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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
25 September 2014 (25.09.2014)

WIPO | PCT

(10) **International Publication Number**
WO 2014/151735 A1

(51) **International Patent Classification:**
C08J 3/20 (2006.01) *C08G 69/04* (2006.01)
C08L 33/24 (2006.01) *C08G 69/46* (2006.01)

(21) **International Application Number:**
PCT/US2014/026353

(22) **International Filing Date:**
13 March 2014 (13.03.2014)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
61/798,641 15 March 2013 (15.03.2013) US

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(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, 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, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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))*

WO 2014/151735 A1

(54) **Title:** POLYMERIZATION COUPLED COMPOUNDING PROCESS

(57) **Abstract**: The present invention provides a process for preparing an improved compounded product and a compounded product prepared by that process.

Title of the Invention: Polymerization Coupled Compounding Process

Background of the Invention

[0001] Polymer compounding is a well-known process for preparing plastic formulations by the mixing and/or blending of polymers, such as polyamides or polyesters, with, for example, additives, fillers, reinforcing agents and modifiers while the polymer is in a melted or semi-melted state. See, *e.g.*, U.S. Patent Nos. 6,149,850; and 5,236,652. Compounding typically takes place in an extruder. The step(s) of mixing and/or blending with, for example, additives, fillers, reinforcing agents and modifiers generally occurs prior to the shaping step, *i.e.*, prior to extrusion, injection molding, *etc.* The additives, fillers, reinforcing agents and modifiers impart preferred properties to the host polymer to which they are added.

[0002] It is desirable that the final plastic product contains as low as possible amount of volatile components such as residual monomers, organic solvents and water. The presence of significant levels of water promotes depolymerization (hydrolysis) and reduces the molecular weight and melt viscosity of the polymer to the point where bubbles form in the extrudate. Degassing of the polymer during the compounding process is the typical means for achieving a low volatile component content. To achieve effective degassing of the volatile components during the compounding process, high vacuum and high temperatures are required, but at high temperatures, degradation of the polymer significantly increases. If, however, temperatures in the extruder are maintained at levels to minimize degradation of the polymer, effective melting and blending of the compound components is negatively impacted, which has a deleterious effect on the quality of the final product. See, *e.g.*, U.S. Patent No. 8,034,269. These problems are particularly prevalent at high throughput rates, where the short exposure time of the polymer to the compounding process is dictated by cost efficiency. Thus, at a high throughput rate, increasingly effective degassing of the volatile components occurs at the expense of an increase in the rate of degradation of the polymer. An economic analysis is required to determine the acceptable balance between these two competing outcomes. It is known, for example, that polyamide resins useful in molding and extrusion applications experience undesirable mold buildup over time, thereby reducing machine uptime and capacity utilization. See, *e.g.*, Plastics Technology (2000) (http://www.ptonline.com/articles/engineering-thermoplastics); page 13 of the DuPont™

ZYTEL® HTN Molding Guide (2001) (http://www.dupont.com/content/dam/assets/products-and-services/plastics-polymers-resins/Documents/H85940.pdf which acknowledge the problems associated with vent plugging. U.S. 6,518,341 refers to vent accumulation, how it relates to burning in the mold and introduces a "shots before burn" term which relates to mold deposits or plate-out and how the productivity of injection molding is adversely impacted by this mold depositing.

[0003] Polyamide resins are routinely compounded by use of an extruder for mixing, for example, additives, fillers, reinforcing agents and modifiers with polyamides such as nylon, including nylon 6, nylon 4/6, nylon 6/6, nylon 6/10, nylon 6/12, nylon 11 and nylon 12, where the polyamide is in a solid (*e.g.*, pelletized or flake or chip) form. Typically, the compounding process comprises introducing nylon feedstock in solid form into the first half of an extruder to achieve melting of the feedstock. After melting has occurred, one or more additives, fillers, reinforcing agents and modifiers are introduced and mixed into the nylon melt. In an extruder containing multiple barrel zones, a vacuum is typically applied to remove undesired volatiles and moisture from the polyamide and the additive, filler, reinforcing agent and/or modifier stream. If not removed, these undesired components foul the customer's mold over time, thereby reducing machine uptime and capacity utilization. See, *e.g.*, A. Dreiblatt, Plastics Technology (2010) (http://www.ptonline.com/columns/in-twin-screw-compounding-distinguish-between-disease-and-illness). U.S. Patent No. 6,518,341 also describes the problems resulting from the presence of deposits in injection molding operations.

[0004] Accordingly, longer exposure time of the polyamide melt to vacuum conditions and to a higher vacuum improves the product quality by decreasing the level of water and any residual impurities such as low molecular weight oligomer content such as nylon oligomer, monomers, stearates and wax components. The removal of impurities is limited by the number of extruder barrel sections that can be used for vacuum exposure, *i.e.*, those barrels not already utilized for nylon melting and glass or additive feed points. The residual content of volatile components is typically determined by means of gas chromatography, with quantitative evaluation carried out using an internal standard.

[0005] It is known that variability in the feedstock significantly contributes to poor process stability and lack of quality control for the compounded product. See, *e.g.*, Extrusion: The Definitive Processing Guide and Handbook (2005) by Harold F. Giles Jr. *et al.* Particularly when the feedstock is stored in a solid form, this undesired variability originates from multiple sources (*e.g.*, differences in moisture levels between samples and the age of the feedstock). As a result, drying of the solid feedstock is frequently required prior to extrusion to achieve a controlled and consistent moisture content necessary to prevent significant reduction of relative viscosity (RV) due to hydrolysis. See, *e.g.*, Extrusion: The Definitive Processing Guide and Handbook (2005) by Harold F. Giles Jr. *et al.*

[0006] Poor warehouse management further contributes to the variability observed in the precursor compounding operation when the feedstock is in solid form as the feedstock is also susceptible to air oxidation over time.

[0007] Thus, there remains a recognized need for a compounded polymer, such as a compounded polyamide, such as compounded nylon66, that exhibits superior stability with improved performance with low variability of impurities, and the process for manufacturing such a product at the lowest possible cost. The compounded polymer prepared by the in-line process described herein shows improved molding performance with significantly lower plate out and longer mold life between cleanings compared to conventionally prepared compounded polymers where the feedstock is introduced to the polymer compounding equipment in solid form. The viscosity and quality control ranges for such a product are also less variable than that resulting from conventional pellet fed compounding. This corresponding improvement in quality directly translates into a superior product for the customer in terms of improved performance and lower cost compared to products prepared from a conventional compounding operations using feedstock in solid form.

Summary of the Invention

[0008] An aspect of the invention is a process for preparing a compounded polyamide, comprising introducing a molten or substantially molten polyamide feedstock directly to one or more (such as 2, 3, 4, 5, *etc.*) polymer compounding devices, where the polyamide feedstock is prepared by a polymerization process, wherein the polymerization process is a continuous polymerization process or a batch polymerization process.

[0009] In an aspect of the invention, the polyamide is selected from the group consisting of nylon 6, nylon 4/6, nylon 6/6, nylon 6/10, nylon 6/12, nylon 11, nylon 12, nylon MXD6, copolymer nylon (a copolymer of caprolactam with hexamethylenediamine adipate), nylon block copolymers, and copolymers comprising these nylons as main components. The methods of preparation of polyamides such as nylon 6/6 are well known. See, *e.g.*, U.S. Patent Nos. 6,197,855; 4,981,906; 4,320,213; 4,346,200; 4,713,415; 4,031,164; 2,071,250; 2,071,251; 2,130,523; 2,130,948; 2,241,322; 2,312,966; 2,512,606; and 3,393,210.

[00010] In an aspect of the invention, the nylon is nylon 6/6 (also referred to herein as nylon 66 or nylon66 or polyamide 66 or PA 66 or PA66).

[00011] In an aspect of the invention the compounded polyamide is a homopolymer.

[00012] In an aspect of the invention the compounded polyamide is a copolymer.

[00013] In an aspect of the invention, the molten polyamide feedstock is at a temperature of about 200°C to 400°C entering the polymer compounding device, such as 250°C to 375°C, such as 275°C to 300°C.

[00014] In an aspect of the invention, the polymer compounding device is an extruder.

[00015] In an aspect of the invention, the extruder is independently a twin-screw extruder or a single-screw extruder.

[00016] In an aspect of the invention, the twin-screw extruder is co-rotating or counter-rotating.

[00017] In an aspect of the invention, the extruder independently contains at least 2 vent ports.

[00018] In an aspect of the invention, the extruder independently contains at least 3 vent ports, such as 4, 5, 6, 7, 8, 9 or 10 vent ports.

