(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 April 2019 (11.04.2019)

(10) International Publication Number
WO 2019/069290 A1

(51) International Patent Classification:
B29C 45/14 (2006.01) *B32B 27/08* (2006.01)

(21) International Application Number:
PCT/IB2018/057763

(22) International Filing Date:
05 October 2018 (05.10.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/569,059 06 October 2017 (06.10.2017) US

(71) Applicant: **PLÁSTICOS TÉCNICOS MEXICANOS, S.A. DE C.V.** [MX/MX]; Carretera México-Tequisquiapan Km. 3.0, Zona Industrial Valle de Oro, San Juan del Río, Querétaro (MX).

(72) Inventors: **PEÑA ZAPATA, José Ricardo**; Av. Mirador de San Juan No. 5, Int. 8, El Marqués, Querétaro (MX). **FEREGRINO MONTES, Ciro**; Plaza Detzani No. 255, Col. Plaza del Sol 2da Sección, Querétaro (MX). **BALBINO TOVAR, Nallely**; Prolongación Venustiano Carranza No. 7, Col. San Pedro Ahuacatlán, San Juan del Río, Querétaro (MX). **ÁVILA RAMÍREZ, Felicitaz Elizabeth**; Emilio Carranza No. 16, Col. Centro, San Juan del Río, Querétaro (MX). **HERNÁNDEZ ZAMUDIO, Hermes**; Emiliano Zapata No. 12, Col. Centro, San Juan del Río, Querétaro (MX).

(74) Agent: **JIMÉNEZ HERNÁNDEZ, Israel** et al.; Calle José María Velasco No. 13, Suite 201, Col. San José Insurgentes, Ciudad De México, 03900 (MX).

(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, JO, 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,

(54) Title: PROCESSES FOR FABRICATING HYBRID METAL-POLYMER PARTS AND THE PRODUCTS DERIVING THEREOF

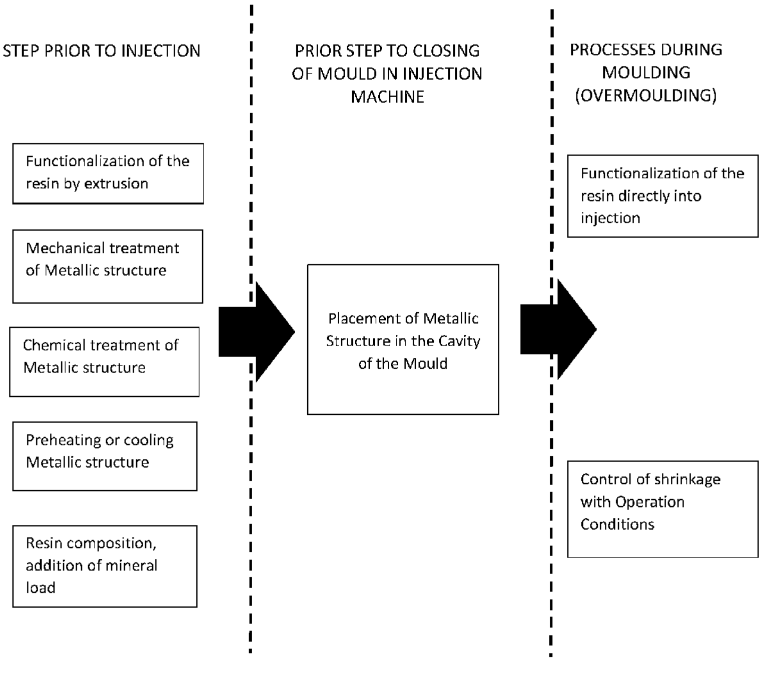

FIGURE 1

(57) **Abstract:** The present invention is directed to processes for fabricating one or more hybrid metal-polymer parts and the products deriving thereof. In a first embodiment of these processes for fabricating one or more hybrid metal-polymer parts sought to be protected by the present invention, the fabrication process comprises a prior injection moulding step, the step of placing of a metallic structure in a moulding cavity prior to the closing of a mould in the injection machine and an overmoulding step. The hybrid metal-polymer parts deriving from the fabricating process are also protected.

