), polyarylenesulfide, fluoropolymer, polyacetal, polycarbonate, styrenic polymer, polyolefins (such as polyethylene (PE), polypropylene (PP)), polyimide (PI), polyetherimide, polyesters preferably polyethylene terephthalate (PET) or polybutylene terephthalate (PBT), polyether ether ketone (PEEK), polyether ketone (PEK), or combinations thereof.

In the said invention, as reinforcing yarn (A) used in forming the stitched fabric, a yarn produced from a material selected from the group comprising glass fiber, carbon fiber, aramid fiber, natural fiber, or a combination thereof is used.

The term “stitched fabric” used in the invention is defined as a system comprised of one or more than one unidirectional fiber layers, and formed by holding these layers together by stitching with a nonstructural stitching yarn, preferably a stitching yarn manufactured from thermoplastic polymer. When the angles of the unidirectional layers forming the stitched fabrics, the fabrics can be unidirectional, biaxial, triaxial or multiaxial.

The term “dtex” used in the invention is the weight in grams per 10000 meters yarn. The term “tex” used in the invention is the weight in grams per 1000 meters yarn.

In the inventive thermoplastic prepreg production method, the resin being in form of yarn manufactured from thermoplastic fiber enables the amount of resin/reinforcing fiber ratio in the thermoplastic prepreg to be adjusted easily.

In the present invention, the wall thickness of the thermoplastic prepregs which are the final products formed by penetrating the resin into the stitched yarn is adjusted to be in range of 0.25 and 8 mm. The wall thickness of the thermoplastic prepregs comprising single layer reinforcing fiber depends on the type of the used reinforcing yarn, areal weight of fabric and the pressure which is applied. The wall thickness of the thermoplastic prepregs manufactured from stitched fabric obtained by holding the system comprising at least “single layer reinforcing yarn” and produced as at least two layers together with a nonstructural stitching yarn depends on the number of the used unidirectional fiber layers, type of the reinforcing yarn, areal weight of the stitched fabric and the pressure.

The present invention comprises application of 0-100 bars, preferably in range of 1-40, of pressure on the resin in step of heating of the resin.

In the present invention, the cooling of the resin penetrating into the reinforcing yarns of the stitched fabric is carried out under 0-100 bars of pressure, preferably in range of 1-40 bars of pressure.

In the present invention, the weight of the thermoplastic resin is in range of 10% to 90%, preferably 30% to 70% of the weight of the yarn manufactured from reinforcing fibers.

In a preferred embodiment of the invention, in order to enable unidirectional (UD) thermoplastic prepreg production, unidirectional and single layered reinforcing yarns (A) and layers comprising thermoplastic yarn (B) on lower and/or upper surface of the said layer are used.

In a preferred embodiment of the invention, in order to enable biaxial thermoplastic prepreg production, biaxial and two layered reinforcing yarns (A) and layers comprising thermoplastic yarn (B) on lower and/or upper surfaces of the said layers are used.

In a preferred embodiment of the invention, in order to enable triaxial thermoplastic prepreg production, triaxial and three layered reinforcing yarns (A) and layers comprising thermoplastic yarn (B) on lower and/or upper surfaces of the said layers are used.

In a preferred embodiment of the invention, in order to enable multiaxial thermoplastic prepreg production, minimum quadraxial and four layered reinforcing yarns (A) and layers comprising thermoplastic yarn (B) on lower and/or upper surfaces of the said layers are used.

In a preferred embodiment of the invention, the stitched fabric is obtained by stitching at least two woven fabrics, which are obtained by weaving thermoplastic yarn and reinforcing yarn together, with a stitching yarn together.

The inventive thermoplastic prepregs can be used as structural and visual material in all industrial fields, mainly aviation, defense industry and automotive. The final product that is obtained is the semi-product called as the thermoplastic prepreg or organosheet.

In thermoplastic prepreg production, discontinuous or continuous methods can be used. The main principle used in both methods is to apply pressure (0-100 bars) at a temperature above softening or melting point of the thermoplastic resin, and to

enable the resin to be impregnated into the reinforcing fibers in this way. Cooling process is applied after temperature and pressure is applied for a determined time between 2 minutes and 120 minutes. Cooling process can be applied without pressure or under pressure (0-100 bar) depending on the structure of the polymer. The cooling temperature is below the glass transition temperature (T_g) of the resin. The machine in which the inventive thermoplastics are produced can be heated up to 450°C depending on the structure of the plastic. The temperature range that can be used in cooling process is between 25°C and 200°C. The wall thickness of the inventive thermoplastic prepregs is in range of 0.25 mm to 8mm. The applications known in the state of the art cannot provide the resin to be homogenously impregnated into the fibers. On the other hand, in the inventive method, since the resin is used in yarn form, the resin/reinforcing fiber ratio can be accurately adjusted. In summary, with the newly developed method, resin homogenization in amount is provided before starting the process. In order to provide the resin/reinforcing fiber ratio homogenously in a desired ratio in everywhere, the different dtex, different filament diameter and number of yarn produced from thermoplastic fibers can be used. With the thermoplastic yarn application, increasing in plastic surface area and regular material orientation enable the resin to be melt more easily relative to especially the powder and granule applications. Therefore, product with higher quality can be obtained in a machine which has lower accuracy. At the same time, the defects related to areal weight of resin that can occur during application are prevented.