[00019] In an aspect of the invention, the extruder vent ports are at atmospheric pressure (*i.e.*, not subjected to vacuum conditions) or, alternatively, are subjected to vacuum conditions. In the case of multiple vent ports, a portion of the vent ports may be at atmospheric pressure and a portion of the vent ports may be subjected to vacuum conditions.

[00020] In an aspect of the invention, the twin-screw extruder has a length to diameter ratio of the screw shaft in the range of 24:1 to 56:1.

[00021] In an aspect of the invention, the twin-screw extruder has a length to diameter ratio of the screw shaft in the range of 36:1 to 48:1.

[00022] In an aspect of the invention, one or more additives, fillers, reinforcing agents or modifiers are introduced into the compounding extruder.

[00023] In an aspect of the invention, fiberglass is compounded with nylon66 in a range of about 5% to about 60% by weight such as about 10% to 55%, such as 15% to 50%, such as 20% to 50%, such as 25% to 50%, such as 35% to 45%.

[00024] In an aspect of the invention, the vent ports are used for removal of moisture or impurities from the compounded polyamide.

[00025] In an aspect of the invention, only a portion (such as, for example, greater than 0% up to about 99%, such as between about 5% up to about 95%, such as between about 15% up to about 85%) of the molten or substantially molten polyamide feedstock is sent directly to the one or more polymer compounding devices.

[00026] In an aspect of the invention, the polymerization process is located less than 500 feet from the polymer compounding device.

[00027] In an aspect of the invention, the compounded polyamide has a relative viscosity (RV) range between about 35 and about 120, such as between about 40 and about 100, such as between about 40 and about 80, such as between about 45 and about 60.

[00028] An aspect of the invention is a polyamide prepared by a process as described herein.

[00029] An aspect of the invention is a compounded polyamide having a plate out value of less than about 3 mg/1,000 shots, such as less than about 2.5 mg/1,000 shots, such as less than about 1.5 mg/1,000 shots, such as less than about 1.0 mg/1,000 shots, such as less than about 0.5 mg/1,000 shots, such as less than about 0.3 mg/1,000 shots, with the lowest value being 0 or a value greater than zero such as, for example, 0.01 mg/1,000 shots or 0.05 mg/1,000 shots or 0.1 mg/1,000 shots.

[00030] An aspect of the invention is a compounded polyamide exhibiting greater than about 200 shots before detection of burn material in the injection mold, such as greater than about 300 shots, such as greater than about 400 shots, such as greater than about 500 shots, such as greater than about 600 shots, such as greater than about 700 shots, such as greater than about 800 shots, and including ranges such as between about 400 to about 800 shots before detection of burn material, such as between about 500 to about 800 shots such as between about 600 to about 800 shots.

[00031] In an aspect of the invention, the compounded polyamide has a relative viscosity (RV) range between samples of less than about 3 units, such as less than about 2 units, such as less than about 1 unit, such as less than about 0.8 units, such as less than about 0.5 units.

Brief Description of the Drawings

[00032] The figures represent exemplary embodiments and are not intended to limit the scope of the present invention as otherwise described herein.

[00033] **Figure 1** represents a schematic of a molten stream fed compounding operation suitable for use in the present invention. Raw materials, comprising hexamethylene diamine (HMD), adipic acid, water, catalyst, modifiers, stabilizers and additives, are fed to a

conventional continuous polymerization process where a nylon polymer comprising PA66 is produced at RV levels between about 35 to about 200. This molten polymer is not allowed to freeze for the purpose of pellet formation or for any other solid method of production – *i.e.*, no significant solidification of the molten polymer is allowed to occur between the continuous polymerization and the subsequent compounding processes. Instead, the molten stream is fed directly to compounding equipment in proximity where any of many types of additives, minerals, reinforcers, modifiers, fillers, *etc.*, are mixed into the polymer to form a new compounded product. This new compounded product is processed through a pelletization system, stored, conveyed and packaged in any combination of conventionally employed containers in the industry.

[00034] **Figure 2** represents a schematic of a molten stream fed compounding operation using a twin screw extruder as the compounding device. Molten polymer from the continuous polymerization process flows directly in to the compounding twin screw extruder. Multiple vent ports are provided for progressing the incremental decrease of absolute pressure in the venting zones. Combi-barrels are used to introduce solid type additives, modifiers, fillers, reinforcers, *etc.*, and injection ports are used to introduce those same components most appropriately introduced in liquid form. Following the compounding unit, the molten product stream is typically fed to a stranding and pelletizing unit with drying and moisture control capabilities known to those skilled in the art. Following the pelletization, the compounded product is conveyed, stored, and packaged in any standard packaging container available for compounded plastics products.

[00035] **Figure 3** represents a schematic of a multi-barrel extruder suitable for use in the present invention as the compounding process. While any of several barrel and screw designs are possible for producing the various compounded products capable of being produced by the described system, the depicted combination has been observed to be highly effective for producing superior plate-out results with 50% glass-filled nylon PA66 with a target RV of 48 and a moisture content of 0.15% by weight.

Detailed Description

Definitions

[00036] Unless defined otherwise, all technical and scientific terms described herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs.

[00037] As described herein, "melt" or "melted" refers to a transition from a solid phase to a liquid phase.

[00038] As described herein, "molten" refers to a material that has never been present in a solid phase.

[00039] As described herein, "substantially melted" means at least 70% melted, such as at least 75% melted, such as at least 80% melted, such as at least 85% melted, such as at least 90% melted, such as at least 95% melted, such as at least 97% melted, such as at least 99% melted.

[00040] As described herein, "substantially molten" means at least 70% molten, such as at least 75% molten, such as at least 80% molten, such as at least 85% molten, such as at least 90% molten, such as at least 95% molten, such as at least 97% molten, such as at least 99% molten.

[00041] As described herein, "polymer compounding device" refers to a device in which polymer compounding occurs. Devolatilization may optionally occur in the polymer compounding device if the polymer compounding device contains a suitable means for devolatilizing the polymer before, during and/or after the compounding process.

[00042] As described herein, "relative viscosity" or "RV" refers to a comparison of the viscosity of a solution of polymer in formic acid with the viscosity of the formic acid itself and is measured using 90% formic acid and glass capillary Ubbelohde viscometers according to ASTM D789. For samples containing fiberglass or other fillers, the weight of sample to be dissolved is adjusted according to the amount of filler to provide the required 11.0 grams of neat resin per 100 ml formic acid. Solutions containing such fillers are filtered before loading into the viscometer.

[00043] As described herein, "dimensional stability" is a measure of the dimensional consistency from shot-to-shot in a molding process.

[00044] As described herein, "weight stability" is a measure of the mass consistency from shot-to-shot in a molding process.

[00045] As defined herein, "warpage" is a measure of the dimensional deviation of a molded part to that of the mold.

[00046] As defined herein, "scrap rate" is a measure of the amount of out-of-spec parts that are produced on a molding process.

[00047] The present invention provides a process for producing an improved compounded polymer such that the compounded polymer exhibits less variability in viscosity, and when used in molding or extrusion operations, results in less injection molding deposits ("plate-out"), thus producing better quality molded parts and extending the operational life of the mold (*i.e.*, the machinery) between overhauls required to remove the deposits. In conventional compounding operations, the polymer (*e.g.*, a polyamide) feedstock is supplied to an extruder in a solid form. In contrast, the present invention introduces a polyamide feedstock in molten form (*e.g.*, from a continuous or batch polymerization process) directly into polymer compounding equipment in a process referred to herein as inline compounding ("ILC"). In an exemplary embodiment, the continuous or batch polymerization process is in proximity to the polymer compounding equipment (*e.g.*, an extruder), such as within 1,000 feet, such as within the same building, such as within 500 feet, such as within 300 feet, such as within 200 feet, such as within 100 feet, such as within 50 feet, such as within 20 feet. By introducing a polyamide feed to polymer compounding equipment where the polyamide feed is already in molten form, additional extruder barrels, normally used for melting the resin, can alternatively be used for increasing vacuum exposure. This increased vacuum exposure in turn results in increased impurity removal and a cleaner product. An additional benefit resulting from applying vacuum in more zones of the polymer compounding equipment (*e.g.*, an extruder) is that the final vacuum zone can operate at a lower pressure (*i.e.*, at a decreased equipment cost) using common vacuum equipment, due to the significant removal of impurities that has already occurred in prior zones.

[00048] In addition, the continuous polymerization or batch polymerization molten feed stream to the polymer compounding equipment results in a compounded polymer with improved

viscosity and/or moisture stability. In an exemplary embodiment, the polyamide feed to extrusion requires less than one hour (such as between 1 and 50 minutes, such as between 1 and 40 minutes, such as between 1 and 30 minutes, such as between 1 and 20 minutes, such as between 1 and 10 minutes) in melt transit to the extruder via a transfer pipe. This molten stream is low in melt history and heat cycles as it is not solidified (in contrast to when the polymer feed stock is present in a solid form) prior to use in the compounding operation. Having at least one less product handling system in place between the polymerization and compounding operations reduces the chance of contamination or foreign body inclusion. Yield improvement and labor cost reduction are also realized with the present invention.

