



(51) International Patent Classification:

C08G 69/20 (2006.01) **B29C 67/00** (2017.01)
C08L 77/02 (2006.01)

(21) International Application Number:

PCT/IL2017/050136

(22) International Filing Date:

05 February 2017 (05.02.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/291,629 05 February 2016 (05.02.2016) US

(71) Applicant: **STRATASYS LTD.** [IL/IL]; 1 Holtzman
Street, Science Park, P.O. Box 2496, 7612401 Rehovot (IL).

(72) Inventors: **KUNO, Lev**; 5/1 Kida Street, 9987500 Tzur-
Hadassah (IL). **YUDOVIN-FARBER, Ira**; 1/9 Neve Alon
Street, 7645501 Rehovot (IL). **DAMARI, Liora**; 16/14
Vilkomich Street, 7644806 Rehovot (IL). **MATZNER, Ey-**

nat; 402 HaBrosh Street, Adi, 1794000 Doar-Na HaMovil
(IL).

(74) Agent: **EHRlich, Gal** et al.; G. E. EHRlich (1995)
LTD., 11 Menachem Begin Road, 5268104 Ramat Gan (IL).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR,
KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

(54) Title: THREE-DIMENSIONAL INKJET PRINTING USING POLYAMIDE-FORMING MATERIALS

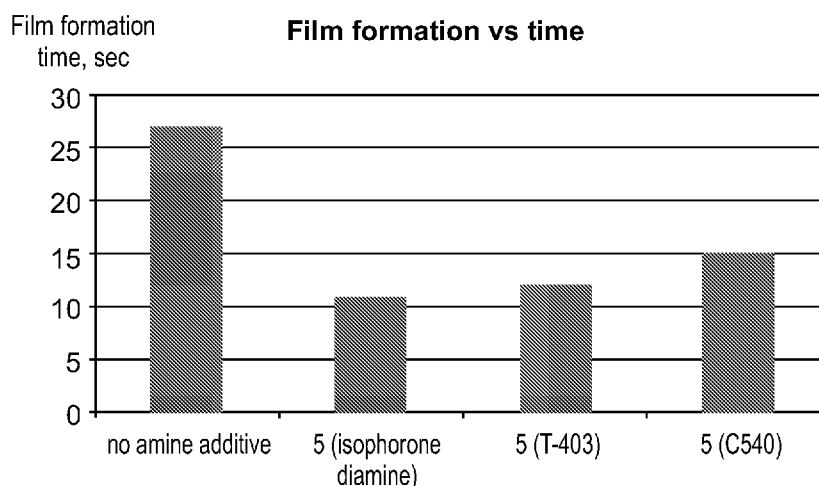


FIG. 3

(57) **Abstract:** Formulation systems usable for fabricating a three-dimensional object made of a polyamide-containing material, by three-dimensional 3D inkjet printing, and methods and systems utilizing same, are provided. The formulation systems are formed of at least a first and second model formulations containing a lactam and a catalyst for inducing anionic ring opening polymerization of the lactam in the first formulation, and an activator for promoting anionic ring opening polymerization of the lactam in the second formulation, and are further characterized as: including in the first and/or second formulation a compound capable of increasing a rate of said polymerization upon exposure to said curing energy; including as an activator a lactam-blocked polyisocyanate; and/or as including in the first model formulation at least one material capable of reducing a melting point of said first model formulation. Formulation systems usable at a selected ratio are also provided.



EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))*

(88) Date of publication of the international search report:

02 November 2017 (02.11.2017)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2017/050136

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G69/20 C08L77/02 B29C67/00
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)

C08G C08L B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KHOSROW KHODABAKHSHI ET AL: "Anionic polymerisation of caprolactam at the small-scale via DSC investigations : A method to be used in an additive manufacturing process", JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY, vol. 115, no. 1, 8 August 2013 (2013-08-08), pages 383-391, XP055377014, NL ISSN: 1388-6150, DOI: 10.1007/s10973-013-3344-4 page 384, paragraph 1; figure 1 page 384, paragraph 2 ----- -/-	1-27,29, 30, 35-41, 44, 46-51, 53-55, 58-61, 64-77



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

2 June 2017

Date of mailing of the international search report

24/08/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Mader, Margarita

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2017/050136

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8, 16-21, 27, 58-61(completely); 9-15, 22-26, 29, 30, 35-41, 44, 46-51
53-55, 64-77(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8, 16-21, 27, 58-61(completely); 9-15, 22-26, 29, 30, 35-41, 44, 46-51, 53-55, 64-77(partially)

Addition of a compound capable of increasing the polymerization rate of a lactam to a multipart 3D printing composition or use of such a compound in the corresponding 3D printing method.

2. claims: 33, 34, 62, 63(completely); 9-15, 35-41, 64-77(partially)

Multipart 3D printing composition or method for lactam-based polyamide parts, wherein the activator is based on a non-blocked polyisocyanate, wherein the formulation comprising the activator is used in a ratio of 1.5-5:1 to the formulation comprising the lactam and the catalyst.

3. claims: 28, 31, 32, 52, 56, 57(completely); 22-26, 29, 30, 40, 41, 53-55, 69-77(partially)

Multipart 3D printing composition or method for lactam-based polyamide parts, wherein the activator is based on a lactam-blocked polyisocyanate.

4. claims: 42, 43, 45(completely); 44, 46-51, 69-77(partially)

Addition of a compound capable of reducing the melting point to a multipart 3D printing composition or use of such a compound in the corresponding 3D printing method.

5. claims: 51, 73-77(all partially)

3D printing method characterized in that the ratio of the formulations in the multipart composition is controlled by depositing voxel blocks

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2017/050136

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2013/065466 A1 (DESBOIS PHILIPPE [US] ET AL) 14 March 2013 (2013-03-14) cited in the application paragraph [0019] - paragraph [0021] paragraph [0034] - paragraph [0036] paragraph [0057] - paragraph [0062] examples 7, 8 claims 18, 20 -----	53-55, 58-61, 64-77 1-27,29, 30, 35-41, 44,46-51
X,P	WO 2016/125170 A1 (STRATASYS LTD [IL]) 11 August 2016 (2016-08-11) claims examples page 54, line 28 - page 56, line 7 -----	1-27,29, 30, 35-41, 44, 46-51, 53-55, 58-61, 64-77

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IL2017/050136

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013065466	A1	14-03-2013	NONE

WO 2016125170	A1	11-08-2016	NONE
