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(54) Title: METHOD FOR MANUFACTURING A THREE-DIMENSIONAL OBJECT

(57) Abstract: The invention pertains to a method for manufacturing a three-dimensional object using an additive manufacturing system, comprising using a combination of a fluorinated thermoplastic elastomer and a thermoplastic vinylidene fluoride polymer, which is effective for printing "soft" shaped part having Shore A hardness of 100 or less.



Description

Method for manufacturing a three-dimensional object

Cross-Reference to Related Application

[0001] This application claims priority to US Provisional Application No. 62/781852 filed on December 19, 2018 and to European Patent Application No 19157417.7, filed on February 15, 2019, the whole content of each of these applications being incorporated herein by reference for all purposes.

Technical Field

[0002] Additive manufacturing technologies, otherwise often referred as 3D printing techniques, including in particular filament fabrication techniques, have rapidly evolved during the past few years, in particular in the field of prototyping, and have gained enormous success because of their well-known advantages in terms of flexibility, accessibility of designs that simply could not be produced physically in any other way, mass customization, tool-less approaches, and sustainability profile.

[0003] Additive manufacturing systems are generally used to print or otherwise build 3D parts from digital representations of the 3D parts using one or more additive manufacturing techniques. Examples of commercially available additive manufacturing techniques include extrusion-based techniques, jetting, selective laser sintering, powder/binder jetting, electron-beam melting, and stereolithography processes. For each of these techniques, a digital representation of the 3D part is initially sliced into multiple horizontal layers. For each sliced layer, a tool path is then generated, which provides instructions for the particular additive manufacturing system to print the given layer.

[0004] For example, in an extrusion-based additive manufacturing system, a 3D part may be printed from a digital representation of the 3D part in a layer-by-layer manner by extruding a flowable part material. The part material is extruded through an extrusion tip carried by a print head of the system, and is deposited as a sequence of roads on a platen in an x-y plane. The

extruded part material fuses to previously deposited part material, and solidifies upon a drop in temperature. The position of the print head relative to the substrate is then incremented along a z-axis (perpendicular to the x-y plane), and the process is then repeated to form a 3D part resembling the digital representation.

- [0005] A variety of materials, thermoplasts or thermosets, have been proposed, and are already presently supplied under different forms, for use in 3D printing devices, including notably under the form of filaments for use in fused filament additive manufacturing devices.
- [0006] Within this area, fluoromaterials are attracting increasing attention because of their performances' profile which may cope with requirements for being used in 3D printing processes.
- [0007] Indeed, fluorinated and fully fluorinated plastomeric materials display high thermal and chemical resistance if compared with non-fluorinated plastics typically used in 3D printing.
- [0008] In this area, **WO 2018/149758** (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) 23.08.2018 is directed to a method for manufacturing a three-dimensional object using an additive manufacturing system, wherein use is made of a fluorinated thermoplastic elastomer, possessing an improved processability profile.
- [0009] Now, when addressing additive manufacturing techniques, processability constraints may render quite arduous the processing of materials, such as the fluorinated thermoplastic elastomers of **WO 2018/149758** above, while endeavouring to strike the proper balance of melt viscosity and filament modulus to match the intended field of use.
- [0010] Further, it is generally acknowledged that printing "soft" compounds with Shore A hardness of 100 or less may be quite delicate especially when using fused filament techniques, where the "soft" filaments tend to buckle at the printer head at high throughput printing conditions.
- [0011] There is hence a continuous quest of solutions for "soft" compounds suitable for providing notably flexible filaments and 3D-printed parts of Shore A hardness of 100 or less, which could be easily processed via additive manufacturing techniques and printed in "soft" shaped parts.

Summary of invention

[0012] The Applicant has now surprisingly found that certain “soft” blends of fluorinated thermoplastic elastomers and vinylidene fluoride thermoplastic polymers, as below detailed, are such to address and cope the challenging requirements expressed above for being processed through additive manufacturing techniques, thanks to their ability to be processed under high throughput/standard conditions in equipment and yet to give rise to shaped parts possessing Shore A hardness of 100 or less.

[0013] The invention hence pertains to a method for manufacturing a three-dimensional object [object (3D)] using an additive manufacturing system, comprising:

- generating a digital representation of the three-dimensional object, and slicing the same into multiple horizontal layers, so as to generate printing instructions for each of the said horizontal layers;

- printing layers of the object (3D) from a part material [composition (C)], said composition (C) comprising:

- (1) at least one fluorinated thermoplastic elastomer [polymer (F-TPE)] comprising:

- at least one elastomeric block (A) consisting of a sequence of recurring units, said sequence comprising recurring units derived from at least one fluorinated monomer, said block (A) possessing a glass transition temperature of less than 25°C, as determined according to ASTM D3418: and

- at least one thermoplastic block (B) consisting of a sequence of recurring units, said sequence comprising recurring units derived from at least one fluorinated monomer,

wherein the crystallinity of said block (B) and its weight fraction in the polymer (F-TPE) are such to provide for a heat of fusion of the polymer (F-TPE) of at least 2.5 J/g and at most 20 J/g, when determined according to ASTM D3418; and

- (2) at least one thermoplastic vinylidene fluoride (VDF) polymer

- [polymer (F)] comprising recurring units derived from VDF in an amount of

at least 85 % moles, with respect to the total moles of recurring units of polymer (F), said polymer (F) possessing a heat of fusion (ΔH_f) of the polymer (F-TPE) of at least 25 J/g, when determined according to ASTM D3418.

[0014] The Applicant has surprisingly found that the above combination of a polymer (F-TPE) and a polymer (F), as above detailed, is particularly advantageous for printing 3D-parts of low Shore A hardness, reproducing target shapes with precision and high resolution, in normal processing conditions, with no buckling at the printer head, even at high throughput.

[0015] The Applicant thinks, without being bound by this theory, that the presence of effective amounts of polymer (F) in admixture with polymer (F-TPE) is such to make possible easy processing under standard thermoplast processing conditions, with substantially no buckling, and delivering precise “soft” parts, thanks to the melt strength/reinforcing effect of polymer (F) and its ability to solidify at higher temperature, so freezing effectively the target shape, as soon as printed.

Description of embodiments

[0016] **The fluorinated thermoplastic elastomer [polymer (F-TPE)]**

[0017] For the purpose of the present invention, the term “elastomeric”, when used in connection with the “block (A)” is hereby intended to denote a polymer chain segment which, when taken alone, is substantially amorphous, that is to say, has a heat of fusion of less than 2.0 J/g, preferably of less than 1.5 J/g, more preferably of less than 1.0 J/g, as measured according to ASTM D3418.

[0018] For the purpose of the present invention, the term “thermoplastic”, when used in connection with the “block (B)”, is hereby intended to denote a polymer chain segment which, when taken alone, is semi-crystalline, and possesses a detectable melting point, with an associated heat of fusion of exceeding 25.0 J/g, as measured according to ASTM D3418.

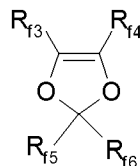
[0019] The fluorinated thermoplastic elastomer of the composition (C) of the invention is advantageously a block copolymer, said block copolymer typically having a structure comprising at least one block (A) alternated to

at least one block (B), that is to say that said fluorinated thermoplastic elastomer typically comprises, preferably consists of, one or more repeating structures of type (B)-(A)-(B). Generally, the polymer (F-TPE) has a structure of type (B)-(A)-(B), i.e. comprising a central block (A) having two ends, connected at both ends to a side block (B).

- [0020] The block (A) is often alternatively referred to as soft block (A); the block (B) is often alternatively referred to as hard block (B).
- [0021] The term “fluorinated monomer” is hereby intended to denote an ethylenically unsaturated monomer comprising at least one fluorine atom.
- [0022] The fluorinated monomer may further comprise one or more other halogen atoms (Cl, Br, I).
- [0023] Any of block(s) (A) and (B) may further comprise recurring units derived from at least one hydrogenated monomer, wherein the term “hydrogenated monomer” is intended to denote an ethylenically unsaturated monomer comprising at least one hydrogen atom and free from fluorine atoms.
- [0024] The polymer (F-TPE) typically comprises, preferably consists of:
- at least one elastomeric block (A) selected from the group consisting of:
 - (1) vinylidene fluoride (VDF)-based elastomeric blocks (A_{VDF}) consisting of a sequence of recurring units, said sequence comprising recurring units derived from VDF and recurring units derived from at least one fluorinated monomer different from VDF, said fluorinated monomer different from VDF being typically selected from the group consisting of:
 - (a) C_2 - C_8 perfluoroolefins such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP);
 - (b) hydrogen-containing C_2 - C_8 fluoroolefins different from VDF, such as vinyl fluoride, trifluoroethylene (TrFE), hexafluoroisobutylene (HFIB), perfluoroalkyl ethylenes of formula $CH_2=CH-R_{f1}$, wherein R_{f1} is a C_1 - C_6 perfluoroalkyl group;
 - (c) C_2 - C_8 chloro- and/or bromo-containing fluoroolefins such as chlorotrifluoroethylene (CTFE);
 - (d) perfluoroalkylvinylethers (PAVE) of formula $CF_2=CFOR_{f1}$, wherein R_{f1} is a C_1 - C_6 perfluoroalkyl group, such as CF_3 (PMVE), C_2F_5 or C_3F_7 ;
 - (e) perfluorooxyalkylvinylethers of formula $CF_2=CFOX_0$, wherein X_0 is a a

