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JPH01254741

(58) Field of Search:
INT CL **B22F, B29B, B29C, B32B, C08J**
Other: **Online: EPODOC, WPI, TXTE, Internet**

(54) Title of the Invention: **A method and apparatus for infusing additive manufactured objects and the like**
Abstract Title: **Method, apparatus and infiltrant for infiltrating an object made by additive manufacturing**

(57) A method of infiltrating an object made by additive manufacturing using a thermoplastics material to at least partially fill pores between particles or sheets used in the additive manufacturing process. Also apparatus suitable for infusing such an object where the apparatus comprises an infusion chamber 12, a reservoir 14 filled with a thermoplastics material, a curing chamber 16, means for controlling the apparatus and either heating means 20 in the reservoir 14 or means 24 & 36 by which the curing chamber 16 can operate at both negative and positive pressure. The thermoplastics material can be a linear or branched semi-crystalline aliphatic polyester with a melting point in the range 40-65 ^{0}C and a solidification/crystallisation point in the range 20-40 65 ^{0}C, for example a polyol polycaprolactone with a molecular weight in the range 2000-100000.

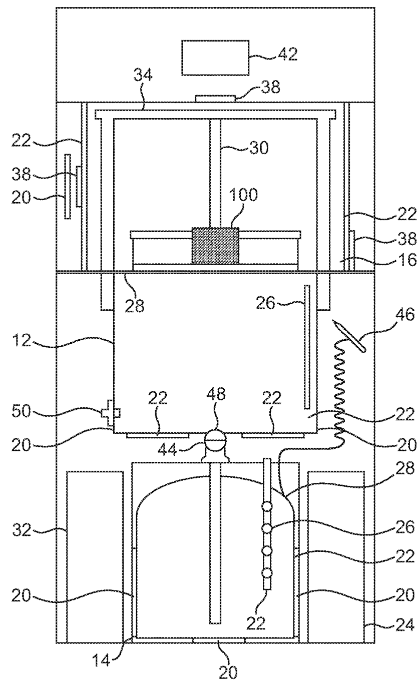

FIG. 2

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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23 06 14

