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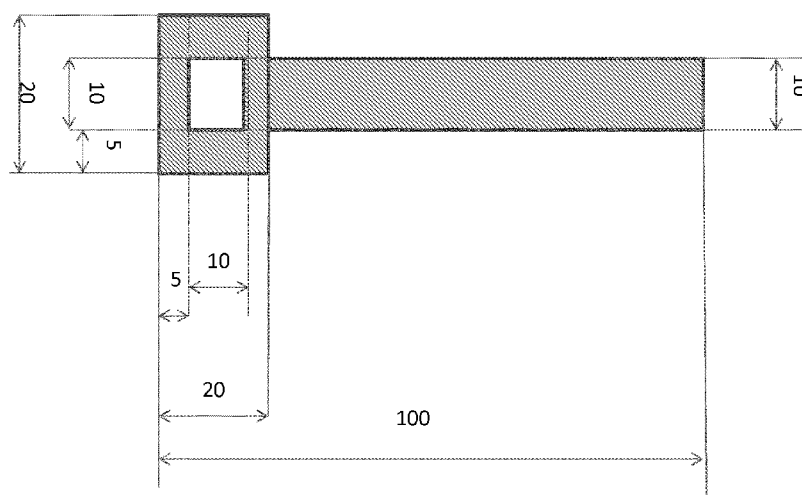
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(54) Title: PROPYLENE BASED FILAMENT FOR 3D PRINTER

FIG 1



(57) Abstract: A consumable filament for use in an extrusion-based additive manufacturing system comprising a propylene ethylene copolymer having: - ethylene derived units content ranging from 3.0 wt% to 12.0 wt%; - MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) from 4 to 20 g/10 min; and - xylene solubles measured at 25°C comprised between 3 wt% and 30 wt%.



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TITLE

PROPYLENE BASED FILAMENT FOR 3D PRINTER

FIELD OF THE INVENTION

[0001] The present disclosure relates to a filament comprising a propylene ethylene copolymer to be used in an extrusion-based 3D printer.

BACKGROUND OF THE INVENTION

[0002] An extrusion-based 3D printer is used to build a 3D model from a digital representation of the 3D model in a layer-by-layer manner by extruding a flowable modeling material. A filament of the modeling material is extruded through an extrusion tip carried by an extrusion head, and is deposited as a sequence of roads on a substrate in an x-y plane. The extruded modeling material fuses to previously deposited modeling material, and solidifies upon a drop in temperature. The position of the extrusion 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 model resembling the digital representation. Movement of the extrusion head with respect to the substrate is performed under computer control, in accordance with build data that represents the 3D model. The build data is obtained by initially slicing the digital representation of the 3D model into multiple horizontally sliced layers. Then, for each sliced layer, the host computer generates a build path for depositing roads of modeling material to form the 3D model.

[0003] In the printing process the filament clearly plays an important role, changing the material of the filament the final mechanical and aesthetic properties of the finished object change. Usually in the art filament of polylactic acid (PLA) or acrylonitrile, butadiene, styrene (ABS) polymer or polyamides are used.

[0004] One of the most important properties of a filament is constant diameter (usually 1.75 mm or 3 mm) otherwise it is not possible to finely tune the amount of material in the printed object. This property is not easily achieved and depends on the characteristics of the polymer.

[0005] Furthermore the filament, once prepared, has to be printable, i.e. it has to be possible to achieve a good adhesion with the plate and among the layers.

[0006] Propylene based polymers has been proposed as polymers suitable for making filaments, however from the tests carried out by the applicant the propylene based filaments available on the market gave poor results in the print test.

[0007] Therefore there is the need for propylene based polymers that can be used as a filament in a 3D printer.

SUMMARY OF THE INVENTION

[0008] The applicant found a consumable filament for use in an extrusion-based additive manufacturing system comprising a propylene ethylene copolymer having:

[0009] -ethylene derived units content ranging from 3.0 wt% to 12.0 wt%;

[0010] -MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) ranging from 4 to 20 g/10 min; and

[0011] - xylene solubles measured at 25°C comprised between 3 wt% and 30 wt% ; .