[00049] Continuous polymerization processes such as those employed by the present invention are well known. See, *e.g.*, U.S. Patent Nos. 3,113,843; 3,947,424; 4,851,466; 5,674,974; and Handbook of Fiber Chemistry (2007) 3rd ed., CRC Press, pp. 35-77.

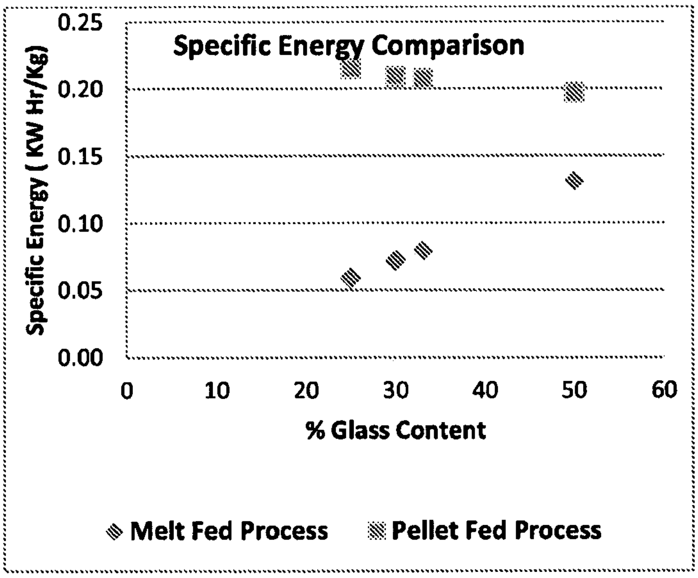
[00050] Batch (also referred to as "clave" or "autoclave") polymerization processes are also suitable for use in the present invention, *e.g.*, as a molten feed directly introduced to a polymerization compounding device. Batch polymerization processes are well known. See, *e.g.*, U.S. Patent Nos. 4,851,466; 5,245,005; and 4,032,517.

[00051] Conventional injection molding, extrusion molding, blow molding, press molding, compression molding and gas assist molding techniques are generally suitable for molding of the compounded polyamides. See, *e.g.*, U.S. Patent No. 8,658,757; 4,707,513; 7,858,172; and 8,192,664.

[00052] The compounded polymer prepared by the ILC process shows improved molding performance with significantly lower plate out and longer mold life between cleanings compared to conventionally prepared compounded polymers where the feedstock is introduced to the polymer compounding equipment in solid form. The viscosity and quality control ranges for such a product are also less variable than that resulting from conventional pellet fed compounding. This corresponding improvement in quality directly translates into a superior product for the customer in terms of improved performance and lower cost compared to products prepared from a conventional compounding operations using feedstock in solid form.

[00053] Also, because the feedstock is conveyed in a molten state to the polymer compounding equipment, the polymer compounding equipment motor size can be reduced since the initial energy required to melt the feedstock is avoided. This advantage translates to lower investment costs and lower energy consumption per pound of product during preparation of the compounded product. In the exemplary embodiment where polyamide PA66 is compounded to provide a product comprising 35% fiberglass, the extruder motor size reduction is approximately 62%. In an exemplary embodiment, the molten polyamide feed stream is introduced directly from a continuous or batch polymerization process to a first portion of a twin-screw extruder with no solidification processing steps prior to introduction to the extruder. By introducing a molten feed to the extruder, the energy consumption of the extruder is reduced relative to an extruder receiving and compounding a solid feedstock. In a particular embodiment, it has been determined that for production of 33% fiberglass-filled nylon, the extruder required a specific energy of 0.071 kw-hr/kg with a molten feedstock, compared to the significantly higher 0.21 kw-hr/kg with conventional pelletized feedstock. This significant difference in energy can be largely attributed to the energy required to initially melt the incoming solid nylon feedstock. Additional savings occur with molten feedstock directly introduced to the extruder since the cumulative costs to pelletize, package, store and handle the feedstock are not incurred. Generally, between about 5 and about 10 cents per pound are saved by implementation of the present invention that consists of a reduced number of steps compared to conventional technologies. Lower feedstock working volumes and lower labor requirements are also included in these savings. In the exemplary embodiment where polyamide PA66 is compounded to provide a product comprising 50% fiberglass, the extruder motor size reduction is approximately 35%. Table 1 shows an exemplary energy comparison.

Table 1



[00054] Since the step of melting the solid feedstock provided to the polymer compounding equipment is no longer necessary in view of the feedstock arriving from the continuous or batch polymerization process in a molten state, the performance of the polymer compounding equipment is enhanced for mixing additives, fillers, reinforcing agents and modifiers, resulting in more flexibility in, for example, the screw of an extruder. For the same cost investment of a typical pellet fed compounding extruder, the molten fed extruder of the present invention is able to achieve greater flexibility in producing higher volumes of different products due to the increased number of barrels available for additive feed and mixing. As a result, compounded products can be prepared in greater amounts and diversity using the molten fed compounding equipment of the present invention.

[00055] While a particular embodiment of this invention is demonstrated using nylon66, other nylons, other polyamides (such as poly(aminoundecanoamide), poly(aminododecanoamide), polyhexamethylene sebacamide, poly(p-xylylene-azeleamide), poly(m-xylylene adipamide), and polyamides from bis(p-aminocyclohexyl)methane and azelaic, sebacic and homologous aliphatic dicarboxylic acids) and the like are also envisioned to benefit from the process of the present invention. Copolymers of polyamides are also suitable for the process of the present invention. See, *e.g.*, U.S. Patent Nos. 3,236,914; 3,472,916; 3,373,223; 3,984,497; and 3,546,319.

[00056] An exemplary embodiment of the present invention comprises an extruder, a molten polyamide feed stream, where the molten feed stream is fed from a continuous polymerization process to an extruder, one or more additive feeds, in a section of the extruder downstream of the melt inlet, one or more vent ports for removal of moisture or impurities, and vacuum equipment for providing vacuum. In an exemplary embodiment, degassing in the course of compounding is facilitated by use of an entraining agent, such as, for example, nitrogen, argon or carbon dioxide. In an exemplary embodiment, the extruder comprises at least two degassing (vacuum) zones (*i.e.*, at least two vent ports or inlets), at least one mixing zone (such as two, three, four or more), one or more metering zones and optionally a melting zone.

[00057] In a particular embodiment during compounding, the vacuum system is a liquid ring vacuum pump which may be used with or without partial seal fluid recycle. Optionally, depending on the level of the vacuum required, a booster compressor may be included in the vacuum skid system. In an exemplary embodiment, a reversing small vent extruder is included for preventing solids from accumulating in the vent area. The vent extruders (also referred to as vent stuffers) allow the vacuum vapors to flow to the downstream vacuum equipment while forcing any condensed material back into the extruder and at a sufficiently rapid rate that the material does not undergo significant degradation or discoloring due to lengthy exposure to high temperatures.

[00058] As defined herein, an extruder includes, but is not limited to, a single- or twin- or multi-shaft screw extruder, such as a twin-shaft screw extruder. In an exemplary embodiment, the extruder is a twin-shaft screw extruder. In another exemplary embodiment, the extruder is a twin-shaft screw extruder with co-rotation of the shafts. In an exemplary embodiment, the extruder is vented. In an exemplary embodiment, the extruder has a length to diameter ratio of the screw shaft in the range of 30:1 to 50:1, such as 32:1 , such as 34:1, such as 36:1, such as 38:1, such as 40:1, such as 42:1, such as 44:1, such as 46:1, such as 48:1 and in all combinations of ranges, such as 32:1 to 50:1 or 32:1 to 34:1 or 42:1 to 46:1, *etc.* In a particular embodiment, the extruder is a Werner & Pfleider Co-rotating Twin Screw Extruder Model ZSK40. The length to diameter ratio of 44:1 is effective in this application. An 11-barrel extruder with a 40 mm diameter represents a particular embodiment for production of a glass-filled product with a PA66 molten feed.

[00059] In an exemplary embodiment, polymer filtration of the molten feedstock is accomplished using filters (such as mesh or fleece filters) in the range of about 5 microns to about 120 microns, such as between about 7 microns to about 100 microns, such as about 20 microns to about 50 microns.