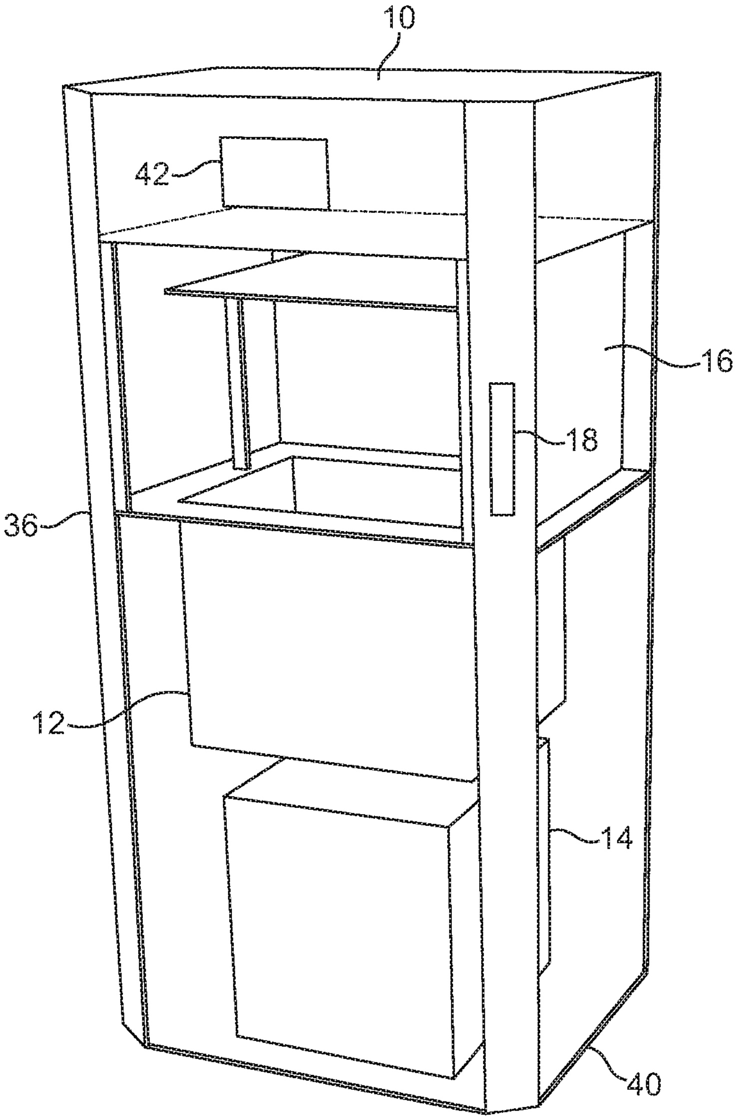

FIG. 1

23 06 14

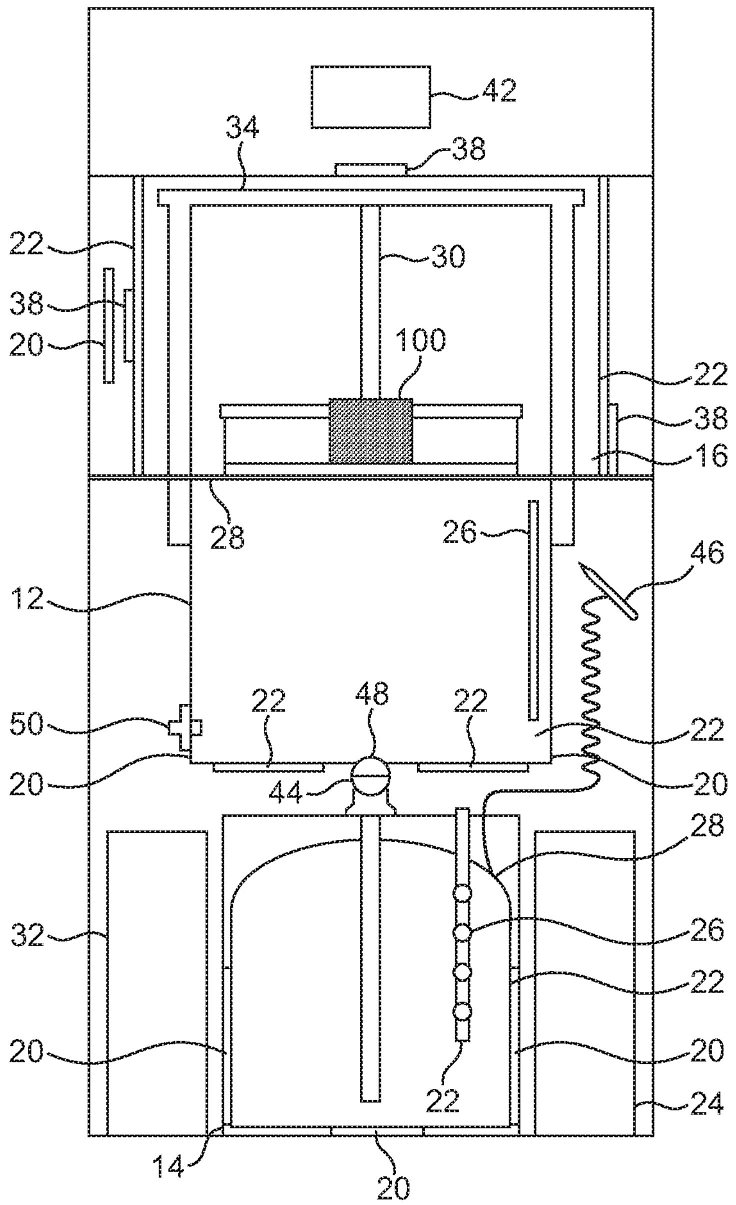
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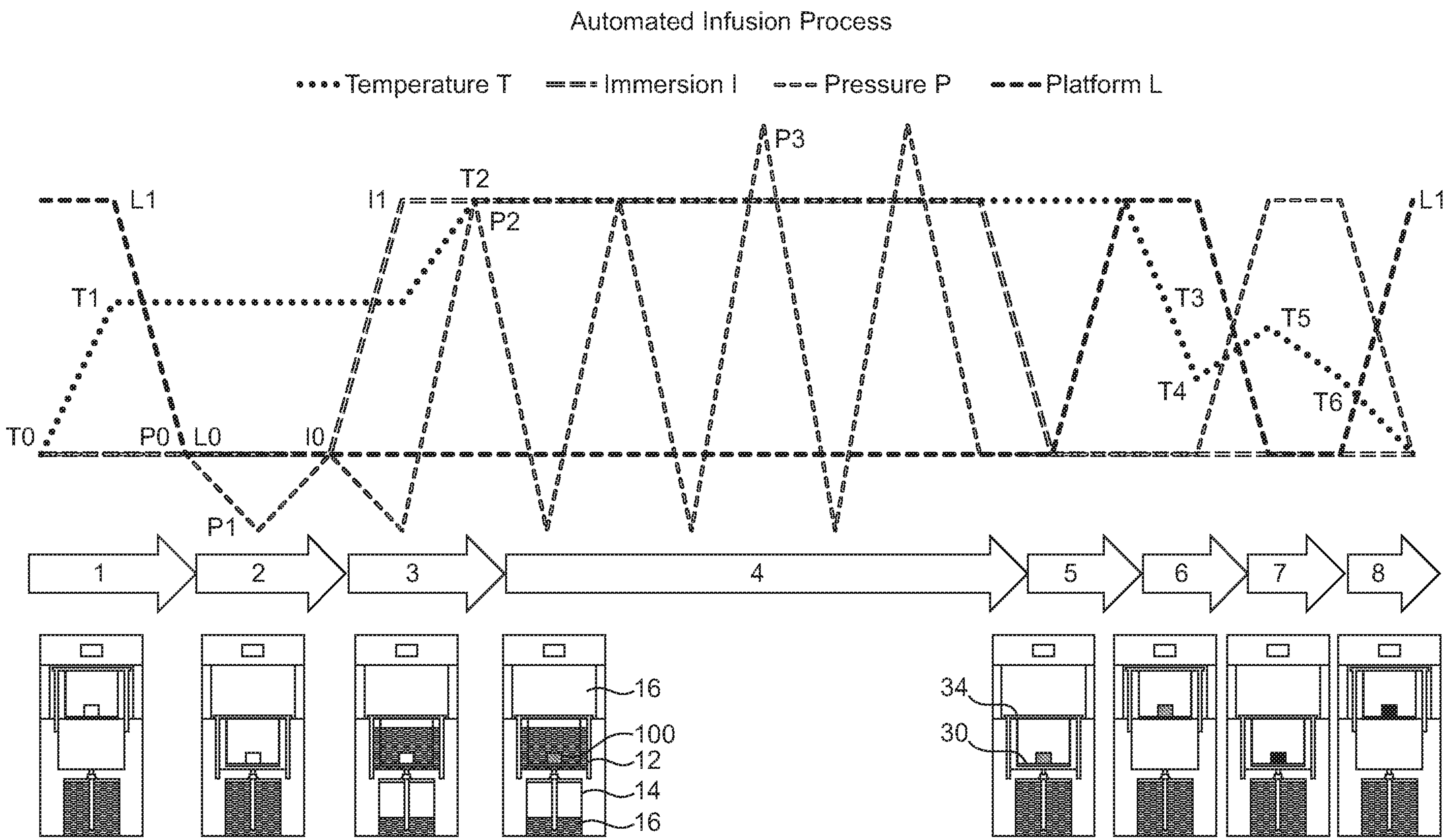
FIG. 2