The thermoplastic resins used in the stitched fabric application are applied in form of yarn on different layers of the fabric. The yarns manufactured from reinforcing fibers (glass, carbon, aramid, natural fiber, etc.) are applied in single layer or different layers of the fabric in the same way, and the obtained hybrid structure is enabled to be appropriate for thermoplastic prepreg production. Two or more kinds of reinforcing yarns (A) can be used in hybrid fabrics. For example, carbon, glass and thermoplastic yarn (B) can be used in the same stitched fabric.

Within the scope of the inventive method, raw material of the thermoplastic prepreg is obtained from the fabric comprising reinforcing yarn (A) and thermoplastic yarn (B) from the multiaxial textiles production machine which is being currently used. Therefore, there is no extra process step required as conventional thermoplastic prepreg production during powder, film or granule coating application, and thus the production is carried out faster.

In production of thermoplastic prepregs, stitched fabrics comprising reinforcing yarn (A) and thermoplastic yarn (B) can be processed in more accurate resin amounts, and they can be processed more easily. The thermoplastic composite structure which is the end product can easily reach the required strength values with the design of stitched fabric layers. By means of the stitched fabric types that are designed differently, thermoplastic prepregs with different mechanical properties can be obtained. By this means the composite structure can be varied compatible with the field of use of the end user.

The stitched fabric application is suitable for being used in wide range of application fields since it allows placing the reinforcing yarn in different axes.

CLAIMS

1. A thermoplastic prepreg material production method **characterized by** the steps of

a)obtaining a fabric by at least two layers comprising reinforcing yarns and thermoplastic yarns being stitching together with stitching yarns,

b) impregnating the said thermoplastic yarns into the said stitched fabric by melting of softening,

c) cooling the said impregnated stitched fabric to a temperature below the glass transition temperature of the said thermoplastic yarns.

2. A thermoplastic prepreg production method according to claim 1, **characterized in that** it comprises the step of applying pressure on the said stitched fabric during melting and softening process of the said thermoplastic yarn.

3. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** it comprises the step of applying pressure in range of 0-100 bars on the said stitched fabric during melting and softening process of the said thermoplastic yarn.

4. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** it comprises the step of applying pressure on the said stitched fabric during the cooling process of the said thermoplastic prepreg material.

5. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** it comprises the step of applying pressure in range of 0-100 bars on the said stitched fabric during the cooling process of the said thermoplastic prepreg material.

6. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said thermoplastic yarns are comprised of polyamide, polyolefin, polyether ketone, polyether ether ketone, polyimide, polyetherimide, polyaryleneketone, polyarylene sulfone, polyarylene ether sulfone, polyarylene sulfide, fluoropolymer, polyacetal, polycarbonate, styrenic polymer, polyester or combinations thereof.

7. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said reinforcing yarns (A) used in forming the said fabric is manufactured from a material selected from the group including glass, carbon, aramid or natural fiber, or a combination thereof.

8. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said stitching yarns are thermoplastic.

9. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said stitched fabric is formed by stitching the said reinforcing yarn layer(s) and the said thermoplastic yarn layer(s) with stitching yarns.

10. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said stitched fabric comprises reinforcing yarn layer(s) formed by stitching with stitching yarns and thermoplastic yarn layer(s) formed by stitching with stitching yarns.

11. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said reinforcing yarn layer(s) and the said thermoplastic yarn layer(s) are unidirectional.

12. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the said unidirectional layers comprised by the said stitched fabric is obtained as unidirectional, biaxial, triaxial or multiaxial by stitching them with different angles to each other.

13. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the layers of the said fabric comprising the said unidirectional reinforcing yarns is formed of same kind or hybrid yarns.

14. A thermoplastic prepreg production method according to claims 1-8, **characterized in that** the said stitched fabric comprises weave fabrics obtained by weaving by using thermoplastic yarn and reinforcing yarn.

15. A thermoplastic prepreg production method according to any one of the preceding claims, **characterized in that** the ratio of the weight of the said thermoplastic yarn to the weight of the said reinforcing yarn is at least 10%.