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is the front view of the sample used in the print tests of the examples. The measure are given in mm, the sample once completely printed is 5 mm thick. .

DETAILED DESCRIPTION OF THE INVENTION

[0013] The applicant found a consumable filament for use in an extrusion-based additive manufacturing system comprising a propylene ethylene copolymer having:

[0014] -ethylene derived units content ranging from 3.0 wt% to 12.0 wt% ; preferably from 3.5 wt% to 10.0 wt%; more preferably from 3.8 wt% to 8.0 wt%;

[0015] -MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) from 4 to 20 g/10 min, preferably from 5 to 10 g/10 min; more preferably from 6 to 8 g/10 min; and

[0016] - xylene solubles measured at 25°C comprised between 3 wt% and 30 wt% ; preferably between 4 wt% and 25 wt%.

[0017] The term copolymer means that the polymer is formed by only to monomers, propylene and ethylene.

[0018] The propylene/ethylene copolymer of the present invention can be extruded in a filament having a constant diameter, the diameter of the filament being that of one used in the art such as 1.75 mm or 3 mm. Other possible diameters can also be used. The variation from the nominal diameter is ± 0.05 mm preferably ± 0.03 mm.

[0019] When amorphous polymeric materials, such as acrylonitrile-butadiene-styrene (ABS) resins and polycarbonate resins are used they have little or no ordered arrangements of their polymer chains in their solid states. This reduces the effects of curling and plastic deformation in the resulting 3D model or support structure.

[0020] Crystalline or semicrystalline polymer exhibits superior mechanical properties but due to the crystallinity when used for building 3D model they show undesirable shrinkage effects both when the extruded road is deposited to form a portion of a layer of a 3D model and when the road is cooled. The shrinkage effects renders the crystalline or semicrystalline polymers not usable for the building of 3D object in an extrusion-based additive manufacturing process.

[0021] The applicant found that the propylene ethylene copolymer of the present disclosure can be advantageously used for building a 3D model comprising semi crystalline polymers as shown by the amount of xylene soluble material.

[0022] The propylene ethylene copolymer of the present disclosure is available in the market. Examples of copolymers can be RP220M sold by LyondellBasell, BOREALIS RD204 CF. Another possible similar polymer is LyondellBasell CLYRELL RC 1908.

[0023] The filament object of the present invention can additionally contain additives normally used in the art such as antioxidants, slipping agents, process stabilizers, antiacid and nucleants.

[0024] The filament can additionally contains fillers known in the art such as talc, calcium carbonate, wollastonite, glass fibers, glass spheres and carbon derived grades.

[0025] Furthermore the filament of the present invention can also contains wood powder, metallic powder marble powder and similar materials normally used for obtaining 3D object having particular aesthetic appearances or improved mechanics.

[0026] The following examples are given to illustrate and not to limit the present invention.

EXAMPLES

[0027] The data of the propylene polymer materials were obtained according to the following methods:

[0028] **Xylene-soluble fraction at 25°C**

[0029] The Xylene Soluble fraction was measured according to ISO 16152, 2005, but with the following deviations (between brackets is what is prescribed by the ISO 16152)

[0030] The solution volume is 250 ml (200 ml)

[0031] During the precipitation stage at 25°C for 30 min, the solution, for the final 10 minutes, is kept under agitation by a magnetic stirrer (30 min, without any stirring at all)

[0032] The final drying step is done under vacuum at 70°C (100 °C)

[0033] The content of said xylene-soluble fraction is expressed as a percentage of the original 2.5 grams and then, by difference (complementary to 100), the xylene insoluble %

[0034] **Ethylene (C2) content**

[0035] **¹³C NMR of propylene/ethylene copolymers**

[0036] ¹³C NMR spectra were acquired on a Bruker AV-600 spectrometer equipped with cryoprobe, operating at 160.91 MHz in the Fourier transform mode at 120°C.