[00060] The materials to be mixed/blended with the polymer include, but are not limited to, glass fibers (*e.g.*, fiberglass, such as in chopped or roving form), waxes, minerals, carbon fibers, aramide fibers, fiber reinforcement, chain terminators, viscosity modifiers, plasticizers, heat stabilizers, UV stabilizers, colorants, catalysts, other polymers and impact modifiers, flame retardants, delusterants, fillers, antimicrobial agents, antistatic agents, optical brighteners, extenders, processing aids, talc, mica, gypsum, wollastonite and other commonly used additives known to those of skill in the art. Preferably, additives are hydrolysis resistant chopped glass, copper heat stabilizers, nucleating agents, Nigrosine and carbon black. Additional suitable additives may be found in Plastics Additives, An A-Z reference, Edited by Geoffrey Pritchard (1998). The optional addition of a stabilizer to the additive dispersion is present in an exemplary embodiment at between about 0.75% and about 7.5% by total dispersion weight. Stabilizers suitable for the additive dispersion include, but are not limited to, polyethoxylates (such as the polyethoxylated alkyl phenol Triton X-100), polypropoxylates, block copolymeric polyethers, long chain alcohols, polyalcohols, alkyl-sulfates, alkyl-sulfonates, alkyl-benzenesulfonates, alkyl-phosphates, alkyl-phosphonates, alkyl-naphthalene sulfonates, carboxylic acids and perfluoronates.

[00061] Suitable vacuum equipment includes, but is not limited to, liquid ring vacuum pumps, dry vacuum pumps and vacuum jets. Liquid ring vacuum pumps are preferred. For sufficiently low vacuum to achieve adequate impurity removal and consequently adequate plate-out molding performance, it is desirable to be below about 1013 mbar absolute, such as below about 500 mbar, such as below about 300 mbar, such as below about 150 mbar, such as below about 65 mbar, with a low end value of about 20 mbar. Depending on the system leaks and vacuum load, the liquid ring vacuum pump system can be supplemented by the dry vacuum booster compressor. In an exemplary embodiment, the booster compressor is not required in normal glass compounding extrusion with nylon PA66.

[00062] In an exemplary embodiment, the molten polyamide feed stream is introduced directly from a continuous or batch polymerization process to a first portion of a twin-screw extruder with no solidification processing steps prior to introduction to the extruder. By introducing a molten feed to the extruder, the energy consumption of the extruder is reduced relative to an extruder receiving and compounding a solid feedstock.

[00063] In an exemplary embodiment, the benefits of low mold plate-out of the product was achieved by extended vacuum time via increased exposure of the molten feedstock to the vacuum zones of the polymer compounding equipment, resulting in a greater degree of impurity removal and moisture removal. By using a molten polymer feed stream (such as a molten polyamide feed stream) rather than the polymer in solid form, a greater portion of the extruder length or space can be utilized for application of vacuum conditions rather than for melting the solid feedstock. The molten feedstock stream directly fed from a continuous or batch polymerization process also imparts a lower moisture load on the vacuum systems, thereby further increasing the ability of the vacuum systems to efficiently remove moisture and impurities from the product.

[00064] In an exemplary embodiment, the lowest capital and operating costs for compounded product are achieved by the elimination of the pelletization, storage, and transportation of polymer feed resin combined with a smaller compounding motor due to the unnecessary step of pelletizing and melting the feed resin. Also, costs are reduced with no required pellet feed storage, raw material handling labor, metering equipment, and no high cost working volume of resin. With less equipment, total operations and maintenance labor are minimized. Fewer spare parts are needed and reliability is higher with the reduced equipment count. Typically, pelletizing units require considerable maintenance upkeep, spare parts, offline calibration, and high repair costs. Also, with the directly coupled molten operation of the compounding operation, fewer lab samples are required to maintain excellent process and product quality control. Another reduction in cost is realized with the lower energy consumption of the compounding operation associated with no melting of the feed resin pellets. Combining the capital and operating cost advantages with the quality improvements such as lower variability, lower volatile content, better plate-out performance, provides for a highly advantaged business structure.

[00065] Examples of applications which would benefit from the in-line process improvements described herein would include articles prepared by injection molding processes, profile extrusion processes, sheet extrusion processes, and other forming processes known to those skilled in the art. These articles may be used in electrical and electronic applications (such as, but not limited to, circuit breakers, terminal blocks, connectors and the like), automotive applications (such as, but not limited to, air handling systems, radiator end tanks, fans, shrouds, and the like) and furniture and appliance parts.

[00066] **Example 1: Method for Injection Molding Resins for Evaluating Plate-Out Performance**
This method determines the amount of plate-out residue in injection molding resins. Plate-out is generated by monomer, lubes, and additives that bloom to the surface during injection molding process. There is a customer expectation of a production length that is linked to product quality of plate-out.

Procedure

1. Install the plate-out tool into the injection molding machine. The mold used in this testing was built according to ISO 294 with the following deviations, mold vents are altered to a land of 0.0005 inches in depth and 0.125 inches in length this is then relieved to 0.005 inches deep and 1.0" in long inches.
2. Completely clean the entire molding surface using a paper towel and methanol.
    a. Mold surface is clean when there is no residue remains on the surface.
3. Mold 600 shots according to ISO 294, except for deviations in injection rate of 50 mm/s and mold temperature to 30°C, the purpose of these changes is to accelerate the build-up of plate-out deposits.

[00067] **Example 2: Method for Measuring Mold Deposits (Plate Out) Collected on Polypropylene Wipes**
A pre-cleaned non-woven polypropylene wipe is used to collect plate out deposits left on surfaces of an injection mold after a known number of injection cycles. The deposits are removed from the wipe with hot methanol under controlled conditions, dried and weighed. The deposits weight is reduced by the weight of background extractables obtained from a clean wipe. This corrected weight is normalized to 1000 shots and reported as milligrams of extractable plate-out per 1000 shots.

I. Preparation of clean wipes

a. Cut non-woven polypropylene cloth sheets into 3x3 inch squares using a sharp scissors to avoid frayed edges.
b. Place about 20 of the 3x3 inch wipes into a 500 mL Erlenmeyer flask with a ground glass stopper and add 200 mL of methanol.
c. Put flask in a large crystallizing dish containing about 2 inches of near-boiling water; place flask and dish on a hot plate set to low heat and allow methanol to reflux gently for 30 minutes.
d. Pour off the methanol, replace with fresh methanol and heat for another 30 minutes
e. Pour off the methanol; using metal forceps, place wipes in a clean crystallizing dish in a fume hood until wipes appear dry.
f. Remove last traces of methanol by drying in oven at 90°C for 30 minutes.
g. Place each wipe inside a folded piece of aluminum foil which has been cleaned on both sides with acetone.
h. Place foil-wrapped wipe in a plastic press-locked bag and label with date cleaned and mg of background extractables for that batch, as determined below.

II. <u>Measurement of background extractables from clean wipes</u> (includes any solvent residue contribution)

a. Record all weights to 0.00000 grams (0.00 mg).
b. Clean an aluminum dish with acetone and methanol rinses inside and out, dry in a 90°C oven, cool and weigh.
c. Rinse an acid digestion vial with methanol and use metal forceps to place a clean wipe into it.
d. Add about 7 mL of methanol, cap the vial and shake or vortex mix for 15 seconds.
e. Place vial in an aluminum heater block set to 80°C for 30 minutes.
f. Using leather gloves or other heat resistant gloves, remove vial from heater block and shake or vortex 15 seconds.
g. Cool vial in running tap water for about 1 minute to bring methanol temperature below boiling point.
h. Open vial and decant methanol into the weighed aluminum dish from step IIb.
i. Add about 3 mL methanol to vial, cap and shake 15 seconds, decant into aluminum dish
j. Put aluminum dish on hot plate with surface temperature 90-110°C and evaporate methanol, removing dish as soon as dry.

k. Repeat steps IId – IIj.

l. Place dish in air oven at ~90°C for 5 minutes.

m. Remove from oven, cool 5 minutes in desiccator and weigh.

n. Repeat steps IIl and IIm. If the weights differ by more than 0.00005 g, let the dish sit on a grounded metal surface for five minutes to discharge static and re-weigh.

o. Calculate background extractables as: average of dried dish weights from step IIn – clean dish weight from step IIb.

p. Check extractables for at least two wipes out of every 40 prepared and use the average extractables for the two wipes as the background extractables level for that batch.

q. Typical background extractables level is approximately 0.5 mg/wipe or less. If background is higher, repeat the cleaning process and re-measure background.

III. Measuring extractable deposits on a used wipe

a. After wiping out the mold, a wipe is put back into the foil wrap and plastic bag and labeled with the number of injection molding cycles ("shots") performed.

b. Perform steps IIa-IIn on the used wipe.

c. Calculate net extractables as the average extractables weight for the used wipe minus the background extractables weight for that batch of wipes.

d. Using the number of molding "shots" noted in IIIa, normalize the net extractables to 1000 shots and report the result to one decimal place as: "extractable plate out = x.x mg/1000 shots".