WO 2019/069290 A1

[Continued on next page]

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, 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).

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))*

PROCESSES FOR FABRICATING HYBRID METAL-POLYMER PARTS AND THE PRODUCTS DERIVING THEREOF

PRIORITY DOCUMENTS

This application claims priority from the U. S. Provisional Patent Application No. US 62/569,059 (filed on October 6, 2017), which is incorporated herein by reference in its entirety for all purposes.

FIELD OF THE INVENTION

The present invention relates generally to the field of manufacturing metal-polymer parts.

BACKGROUND OF THE INVENTION

Polymeric materials have been extending their use and replacing other traditional materials thanks to some of their properties such as lower density, greater degree of safety, lower energy cost when processed, etc. However, its use is limited in some applications that require a greater mechanical requirement of the material. For example, the Young's modulus of an HDPE oscillates between 700-1000 MPa, while that of steel is around 210,000 MPa (more than 200 times). Due to this, it is common to find in applications such as pallets the use of steel or aluminum reinforcements incorporated in plastic parts. The disadvantage of this type of reinforcement is that the assembly represents a complicated additional process. In addition, the reinforcement does not adhere to the plastic surface and can present movement, separation of the components, corrosion if it becomes exposed to the environment, etc.

In the state of the art there are documents which reveal only the coupling of metal parts with a plastic material:

US application 2016/0023389 A1 discloses a method for the manufacture of a structural part comprising a metal component and a plastic component wherein the metal component is coated with a precured bonding agent system.

US patent 6893590 B1 is referred to a process for effecting a coupling between a plastic material and a metal surface comprising the steps of applying a powder of an adhesive polymer composition to the metal surface; then overmoulding the metal surface with a plastic material by injection moulding; and finally applying heat to the metal surface.

US patent 5672405 discloses a metal-reinforced, molded-plastic composite structure having an end use such as an automobile bumper, the reinforcement being constituted by a sheet of ductile metal having an array of holes punched therein, each bordered by a metal projection. In forming the composite structure, the metal sheet is supported within the cavity of a mold whose shape is appropriate to the end use. Molten plastic injected into the mold is caused to flow through the holes and to envelop the projections therefrom whereby when the plastic solidifies, the metal sheet is then fully integrated with the resultant plastic body and serves to enhance the resistance of the body to impact and other forces which in the absence of the reinforcing sheet would fracture the body.

US application 2003/0077409 A1 relates to a composite component and to a process for its production. The composite component is composed of a hollow-profile base (1), which has a hollow-profile cross section and is advantageously produced by the HF process, and of at least one plastic element (2) which has been securely connected to the hollow-profile base (1). The plastic element (2) has been molded onto the hollow-profile base (1) and its connection to the hollow-profile base (1) takes place at discrete connection sites (3, 6) by partial or complete jacketing of the hollow-profile base (1) at the connection sites (3, 6, 6 a , 6 b , 10, 12) by the molded-on plastic for the plastic element (2).

US application 2011/0049747 A1 discloses a process that includes preparing the metal frame that is overlaid with an adhesive. The adhesive is heated thereafter, and the adhesive becomes solidified and thus engaged securely with the metal frame. The adhesive is injection molded thereafter, and the molten resin is delivered onto the solidified adhesive to melt the adhesive so as to enable the adhesive to adhere the resin, and after the adhesive and the resin become solid, the resin forms a plastic member securely bound with the metal frame, thus forming the finished product

SUMMARY OF THE INVENTION

The present invention is directed to processes for fabricating one or more hybrid metal-polymer parts and the products deriving thereof.

Some embodiments of these processes for fabricating one or more hybrid metal-polymer parts sought to be protected by the present invention, the fabrication process comprises a step prior to moulding, then a step of placing of a metallic structure in a moulding cavity prior to the closing of a mould in the injection machine and an overmoulding step. The hybrid metal-polymer parts deriving from the fabricating process are also protected.