[0037] The peak of the S_{ββ} carbon (nomenclature according to “Monomer Sequence Distribution in Ethylene-Propylene Rubber Measured by ¹³C NMR. 3. Use of Reaction Probability Mode ” C. J. Carman, R. A. Harrington and C. E. Wilkes, Macromolecules, 1977, 10, 536) was used as internal reference at 29.9 ppm. The samples were dissolved in 1,1,2,2-tetrachloroethane-d₂ at 120°C with a 8 % wt/v concentration. Each spectrum was acquired with a 90° pulse, 15 seconds of delay between pulses and CPD to remove 1H-¹³C coupling. 512 transients were stored in 32K data points using a spectral window of 9000 Hz.

[0038] The assignments of the spectra, the evaluation of triad distribution and the composition were made according to Kakugo (“Carbon-13 NMR determination of monomer sequence distribution in ethylene-propylene copolymers prepared with δ-titanium trichloride-diethylaluminum chloride” M. Kakugo, Y. Naito, K. Mizunuma and T. Miyatake, Macromolecules, 1982, 15, 1150) using the following equations:

$$\begin{aligned}
 \text{PPP} &= 100 \text{ T}_{\beta\beta}/\text{S} & \text{PPE} &= 100 \text{ T}_{\beta\delta}/\text{S} & \text{EPE} &= 100 \text{ T}_{\delta\delta}/\text{S} \\
 \text{PEP} &= 100 \text{ S}_{\beta\beta}/\text{S} & \text{PEE} &= 100 \text{ S}_{\beta\delta}/\text{S} & \text{EEE} &= 100 (0.25 \text{ S}_{\gamma\delta} + 0.5 \text{ S}_{\delta\delta})/\text{S} \\
 \text{S} &= \text{T}_{\beta\beta} + \text{T}_{\beta\delta} + \text{T}_{\delta\delta} + \text{S}_{\beta\beta} + \text{S}_{\beta\delta} + 0.25 \text{ S}_{\gamma\delta} + 0.5 \text{ S}_{\delta\delta}
 \end{aligned}$$

The molar percentage of ethylene content was evaluated using the following equation:

$E\% \text{ mol} = 100 * [PEP+PEE+EEE]$ The weight percentage of ethylene content was evaluated using the following equation:

$$E\% \text{ wt.} = \frac{100 * E\% \text{ mol} * MW_E}{E\% \text{ mol} * MW_E + P\% \text{ mol} * MW_P}$$

[0039] where $P\% \text{ mol}$ is the molar percentage of propylene content, while MW_E and MW_P are the molecular weights of ethylene and propylene, respectively.

[0040] The product of reactivity ratio $r_1 r_2$ was calculated according to Carman (C.J. Carman, R.A. Harrington and C.E. Wilkes, *Macromolecules*, **1977**; *10*, 536) as:

$$r_1 r_2 = 1 + \left(\frac{EEE + PEE}{PEP} + 1 \right) - \left(\frac{P}{E} + 1 \right) \left(\frac{EEE + PEE}{PEP} + 1 \right)^{0.5}$$

[0041]

[0042] The tacticity of Propylene sequences was calculated as mm content from the ratio of the PPP $mmT_{\beta\beta}$ (28.90-29.65 ppm) and the whole $T_{\beta\beta}$ (29.80-28.37 ppm)

[0043] **Melt flow rate (MFR)**

[0044] The melt flow rate MFR of the polymer was determined according to ISO 1133 (230°C, 2.16 Kg).

[0045] **The following polymers have been used**

[0046] PP1

Propylene homopolymer having an MFR 6,5 and a fraction soluble in xylene at 25°C of < 4%

[0047] PP2

Commercial filament of diameter 1.75 mm sold under the tradename PP REPRAP BLACK FILAMENT German RepRap PP Filament 600g, a random propylene ethylene copolymer having an ethylene content of 3 wt% an MFR of 2 dl/10 min and a fraction soluble in xylene at 25°C of 6.2 wt%.