IV. Chemicals and consumable materials

a. Non-woven polypropylene fiber cleaning cloths, Berkshire Pro-Wipe® 880 or equivalent 12" x 12".

b. Methanol, Fisher Scientific HPLC grade or equivalent, with evaporation residue 0.5 ppm or less.

c. Acid digestion vial, borosilicate glass with inert lined screw-on phenolic cap; vial dimensions approximately 19 cm long x 1.6 cm diameter, 12 mL volume.

d. Aluminum weighing dishes, approximately 70 mm wide by 15 mm tall, weighing about 2 grams; VWR Scientific catalog number 25433-085 or equivalent.

[00068] Table 2 shows the impact of increasing melt exposure and vacuum on the molding performance plate-out of a compounded nylon resin. It is clear from the results that superior

performance is achieved with the present invention compared to conventional methods. Melt vacuum exposure time was determined according to the calculations below:

Variables:
N=number of screws
ID = inner diameter of screws (mm)
OD = outer diameter of screws (mm)
F = % fill in the vacuum section
L = length under vacuum (mm)
R = flow rate through extruder (kg/hr)
D = density of compound (g/cm^3)
Vf = volumetric flow rate = (R*1000)/(D*3600)
C = total cross sectional area = N* PI*(OD/2)^2-PI*(ID/2)^2
Cp = total cross sectional area filled with polymer given = C*F
Vv = total volume in vacuum section = Cp*L/1000
Vacuum Exposure Time = Vv/Vf (seconds)

The following constants were used for these calculations:

# screws:	2
ID:	70 mm
OD:	96 mm
Density:	1.6 g/cm^3
% Fill (F):	25%
Length under vacuum (L):	768 mm

Additional information relating to the devolatilization performance of a twin screw extruder can be found, for example, in Polymer Extrusion, (2001) 4th Edition, by Chris Rauwendaal, pp. 618-622. The high surface renewal and thin film generation in the extruder enhances devolatilization effectively with low overall residence time.

Table 2

Operating Conditions			Molding Performance	
Conventional Process				
Compounding Rate (lbs/hr)	Vacuum (in Hg)	Vacuum Exposure Time (s)	Shots Until Burning	Plate Out (mg/100 shots)
2500	25	1.52	>600 shots	1.8
3000	25	1.36	341	2.8
3500	25	1.21	318	2.7
3700 (high plateout conditions)	20	1.14	88	5.8
Improved ILC Process				
6000	28	2.75	>600 shots	0.77
6000	28	2.75	>600 shots	0.62

[00069] Reviewing the results of Table 2, it is apparent that the present invention results in significantly improved molding performance compared to the conditions in which the nylon feedstock is introduced in a pelletized (i.e., solid) form (conventional process). For example, a solid feedstock exposed to the least amount of vacuum time exhibited the lowest number of shots until burning (88) and the highest plate-out value (5.8). In contrast, the molding performance of the molten nylon feedstock (ILC process) showed no burning in the mold and, more significantly, the least amount of plate-out (0.7 or less) compared to all tests using solid feedstock. For the customer, these improvements translate into extended up-time on equipment since there are fewer overhauls of the molds, allowing the equipment to produce more parts with the same capital cost and lower operating costs. Product quality also is improved with less plate-out as the deposits can contaminate the product and impart surface defects on the produced molded parts. In customer molding applications exhibiting complicated or intricate mold venting manifolds, this benefit has even more impact in improving product quality and process output or yield. Cost savings and earnings for these plants could be increased as much as 50% or more given the potential for lower plate-out. In a particular

embodiment, a customer typically operates Monday through Friday producing injection molded parts by conventional means with a compounded product feedstock. Then they schedule a necessary cleaning of the molding equipment over the two-day weekend. Employing the low plate-out compounded product of the present invention as the feedstock, this molding customer can operate continuously for at least two weeks before needing to shut down to clean the their equipment, thus allowing for the significant increase in productivity of 2 days out of 14 days, an increase of about 15%.

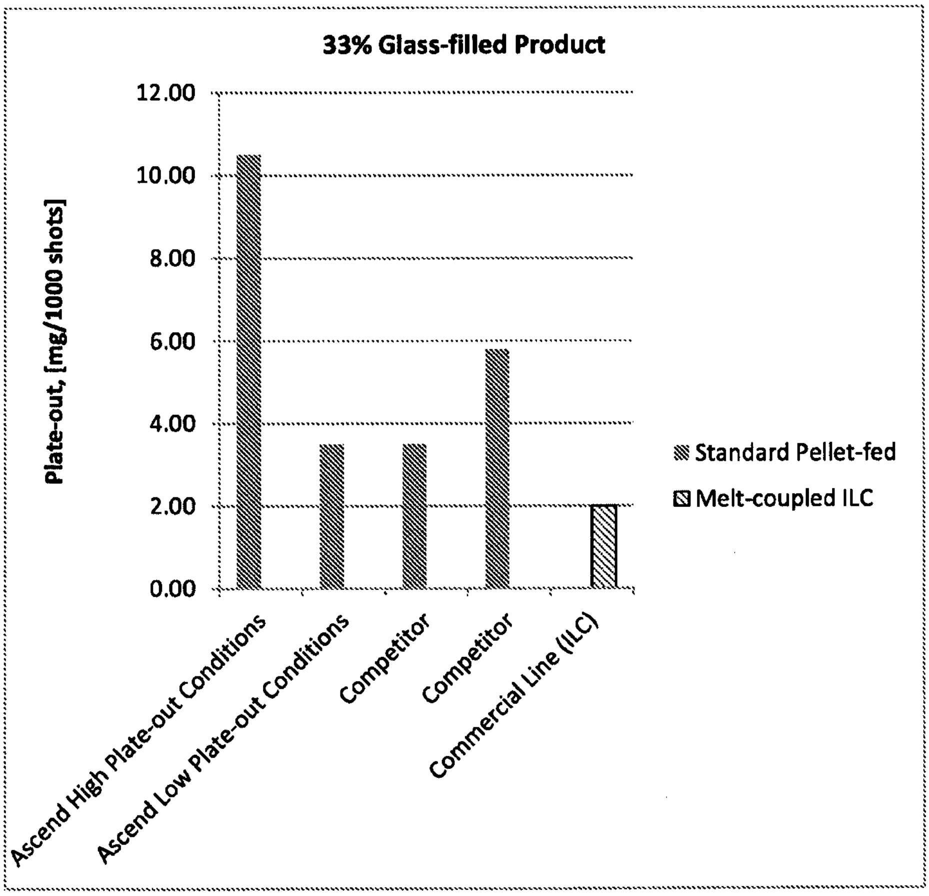
[00070] In Table 3, comparisons are made with conventionally prepared products (standard pellet fed configuration) and a product prepared from the ILC process of the invention. Clearly, the plate-out results indicate that an inline molten feed produces a material substantially superior to that obtained from standard pellet fed operations. Unlike the products prepared from the pellet fed operations, the ILC product has substantially lower plate-out performance which would be realized as increased uptime and productivity for customers using this material.

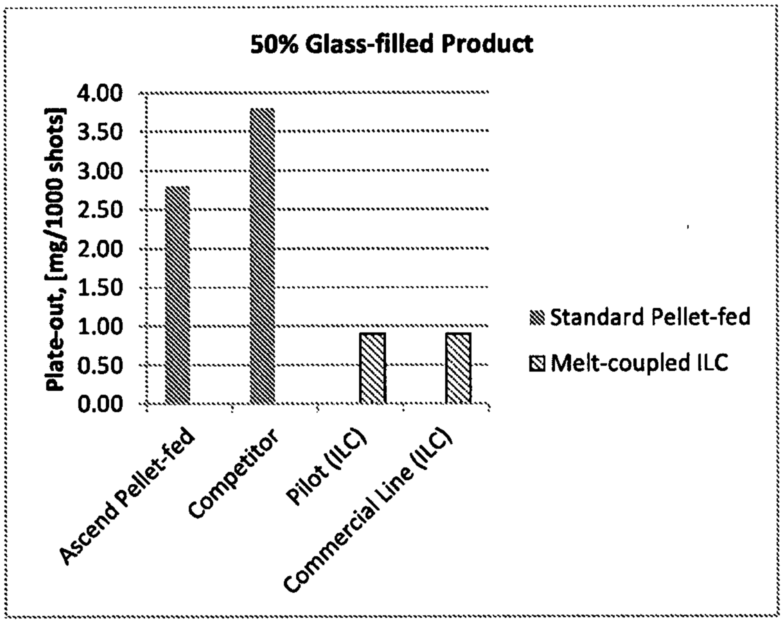
Table 3

Source	Glass %FG	Plate-out mg/1000 Shots
Pellet-fed – High Plate-out Conditions	33	10.50
Pellet-fed – Low Plate-out Conditions	33	3.50
Competitor A nylon product	33	3.50
Competitor B nylon product	33	5.80
Continuous Polymerization (ILC) Molten Fed Commercial Line	33	2.00
Pellet-fed Normal Conditions	50	2.80
Competitor A nylon product	50	3.80
Continuous Polymerization (ILC) side stream Molten fed Pilot Line	50	0.90
Continuous Polymerization (ILC) Molten Fed Commercial Line	50	0.90

[00071] In Table 3, "ILC" refers to inline compounding. Competitor A and B products refer to commercial nylon products and are tested to illustrate the superior performance achieved using the ILC process of the invention with regards to plate-out.