C₁-C₁₂ perfluorooxyalkyl group comprising one or more than one ethereal oxygen atom, including notably perfluoromethoxyalkylvinylethers of formula CF₂=CFOCF₂OR_{f2}, with R_{f2} being a C₁-C₃ perfluoro(oxy)alkyl group, such as -CF₂CF₃, -CF₂CF₂-O-CF₃ and -CF₃; and

(f) (per)fluorodioxoles of formula:



wherein each of R_{f3}, R_{f4}, R_{f5} and R_{f6}, equal to or different from each other, is independently a fluorine atom, a C₁-C₆ perfluoro(oxy)alkyl group, optionally comprising one or more oxygen atoms, such as -CF₃, -C₂F₅, -C₃F₇, -OCF₃ or -OCF₂CF₂OCF₃; and

(2) tetrafluoroethylene (TFE)-based elastomeric blocks (A_{TFE}) consisting of a sequence of recurring units, said sequence comprising recurring units derived from TFE and recurring units derived from at least one fluorinated monomer different from TFE, said fluorinated monomer being typically selected from the group consisting of those of classes (b), (c), (d), (e) as defined above;

- at least one thermoplastic block (B) consisting of a sequence of recurring units derived from at least one fluorinated monomer.

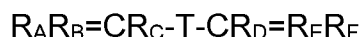
[0025] Any of block(s) (A_{VDF}) and (A_{TFE}) may further comprise recurring units derived from at least one hydrogenated monomer, which may be selected from the group consisting of C₂-C₈ non-fluorinated olefins such as ethylene, propylene or isobutylene.

[0026] Should the elastomeric block (A) be a block (A_{VDF}), as above detailed, said block (A_{VDF}) typically consists of a sequence of recurring units comprising, preferably consisting of:

- from 45% to 90% by moles of recurring units derived from vinylidene fluoride (VDF),
- from 5% to 50% by moles of recurring units derived from at least one fluorinated monomer different from VDF, and
- optionally, up to 30% by moles of recurring units derived from at least one hydrogenated monomer,

with respect to the total moles of recurring units of the sequence of block (A_{VDF}).

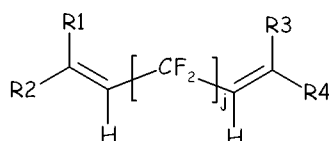
[0027] The elastomeric block (A) may further comprise recurring units derived from at least one bis-olefin [bis-olefin (OF)] of formula:



wherein R_A , R_B , R_C , R_D , R_E and R_F , equal to or different from each other, are selected from the group consisting of H, F, Cl, C_1 - C_5 alkyl groups and C_1 - C_5 (per)fluoroalkyl groups, and T is a linear or branched C_1 - C_{18} alkylene or cycloalkylene group, optionally comprising one or more than one ethereal oxygen atom, preferably at least partially fluorinated, or a (per)fluoropolyoxyalkylene group.

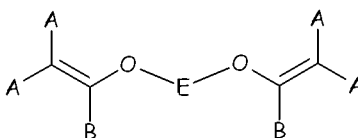
[0028] The bis-olefin (OF) is preferably selected from the group consisting of those of any of formulae (OF-1), (OF-2) and (OF-3):

(OF-1)



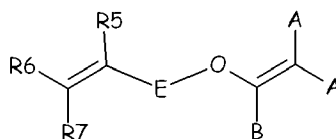
wherein j is an integer comprised between 2 and 10, preferably between 4 and 8, and R_1 , R_2 , R_3 and R_4 , equal to or different from each other, are selected from the group consisting of H, F, C_1 - C_5 alkyl groups and C_1 - C_5 (per)fluoroalkyl groups;

(OF-2)



wherein each of A, equal to or different from each other and at each occurrence, is independently selected from the group consisting of H, F and Cl; each of B, equal to or different from each other and at each occurrence, is independently selected from the group consisting of H, F, Cl and OR_B , wherein R_B is a branched or straight chain alkyl group which may be partially, substantially or completely fluorinated or chlorinated, E is a divalent group having 2 to 10 carbon atoms, optionally fluorinated, which

may be inserted with ether linkages; preferably E is a $-(CF_2)_m-$ group, wherein m is an integer comprised between 3 and 5; a preferred bis-olefin of (OF-2) type is $F_2C=CF-O-(CF_2)_5-O-CF=CF_2$;
(OF-3)



wherein E, A and B have the same meaning as defined above, R5, R6 and R7, equal to or different from each other, are selected from the group consisting of H, F, C_1 - C_5 alkyl groups and C_1 - C_5 (per)fluoroalkyl groups.

[0029] Should the block (A) consist of a recurring units sequence further comprising recurring units derived from at least one bis-olefin (OF), said sequence typically comprises recurring units derived from the said at least one bis-olefin (OF) in an amount comprised between 0.01% and 1.0% by moles, preferably between 0.03% and 0.5% by moles, more preferably between 0.05% and 0.2% by moles, based on the total moles of recurring units of block (A).

[0030] The elastomeric block (A) is preferably a block (A_{VDF}), as above detailed, said block (A_{VDF}) typically consisting of a sequence of recurring units comprising, preferably consisting of:

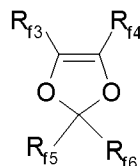
- from 45% to 80% by moles of recurring units derived from vinylidene fluoride (VDF),
- from 5% to 50% by moles of recurring units derived from at least one fluorinated monomer different from VDF,
- optionally, up to 1.0 % by moles of recurring units derived from at least one bis-olefin (OF), as above detailed; and
- optionally, up to 30% by moles of recurring units derived from at least one hydrogenated monomer,

with respect to the total moles of recurring units of the sequence of block (A_{VDF}).

[0031] Block (B) may consist of a sequence of recurring units, said sequence comprising:

- recurring units derived from one or more than one fluoromonomer, preferably selected from the group consisting of:

- (a) C₂-C₈ perfluoroolefins such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP);
- (b) hydrogen-containing C₂-C₈ fluoroolefins, such as vinylidene fluoride (VDF), vinyl fluoride, trifluoroethylene (TrFE), hexafluoroisobutylene (HFIB), perfluoroalkyl ethylenes of formula CH₂=CH-R_{f1}, wherein R_{f1} is a C₁-C₆ perfluoroalkyl group;
- (c) C₂-C₈ chloro- and/or bromo-containing fluoroolefins such as chlorotrifluoroethylene (CTFE);
- (d) perfluoroalkylvinylethers (PAVE) of formula CF₂=CFOR_{f1}, wherein R_{f1} is a C₁-C₆ perfluoroalkyl group, such as CF₃ (PMVE), C₂F₅ or C₃F₇;
- (e) perfluorooxyalkylvinylethers of formula CF₂=CFOX₀, wherein X₀ is a C₁-C₁₂ perfluorooxyalkyl group comprising one or more than one ethereal oxygen atom, including notably perfluoromethoxyalkylvinylethers of formula CF₂=CFOCF₂OR_{f2}, with R_{f2} being a C₁-C₃ perfluoro(oxy)alkyl group, such as -CF₂CF₃, -CF₂CF₂-O-CF₃ and -CF₃; and
- (f) (per)fluorodioxoles of formula:



wherein each of R_{f3}, R_{f4}, R_{f5} and R_{f6}, equal to or different from each other, is independently a fluorine atom, a C₁-C₆ perfluoro(oxy)alkyl group, optionally comprising one or more oxygen atoms, such as -CF₃, -C₂F₅, -C₃F₇, -OCF₃ or -OCF₂CF₂OCF₃; and

- optionally, recurring units derived from one or more than one hydrogenated monomer, as above detailed, including notably ethylene, propylene, (meth)acrylic monomers, styrenic monomers.

[0032] More specifically, block (B) may be selected from the group consisting of:

- blocks (B_{VDF}) consisting of a sequence of recurring units derived from vinylidene fluoride and optionally from one or more than one additional fluorinated monomer different from VDF, e.g. HFP, TFE or CTFE, and optionally from a hydrogenated monomer, as above detailed, e.g. a

(meth)acrylic monomer, whereas the amount of recurring units derived from VDF is of 85 to 100 % moles, based on the total moles of recurring units of block (B_{VDF});

- blocks (B_{TFE}) consisting of a sequence of recurring units derived from tetrafluoroethylene, and optionally from an additional perfluorinated monomer different from TFE, whereas the amount of recurring units derived from TFE is of 75 to 100 % moles, based on the total moles of recurring units of block (B);

- blocks ($B_{E/(C)TFE}$) consisting of a sequence of recurring units derived from ethylene and recurring units derived from CTFE and/or TFE, possibly in combination with an additional monomer.