Some embodiments of these processes disclose the generation of hybrid metal-polymer parts. To manufacture these parts, a thermoplastic material is overmould by injection on metallic structures held within the mold cavity. Additionally, in the present invention is described a step prior to moulding the piece, based on one or more mechanisms, which aims to increase the surface adhesion between the polymer and metal phases, as well as controlling the shrinkage phenomena, and thermal expansion.

These mechanisms represent the main advantage of the present invention. The mechanisms according to the present invention are necessary for obtaining metal-polymer hybrid pieces resistant to cracking caused by release of residual stress, differences in the coefficients of thermal expansion and shrinkage of the plastic part after the moulding.

In some embodiments, the above-mentioned mechanisms may comprise mechanical treatment, chemical treatment, preheating or cooling which are applied to the metallic part, and resin composition (addition of mineral/organic load).

Some embodiments disclose pieces obtained by the process described in the present invention which combine the resistance to tensile stress, compression and bending of metallic materials such as steel and aluminum with the impact resistance and low density of plastic materials such as HDPE, PP, ABS, etc.

The processes of the present invention provide an advantage in articles subjected to high efforts and rough use, such as pallets, grills, racks, gondolas, trays, etc. Showing an excellent performance and prolonged life time, due to good interfacial adhesion and dimensional control.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows a flow chart of several different embodiments of the processes for fabricating one or more hybrid metal-polymer parts of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The following detailed description is of the best currently contemplated modes of carrying out the invention. The description is not to be taken in a limiting sense but is made merely for the purpose of illustrating the general principles of the invention, since the scope of the invention is best defined by the appended claims.

The present invention is directed to processes for fabricating one or more hybrid metal-polymer parts and the products deriving thereof. In a first embodiment of these processes for fabricating one or more hybrid metal-polymer parts sought to be protected by the present invention, the fabrication process comprises a step prior to moulding in order to increase the surface adhesion between the polymer and metal phases, a step of placing of a metallic structure in a moulding cavity prior to the closing of a mould in the injection machine and an overmoulding step. The hybrid metal-polymer parts deriving from the fabricating process are also protected.

In some embodiments a thermoplastic material is overmould by injection on metallic structures held within a mold cavity.

The metallic structures can be profiles (hollow or open) or monolithic structures. In case the metallic structures are profiles, they may or may not be in contact with each other.

In some embodiments, the metallic structures can be made of iron, cast iron, aluminum alloy, steel, copper or bronze and others.

In some embodiments, the thermoplastic material (or also described herein as resin) can be selected among (but not limited to) polyamide (PA), polycarbonate (PC), high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET), polypropylene (PP) and high-density polyethylene (HDPE) as well as mixtures thereof and may or may not include organic/mineral loads such as (but not limited to) natural corncob “olote” fiber, barley husk, sugarcane or mica, talcum, $CaCO_3$, iron oxide, fiberglass, etc; in order to improve the interaction of the polymer with the surface of the metallic part.

In some embodiments, the resins can have in their formulation polar groups and/or repetitive units unbalanced electrically.

In some embodiments, to obtain the hybrid metal-polymer parts according to the processes of the present invention, the metallic structures are placed inside the mold cavity, where they can be held by bolts, pins or magnets placed in strategic areas. Once the structure is placed in the cavity, thermoplastic material is overmoulded to generate pieces where the metal structure is totally or partially embedded in the thermoplastic material.

Now, the interfacial adhesion and the interaction between the polymer with the surface of the metallic part can be enhanced by means of one or more of the following mechanisms which corresponds a step prior to moulding.

In some embodiments of the processes of the present invention, the mechanisms may comprise a mechanical treatment of the metallic surface for generating roughness and porosity. This mechanical treatment step is carried out over the metallic structure before the metallic structure is placed inside the mould. In some examples the mechanical treatment may include, but not limited to, abrasive blasting (sandblasting), EDM (electrical discharge machining), sanding, roughing, or related treatments.