Automated Infusion Process
Temperature T
Immersion I
Pressure P
Platform L
L1
T0
T1
P0
L0
P1
I0
I1
T2
P2
P3
T3
T4
T5
T6
L1
1
2
3
4
5
6
7
8
16
100
12
14
16
34
30

FIG. 3

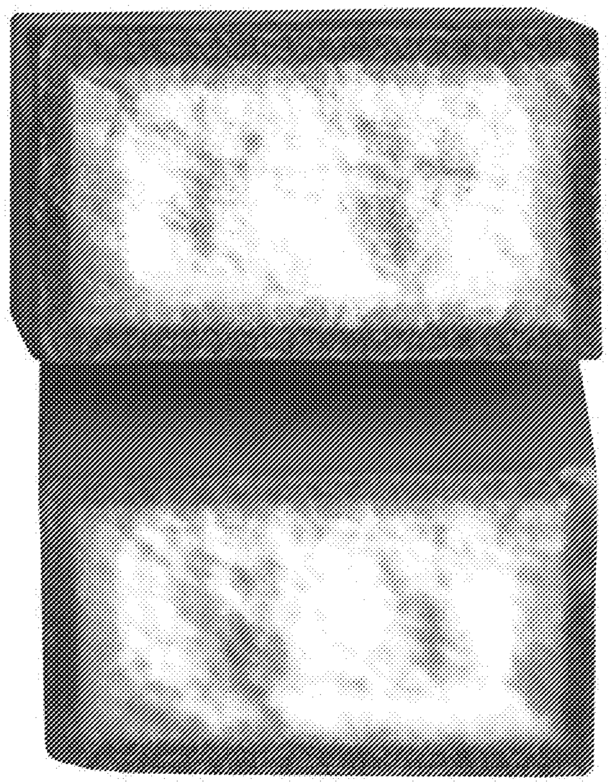


FIG. 4a

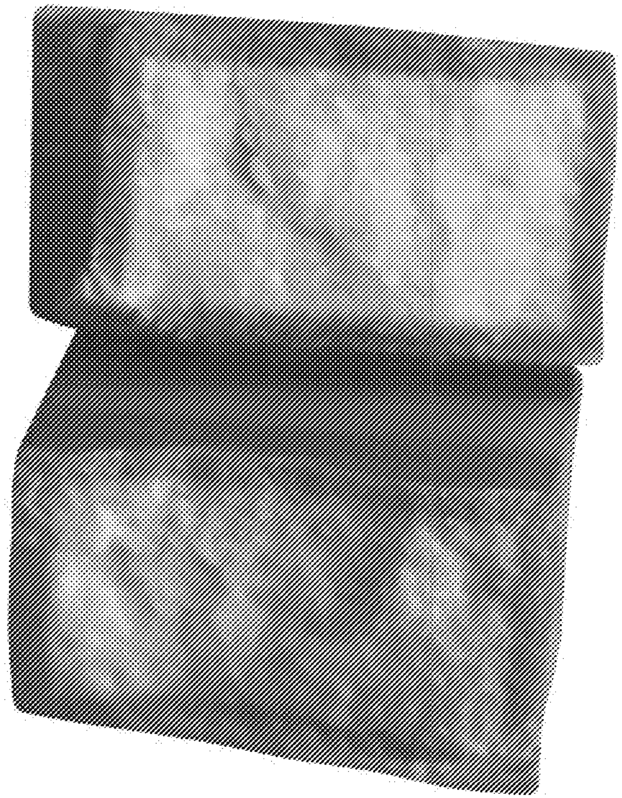


FIG. 4b

A METHOD AND APPARATUS FOR INFUSING ADDITIVE MANUFACTURED OBJECTS AND THE LIKE

INTRODUCTION

[0001] This invention relates to a method of infusing three dimensional printed, free-form fabricated, or additive manufactured objects; an apparatus for infusing three dimensional printed, free-form fabricated, or additive manufactured objects; to novel functional polymers for use with said method, and to objects infused by said polymers.