[0033] The weight ratio between blocks (A) and blocks (B) in the fluorinated thermoplastic elastomer is typically comprised between 95:5 and 10:90.

[0034] According to certain preferred embodiments, the polymers (F-TPE) comprise a major amount of blocks (A); according to these embodiments, the polymer (F-TPE) used in the method of the present invention is characterized by a weight ratio between blocks (A) and blocks (B) of 95:5 to 65:35, preferably 90:10 to 70:30.

[0035] The crystallinity of block (B) and its weight fraction in the polymer (F-TPE) are such to provide for a heat of fusion (ΔH_f) of the polymer (F-TPE) of at most 20 J/g, preferably at most 18 J/g, more preferably at most 15 J/g, when determined according to ASTM D3418; on the other side, polymer (F-TPE) combines thermoplastic and elastomeric character, so as to possess a certain crystallinity, delivering a heat of fusion of at least 2.5 J/g, preferably at least 3.0 J/g, when determined according to same method.

[0036] Preferred polymers (F-TPE) are those comprising:

- at least one elastomeric block (A_{VDF}), as above detailed, and
- at least one thermoplastic block (B_{VDF}), as above detailed, and

wherein the crystallinity of said block (B) and its weight fraction in the polymer (F-TPE) are such to provide for a heat of fusion of the polymer (F-TPE) of at most 15 J/g, when determined according to ASTM D3418.

[0037] *The polymer (F)*

- [0038] The expression vinylidene fluoride polymer and polymer (F) are used within the frame of the present invention for designating polymers essentially made of recurring units, more than 85 % by moles of said recurring units being derived from vinylidene fluoride (VDF).
- [0039] Polymer (F) has a substantial crystalline character, and possesses a heat of fusion (ΔH_f) of more than 25 J/g, preferably of more than 27 J/g, more preferably more than 30 J/g, when determined according to ASTM D3418.
- [0040] The vinylidene fluoride polymer [polymer (F)] is preferably a polymer comprising :
- (a') at least 85 % by moles of recurring units derived from vinylidene fluoride (VDF);
 - (b') optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of recurring units derived from a fluorinated monomer different from VDF; and
 - (c') optionally from 0.1 to 5 %, by moles, preferably 0.1 to 3 % by moles, more preferably 0.1 to 1% by moles of recurring units derived from one or more hydrogenated comonomer(s),
- all the aforementioned % by moles being referred to the total moles of recurring units of the polymer (F).
- [0041] The said fluorinated monomer is advantageously selected in the group consisting of vinyl fluoride (VF_1); trifluoroethylene (VF_3); chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl)vinyl ethers, such as perfluoro(methyl)vinyl ether (PMVE), perfluoro(ethyl) vinyl ether (PEVE) and perfluoro(propyl)vinyl ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD). Preferably, the possible additional fluorinated monomer is chosen from chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF_3) and tetrafluoroethylene (TFE).
- [0042] The choice of the said hydrogenated comonomer(s) is not particularly limited; alpha-olefins, (meth)acrylic monomers, vinyl ether monomers, styrenic monomers may be used; nevertheless, to the sake of optimizing chemical resistance, embodiment's wherein the polymer (F) is

essentially free from recurring units derived from said hydrogenated comonomer(s) are preferred.

- [0043] Accordingly, the vinylidene fluoride polymer [polymer (F)] is more preferably a polymer consisting essentially of :
- (a') at least 85 % by moles of recurring units derived from vinylidene fluoride (VDF);
 - (b') optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of a fluorinated monomer different from VDF; said fluorinated monomer being preferably selected in the group consisting of vinylfluoride (VF₁), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), tetrafluoroethylene (TFE), perfluoromethylvinylether (MVE), trifluoroethylene (TrFE) and mixtures therefrom,
- all the aforementioned % by moles being referred to the total moles of recurring units of the polymer (F).
- [0044] Defects, end chains, impurities, chains inversions or branchings and the like may be additionally present in the polymer (F) in addition to the said recurring units, without these components substantially modifying the behaviour and properties of the polymer (F).
- [0045] As non-limitative examples of polymers (F) useful in the present invention, mention can be notably made of homopolymers of VDF, VDF/TFE copolymers, VDF/TFE/HFP copolymers, VDF/TFE/CTFE copolymers, VDF/TFE/TrFE copolymers, VDF/CTFE copolymers, VDF/HFP copolymers, VDF/TFE/HFP/CTFE copolymers and the like.
- [0046] VDF homopolymers are particularly advantageous for being used as polymer (F) in the composition (C).
- [0047] The melt index of the polymer (F) is advantageously at least 0.01, preferably at least 0.05, more preferably at least 0.1 g/10 min and advantageously less than 50, preferably less than 30, more preferably less than 20 g/10 min, when measured in accordance with ASTM test No. 1238, run at 230°C, under a piston load of 2.16 kg.
- [0048] The melt index of the polymer (F) is advantageously at least 1, preferably at least 2, more preferably at least 5 g/10 min and advantageously less

than 70, preferably less than 50, more preferably less than 40 g/10 min, when measured in accordance with ASTM test No. 1238, run at 230°C, under a piston load of 5 kg.

- [0049] The polymer (F) has advantageously a melting point (T_{m2}) advantageously of at least 120°C, preferably at least 125°C, more preferably at least 130°C and of at most 190°C, preferably at most 185°C, more preferably at most 180°C, when determined by DSC, at a heating rate of 10°C/min, according to ASTM D 3418.
- [0050] The part material [composition (C)]
- [0051] Within the frame of the present invention, the expression “part material” (otherwise referred to as “composition (C)”), as used in connection with the method of the present invention is understood to designate the composition of matter intended to be the constituent material of the three-dimensional object obtained from the said method.
- [0052] As said the part material (otherwise referred to as “composition (C)”) comprises at least one polymer (F-TPE) and at least one polymer (F), as above detailed. One or more than one polymer (F-TPE) and/or one or more than one polymer (F) may be used in the part material.
- [0053] The amount of polymer (F-TPE) in the composition (C) is generally of at least 50 % wt, preferably at least 60 % wt, most preferably of at least 70 % wt; and/or is advantageously of at most 97 % wt, preferably at most 95 % wt, more preferably at most 94 % wt, with respect to the total weight of polymer (F) and polymer (F-TPE).
- [0054] The amount of polymer (F) in the composition (C) is of at least 3 % wt, preferably of at least 5 % wt, more preferably at least 6 % wt; and/or is of at most 50 % wt, preferably at most 40 % wt, more preferably at most 30 % wt, with respect to the total weight of polymer (F) and polymer (F-TPE).
- [0055] The part material may comprise the polymer (F-TPE) and polymer (F) as above detailed in combination with other materials/ingredients, or may essentially consist of the said blend of polymer (F-TPE) and polymer (F), being understood that minor amounts (e.g. < 1% wt on total part material) of components other than the said main ingredients of the blend may be

present, without these components substantially affecting the performances and the properties of the polymer (F-TPE) and polymer (F) blend.

[0056] Further, the composition (C) may comprise one or more than one ingredient, such as those selected from the group consisting of thermal stabilizers, UV stabilizers, fillers, colouring compounds, plasticizers, curing systems, acid acceptors and flame retardants.

[0057] Among UV stabilizers suitable for being used in the composition (C), mention can be made, as categorized by their mode of action to prevent photo-degradation, of:

1. Quenchers, which are able to bring back “excited” chromophores (due to photon absorption) to a stable state;
2. Radical scavengers, such as HALS (hindered aromatic amine compounds), which are reactive towards free radicals formed after decomposition of “excited” chromophores (typically through generation of hydroperoxy radicals, and hence hydroperoxides and free radicals, by interaction with oxygen);
3. UV absorbers, which filter out harmful UV radiation, quickly transforming the same into vibrational and rotational energy of the molecule (hence into harmless heat), thus preventing the photo-degradation of the polymer components of composition (C).

[0058] In other terms, compounds of this latter class are chromophores that can go back to their stable state after light absorption without creating harmful free radicals (deactivation of the excited state by electronic rearrangement and heat dissipation).

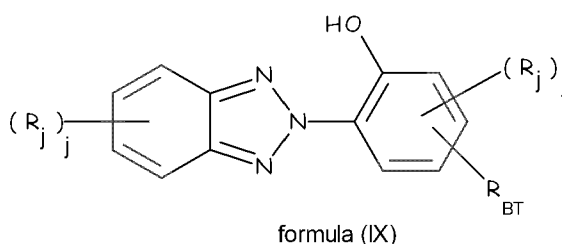
[0059] For a UV absorber to be effective in a polymer matrix, it is thus necessary for the UV absorber to absorb UV radiation through a chromophore group present in the molecule more quickly and more efficiently than the chromophores present in the polymer. The most important UV absorbers which have been found effective in the composition (C) are:

- a) 2-(2-hydroxyphenyl)-benzotriazoles
- b) 2-hydroxy-benzophenones
- c) 2-hydroxyphenyl-triazines

d) oxalanilides

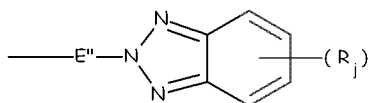
e) cyanoacrylates.