In some embodiments of the processes of the present invention, the mechanisms may comprise chemical treatment and/or attack of the metallic surface. This chemical treatment and/or attack also takes place before the metallic structure is placed inside the mould. The purpose of the chemical treatment and/or attack is to generate roughness and/or porosity and to eliminate oxides or contaminants and/or producing chemical interaction zones with the thermoplastic resin. In some examples the chemical treatment may include, but not limited to, treatment with acids such as pickling with mixtures of 25% nitric acid and 8% hydrofluoric acid, cleaning with chelating agents, cleaning with acetone, coating with silanes, or related treatments.

In some embodiments of the processes of the present invention the mechanisms may comprise shrinkage control and thermal expansion in both metallic and polymeric phases. The shrinkage control may be achieved with the process conditions during the moulding, the composition of the resin when adding mineral loads, and the pre-heating and cooling of the metallic structure prior to being moulded. The purpose of is to balance the shrinkage of the polymer over the metal in such a way that sufficient pressure is exerted over it to sustain it without generating excess pressure that may damage the part.

Furthermore, in some embodiments of the processes of the present invention, the mechanisms may comprise the addition of polar or ionomer functional groups into the resin. This addition step comprises the addition of a polar phase into the resin which shows the best chemical interaction with the metallic surface. Prior to the injection (or during the injection), the resin is mixed in molten state with another polymer which contains polar groups or electrically unbalanced repetitive units (ionomers).

The purpose of the above mechanisms of the processes of the present invention is to ensure proper interfacial adhesion and may be promoted by one or more of the different embodiments described above. The advantages of promoting proper interfacial adhesion include the part showing reinforcement transmission through the interface, thereby helping the mechanical performance of the part, and the increase in durability of the part. Without a proper interfacial adhesion, be it through fatigue or macromolecular relaxation, the metallic part will separate from the polymeric part leading to slippage which eventually lead the part to fail prematurely.

Once the metallic structure has been placed in the moulding cavity, it is overmoulded with thermoplastic material creating hybrid parts in which the metallic structure is partially or completely embedded in the thermoplastic material. In one embodiment, the overmoulding step may comprise the functionalization of the resin directly in the injection. In another embodiment the overmoulding step may comprise the shrinkage control with operation conditions.

The field of application of the structural system of hybrid metal-polymer part produced by the processes for fabricating one or more hybrid metal-polymer parts of the present invention where the technical advantages are being identified is in products fabricated primarily from thermoplastic materials, as it can be the case for materials handling, display and furniture, and which have surfaces which are subject to loads that can result in undesirable bends/deflections and which affect the functionality and/or structural performance of the products.

Figure 1 shows a schematic view of the steps of the processes of the present invention, which may have one or more steps in each stage.

EXAMPLES

The following examples illustrate the practice of the present invention and are not intended as a limitation of the scope thereof.

Example 1

1018 steel treated by sandblasting, coated with a hydrophobic layer of silanes embedded in a HDPE base resin with 10-20% talc and 2-4% of polyolefin elastomer (impact resistance) to reduce the percentage of shrinkage and the linear thermal expansion coefficient.

Example 2

Aluminum 6005 sanded and cleaned with acetone, preheated to 80 °C, embedded in a PET base resin with 5-18% polyolefin elastomer, with 2-4% compatibilizing agent and 1-10% mica to reduce the percentage of shrinkage and the coefficient of linear thermal expansion.

Example 3

Steel treated with a solution of 25% nitric acid and 8% hydrofluoric acid embedded in ABS base resin containing 8-15% SEBS-gMA resin to promote interaction with the metal.

CLAIMS

1.- A process for fabricating one or more hybrid metal-polymer parts, comprising:

(a) A prior injection moulding step in order to enhance the adhesion and interaction between the polymer and a metallic part;

(b) Placing a metallic structure in a moulding cavity prior to the closing of a mould in an injection machine; and

(c) An overmoulding step.