BACKGROUND

[0002] Three dimensional printing, free-form fabrication, or additive manufactured objects can be produced fairly simply using known methods, including but not limited to, the deposit of particles, such as plaster or plastics, or layers, such as paper, plastic or fabrics. However, the resulting products may be porous, “soft” and easily damaged. It is therefore desirable to develop improved methods for strengthening or otherwise protecting such objects, and/ or providing quality finishes thereto.

[0003] Current approaches to strengthening/ protecting such manufactured objects fall into the following generalised categories:

[0004] Impregnation of the manufactured objects with an acrylic resin.

In general, the acrylic resin is a cyanoacrylate (not favored due to its toxicity) and it is absorbed into pores or voids in the object where it rapidly polymerizes, in the presence of water (specifically hydroxide ions), forming long strong chains which join and bond the particles and/ or layers together. However, because the presence of moisture causes the cyanoacrylate to set, exposure to moisture in the air can cause containers of cyanoacrylate to rapidly deteriorate and become unusable over time. To prevent this, the cyanoacrylate must be stored in an airtight container with a package of a desiccant such as silica gel.

[0005] Impregnation of the manufactured objects with waxes.

Whilst waxes are safer to handle than cyanoacrylates, and can be “re-melted” allowing reprocessing of the object, they “shrink” in the pores and consequently, generally provide an unsatisfactory finish. Furthermore their hydrophobic nature makes the wax impregnated object difficult to finish.

[0006] Impregnation of the manufactured objects with a curable resin.

Curable resins, such as, heat cured or UV cured resins, like cyanoacrylate, form a permanent finish and can’t be reworked if the finish is unsatisfactory. They also shrink in the pores and, due to their viscous nature, often only impregnate the outermost surfaces, meaning the cured product lacks good structural integrity; and

[0007] Impregnation of the manufactured objects with two-part component resins.

Typically the two components are pre-mixed so that they will “set”, and are used to impregnate the object whilst they are workable. Examples include: polyesters, epoxy resins, and polyacrylates. Disadvantages include the fact they set in a non-reversible manner, suffer from a poor quality finish and mixing results in wastage.

[0008] The disadvantages with these alternative impregnating materials and methods are overcome through the use of a thermoplastic polymer which will impregnate the pores and voids in a molten state in a first defined temperature range and set at a second temperature range (lower than said first).

[0009] By the use of e.g. pressure, they can be caused to impregnate the pores and voids deeply (and not just the outer surface), resulting in less shrinkage and greater structural integrity providing a better quality of finish. By deeply is meant able to penetrate the pores by greater than 10%, through 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%, to 100% impregnation, depending on the thickness of the object.

[0010] Furthermore, unlike cyanoacrylate, the current “gold standard”, they are safe to handle and do not suffer from premature spoiling. More significantly still, unlike cyanoacrylate and cured resins, the impregnation with a thermoplastic can be reversed, if a good finish is not achieved first time around.

[0011] It is a first object of the present invention is to provide improved methods for infusing three dimensional printed, free form fabricated or additive manufactured objects.

[0012] It is a separate and yet further object to identify functional polymers which are safer and have greater versatility for use with said method, and to provide stronger and / or better finished objects infused by said polymers.

[0013] It is yet a further and independent object to provide improved apparatus for the automated infusion of three dimensional printed, free form fabricated or additive manufactured objects.

BRIEF SUMMARY OF THE DISCLOSURE

[0014] In accordance with a first aspect of the present invention there is provided a method of infusing, infiltrating or impregnating a free-form fabricated or additive manufactured object comprising pores or voids in or between particles or sheets of material from which the object is manufactured characterised in that the object is infused with a thermoplastics material to, at least partially fill the pores or voids and to bond particles or sheets of material from which the object is manufactured.

[0015] Preferably the particles or sheets of material are deposited in layers.

[0016] In one embodiment the sheets comprise paper, plastic, fabric or another compressed or woven material.

[0017] In another embodiment the particles comprise a colour absorbent or colour coatable material, preferably plaster or a plastics. The plaster is usually a modified plaster and preferred forms comprise a solvent based co-polymer, typically one in which the co-polymer is polyvinyl acetate (PVA). They may also comprise a colorant.

[0018] In one embodiment the thermoplastic is introduced under controlled conditions of temperature at atmospheric pressure. However, in a favoured embodiment the thermoplastic is introduced under controlled conditions of non-atmospheric pressure.

[0019] Preferred thermoplastics for use in the method of the invention are linear or branched semi-crystalline aliphatic polyester thermoplastics with a melting point between 40 ºC and 65 ºC and a solidification/crystallisation point of between 20 ºC and 40 ºC.

[0020] Most preferred are caprolactones.