[0060] According to certain embodiments, composition (C) comprises at least one UV absorber selected from the group consisting of benzotriazole compounds [compounds (BT)] of formula (IX):

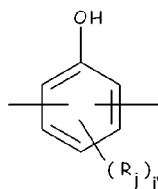


wherein:

- R_{BT} is independently H; C_1 - C_{18} alkyl; C_3 - C_6 alkenyl; C_5 - C_{12} cycloalkyl; phenyl; naphthyl; biphenyl; C_7 - C_{11} phenylalkyl; C_7 - C_{14} alkylphenyl; or is a group of formula:



wherein E'' is a hydrocarbon group, preferably an aromatic group, more preferably a group of formula:

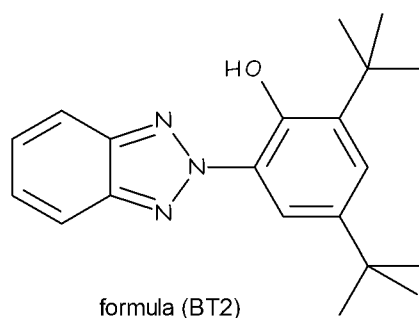
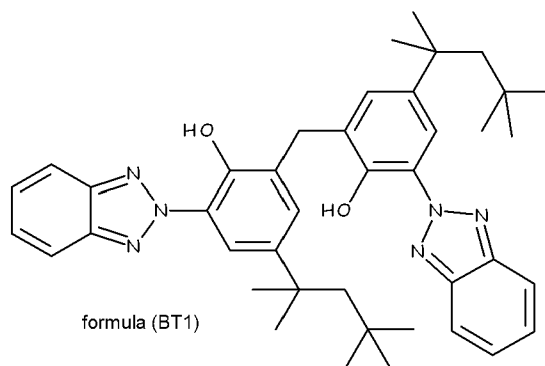


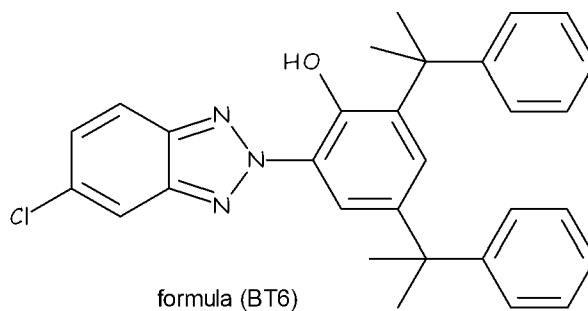
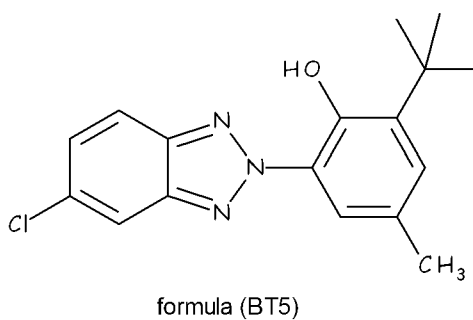
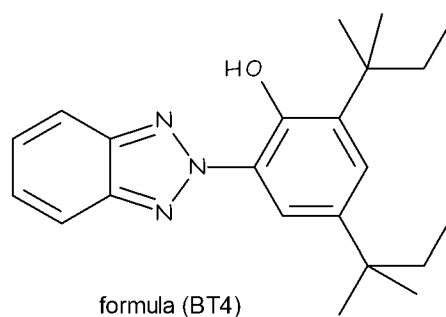
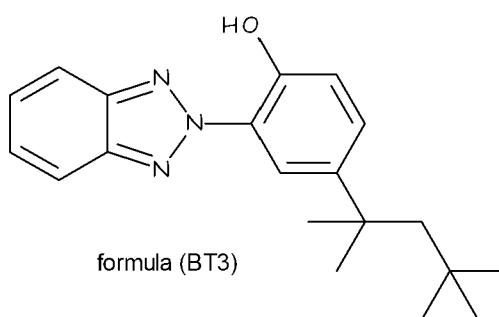
- j is zero or an integer of 0 to 4; j' is zero or an integer of 0 to 3;
- each of R_j , equal to or different from each other, is independently C_1 - C_{18} alkyl; C_3 - C_6 alkenyl; C_5 - C_{12} cycloalkyl; phenyl; naphthyl; biphenyl; C_7 - C_{11} phenylalkyl; C_7 - C_{14} alkylphenyl; halogen; C_1 - C_{18} haloalkyl; or C_1 - C_{18} alkoxy; or is NH_2 , NHR_{cn2} , $-N(R_{cn2})(R_{cn3})$, $NH-CO-R_{cn4}$, $-S-R_{cn5}$, or $-OR_{cn5}$; wherein:
 - R_{cn2} and R_{cn3} , equal to or different from each other, are independently C_1 - C_{12} alkyl; C_3 - C_{12} alkoxyalkyl; C_4 - C_{16} dialkylaminoalkyl; or C_5 - C_{12} cycloalkyl; or, when simultaneously present, may together form C_3 - C_9 -alkylene, -oxaalkylene or -azaalkylene;
 - R_{cn4} is independently H; C_1 - C_{18} alkyl; C_1 - C_{18} alkyl substituted by $COOH$ or

by $\text{COOR}_{\text{cn}2}$; $\text{C}_2\text{-C}_{18}$ alkenyl; $\text{C}_2\text{-C}_{18}$ alkenyl substituted by COOH or by $\text{COOR}_{\text{cn}2}$; $\text{C}_5\text{-C}_{12}$ cycloalkyl; phenyl; $\text{C}_7\text{-C}_{11}$ phenylalkyl; $\text{C}_6\text{-C}_{15}$ bicycloalkyl; $\text{C}_6\text{-C}_{15}$ bicycloalkenyl; or $\text{C}_6\text{-C}_{15}$ tricycloalkyl;

- $\text{R}_{\text{cn}5}$ is independently H, $\text{C}_1\text{-C}_{18}$ alkyl; $\text{C}_5\text{-C}_{12}$ cycloalkyl; $\text{C}_3\text{-C}_{18}$ alkenyl; phenyl; $\text{C}_1\text{-C}_{18}$ alkyl that is substituted by phenyl, OH, $\text{C}_1\text{-C}_{18}$ alkoxy, $\text{C}_5\text{-C}_{12}$ cycloalkoxy, $\text{C}_3\text{-C}_{18}$ alkenyloxy, halogen, $-\text{COOH}$, $-\text{COOR}_{\text{cn}2}$, $-\text{O-CO-R}_{\text{cn}2}$, $-\text{O-CO-O-R}_{\text{cn}2}$, $-\text{CO-NH}_2$, $-\text{CO-NHR}_{\text{cn}2}$, $-\text{CO-N(R}_{\text{cn}2})(\text{R}_{\text{cn}3})$, CN, NH_2 , $\text{NHR}_{\text{cn}2}$, $-\text{N(R}_{\text{cn}2})(\text{R}_{\text{cn}3})$, $-\text{NH-CO-R}_{\text{cn}2}$, phenoxy, $\text{C}_1\text{-C}_{18}$ alkyl-substituted phenoxy, phenyl- $\text{C}_1\text{-C}_4$ -alkoxy, $\text{C}_6\text{-C}_{15}$ bicycloalkoxy, $\text{C}_6\text{-C}_{15}$ bicycloalkyl-alkoxy, $\text{C}_6\text{-C}_{15}$ bicycloalkenyl-alkoxy and/or by $\text{C}_6\text{-C}_{15}$ -tricycloalkoxy; $\text{C}_5\text{-C}_{12}$ cycloalkyl that is substituted by OH, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_2\text{-C}_6$ alkenyl and/or by $-\text{O-CO-R}_{\text{cn}2}$; $-\text{CO-R}_{\text{cn}2}$ or $-\text{SO}_2\text{-R}_{\text{cn}2}$; or $\text{C}_3\text{-C}_{50}$ alkyl that is interrupted by one or more oxygen atoms and is unsubstituted or substituted by OH, phenoxy and/or by $\text{C}_7\text{-C}_{18}$ alkylphenoxy.

[0061] Among compounds (BT) which can be used in the composition (C), mention can be notably made of compounds complying with any of formulae below:





[0062] Of above mentioned compounds (BT), compound of formula (BT5), otherwise known as Bumetrizole, notably commercially available as TINUVIN® 326, has been found particularly advantageous.