[00072] The graphs below represent the data from Table 3 in bar graph format. The graphs clearly illustrate the significant plate-out (amount of mold vent deposits) associated with the direct molten fed compounded lines (ILC) in both the pilot unit rated at 400 pounds per hour of a 50% glass product and the commercial-sized ILC line capable of more than 6,000 pounds per hour of a 50% glass product.





[00073] As described herein, a continuous feed from a continuous polymerization process provides a more stable feedstock for compounding. This low variability translates into lower variability in the compounded product.

[00074] In an exemplary embodiment of the invention, a polyamide prepared by the process described herein has a plate-out value of less than about 2 mg/1000 shots, such as less than about 1.5 mg/1000 shots, such as less than about 1.0, such as less than about 0.5 mg/1000 shots, wherein 0.1 mg/1000 shots is considered as the minimum value.

[00075] Table 4 compares viscosity standard deviation for a typical pellet fed compounding product and a product of the present process produced in a 150-kilogram per hour pilot operation. Unlike conventional pellet-fed compounding lines, the inline molten-coupled compounding line exhibits the low variability within the continuous polymerization line, free of the variability arising from multiple resin sources, multiple moisture levels in the resin, and multiple ages of the resin feedstock. This consistent feed leads to lower variability as demonstrated with the pilot line results below. The molten-coupled compounding is uniquely enabled to provide the least variable product of any compounding operation tested.

Table 4

	Conventional Pellet-Fed Compounding	**Molten-Fed Compounding (ILC)**	**% Reduction**
Standard Deviation of Relative Viscosity	**1.9**	**0.9**	**53%**

[00076] As a result of the reduced compounded product variability, the customer in a molding operation is expected to have better shot to shot consistency, leading to greater dimensional and weight stability, less warpage, and lower scrap rates, i.e., higher yield. On any given run, parts produced on an injection molding process will have a distribution of dimensions, in which the variation can be caused by viscosity variations with the compounded material. Variation can also be caused by other factors (ambient conditions, machine wear, *etc.*). On any given run, parts produced on an injection molding process will have a distribution of masses, in which the variation can be caused by viscosity variations with the compounded material. Variation can also be caused by other factors (ambient conditions, machine wear, *etc.*).

[00077] Additionally, the lower variability is expected to result in more consistent pressures and feeding rates in the customers' molding processes, which lead to lower scrap rates, *i.e.*, higher yields, and faster cycle times resulting in higher production rate or throughput. As a result, the customer is able to produce more products with lower investment. Also, the products are expected to exhibit improved product color, typically visualized as being less yellow. The products also are expected to have higher tensile strength because of the lower heat history (factors of, for example, temperature and residence time) resulting from the faster cycle times attributable to lower feed variability and no melting step between the continuous polymerization and compounding processes.

[00078] All published documents (*e.g.* patents, journal articles, books) cited herein are incorporated by reference in their entireties. Embodiments of the present disclosure employ, unless otherwise indicated, chemical and engineering techniques which are within the skill of

the art. Such techniques are fully explained in the literature. As would be apparent to those of skill in the art, several of the embodiments described herein have components and features that may be readily separated from or combined with the features of other embodiments without departing from the scope or spirit of the present disclosure.

What is Claimed Is:

1. A process for preparing a compounded polyamide, comprising introducing a molten polyamide feedstock directly to one or more polymer compounding devices, where the molten feedstock is prepared by a polymerization process.

2. The process according to claim 1, wherein the polymerization process is a continuous process.

3. The process according to claim 1, wherein the polymerization process is a batch process.

4. The process according to claim 1, wherein the molten polyamide feedstock is a molten nylon66 feedstock.

5. The process according to claim 1, wherein the polymer compounding device is an extruder.

6. The process according to claim 5, wherein the extruder is a twin-screw extruder.

7. The process according to claim 6, wherein the twin-screw extruder contains at least 2 vent ports.

8. The process according to claim 6, wherein the twin-screw extruder contains at least 3 vent ports.

9. The process according to claim 7, wherein the vent ports are at atmospheric pressure.

10. The process according to claim 7, wherein the vent ports are subjected to vacuum conditions.

11. The process according to claim 6, wherein the twin-screw extruder has a length to diameter ratio of the screw shaft in the range of 24:1 to 56:1.

12. The process according to claim 6, wherein the twin-screw extruder has a length to diameter ratio of the screw shaft in the range of 36:1 to 48:1.

13. The process according to claim 1, wherein only a portion of the molten feedstock is sent directly to the one or more polymer compounding devices.

14. The process according to claim 1, further comprising introducing one or more additives, fillers, reinforcing agents and modifiers into the one or more polymer compounding devices.

15. The process according to claim 1, wherein the polymer polymerization process occurs less than 50 feet from the one or more polymer compounding devices.

16. The process according to claim 1, wherein the compounded polyamide has a relative viscosity (RV) range between samples of less than about 3 units.

17. The process according to claim 16, wherein the compounded polyamide has a relative viscosity (RV) range between samples of less than about 2 units.

18. The process according to claim 1, wherein the compounded polyamide has a relative viscosity (RV) range between samples of less than about 1 unit.

19. A compounded polyamide prepared by the process of claim 1, claim 2 or claim 3.

20. A compounded polyamide having a plate-out value of less than about 2.0 mg/1,000 shots.

21. The compounded polyamide according to claim 20, having a plate-out value of less than about 1.0 mg/1,000 shots.

22. The compounded polyamide of claim 20 or claim 21, having a relative viscosity (RV) range between samples of less than about 2 units.

23. The compounded polyamide of claim 20 or claim 21, having a relative viscosity (RV) range between samples of less than about 1 unit.

24. The compounded polyamide according to claim 20 exhibiting greater than about 500 shots before detection of burn material in a mold for mold injection.

25. The compounded polyamide according to claim 20 exhibiting greater than about 600 shots before detection of burn material in a mold for mold injection.

26. The compounded polyamide according to claim 21 exhibiting greater than about 500 shots before detection of burn material in a mold for mold injection.

27. The compounded polyamide according to claim 21 exhibiting greater than about 600 shots before detection of burn material in a mold for mold injection.