[0048] PP3

Propylene ethylene copolymer sold under the tradename MOPLen RP220M being a random propylene ethylene copolymer having an ethylene content of 4 wt% an MFR of 7 and a fraction soluble in xylene at 25°C of 7%

[0049] Polymers PP1 and PP3 have been extruded to form a filament having 1.75 mm of diameter. In order to be able to extrude PP1 10 wt% of talc has been added.

[0050] **Print test**

[0051] The printer was a 3D Rostock delta printer. The printer conditions are the followings:

[0052]

Filament diameter	mm	1,75 ±0.03
Nozzle diameter	mm	0,4
Temperature first layer	°C	245
Temperature other layers	°C	245
		1
Layer high	mm	0,2
Temperature plate	°C	100
Support material to adhere on the plate		vinyl glue
Plate material.		glass
Infill		100%
printer speed	mm/min	3600
Speed first layer		60%
Speed other layers		100%
Speed infill	mm/min	4.000

[0053] The sample to be printed is reported in Fig 1. For each filament 5 printer tests have been carried out, the print has been stopped when one side of the object is detached from the plane and thus the print of the object was no longer possible. The results are reported on table 1

Table 1

material	height before detach (Z) (mm) (average measure)
PP1*	0.8
PP2*	1.2
PP3	full (5 mm)

[0054] * comparative

[0055] From table 1 clearly results that only PP3, that is the material according to the invention, can be used to fully print the sample.

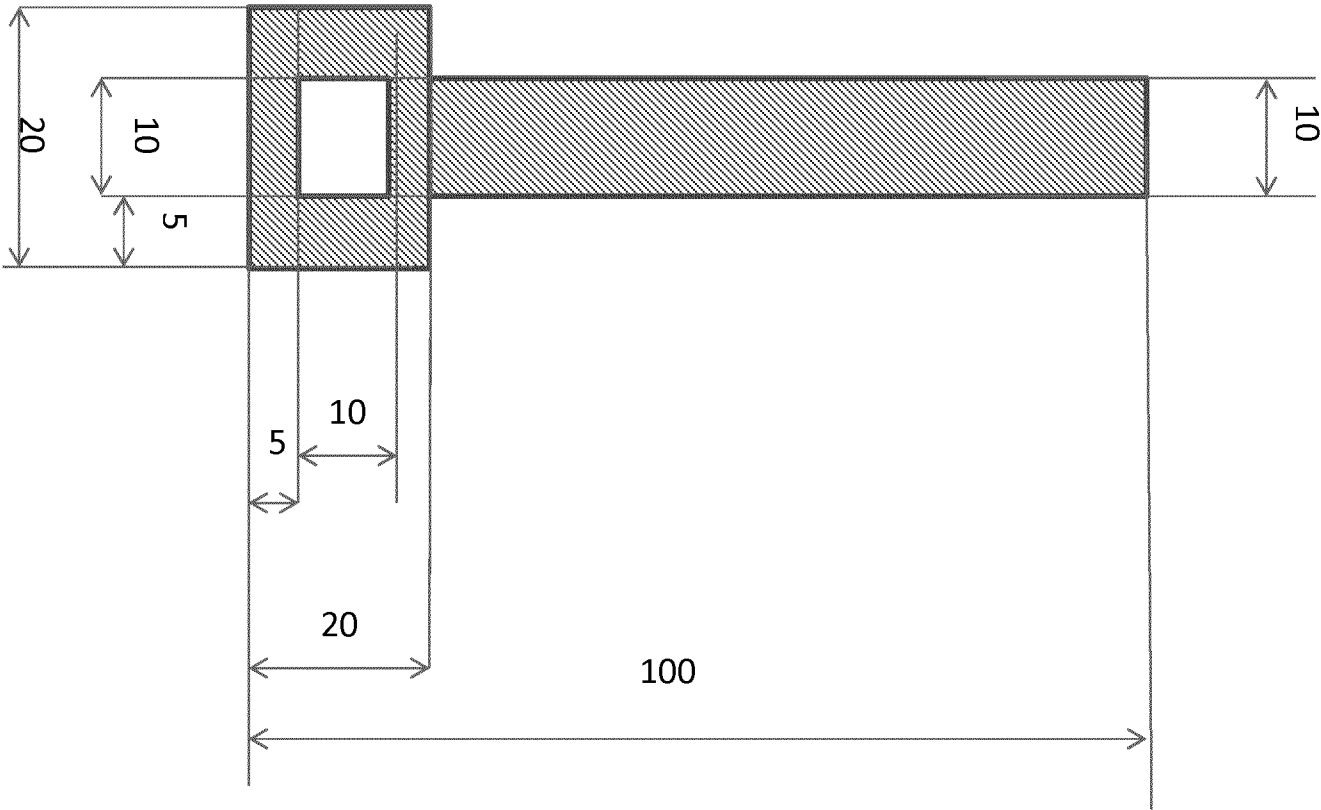
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CLAIMS