- [0063] The composition (C) may comprise at least one acid acceptor selected from the group consisting of:
- (a) oxides or hydroxides of divalent metals, for instance oxides or hydroxides of Mg, Zn, Ca or Pb;
 - (b) metal salts of a weak acid, for instance Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates or phosphites; preferably Ca salts, and more preferably calcium carbonate;
 - (c) nitrogen-containing organic basic compounds, such as 1,8-bis(dimethylamino)naphthalene, octadecylamine, etc., as notably described in EP 708797 A (DU PONT) 1/05/1996.
- [0064] Generally, to the aim of fabricating a coloured three-dimensional object, the composition (C) will comprise one or more than one colouring compound, whose choice is not particularly limited. As used herein, the term "colouring compound" is intended to denote a compound that changes the colour of reflected or transmitted light as the result of wavelength-selective absorption of the electromagnetic radiation.
- [0065] The colouring compound maybe typically selected from the group consisting of organic colouring compounds and inorganic colouring compounds. Mixtures of one or more organic colouring compounds and one or more inorganic colouring compounds may be used in the composition (C) as above detailed. Otherwise, organic colouring compounds or inorganic colouring compounds may be separately used.
- [0066] Non-limiting examples of suitable inorganic compounds (N-L) include inorganic pigments such as metal salts and metal oxides, preferably selected from the group consisting of cadmium sulfide, zinc sulfide, cadmium selenite, lead chromate, zinc chromate, aluminosilicate sulfur complex, ferric oxide, ferric oxide molybdenate, chromium oxide, copper oxide, cobalt oxide, alumina, lead oxide, carbon black and mixtures thereof.
- [0067] Composition (C) may comprise at least one white inorganic colouring compound, also referred to as a white pigment; the use of a white pigment is advantageous in that it absorbs limited incident visible radiation and scatters most of said incident visible radiation. Otherwise stated, the white

pigments which can be used in the composition (C) generally absorb essentially no light in the visible region (wavelength 400 - 800 nm), and in certain cases some of them generally absorb no light in the UV region (wavelength 100-400 nm), but they disperse incident radiation in this region as completely as possible.

- [0068] The white pigments may be selected from the group consisting of titanium dioxide (TiO_2), zinc disulfide (ZnS_2), zinc oxide (ZnO) and barium sulfate (BaSO_4), among which TiO_2 is preferred. Suitable titanium dioxide pigments can be supplied from a variety of commercial sources, including notably Chemours, ISK, and the like. The nature of the titanium dioxide pigment is not particularly limited, and a variety of crystalline forms such as the anatase form, the rutile form and the monoclinic type can be advantageously used. However, the rutile form is generally preferred due to its higher refraction index and its superior light stability. Titanium dioxide pigment may be treated on its surface with at least one treatment agent, even if embodiments wherein titanium dioxide pigments have no surface treatment are also suitable.
- [0069] The colouring compound may be a luminescent colouring compound [compound (L)] or a non-luminescent colouring compound [compound (N-L)].
- [0070] For the purpose of the present invention, the term "luminescent colouring compound [compound (L)]" is intended to denote either a fluorescent colouring compound [compound (L-F)] or a phosphorescent colouring compound [compound (L-P)].
- [0071] The terms "luminescent", "fluorescent" and "phosphorescent" are used in the present invention according to their usual meanings.
- [0072] The compound (L) is usually able to re-emit the absorbed electromagnetic radiation from an excited state to a ground state. In particular, the compound (L-F) usually absorbs electromagnetic radiation in the ultraviolet (UV) region and re-emits it in the visible region of the electromagnetic spectrum.
- [0073] For the purpose of the present invention, the term "non-luminescent colouring compound [compound (N-L)]" is intended to denote a non-

luminescent colouring compound which selectively absorbs electromagnetic radiation in the visible region of the electromagnetic spectrum.

[0074] According to an embodiment of the present invention, mixtures of one or more compounds (L) and one or more compounds (N-L) may be used in the composition (C) of the invention.

[0075] Non-limiting examples of suitable organic compounds (N-L) include, for instance, azo pigments and polycyclic aromatic pigments, said polycyclic aromatic pigments being preferably selected from those based on cyanine, phthalocyanine such as copper phthalocyanine, anthraquinone, quinacridone, perylene, perinone, thioindigo, dioxazine, isoindolinone, isoindoline, diketopyrrolopyrrole, triarylcarbonium and quinophthalone.

[0076] Non-limiting examples of suitable organic compounds (L-F) typically include polycyclic aromatic dyes such as those based on xanthene, thioxanthene, benzoxanthene, naphthalimide, coumarin, naphtholactam, hydrazam, azlactone, methine, oxazine and thiazine.

[0077] Non-limiting examples of suitable inorganic compounds (L-F) typically include inorganic compounds comprising at least one element selected from the group consisting of rare earth metals, Zn and Mn.

[0078] The composition (C) may comprise one or more than one filler; the filler may be at least one selected from the group consisting of calcium carbonate, mica, kaolin, talc, carbon black, carbon fibers, carbon nanotubes, magnesium carbonate, sulfates of barium, calcium sulfate, titanium, nano clay, carbon black, hydroxides of aluminium or ammonium or magnesium, zirconia, nanoscale titania, and combinations thereof. While silica and glass fibers are generally not preferred fillers, they may be used in the composition (C), when the components of the said composition (C) are not generating amounts of HF which may react with the said SiO₂-based fillers.

[0079] **The method for manufacturing a three-dimensional object**

[0080] As said, the method includes a step of printing layers of the part material, as above detailed.

- [0081] Techniques for printing the said layers are not particularly limited, and may be selected notably from extrusion-based techniques, jetting, selective laser sintering, powder/binder jetting, electron-beam melting and stereolithography.
- [0082] Depending upon the printing technique which is used, the part material may be provided under different morphology for being used for printing layers in the additive manufacturing system. For instance, the part material may be provided under the form of loose particles; it may be provided under the form of fluid-state thermally solidifiable material or meltable precursor thereof, or may be provided under the form of a thermosettable liquid solution.
- [0083] The method may include printing layers of a support structure from a support material, and printing layers of the three-dimensional object from the said part material in coordination with the printing of the layers of the support structure, where at least a portion the printed layers of the support structure support the printed layers of the three-dimensional object, and then removing at least a portion of the support structure for obtaining the object (3D).
- [0084] According to certain preferred embodiments, the printing technique is an extrusion-based technique. According to these embodiment's, the method of the invention comprises:
- (i) a step of introducing a supply of the part material , as above detailed, in a fluid state into a flow passage of a discharge nozzle on a mechanically moveable dispensing head, said nozzle having a dispensing outlet at one end thereof in fluid-flow communication with said flow passage;
 - (ii) dispensing said part material from said dispensing outlet as a continuous, flowable fluid stream at a predetermined temperature above the temperature at which it solidifies onto a base member positioned in close proximity to said nozzle;
 - (iii) simultaneously with the dispensing of said part material onto said base member, mechanically generating relative movement of said base member and said dispensing head with respect to each other in a predetermined pattern to form a first layer of said material on said base member; and

- (iv) displacing said dispensing head a predetermined layer thickness distance from said first layer, and
- (v) after the portion of said first layer adjacent said nozzle has cooled and solidified, dispensing a second layer of said part material in a fluid state onto said first layer from said dispensing outlet while simultaneously moving said base member and said dispensing head relative to each other, whereby said second layer solidifies upon cooling and adheres to said first layer to form a three-dimensional article; and
- (vi) forming multiple layers of said part material built up on top of the previously generated layer in multiple passes by repeated sequences of steps (i) to (v), as above detailed.

[0085] Although this not being required, the object (3D) generated in the method as above detailed, maybe submitted to a further step causing the polymer (F-TPE) and/or the polymer (F) comprised in composition (C) to chemically crosslink.

[0086] This can be achieved through different techniques, including notably irradiation, e.g. with beta-radiation or gamma-radiation, thermal treatment, or any combination of the same.

[0087] To this aim, composition (C) may advantageously comprise suitable curing systems facilitating cross-linking of the polymer (F-TPE) and/or polymer (F).

[0088] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0089] The invention will be now described in more detail with reference to the following examples whose purpose is merely illustrative and not limitative of the scope of the invention.

[0090] **Examples**

[0091] **Raw Materials**

[0092] The following materials were used :

[0093] F-TPE-A is a thermoplastic elastomer based on VDF and HFP, possessing a heat of fusion of 8-9 J/g, and possessing a weight averaged molecular

weight of 296 000 g/mol (F-TPE-A, hereinafter), which can be prepared according to the teachings of .