28. The compounded polyamide according to any one of claims 19 to 27, wherein the polyamide is nylon66.

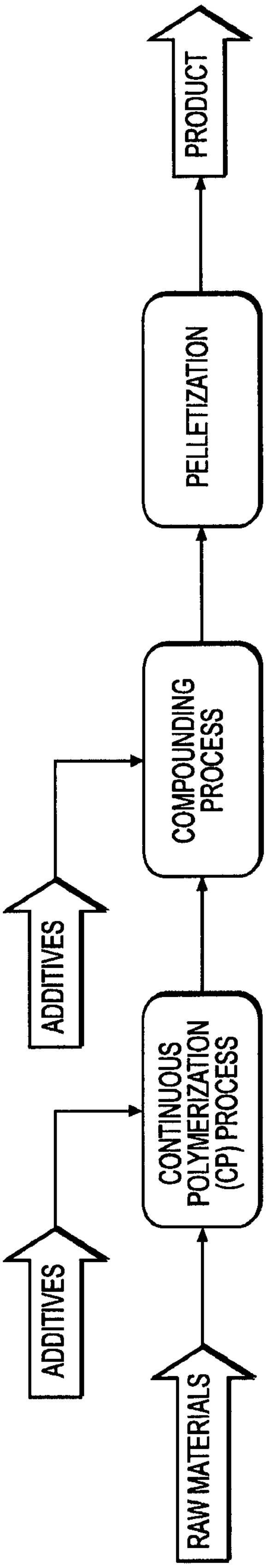

SCHEMATIC OF PROCESS INVENTION

FIG. 1

SCHEMATIC OF COMPOUNDING PROCESS EXAMPLE

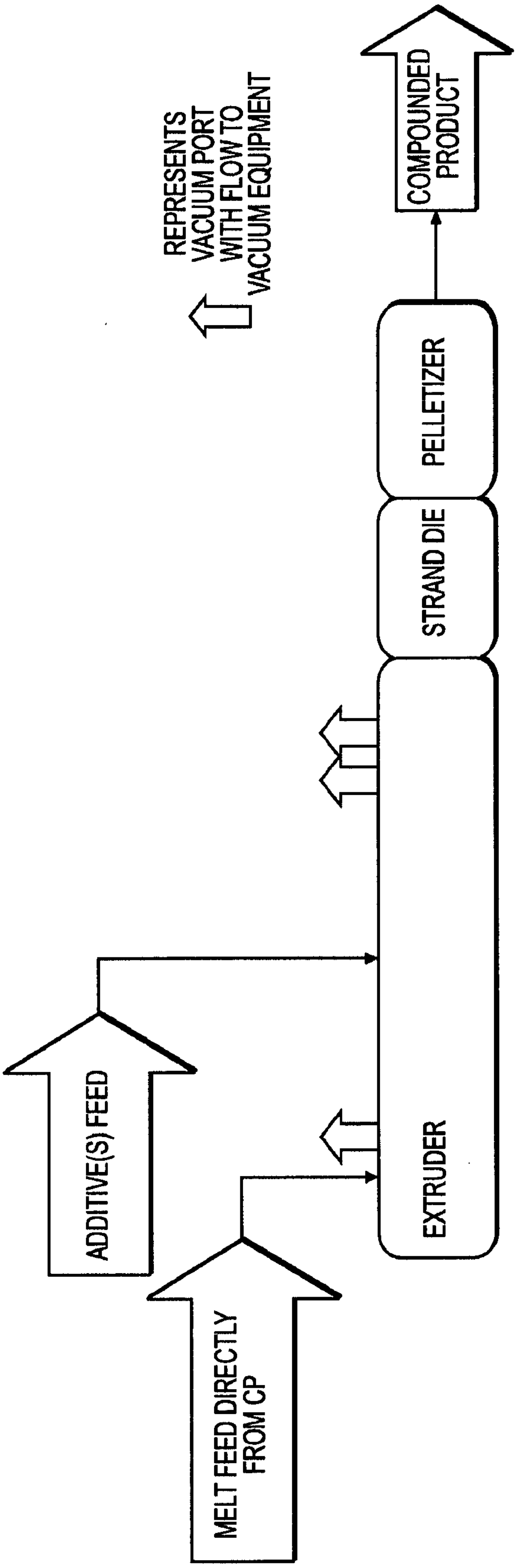


FIG. 2

EXTRUDER BARREL AND SCREW CONFIGURATION EXAMPLE

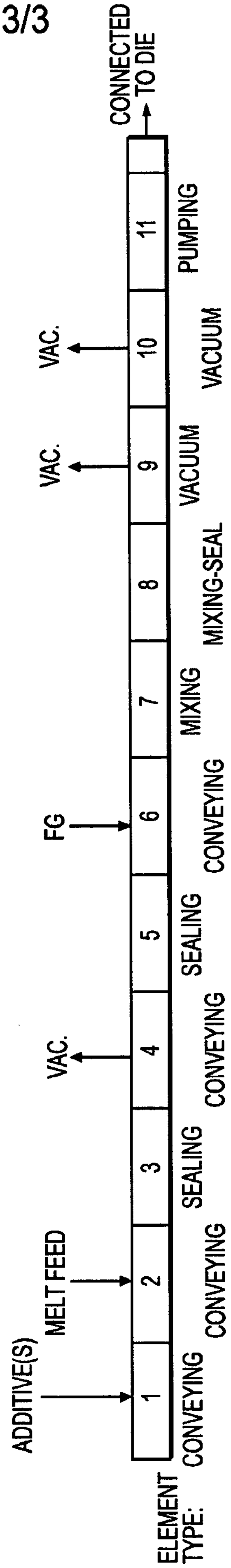


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US14/26353

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08J 3/20; C08L 33/24; C08G 69/04, 69/46 (2014.01)
USPC - 525/183; 425/110, 113; 264/37.26, 173.12, 173.14, 102
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)
IPC(8): C08J 3/00, 3/20, 5/00; C08L 33/24, 77/00; C08G 69/00, 69/04, 69/46 (2014.01)
USPC: 525/183; 425/110, 113; 264/37.26, 173.12, 173.14, 102

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)
MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; IP.com; Google/Google Scholar; Key Words: compound*, polyamide*, molten, feed, feed*stock, direct*, polymeriz*, extruder, continuous, batch, nylon66, twin*screw, vent ports, vacuum, pressure, length to diameter ratio, additive*, distance, reactor, vessel, relative viscosity, RV, plate*out

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 3,391,232 A (JACKSON, R) 02 July 1968; column 2, lines 24-26, 37-45, 50-54; column 4, lines 48-50; column 5, lines 20-23; column 7, lines 19-24; example 1; claim 1	1, 4-8, 10, 14, 19/1 -------------------- 2-3, 9, 11-13, 15-18, 19/2-3
Y	US 2009/0258226 A1 (SCHWINN, GA) 15 October 2009; paragraph [0041]	2-3, 19/2-3
Y	US 7,132,498 B2 (MCCLOSKEY, PJ et al.) 07 November 2006; column 18, lines 16-25	9
Y	US 8,262,925 B2 (FIEBACK, K et al.) 11 September 2012; column 5, lines 33-37	11-12
Y	US 2,273,188 A (GRAVES, GW, DE) 17 February 1942; column 2, lines 38-42, 45-55	13
Y	US 2005/0272914 A1 (MCELVAIN, RR et al.) 08 December 2005; paragraph [0028]; claims 9, 18	15
Y	US 2008/0287643 A1 (STRAUCH, J et al.) 20 November 2008; paragraphs [0012], [0078]	16-18, 22/20-21, 23/20-21
Y	US 4,977,216 A (ELIA, AE) 11 December 1990; abstract; column 5, lines 58-61; column 6, lines 23-40; table II	20-21, 22/20-21, 23/20-21, 24-27
Y	US 2006/0258816 A1 (ENDO, S) 16 November 2006; paragraph [0110]; table 3	20-21, 22/20-21, 23/20-21, 24-27
Y	US 6,518,341 B1 (HURLEY, JM et al.) 11 February 2003; column 3, lines 11-21; column 13, lines 12-22; table 1	24-27

☒ Further documents are listed in the continuation of Box C. ☐

* 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 02 June 2014 (02.06.2014)	Date of mailing of the international search report 11 JUL 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US14/26353

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2,810,630 A (HERELE, L) 22 October 1957; entire document	1-18, 19/1-3, 20-21, 22/20-21, 23/20-21, 24-27
A	US 2,361,717 A (TAYLOR, GB) 31 October 1944; entire document	1-18, 19/1-3, 20-21, 22/20-21, 23/20-21, 24-27
A	US 2011/0015328 A1 (ORIHASHI, Y) 20 January 2011; entire document	1-18, 19/1-3, 20-21, 22/20-21, 23/20-21, 24-27

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US14/26353

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.: 28
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:

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 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.:

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.

(19) 中华人民共和国国家知识产权局

(12) 发明专利申请

(10) 申请公布号 CN 105246950 A
(43) 申请公布日 2016.01.13

(21) 申请号 201480022596.3
(22) 申请日 2014.03.13
(30) 优先权数据
61/798,641 2013.03.15 US
(85) PCT国际申请进入国家阶段日
2015.10.21
(86) PCT国际申请的申请数据
PCT/US2014/026353 2014.03.13
(87) PCT国际申请的公布数据
WO2014/151735 EN 2014.09.25

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(51) Int. Cl.
C08J 3/20(2006.01)
C08L 33/24(2006.01)
C08G 69/04(2006.01)
C08G 69/46(2006.01)