[0021] In a favoured method, prior to infusion with a thermoplastics, the object is heated to a first temperature (T1) and held at a negative pressure (P1) to drive off water and or other volatiles from the pores or voids therby ensuring the thermoplastics can best penetrate the object. The object is then immersed in the thermoplastics and taken to a second viscosity lowering temperature (T2) typically from 90 ºC to 160 ºC, under a vacuum (P1) or at atmospheric pressure (P0).

[0022] Preferably, though not essentially, when the second viscosity lowering temperature (T2) is reached the infusion process begins and the pressure is oscillatied between a negative pressure (P1) and a positive pressure (P2) or an over pressure (P3).

[0023] Once treated the second viscosity lowering temperature (T2) is maintained and the thermoplastics is drained under a positive pressure (P2). The object is then moved through various orientations at the second viscosity lowering temperature (T2) to displace surplus thermoplastics material.

[0024] The object may then be presented for inspection, the temperature dropped from the second temperature (T2) to a third handlable temperature (T3), intermediate between the first and second viscosity lowering temperatures (T1 and T2), and if required, surplus material can be removed using a novel thermoplastic removal device.

[0025] Finally the object is tempered under positive pressure (P2) by moving between one or more further intermediate temperatures (T4 and T5).

[0026] In accordance with a second aspect of the present invention there is provided an apparatus (10), for infusing three dimensional printed, free-form fabricated or additive manufactured objects (100), comprising:

a) an infusion chamber (12), in which the object to be infused with a thermoplastics (110) is infused;

b) a reservoir (14) which is filled with the thermoplastics;

c) a curing chamber (16) for heating and curing the object; and

d) a controller (18) for controlling the operative functions of the apparatus;

characterised in that the reservoir comprises a heating means (20) and sensors (22, 26, 28) such that the thermoplastics can be melted within defined parameters of temperature (T).

[0027] In accordance with a third aspect of the present invention there is provided an apparatus (10), for infusing three dimensional printed, free-form fabricated or additive manufactured objects (100), comprising:

a. an infusion chamber (12), in which the object to be infused with a thermoplastics (110) is infused;

b. a reservoir (14) which is filled with the thermoplastics;

c. a curing chamber (16) for heating and curing the object; and

d. a controller (18) for controlling the operative functions of the apparatus;

characterised in that the curing chamber is constructed such that reactions can be conducted under both negative pressure (P1) and positive pressure (P2/P3).

[0028] In the apparatus of both the second and third aspects there are a number of common features.

[0029] In one embodiment it is preferred that the curing chamber has associated therewith a vacuum pump and one or more of at least one heat sensor(s), pressure sensor(s) and / or level sensor(s).

[0030] Prefererably the apparatus further comprises a platform, container or arm for supporting the object and a compressor to pressurise the infusion chamber and assist other operative functions.

[0031] More preferably the apparatus also comprises heat means associated with one or more of the infusion chamber and curing chamber.

[0032] In a preferred embodiment a lid seals the reaction chamber and provides support for the platform and the apparatus further comprises a viewing window and one or more fans.

[0033] In accordance with a forth aspect of the present invention there is provided a functional polymer, for use with said method of the invention, which is a linear or branched semi-crystalline aliphatic polyester thermoplastic with a melting point between 40 ºC and 65 ºC and a solidification/crystallisation point of between 20 ºC and 40 ºC.

[0034] Preferably thefunctional polymer is a polycaprolactone. Most preferably it is a polyol, more preferably still a diol, triol, or tetrol.

[0035] The polycaprolactone may have a molecular weight of from between 2000 to 100,000.

[0036] In accordance with a fifth aspect of the invention there is provided an object infused with a thermoplastic polymer of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0037] The various aspects of the invention are further described, by way of example only, with reference to the following drawings and Example in which:

Fig 1 is a “simple” perspective view of an infusion apparatus according to one aspect of the invention;

Fig 2 is a plan view (from the front) of an infusion apparatus of the invention;

Fig 3 is a schematic showing exemplary process stages (1-8) together with representations of the infusion apparatus at the different stages of processing; and

Figs 4a and 4b are photographic representation of an object processed without pressure a) according to one aspect of the invention and with pressure b) according to a preferred aspect of the invention.

Detailed Description

[0038] Referring to Fig 1 the infusion apparatus (10) of the invention can, simplistically, be seen to comprise three functional chambers (12, 14, 16), which in the embodiment illustrated are stacked one above another, in a housing (40).

[0039] At the bottom of the stack is a reservoir (14) which, in use, is filled with a thermoplastics (110), see Fig 3, which thermoplastics provides many of the benefits attained using the method of the invention. Positioned above it is an infusion chamber (12), in which an object (100) (Fig 3) to be infused with the thermoplastics (110) is, in use, infused. Immediately above the infusion chamber is the curing chamber (16), for heating and curing the object and this is provided with a viewing window/ door (36).

[0040] Above the curing chamber (16) there are provided the “controls”, not shown, which are operated via a control panel (18) and a display (42).

[0041] Referring to Fig 2, there is provided more detail on the inter-relationship between the key components and additional features providing functionality.

[0042] Housed at the bottom of the apparatus on either side of the reservoir (14) are a vacuum pump (24) and compressor (32) whose function will be better understood with reference to the later described processing. Briefly, however, the compressor enables pneumatic control of the door (36), lid (34), ball valve (44), reservoir (14), infusion chamber (12) and material removal device (46).