- [0094] F-TPE-B is another thermoplastic elastomer based on VDF and HFP, possessing a heat of fusion of 8-9 J/g, and possessing a weight averaged molecular weight of 230 000 g/mol (F-TPE-B, hereinafter).
- [0095] SOLEF® 9009 is a VDF homopolymer having a MIFI (230°C/5kg) of 24 g/10 min and a heat of fusion of about 55-60 J/g (PVDF-9009, herein after), commercially available from Solvay Specialty Polymers Italy SpA.
- [0096] BLEND-C is a 50:50 weight ratio of F-TPE-A and PVDF-9009, provided in pelletized form (BLEND-C, herein after).
- [0097] TINUVIN® 326 (Bumetrizole) is a UV absorber (326, herein below), calcium carbonate is a mineral (R013, herein below), and Ti-Pure R-350 is TiO₂, a pigment (R-350, herein below).
- [0098] **Blend Compounding: general procedure**
- [0099] A co-rotating partially intermeshing twin screw extruder having an L/D ratio of 48:1 and 26 mm screws was used. The barrel sections 2 through 12 and the die were heated to set point temperatures between 160-180°C to generate a melt temperature of 180-210°C. In each case, the resin blends and additives were fed at barrel section 1 using gravimetric feeders at throughput rates in the range 10 lb/hr (4.53 Kg/h). The extruder was operated at screw speeds of around 150 RPM. No vacuum was applied. A single-hole die was used for all the compounds to give a filament approximately 2.6 to 2.7 mm in diameter and the polymer filament exiting the die was cooled in ice water and fed to the pelletizer to generate pellets approximately 2.7 mm in length.
- [00100] **Formulation Preparation: general procedure**
- [00101] Samples 50/50 w/w F-TPE-A / BLEND-C and 75/25 wt/wt F-TPE-B / PVDF-9009 were formulated as follows. For 50/50 w/w F-TPE-A / BLEND-C, a mixture of compounded F-TPE-A pellets and BLEND-C pellets were comingled and mixed on a bucket shaker (Agitar 05995PB) for 2 minutes and subsequently employed as a feedstock for the Brabender®, described below. For 75/25 wt/wt F-TPE-BH / PVDF-9009, F-

TPE-B powder and PVDF-9009 pellets were comingled and mixed on the same bucket shaker for 2 minutes.

[00102] Additive Manufacturing Filament Preparation: general procedure

[00103] Filament of diameter of 1.75 mm was prepared for each composition using a Brabender® Intelli-Torque Plasti-Corde® Torque Rheometer extruder equipped with a 0.75" (1.905 cm) 32 L/D general purpose single screw, a filament head adapter, a 2.5-mm nozzle and ESI-Extrusion Services downstream equipment comprising a cooling tank, a belt puller, and a Dual Station Coiler. A Beta LaserMike® 5012 with DataPro 1000 data controller was used to monitor filament dimensions. The melt strand was cooled with air. The Brabender® zone set point temperatures were as follows: zone 1, 185°C; zone 2 and zone 3, 180°C; zones 4, 170°C. The Brabender® speed ranged from 60 to 70 rpm and the puller speed from 22 to 34 feet per minute (6.706 to 10.363 meters per minute).

[00104] 3D printing FFF tensile and flex specimen: general procedure

[00105] Test bars (i.e. ASTM D638 Type V tensile bars and ASTM D256 flex bars, i.e. 0.125" x 0.5" x 2.5", corresponding to 3.175 mm x 12.7 mm x 63.5 mm) were printed from filament of 1.75 mm in diameter on a Hydra 16A printer from Hyrel, LLC, equipped with a 0.5 mm diameter nozzle. Bars were oriented in the XY direction on the build platform during printing. Test bars were printed with no brim, a 1-2 loop perimeter, and a 1-loop contour for each layer. The infill was a cross-hatch pattern with a 45° angle with respect to the long axis of the part. The build plate temperature for all bars was 120°C, and the build plate consisted of a glass plate with Dimafix glue applied to the surface (Dima3D, Spain). The nozzle and extruder temperature was 250°C for all FFF examples. The speed of the nozzle was varied from 9 to 15 mm/s. Layer height for all layers was 0.25 mm, with 100% fill density, an extrusion width of 0.5 mm for infill and 0.42 mm for perimeters.

[00106] Injection molded bars (comparative)

[00107] ASTM D638 Type V bars and ASTM D790 (i.e. 0.125" x 0.5" x 5.0", corresponding to 3.175 mm x 12.7 mm x 127 mm) impact bars were also obtained by injection molding. BLEND-C was processed in a mold

regulated at 38°C. A mold temperature of 38°C was employed for molded F-TPE-A.

[00108] Characterization of materials produced in the examples

[00109] Determination of thermal properties

[00110] Thermal properties have been determined by differential scanning calorimetry pursuant to ASTM D3418 standard. The supplied melting point data are from second heat scans.

[00111] Determination of physical / mechanical properties

[00112] Tensile strength and modulus were determined according to the ASTM D638 method with Type V bars. The components and their respective amounts in the test bars (according to the present invention or comparative) and the mechanical properties of the same are reported in Tables 3 below (5 test bars/mean value). Hardness measurements were performed with a durometer on the Shore A scale, pursuant to ASTM D2240, with an average of five tests per mean value. Specific gravity/density measurements were performed pursuant to ASTM D792, with an average of two test bars per mean value.

[00113] Table 1 provides an overview of the compositions of the filaments used in Examples 1C, 2 to 4 and 5C.

Table 1

Example		1c	2	3	4	5c
Ingredients	Processing	Injection Molded	3D Printed	3D Printed	3D Printed	3D Printed
F-TPE-A	wt%	49.83	49.83	74.83		100
326	wt%	0.07	0.07	0.07		
R013	wt%	0.1	0.1	0.1		
PVDF-9009	wt%	50	50	25		
R-350	pph	1	1	1		
F-TPE-B	wt%				75	
PVDF-9009	wt%				25	

[00114] Standard deviations of measured parameters are shown in parentheses in Table above.

[00115] 3D printing processing parameters are summarized in Table 2, herein below; it is noticeable that while filament of Ex. 5C (F-TPE alone) could not

be satisfactorily printed, in exactly same conditions, filament of Ex. 2 (combining F-TPE and PVDF) could be printed to provide parts having essentially same density as corresponding injection molded parts, so representative of faults-less/voids-less 3D printed parts.

Table 2

Printing conditions	Ex. 2/Ex. 5C	Ex. 3	Ex. 4
Printer	Hyrel Hydra	Hyrel Hydra	Hyrel Hydra
Filament diameter, mm	1.75	1.75	1.75
Extruder temperature, T°C	240	250	250
Bed, T°C	100	120	120
Bed surface	Glass + Dimafix	Glass + Dimafix	Glass + Dimafix
Nozzle Diameter (mm)	0.5	0.5	0.5
Fill density (% infill)	100	100	100
Fill angle, °	+/- 45 alt	+/- 45 alt	+/- 45 alt
Layer Height, mm	0.1	0.25	0.25
Number of perimeters/shells	1	1	1
Speed, mm/sec	30	15	9

[00116] Table 3 herein below shows the results of characterization carried out on printed and comparative injection molded samples, well demonstrating the effectiveness of the inventive solution of incorporating PVDF into F-TPE for enhancing 3D printing processability, while maintaining Shore A hardness of less than 100.

Table 3

Test		1C	2	3	4	5C
Melting point filament	°C	166	166	167	166	165
Specific Gravity	g/cm ³	1.8 (0.01)	1.78 (0.01)	1.78 (0.01)	1.73 (0.01)	(*)
Shore A	-	95.6 (0.6)	95.4 (0.6)	93.4 (0.55)	91.6 (0.55)	
Tensile Strain @ Break	%	170 (43)	52 (8)	261 (32)	159 (12)	
Modulus of Elasticity	ksi	82.8 (3.3)	60.1 (6.1)	13.5 (2.8)	8.5 (1.2)	

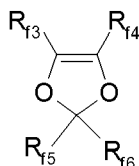
(*) means that the filament failed to be printed in explored conditions (buckles at the print head), so that no meaningful part for testing was obtained.

Claims

- Claim 1. A method for manufacturing a three-dimensional object [object (3D)] using an additive manufacturing system, comprising:
- generating a digital representation of the three-dimensional object, and slicing the same into multiple horizontal layers, so as to generate printing instructions for each of the said horizontal layers;
 - printing layers of the object (3D) from a part material [composition (C)] comprising:
 - (1) at least one fluorinated thermoplastic elastomer [polymer (F-TPE)] comprising:
 - at least one elastomeric block (A) consisting of a sequence of recurring units, said sequence comprising recurring units derived from at least one fluorinated monomer, said block (A) possessing a glass transition temperature of less than 25°C, as determined according to ASTM D3418; and
 - at least one thermoplastic block (B) consisting of a sequence of recurring units, said sequence comprising recurring units derived from at least one fluorinated monomer,wherein the crystallinity of said block (B) and its weight fraction in the polymer (F-TPE) are such to provide for a heat of fusion of the polymer (F-TPE) of at least 2.5 J/g and at most 20 J/g, when determined according to ASTM D3418; and
 - (2) at least one thermoplastic vinylidene fluoride (VDF) polymer [polymer (F)] comprising recurring units derived from VDF in an amount of at least 85 % moles, with respect to the total moles of recurring units of polymer (F), said polymer (F) possessing a heat of fusion (ΔH_f) of the polymer (F-TPE) of at least 25 J/g, when determined according to ASTM D3418.
- Claim 2. The method of Claim 1, wherein polymer (F-TPE) comprises, preferably consists of:
- at least one elastomeric block (A) selected from the group consisting of:
 - (1) vinylidene fluoride (VDF)-based elastomeric blocks (A_{VDF}) consisting of a sequence of recurring units, said sequence comprising recurring units derived from VDF and recurring units derived from at least one fluorinated monomer

different from VDF, said fluorinated monomer different from VDF being typically selected from the group consisting of:

- (a) C₂-C₈ perfluoroolefins such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP);
- (b) hydrogen-containing C₂-C₈ fluoroolefins different from VDF, such as vinyl fluoride, trifluoroethylene (TrFE), hexafluoroisobutylene (HFIB), perfluoroalkyl ethylenes of formula CH₂=CH-R_{f1}, wherein R_{f1} is a C₁-C₆ perfluoroalkyl group;
- (c) C₂-C₈ chloro- and/or bromo-containing fluoroolefins such as chlorotrifluoroethylene (CTFE);
- (d) perfluoroalkylvinylethers (PAVE) of formula CF₂=CFOR_{f1}, wherein R_{f1} is a C₁-C₆ perfluoroalkyl group, such as CF₃ (PMVE), C₂F₅ or C₃F₇;
- (e) perfluorooxyalkylvinylethers of formula CF₂=CFOX₀, wherein X₀ is a C₁-C₁₂ perfluorooxyalkyl group comprising one or more than one ethereal oxygen atom, including notably perfluoromethoxyalkylvinylethers of formula CF₂=CFOCF₂OR_{f2}, with R_{f2} being a C₁-C₃ perfluoro(oxy)alkyl group, such as -CF₂CF₃, -CF₂CF₂-O-CF₃ and -CF₃; and
- (f) (per)fluorodioxoles of formula:



wherein each of R_{f3}, R_{f4}, R_{f5} and R_{f6}, equal to or different from each other, is independently a fluorine atom, a C₁-C₆ perfluoro(oxy)alkyl group, optionally comprising one or more oxygen atoms, such as -CF₃, -C₂F₅, -C₃F₇, -OCF₃ or -OCF₂CF₂OCF₃; and

- (2) tetrafluoroethylene (TFE)-based elastomeric blocks (A_{TFE}) consisting of a sequence of recurring units, said sequence comprising recurring units derived from TFE and recurring units derived from at least one fluorinated monomer different from TFE, said fluorinated monomer being typically selected from the group consisting of those of classes (b), (c), (d), (e) as defined above;
- at least one thermoplastic block (B) consisting of a sequence of recurring units derived from at least one fluorinated monomer.

Claim 3. The method of Claim 2, wherein the elastomeric block (A) be a block (A_{VDF}), said block (A_{VDF}) consisting of a sequence of recurring units

comprising, preferably consisting of:

- from 45% to 90% by moles of recurring units derived from vinylidene fluoride (VDF),
- from 5% to 50% by moles of recurring units derived from at least one fluorinated monomer different from VDF, and
- optionally, up to 30% by moles of recurring units derived from at least one hydrogenated monomer,

with respect to the total moles of recurring units of the sequence of block (A_{VDF}); and wherein the elastomeric block (A) is preferably a block (A_{VDF}), said block (A_{VDF}) consisting of a sequence of recurring units comprising, preferably consisting of:

- from 45% to 80% by moles of recurring units derived from vinylidene fluoride (VDF),
- from 5% to 50% by moles of recurring units derived from at least one fluorinated monomer different from VDF,
- optionally, up to 1.0 % by moles of recurring units derived from at least one bis-olefin (OF); and
- optionally, up to 30% by moles of recurring units derived from at least one hydrogenated monomer,

with respect to the total moles of recurring units of the sequence of block (A_{VDF}).

Claim 4. The method of anyone of the preceding Claims, wherein block (B)

consists of a sequence of recurring units, said sequence comprising:

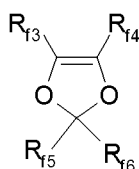
- recurring units derived from one or more than one fluoromonomer, preferably selected from the group consisting of:

(a) C_2 - C_8 perfluoroolefins such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP);

(b) hydrogen-containing C_2 - C_8 fluoroolefins, such as vinylidene fluoride (VDF), vinyl fluoride, trifluoroethylene (TrFE), hexafluoroisobutylene (HFIB), perfluoroalkyl ethylenes of formula $CH_2=CH-R_{f1}$, wherein R_{f1} is a C_1 - C_6 perfluoroalkyl group;

(c) C_2 - C_8 chloro- and/or bromo-containing fluoroolefins such as chlorotrifluoroethylene (CTFE);

- (d) perfluoroalkylvinylethers (PAVE) of formula $\text{CF}_2=\text{CFOR}_{f1}$, wherein R_{f1} is a $\text{C}_1\text{-C}_6$ perfluoroalkyl group, such as CF_3 (PMVE), C_2F_5 or C_3F_7 ;
- (e) perfluorooxyalkylvinylethers of formula $\text{CF}_2=\text{CFOX}_0$, wherein X_0 is a $\text{C}_1\text{-C}_{12}$ perfluorooxyalkyl group comprising one or more than one ethereal oxygen atom, including notably perfluoromethoxyalkylvinylethers of formula $\text{CF}_2=\text{CFOCF}_2\text{OR}_{f2}$, with R_{f2} being a $\text{C}_1\text{-C}_3$ perfluoro(oxy)alkyl group, such as $-\text{CF}_2\text{CF}_3$, $-\text{CF}_2\text{CF}_2\text{-O-CF}_3$ and $-\text{CF}_3$; and
- (f) (per)fluorodioxoles of formula:



wherein each of R_{f3} , R_{f4} , R_{f5} and R_{f6} , equal to or different from each other, is independently a fluorine atom, a $\text{C}_1\text{-C}_6$ perfluoro(oxy)alkyl group, optionally comprising one or more oxygen atoms, such as $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$, $-\text{OCF}_3$ or $-\text{OCF}_2\text{CF}_2\text{OCF}_3$; and

- optionally, recurring units derived from one or more than one hydrogenated monomer, as above detailed, including notably ethylene, propylene, (meth)acrylic monomers, styrenic monomers.

Claim 5. The method of Claim 4, wherein block (B) is selected from the group consisting of:

- blocks (B_{VDF}) consisting of a sequence of recurring units derived from vinylidene fluoride and optionally from one or more than one additional fluorinated monomer different from VDF, e.g. HFP, TFE or CTFE, and optionally from a hydrogenated monomer, as above detailed, e.g. a (meth)acrylic monomer, whereas the amount of recurring units derived from VDF is of 85 to 100 % moles, based on the total moles of recurring units of block (B_{VDF});
- blocks (B_{TFE}) consisting of a sequence of recurring units derived from tetrafluoroethylene, and optionally from an additional perfluorinated monomer different from TFE, whereas the amount of recurring units derived from TFE is of 75 to 100 % moles, based on the total moles of recurring units of block (B);
- blocks ($\text{B}_{\text{E(C)TFE}}$) consisting of a sequence of recurring units derived from

ethylene and recurring units derived from CTFE and/or TFE, possibly in combination with an additional monomer.

Claim 6. The method according to Claim 5, wherein polymer (F-TPE) is selected from the group consisting of those comprising:

- at least one elastomeric block (A_{VDF}), and
- at least one thermoplastic block (B_{VDF}), and

wherein the crystallinity of said block (B) and its weight fraction in the polymer (F-TPE) are such to provide for a heat of fusion of the polymer (F-TPE) of at most 15 J/g, when determined according to ASTM D3418.

Claim 7. The method according to anyone of the preceding Claims, wherein polymer (F) is a polymer comprising :

- (a') at least 85 % by moles of recurring units derived from vinylidene fluoride (VDF);
- (b') optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of recurring units derived from a fluorinated monomer different from VDF; and
- (c') optionally from 0.1 to 5 %, by moles, preferably 0.1 to 3 % by moles, more preferably 0.1 to 1% by moles of recurring units derived from one or more hydrogenated comonomer(s),

all the aforementioned % by moles being referred to the total moles of recurring units of the polymer (F),

wherein said fluorinated monomer is selected in the group consisting of vinyl fluoride (VF_1); trifluoroethylene (VF_3); chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl)vinyl ethers, such as perfluoro(methyl)vinyl ether (PMVE), perfluoro(ethyl) vinyl ether (PEVE) and perfluoro(propyl)vinyl ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD); and

wherein polymer (F) is preferably a polymer consisting essentially of :

- (a') at least 85 % by moles of recurring units derived from vinylidene fluoride (VDF);
- (b') optionally from 0.1 to 15%, preferably from 0.1 to 12%, more preferably from 0.1 to 10% by moles of a fluorinated monomer different from VDF; said fluorinated monomer being preferably selected in the group

consisting of vinylfluoride (VF₁), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), tetrafluoroethylene (TFE), perfluoromethylvinylether (MVE), trifluoroethylene (TrFE) and mixtures therefrom, all the aforementioned % by moles being referred to the total moles of recurring units of the polymer (F).