2.- The process in accordance with claim 1, wherein the step (a) comprises a treatment by means of mechanisms such as mechanical treatment, chemical treatment, addition of polar or ionomer functional, and preheating or cooling the metallic part.

3. The process in accordance with claim 2, wherein the metallic treatment comprises abrasive blasting, EDM, sanding, roughing or related treatments.

4. The process in accordance with claim 2, wherein the chemical treatment comprises treatment with acid, cleaning with chelating agents, cleaning with acetone, coating with silanes or related treatments.

5. The process in accordance with claim 2, wherein the addition of a polar phase into the resin comprises mixing the resin in molten state with another polymer containing polar groups or electrically unbalanced repetitive units.

6. The process in accordance to claim 1, wherein the step (a) further comprises a shrinkage control and thermal expansion in both metallic part and polymer.

7. The process in accordance to claim 6, wherein the shrinkage control and thermal expansion is achieved by adding mineral or organic loads and pre-heating and cooling the metallic structure.

8.- The process in accordance with claim 1, wherein the prior injection moulding step comprises the functionalization of the resin directly in the injection.

9. The process in accordance with claim 1, wherein the one or more metallic structures may be hollow or open profiles or monolithic structures.

10.- The process in accordance with claim 1, wherein the one or more metallic structures may or may not be in contact with each other.

11.- The process in accordance with claim 1, wherein the polymer may be thermoplastic material selected among polyamide (PA), polycarbonate (PC), high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET), polypropylene (PP) and high-density polyethylene (HDPE) as well as mixtures thereof.

12.- The process in accordance with claim 1, wherein the polymer may or may not include mineral loads but not limited to mica, talc, calcium carbonate, iron oxide and fiberglass.

13.- The process in accordance with claim 1, wherein the polymer may or may not include organic loads but not limited to natural corncob fiber, barley husk and sugarcane.