[0043] Associated with the reservoir (14) are a heating means (20) for heating the thermoplastics to make it liquid, and heat sensors (22), level sensors (26) and pressure sensors (28) allowing control of both temperature and pressure and the flow of the thermoplastic to and from the infusion chamber (12).

[0044] The infusion chamber is also heated by heat means (20) and has sensors to monitor liquid levels (26) and pressure (28). It is also fitted with a filter (48) to prevent particles entering the chamber.

[0045] A material removal device (46) is also provided.

[0046] The upper curing chamber (16) has a clear (viewing) door (36) which can be opened so as to place an object (100) onto a platform (30) which is connected to a lid (34) which can be raised and lowered into the infusion chamber and moved in X, Y and Z planes for optimum handling. It too has a heating means (20) and additionally at least one fan (38) associated therewith to maintain an even temperature.

[0047] The method of the invention can be applied with or without positive pressures, including over pressures which can be achieved hydraulically with the aid of a ram (50).

[0048] A method of the invention (utilising positive pressure) is described with reference to Fig 3.

[0049] **Stage 1** An object (100) to be treated is placed on the platform (30) (securely clamped if required) at level L1 or in a container that is mechanically attached to the lid (34). The object is heated from room temperature T0 to a “first target temperature” (T1) (e.g. 60ºC) for a sufficient time to allow complete uniformity of temperature through the object to be reached at atmospheric pressure (P0). The skilled person will appreciate the target Temperature (T1) will vary with the object to be infused and the thermoplastics being used.

[0050] Stage 2 When the first Target temperature (T1) is reached, the object is lowered on the platform to position L0 in the infusion chamber (12) for desiccation under negative pressure P1 (e.g. -1 Bar). Pressure sensors (28, Fig 2) detect the absence of water or solvent.

[0051] Stage 3 Whilst under negative or atmospheric pressure (P1 or P0) the infusion chamber (12) is filled from empty (I0) with the infusion material (110) such that the object is fully immersed (I1). The fill level is controlled through the use of level sensors (26, Fig 2) in the reservoir. Once at the desired fill level (I1) (object immersed), the thermoplastic infusion material (110) is heated to a second target temperature (T2) which is selected such that the viscosity of the thermoplastics is low enough that the thermoplastics will drain from the object. Typically, this will be between, e.g. 90ºC and 150 ºC, for the favoured caprolactones, but with higher molecular weight polymers (greater than 10,000) increased temperatures and pressures (P2) may be used.

[0052] Stage 4 Once the second target temperature (T2) in the infusion chamber is reached, the pressure may be oscillated between negative (P1) (or atmospheric P0) and positive pressures (P2) including over pressures (P3) which may be achieved hydraulically via component (50), e.g. -1 bar to 1000 bar. The frequency and amplitude of oscillation can be varied to suit the geometry and material properties of the object being treated. Level sensors (26, Fig 2) in the chamber detect and control excessive foaming and ensure sufficient infusion material (110) is present.

[0053] Stage 5 Once infused, the infusion material (110) is drained to the reservoir via positive pressure or gravity at normal atmospheric pressure (P0).

[0054] Stage 6 The platform is raised to position (L1) into the cure chamber and may be caused to rotate through any orientation (X, Y, Z planes) to ensure all infusion material (110) is reclaimed. The speed of the platform can be increased to aid material removal.

[0055] Stage 7 Once all available infusion material is reclaimed the object is cooled to one or more intermediate temperatures (T3) at which the object may be handled e.g. between 40ºC and 90ºC for inspection. During inspection unset material can be removed with the assistance of a novel handheld air blow and vacuum device (46) with access via open window (36, Fig 2). The temperate of the air blown through the device is maintained at a temperature at or above T3. This is particularly useful where the object has geometries and cavities which might retain unwanted thermoplastic material. Once inspection is complete the object is lowered into the infusion chamber (12) and cooled under positive pressure (P2) at one or multiple tempering temperatures (T4; T5; T6) which are lower than intermediate temperature T3 where the material is tempered for maximum crystalline structure. Tempering may involve raising and lowering the temperature above and below T4, T5 or T6.

[0056] Stage 8 Once tempered the platform is raised to L1 and the object may be removed.

[0057] The skilled person will appreciate that the use of pressure is an optional, but preferred, feature of the invention, and it is possible to merely immerse the object in thermoplastics, remove the object, and cure it by selection of an appropriate thermoplastics. However, the use of pressure allows a wider range of thermoplastics to be used since they can be made less viscous under pressure thereby allowing greater penetration to be achieves as illustrated in Example 1 below:

Example 1

[0058] The benefits of using pressure are illustrated in the following example in which an object was treated:

a) With a caprolactone (molecular weight 25,000) at 120 ºC, (Fig 4a); and

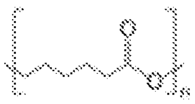
b) With the same caprolactone at 120 ºC, at oscillating pressures between -1 Bar and 4 Bar (Fig 4b).