Figure 1

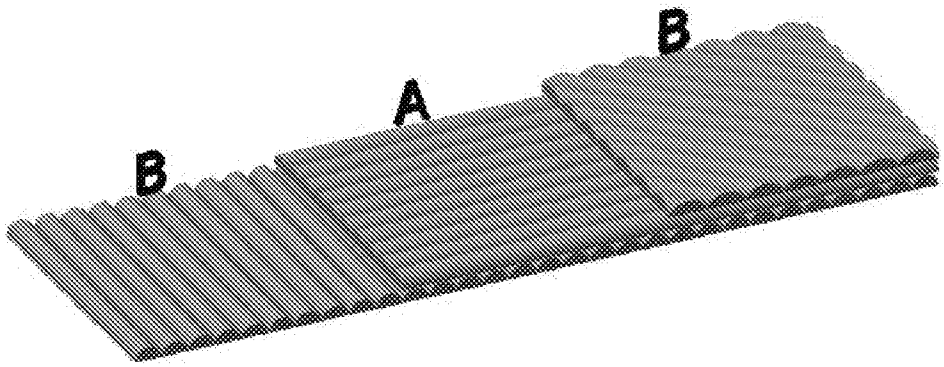


Figure 2

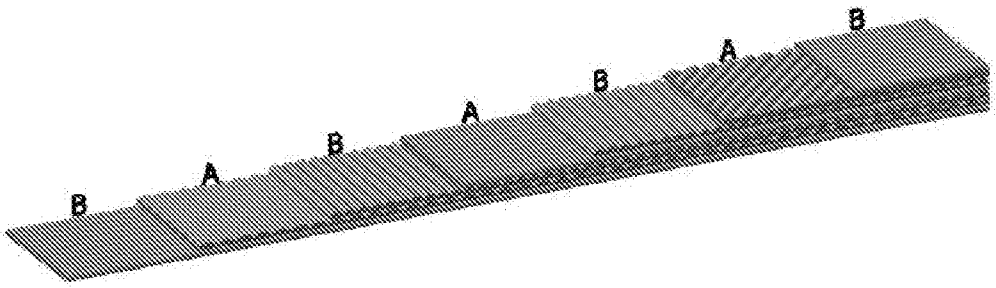


Figure 3

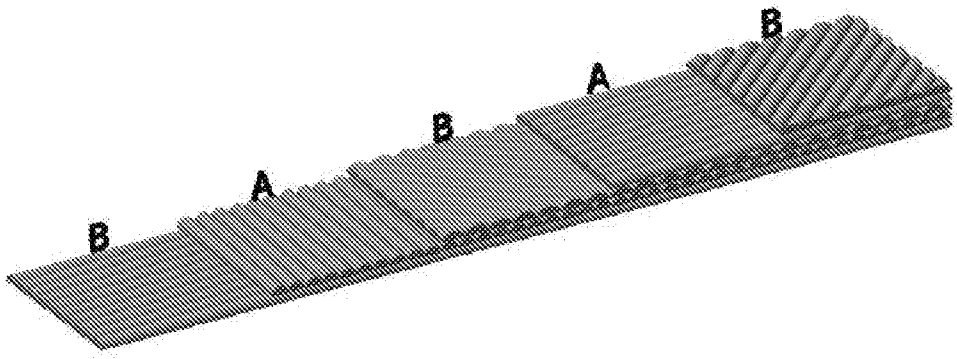
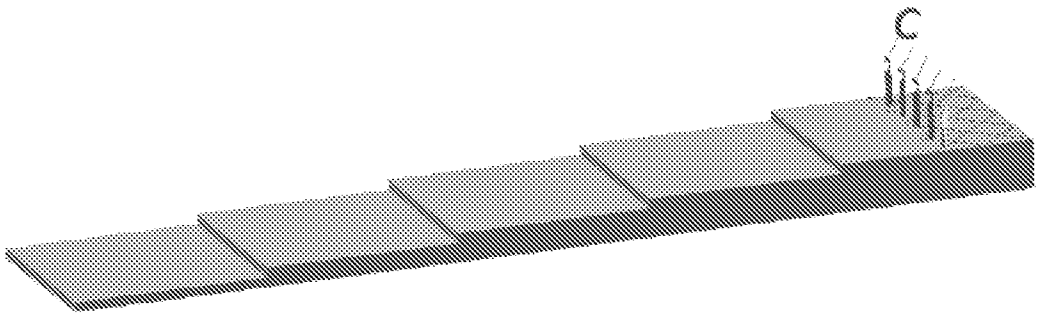


Figure 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/TR2016/050341

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29B15/12 D04H3/115 D04H3/14
ADD. B29K101/12

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)
B29B D04H B29K

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 2012/152242 A1 (SKL SCHWERGEWEBEKONFEKTION LICHTENSTEIN GMBH [DE]; SCHEIKA MIKE [DE];) 15 November 2012 (2012-11-15) pages 3,4 pages 8,9 figures 1,2	1-15
X	DE 10 2011 102342 A1 (CRAMER WEBEREI C [DE]) 29 November 2012 (2012-11-29) paragraph [0008] - paragraph [0011]	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/TR2016/050341

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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