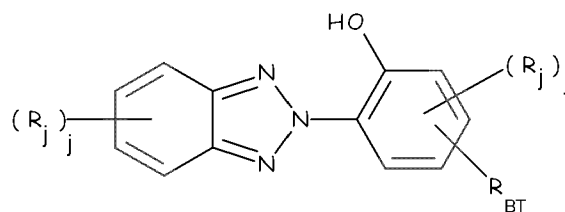
Claim 8. The method of anyone of the preceding claims, wherein:

- the amount of polymer (F-TPE) in the composition (C) is of at least 50 % wt, preferably at least 60 % wt, most preferably of at least 70 % wt; and/or is of at most 97 % wt, preferably at most 95 % wt, more preferably at most 94 % wt, with respect to the total weight of polymer (F) and polymer (F-TPE); and/or
- the amount of polymer (F) in the composition (C) is of at least 3 % wt, preferably of at least 5 % wt, more preferably at least 6 % wt; and/or is of at most 50 % wt, preferably at most 40 % wt, more preferably at most 30 % wt, with respect to the total weight of polymer (F) and polymer (F-TPE).

Claim 9. The method of anyone of the preceding claims, wherein the composition (C) comprises one or more than one colouring compound, selected from the group consisting of a luminescent colouring compound [compound (L)] or a non-luminescent colouring compound [compound (N-L)].

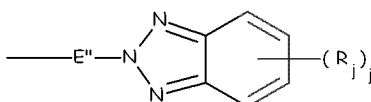
Claim 10. The method of anyone of the preceding claims, wherein the composition (C) comprises:

- at least one UV absorber, which is preferably selected from the group consisting of benzotriazole compounds [compounds (BT)] of formula (IX):

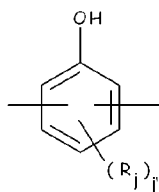


wherein:

- R_{BT} is independently H; C₁-C₁₈ alkyl; C₃-C₆ alkenyl; C₅-C₁₂ cycloalkyl; phenyl; naphthyl; biphenyl; C₇-C₁₁ phenylalkyl; C₇-C₁₄ alkylphenyl; or is a group of formula:



wherein E" is a hydrocarbon group, preferably an aromatic group, more preferably a group of formula:



;

- j is zero or an integer of 0 to 4; j' is zero or an integer of 0 to 3;
- each of R_j, equal to or different from each other, is independently C₁-C₁₈ alkyl; C₃-C₆ alkenyl; C₅-C₁₂ cycloalkyl; phenyl; naphthyl; biphenyl; C₇-C₁₁ phenylalkyl; C₇-C₁₄ alkylphenyl; halogen; C₁-C₁₈ haloalkyl; or C₁-C₁₈ alkoxy; or is NH₂, NHR_{cn2}, -N(R_{cn2})(R_{cn3}), NH-CO-R_{cn4}; -S-R_{cn5}, or -OR_{cn5}; wherein:
 - R_{cn2} and R_{cn3}, equal to or different from each other, are independently C₁-C₁₂ alkyl; C₃-C₁₂ alkoxyalkyl; C₄-C₁₆ dialkylaminoalkyl; or C₅-C₁₂ cycloalkyl; or, when simultaneously present, may together form C₃-C₉-alkylene, -oxaalkylene or -azaalkylene;
 - R_{cn4} is independently H; C₁-C₁₈ alkyl; C₁-C₁₈ alkyl substituted by COOH or by COOR_{cn2}; C₂-C₁₈ alkenyl; C₂-C₁₈ alkenyl substituted by COOH or by COOR_{cn2}; C₅-C₁₂ cycloalkyl; phenyl; C₇-C₁₁ phenylalkyl; C₆-C₁₅ bicycloalkyl; C₆-C₁₅ bicycloalkenyl; or C₆-C₁₅ tricycloalkyl;
 - R_{cn5} is independently H, C₁-C₁₈ alkyl; C₅-C₁₂ cycloalkyl; C₃-C₁₈ alkenyl; phenyl; C₁-C₁₈ alkyl that is substituted by phenyl, OH, C₁-C₁₈ alkoxy, C₅-C₁₂ cycloalkoxy, C₃-C₁₈ alkenyloxy, halogen, -COOH, -COOR_{cn2}, -O-CO-R_{cn2}, --O-CO-O-R_{cn2}, -CO-NH₂, -CO-NHR_{cn2}, -CO-N(R_{cn2})(R_{cn3}), CN, NH₂, NHR_{cn2}, -N(R_{cn2})(R_{cn3}), -NH-CO-R_{cn2}, phenoxy, C₁-C₁₈ alkyl-substituted phenoxy, phenyl-C₁-C₄-alkoxy, C₆-C₁₅ bicycloalkoxy, C₆-C₁₅ bicycloalkyl-alkoxy, C₆-C₁₅ bicycloalkenyl-alkoxy and/or by C₆-C₁₅-tricycloalkoxy; C₅-C₁₂ cycloalkyl that is substituted by OH, C₁-C₄ alkyl, C₂-C₆ alkenyl and/or by -O-CO-R_{cn2}; -CO-R_{cn2} or -SO₂-R_{cn2}; or C₃-C₅₀ alkyl that is interrupted by one or more oxygen atoms and is unsubstituted or substituted by OH, phenoxy and/or by C₇-C₁₈ alkylphenoxy; and/o
- at least one acid acceptor, which is preferably selected from the group consisting of:
 - (a) oxides or hydroxides of divalent metals, for instance oxides or hydroxides of

Mg, Zn, Ca or Pb;

(b) metal salts of a weak acid, for instance Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates or phosphites; preferably Ca salts, and more preferably calcium carbonate;

(c) nitrogen-containing organic basic compounds.

Claim 11. The method according to anyone of the preceding claims, wherein the method includes a step of printing layers of the part material, according to a technique selected from the group consisting of extrusion-based techniques, jetting, selective laser sintering, powder/binder jetting, electron-beam melting and stereolithography.

Claim 12. The method according to anyone of the preceding claims, wherein the method includes printing layers of a support structure from a support material, and printing layers of the three-dimensional object from the said part material in coordination with the printing of the layers of the support structure, where at least a portion the printed layers of the support structure support the printed layers of the three-dimensional object, and then removing at least a portion of the support structure for obtaining the object (3D).

Claim 13. The method according to anyone of the preceding claims, said method comprising:

(i) a step of introducing a supply of the part material, as above detailed, in a fluid state into a flow passage of a discharge nozzle on a mechanically moveable dispensing head, said nozzle having a dispensing outlet at one end thereof in fluid-flow communication with said flow passage;

(ii) dispensing said part material from said dispensing outlet as a continuous, flowable fluid stream at a predetermined temperature above the temperature at which it solidifies onto a base member positioned in close proximity to said nozzle;

(iii) simultaneously with the dispensing of said part material onto said base member, mechanically generating relative movement of said base member and said dispensing head with respect to each other in a predetermined pattern to form a first layer of said material on said base member; and

(iv) displacing said dispensing head a predetermined layer thickness distance from said first layer, and

(v) after the portion of said first layer adjacent said nozzle has cooled and solidified, dispensing a second layer of said part material in a fluid state onto said first layer from said dispensing outlet while simultaneously moving said base member and said dispensing head relative to each other, whereby said second layer solidifies upon cooling and adheres to said first layer to form a three-dimensional article; and

(vi) forming multiple layers of said part material built up on top of the previously generated layer in multiple passes by repeated sequences of steps (i) to (v), as above detailed.

Claim 14. The method according to anyone of the preceding claims, said method comprising a further step wherein the object (3D) is submitted to a further step causing the polymer (F-TPE) to chemically crosslink.

Claim 15. The method of claim 14, wherein composition (C) comprises curing systems facilitating cross-linking of the polymer (F-TPE).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/085241

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/106 B33Y70/00 B33Y10/00 B29C64/00 C08F293/00
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)
C09D B29C B33Y C09J C08F

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.
A	WO 2018/149758 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 23 August 2018 (2018-08-23) cited in the application claims; examples -----	1-15
A	WO 2018/149757 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 23 August 2018 (2018-08-23) claims; examples -----	1-15
A	"ADDITIVE PROCESSING OF FLUOROPOLYMERS", IP.COM JOURNAL, IP.COM INC., WEST HENRIETTA, NY, US, 28 February 2017 (2017-02-28), XP013174570, ISSN: 1533-0001 the whole document -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"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

20 February 2020

Date of mailing of the international search report

02/03/2020

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/085241

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2018149758 A1	23-08-2018	CN 110300768 A EP 3583143 A1 KR 20190116310 A US 2019381727 A1 WO 2018149758 A1	01-10-2019 25-12-2019 14-10-2019 19-12-2019 23-08-2018
WO 2018149757 A1	23-08-2018	CN 110312746 A EP 3583142 A1 KR 20190115446 A WO 2018149757 A1	08-10-2019 25-12-2019 11-10-2019 23-08-2018