[0059] As can be seen from the comparative figures, Figs 4a and 4b the provision of pressure ensured that the material was fully infused as evidenced by the darker uniform centre in Fig 4b.

[0060] The preferred thermoplastics for use with the methods of the invention are linear or branched semi - crystalline aliphatic polyester thermoplastics with a melting point between 40 ºC and 65 ºC and a solidification/crystallisation point of between 20 ºC and 40 ºC.

[0061] Preferred polyesters for use in the invention are the polycaprolactones.

[0062] The general Formula of Polycaprolactone is shown in Formula 1 below:



[0063] Polycaprolactones are normally defined as “thermoplastic” at a molecular weight of 10,000 and above, where they have a viscosity of 9,300 Mpas and a melting range of 58-60 ºC.

[0064] However, lower molecular weight polyols, including diols, triols and tetrols, and some copolymers thereof, have melting ranges above room temperature, more preferably above 30 ºC, such as typically 40-50 ºC and with much lower viscosities (as low as 400-500 Mpas) are particularly suitable for the present applications.

CLAIMS

1. A method of infusing, infiltrating or impregnating a free-form fabricated or additive manufactured object comprising pores or voids in or between particles or sheets of material from which the object is manufactured characterised in that the object is infused with a thermoplastics material to, at least partially fill the pores or voids and to bond particles or sheets of material from which the object is manufactured.
2. A method as claimed in claim 1 wherein the particles or sheets of material have been deposited in layers.
3. A method as claimed in claim 2 wherein the sheets comprise paper, plastic, fabric or another compressed or woven material.
4. A method as claimed in claim 1 wherein the particles comprise a colour absorbent or colour coatable material.
5. A method as claimed in claim 4 wherein the colour absorbent or colour coatable material is plaster or plastics.
6. A method as claimed in claim 5 wherein the plaster further comprises a solvent based co-polymer.
7. A method as claimed in claim 6 wherein the solvent based co-polymer is polyvinyl acetate (PVA).
8. A method as claimed in claim 1 wherein the particles or sheets are coloured.
9. A method as claimed in any of the preceding claims wherein the thermoplastic is introduced under controlled conditions of temperature.
10. A method as claimed in claim 9 wherein the thermoplastics is introduced under controlled conditions of non-atmospheric pressure.
11. A method as claimed in claim 9 or 10 wherein for a thermoplastics is a linear or branched semi-crystalline aliphatic polyester with a melting point between 40 ºC and 65 ºC and a solidification / crystalisation point between 20 ºC and 40 ºC.

12. A method as claimed in claim 11 wherein the thermoplastics is a caprolactone.

13. A method as claimed in claim 10 wherein prior to infusion of the thermoplastics the object is heated to a first temperature (T1) and held at negative pressure (P1) to drive off water and or other volatiles from the pores or voids.

14. A method as claimed in claim 9 or 10 wherein the object is immersed in the thermoplastics and taken to a second viscosity lowering temperature (T2) of from 90 ºC to 220 ºC under a vaccum (P1) or atmospheric pressure (P0).

15. A method as claimed in claim 14 wherein when the second temperature (T2) is reached, the infusion process begins and the pressure is oscillatied between a negative pressure (P1) and a positive pressure (P2/P3) to force the thermoplastics material into the object.

16. A method as claimed in claim 15 wherein, to drain the thermoplastics, the second viscosity lowering temperature (T2) is maintained, and the thermoplastics is drained under a positive pressure (P2/P3).

17. A method as claimed in claim 16 wherein the object is moved through various orientations at the second viscosity lowering temperature (T2) to displace thermoplastics material.

18. A method as claimed in claim 16 wherein the object is presented for inspection, the temperature is dropped from the second viscosity lowering temperature (T2) to a third handlable temperature (T3), intermediate between the first and second viscosity lowering temperatures (T1 and T2), and if required, material can be removed using a thermoplastic removal device (46).

19. A method as claimed in claim 18 wherein the object is tempered under positive pressure (P2/P3) by moving between one or more further intermediate temperatures (T4 and T5).

20. An apparatus (10), for infusing three dimensional printed, free-form fabricated or additive manufactured objects (100), comprising:

a) an infusion chamber (12), in which the object to be infused with a thermoplastics (110) is infused;

b) a reservoir (14) which is filled with the thermoplastics;

c) a curing chamber (16) for heating and curing the object; and

d) a controller (18) for controlling the operative functions of the apparatus;

characterised in that the reservoir comprises a heating means (20) and sensors (22, 26, 28) such that the thermoplastics can be melted within defined parameters of temperature (T).

21. An apparatus (10), for infusing three dimensional printed, free-form fabricated or additive manufactured objects (100), comprising:

a) an infusion chamber (12), in which the object to be infused with a thermoplastics (110) is infused;

b) a reservoir (14) which is filled with the thermoplastics;

c) a curing chamber (16) for heating and curing the object; and

d) a controller (18) for controlling the operative functions of the apparatus;

characterised in that the curing chamber is constructed such that reactions can be conducted under both negative pressure (P1) and positive pressure (P2/P3).

22. An apparatus as claimed in claim 20 or 21 wherein the curing chamber (16) has associated therewith a vacuum pump (24).