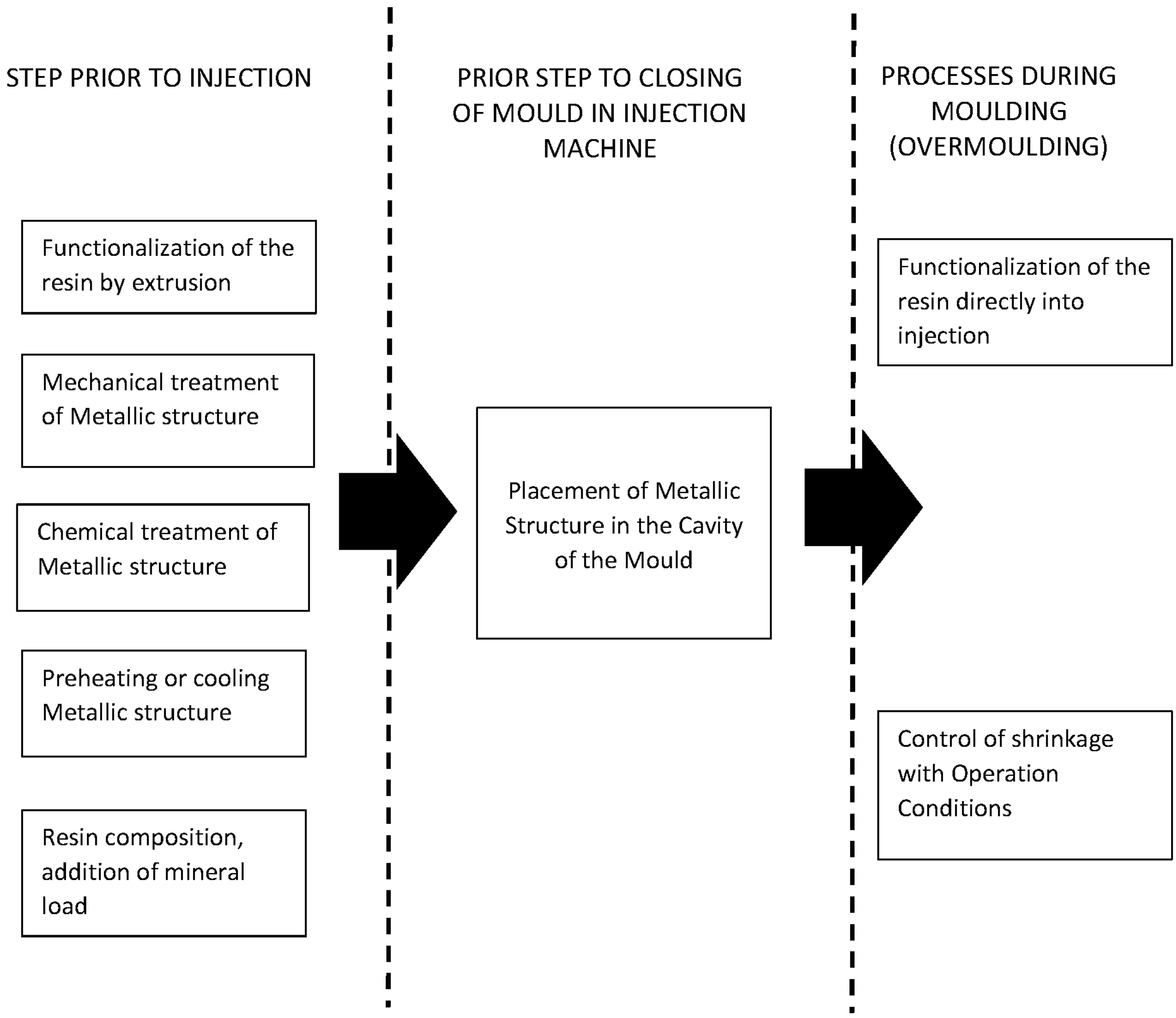
STEP PRIOR TO INJECTION
PRIOR STEP TO CLOSING OF MOULD IN INJECTION MACHINE
PROCESSES DURING MOULDING (OVERMOULDING)
Functionalization of the resin by extrusion
Mechanical treatment of Metallic structure
Chemical treatment of Metallic structure
Preheating or cooling Metallic structure
Resin composition, addition of mineral load
Placement of Metallic Structure in the Cavity of the Mould
Functionalization of the resin directly into injection
Control of shrinkage with Operation Conditions

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 18/57763

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B29C 45/14; B29C 45/14; B32B 27/08 (2018.01)
CPC - C08J 5/128; B29K 2705/12; C08L 67/00; C08L 75/04; C09J 5/06; C09J 2205/114

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)
See Search History Document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y --- A	WO 2017/102943 A1 (DSM IP Assets B.V.) 22 June 2017 (22.06.2017) pg 1 ln 4-13, pg 2 ln 4-5, pg 3 ln 20-34, pg 4 ln 15-34, pg 8 ln 23-30, pg 12 ln 21-34, and Figure 1.	1-2, 4, 9-13 ------------------------ 3, 5 ----- 6-8
Y --- A	US 2016/0023389 A1 (Rehau AG & Co.) 28 January 2016 (28.01.2016) Abstract, para [0012], [0014]-[0017], [0037], [0044], [0119].	3 --- 8
Y	US 5,709,948 A (Perez et al.) 20 January 1998 (20.01.1998) Abstract, col 3 ln 58-59, col 4 ln 26-31, col 10 ln 26-28, col 11 ln 28-29.	5
A	US 2014/0240989 A1 (Sabic Innovative Plastic IP B.V.) 28 August 2014 (28.08.2014) Abstract, para [0049]-[0050], and Figure 1.	6-7
A	US 2015/0361316 A1 (Evonik Industries AG) 17 December 2015 (17.12.2015) Entire Document.	1-13
A	US 6,893,590 B1 (Rigosi et al.) 17 May 2005 (17.05.2005) Entire Document.	1-13

☐ 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	Date of mailing of the international search report
7 January 2018	28 JAN 2019

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774