What is claimed is:

1. Use of a consumable filament comprising a propylene ethylene copolymer having:
 - ethylene derived units content ranging from 3.0 wt% to 12.0 wt%;
 - MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) from 4 to 20 g/10 min; and
 - xylene solubles measured at 25°C comprised between 3 wt% and 30 wt%;in an extrusion-based additive manufacturing system.
2. Use of the consumable filament according to claim 1 wherein in the propylene copolymer the ethylene derived units content ranges from 3.5 wt% to 10.0 wt%.
3. Use of the consumable filament according to claims 1 or 2 wherein in the propylene copolymer has a MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) ranging from 5 to 10 g/10 min.
4. Use of the consumable filament according to anyone of claims 1-3 wherein in the propylene copolymer the xylene solubles measured at 25°C is comprised between 4 wt% and 25 wt%.
5. Use of the consumable filament according to anyone of claims 1-4 wherein in the propylene copolymer the ethylene derived units content ranges from 3.8 wt% to 8.0 wt%.
6. Use of the consumable filament according to claims 1 or 5 wherein in the propylene copolymer has a MFR L (Melt Flow Rate according to ISO 1133, condition L, i.e. 230°C and 2.16 kg load) ranging from 6 to 8 g/10 min.
7. Use of the consumable filament according to anyone of claims 1-6 wherein the consumable filament has a constant diameter having a variation of +/- 0.05 mm.
8. Use of the consumable filament according to anyone of claims 1-7 wherein the consumable filament has a constant diameter having a variation of +/- 0.03 mm.
9. Use of the consumable filament according to anyone of claims 1-8 wherein the consumable filament has a diameter of 1.75 mm or 3 mm +/- 0.05 mm.
10. Use of the consumable filament according to anyone of claims 1-8 wherein the consumable filament has a diameter of 1.75 mm or 3 mm +/- 0.03 mm.
11. Use of the consumable filament of claims 1-10 for the production of 3D printed articles.

FIG 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/056495

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F210/06 B33Y70/00 D01F6/30
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)

C08F B33Y D01F

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	EP 1 270 628 A1 (BOREALIS TECH OY [FI]) 2 January 2003 (2003-01-02) table 2 claim 27	1-11
A	EP 1 484 345 A1 (BOREALIS TECH OY [FI]) 8 December 2004 (2004-12-08) example 4 claim 1	1-11
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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

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/056495

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>O.S. CARNEIRO ET AL: "Fused deposition modeling with polypropylene", MATERIALS & DESIGN, vol. 83, 20 June 2015 (2015-06-20), pages 768-776, XP055312954, AMSTERDAM, NL ISSN: 0264-1275, DOI: 10.1016/j.matdes.2015.06.053 the whole document</p> <p>-----</p>	1-11
A	<p>Manfred Kohlen: "ITespresso.de German RepRap liefert lebensmittelkonformes 3D-Druckmaterial - ITespresso.de", 16 January 2014 (2014-01-16), XP055258389, Retrieved from the Internet: URL:http://www.itespresso.de/2014/01/16/german-reprap-liefert-lebensmittelkonformes-3d-druckmaterial/?print=1 [retrieved on 2016-03-15] the whole document</p> <p>-----</p>	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/056495

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