23. An apparatus as claimed in claim 20 or 21 wherein the curing chamber (16) comprises one or more of at least one heat sensor(s) (22), pressure sensor(s) (26) and / or level sensor(s) (28).

24. An apparatus as claimed in any of claims 20 to 23 further comprising a platform, container or arm (30) for supporting the object.

25. An apparatus as claimed in any of claims 20 to 24 further comprising a compressor (32) to pressurise the infusion chamber and assist other operative functions.

26. An apparatus as claimed in any of claims 20 to 25 further comprising heat means (20) associated with one or more of the infusion chamber (12) and curing chamber (16).

27. An apparatus as claimed in any of claims 20 to 26 further comprising a lid (34) which seals the reaction chamber and provides support for the platform (30).

28. An apparatus as claimed in any of claims 20 to 27 further comprising a viewing window (36).

29. An apparatus as claimed in any of claims 20 to 28 further comprising one or more fans (38).

30. A functional polymer, for use with said method of claims 1-19, which is a linear or branched semi-crystalline aliphatic polyester thermoplastic with a melting point between 40 ºC and 65 ºC and a solidification/crystallisation point of between 20 ºC and 40 ºC.

31. A functional polymer as claimed in claim 30 wherein the thermoplastics is a polycaprolactone.

32. A functional polymer as claimed in claim 31 which is a polyol.

33. A functional polymer as claimed in claim 32 wherein the polyol is a diol, triol, or tetrol.

34. A functional polymer as claimed in any of claims 30-34 wherein the polycaprolactone has a molecular weight of from 2000 to 100,000.

35. An object (100) infused with a thermoplastic polymer as claimed in any of claims 30-34.

36. An object as claimed in claim 35 wherein the thermoplastic polymer penetrates the object by at least 10%.

Intellectual Property Office

Application No:	GB1305619.7	**Examiner:**	Matthew Lawson
Claims searched:	1-19	**Date of search:**	13 December 2013

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1,2,4,5,8, 9	US 2005/0059757 A1 (BREDT) - paragraphs [0023], [0081], [0093]-[0094] & [0202].
X	1-3,8,9	GB 2283966 A (BOWATER) - page 6 lines 24-35, page 10 lines 1-22, page 17 lines 24-34, page 19 lines 11-13 & 29-31 and figures 4 & 5.
X	1,2,4,5,8, 9	DE 19927923 A1 (DAIMLER) - WPI Abstract Accession No. 00-506852 and the figures.
X	1,2,4-10	US 2003/0186042 A1 (DUNLAP) - paragraphs [0005], [0006] & [0031].

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

B22F; B29C; B32B; C08J

The following online and other databases have been used in the preparation of this search report

Online: EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
B29C	0067/00	01/01/2006
B29C	0071/00	01/01/2006
C08G	0063/08	01/01/2006

Intellectual Property Office

Application No:	GB1305619.7	**Examiner:**	Matthew Lawson
Claims searched:	20 and 22-29 in part	**Date of search:**	28 February 2014

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	20,222-26,28,29	US 3384505 A (PALMER) - the whole document.
X	20,23,24,26,29	JPH01254741 A (MITSUBISHI) - WPI Abstract Accession No. 89-343298 and figures 1 & 2.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

B29B; B29C; B32B; C08J

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Online: EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
B29C	0067/00	01/01/2006
B29C	0071/00	01/01/2006
C08G	0063/08	01/01/2006
C08L	0067/04	01/01/2006

Intellectual Property Office

Application No:	GB1305619.7	**Examiner:**	Matthew Lawson
Claims searched:	30-35	**Date of search:**	28 February 2014

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	30,31,34	US 5977203 A (MAKUUCHI) - column 2 lines 39-46 and column 2 line 67 - column 3 line 5.
X	30	US 2007/0111037 A1 (ECONOMY) - paragraphs [0007], [0068], [0070], [0072] & [0075]-[0078]
X,Y	X:30-34 Y:35,36	https://www.perstorp.com/~/media/Files/Perstorp/PB/CAPA_eng.ashx - the diols, triols & tertols of the product data summary.
X,Y	X:30,31,34 Y:35,36	http://photos.imageevent.com/bolt/plastics/Processing%20CAPA%20Thermoplastics%20Pp.pdf - CAPA RTM 6500 & CAPA RTM 6800.
Y	35,36	JP 2007070517 A (NAGASE) - WPI Abstract Accession No. 07-297497.

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Field of Search:

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Worldwide search of patent documents classified in the following areas of the IPC

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Online: EPODOC, WPI, TXTE, Internet

International Classification:

Subclass	Subgroup	Valid From
B29C	0067/00	01/01/2006

Intellectual
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Subclass	Subgroup	Valid From
B29C	0071/00	01/01/2006
C08G	0063/08	01/01/2006
C08L	0067/04	01/01/2006

Intellectual Property Office

Application No:	GB1305619.7	**Examiner:**	Matthew Lawson
Claims searched:	21 and 22-29 in part	**Date of search:**	28 February 2014

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US 3384505 A (PALMER)
A	-	JPH01254741 A (MITSUBISHI)

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C08G	0063/08	01/01/2006
C08L	0067/04	01/01/2006