权利要求书2页 说明书14页 附图2页

(54) 发明名称

聚合经耦合的配混方法

(57) 摘要

本发明提供制备改进的配混产物的方法和由该方法制备的配混产物。

1. 一种制备经配混的聚酰胺的方法，该方法包括将熔融聚酰胺原料直接引入到一个或多个聚合物配混装置中，其中该熔融原料通过聚合工艺制备。

2. 权利要求 1 的方法，其中该聚合工艺是连续法。

3. 权利要求 1 的方法，其中该聚合工艺是间歇法。

4. 权利要求 1 的方法，其中该熔融聚酰胺原料是熔融的尼龙 66 原料。

5. 权利要求 1 的方法，其中该聚合物配混装置是挤出机。

6. 权利要求 5 的方法，其中挤出机是双螺杆挤出机。

7. 权利要求 6 的方法，其中双螺杆挤出机包括至少 2 个排气口。

8. 权利要求 6 的方法，其中双螺杆挤出机包括至少 3 个排气口。

9. 权利要求 7 的方法，其中排气口处于大气压下。

10. 权利要求 7 的方法，其中排气口经受真空条件。

11. 权利要求 6 的方法，其中双螺杆挤出机的螺旋轴具有范围为 24:1 至 56:1 的长度与直径的比。

12. 权利要求 6 的方法，其中双螺杆挤出机的螺旋轴具有范围为 36:1 至 48:1 的长度与直径的比。

13. 权利要求 1 的方法，其中仅仅一部分熔融原料被直接输送到一个或多个聚合物配混装置中。

14. 权利要求 1 的方法，进一步包括引入一种或多种添加剂，填料，增强剂和改性剂到一个或多个聚合物配混装置中。

15. 权利要求 1 的方法，其中聚合物聚合工艺在离一个或多个聚合物配混装置小于 50 英尺处发生。

16. 权利要求 1 的方法，其中经配混的聚酰胺样品间的相对粘度 (RV) 范围为小于约 3 个单位。

17. 权利要求 16 的方法，其中经配混的聚酰胺样品间的相对粘度 (RV) 范围为小于约 2 个单位。

18. 权利要求 1 的方法，其中经配混的聚酰胺样品间的相对粘度 (RV) 范围为小于约 1 个单位。

19. 通过权利要求 1，2 或 3 的方法制备的经配混的聚酰胺。

20. 一种经配混的聚酰胺，其积垢值小于约 2.0mg/1,000 次注射。

21. 权利要求 20 的经配混的聚酰胺，其积垢值小于约 1.0mg/1,000 次注射。

22. 权利要求 20 或 21 的经配混的聚酰胺，其样品间的相对粘度 (RV) 范围为小于约 2 个单位。

23. 权利要求 20 或 21 的经配混的聚酰胺，其样品间的相对粘度 (RV) 范围为小于约 1 个单位。

24. 权利要求 20 的经配混的聚酰胺，在用于模塑的模具中检测到燃烧材料之前显示大于约 500 次注射。

25. 权利要求 20 的经配混的聚酰胺，在用于模塑的模具中检测到燃烧材料之前显示大于约 600 次注射。

26. 权利要求 21 的经配混的聚酰胺，在用于模塑的模具中检测到燃烧材料之前显示大

于约 500 次注射。

27. 权利要求 21 的经配混的聚酰胺，在用于模塑的模具中检测到燃烧材料之前显示大于约 600 次注射。

28. 权利要求 19-27 任何一项的经配混的聚酰胺，其中聚酰胺是尼龙 66。

聚合经耦合的配混方法

技术领域

[0001]　聚合物配混是用于制备塑料配方的公知方法，该方法通过在聚合物处于熔融或半熔融状态的同时，混合和／或共混聚合物，例如聚酰胺或聚酯与例如添加剂，填料，增强剂和改性剂而进行，参见，例如美国专利 Nos. 6, 149, 850 ；和 5, 236, 652。配混典型地在挤出机内发生。与例如添加剂，填料，增强剂和改性剂混合和／或共混的步骤通常在成型步骤之前，即在挤出、注塑等之前发生。添加剂，填料，增强剂和改性剂赋予它们向其中添加的主体聚合物以优选的性能。

背景技术

[0002]　期望最终的塑料产品含有尽可能低含量的挥发性组分，例如残留单体，有机溶剂和水。存在显著量水会促进解聚（水解）并降低聚合物的分子量和熔体粘度到在挤出物内形成气泡的程度。在配混工艺期间使聚合物脱气是实现低挥发性组分含量的典型方式。为了实现配混工艺期间挥发性组分有效的脱气，要求高真空和高温，但在高温下，聚合物的降解显著增加。然而，若挤出机内的温度维持在最小化聚合物降解的水平下，则会负面影响化合物组分的有效熔融和共混，这对最终产品的品质具有有害影响。参见例如美国专利 No. 8, 034, 269。这些问题在高产出率时尤其普遍，在高产出率的情况下，聚合物曝露于配混工艺下短的时间由成本效益决定。因此，在高产出率下，挥发性组分的日益有效的脱气以增加聚合物降解速率为代价。需要进行经济分析以确定这两种竞争性结果之间的可接受的平衡。例如，已知可用于模塑和挤出应用的聚酰胺树脂会随着时间经历非所需的模具累积，从而降低机器的正常运行时间和容量使用率。参见例如 Plastics Technology (2000) (http://www.ptonline.com/articles /engineering-thermoplastics)；DuPont™ **ZYTEL®** HTN Molding Guide (2001) (http://www.dupont.com/content/dam/assets/products-and-services/plastics-polymers-resins/Documents/H8 5940.pdf，第 13 页，其认识到与排气口堵塞 (vent plugging) 有关的问题。U. S. 6, 518, 341 提到排气累积 (vent accumulation)，其如何涉及在模具中烧结 (burning)，并引入与模具沉积物或积垢 (plate-out) 有关的术语“烧结之前的注射量 (shots before burn)”，以及注塑的生产率如何受到该模具沉积的不利影响。

[0003]　常规地通过使用用于混合例如添加剂，填料，增强剂和改性剂与聚酰胺，例如尼龙，其中包括尼龙 6，尼龙 4/6，尼龙 6/6，尼龙 6/10，尼龙 6/12，尼龙 11 和尼龙 12 的挤出机，配混聚酰胺树脂，其中聚酰胺为固态（例如，颗粒或薄片或切片）形式。典型地，配混工艺包括将呈固体形式的尼龙原料引入到挤出机的前半部分中，以实现该原料的熔融。在出现熔融之后，引入一种或多种添加剂，填料，增强剂和改性剂，并混合到尼龙熔体内。在含有多个机筒区段的挤出机内，典型地施加真空，从聚酰胺和添加剂，填料，增强剂和／或改性剂物流中除去非所需的挥发物和水分。如果没有除去的话，则这些非所需的组分随着时间流逝会堵塞客户的模具，从而减少机器的正常运行时间和容量使用率。参见例如 A. Dreiblatt, Plastics Technology (2010) (http://www.ptonline.com/columns/in-twin-screw-compo unding-distinguish-between-disease-and-illness)。美国专利 No. 6,518,341 还描述了在注塑操作中由于存在沉积物而产生的问题。

[0004] 因此，聚酰胺熔体较长时间曝露于真空条件下和较高真空可通过降低水与任何残留杂质，例如低分子量低聚物，例如尼龙低聚物，单体，硬脂酸盐和蜡组分的含量而改进产品品质。除去杂质受到可用于真空曝露的挤出机机筒部分（亦即，尚未用于尼龙熔融以及玻璃或添加剂进料点的那些机筒）的数量限制。典型地通过气相色谱法和利用内部标准进行的定量评估，测定挥发性组分的残留含量。

[0005] 已知原料的可变性会对配混产品明显造成不良的加工稳定性和品质控制不足。参见例如，Harold F.Giles Jr. 等人的 Extrusion:The Definitive Processing Guide and Handbook(2005)。尤其当原料以固体形式储存时，这种非所需的可变性源于多种原因（例如，样品之间水分含量的差异和原料使用期限的差异）。结果，常常要求在挤出之前干燥固体原料，以实现防止由于水解而引起相对粘度 (RV) 显著下降所必需的受控且一致的水分含量。参见，例如 Harold F.Giles Jr. 等人的 Extrusion:The Definitive Processing Guide and Handbook(2005)。

[0006] 当原料呈固体形式时，仓库管理不佳会进一步造成在前体配混操作中观察到的可变性，因为该原料还容易随着时间流逝受到空气氧化。

[0007] 因此，认识到仍然需要一种呈现优异稳定性和改进的性能以及低杂质可变性的配混聚合物，例如配混的聚酰胺，例如配混的尼龙 66，以及以最低可能的成本制造该产品的方法。通过与常规地制备的配混聚合物（其中原料以固体形式引入到聚合物配混设备内）相比，通过本文描述的直接插入 (inline) 方法制备的配混聚合物显示出改进的模塑性能和显著更低的积垢和在清洁之间的更长模具寿命。这种产品的粘度和品质控制范围也比由常规的粒料进料配混所产生的产品具有更低的可变性。与利用固体形式的原料由常规的配混操作所制造的产品相比，这种品质方面的相应改进直接为客户提供具有改进的性能和更低成本的优异产品。

发明内容

[0008] 本发明的一个方面是制备配混聚酰胺的方法，该方法包括将熔融或者基本上熔融的聚酰胺原料直接引入到一个或多个（例如 2,3,4,5 等）聚合物配混装置中，其中该聚酰胺原料通过聚合方法制备，其中该聚合方法是连续聚合法或者间歇聚合法。

[0009] 在本发明的一个方面中，聚酰胺选自尼龙 6，尼龙 4/6，尼龙 6/6，尼龙 6/10，尼龙 6/12，尼龙 11，尼龙 12，尼龙 MXD6，共聚尼龙（己内酰胺与己二胺己二酸酯的共聚物），尼龙嵌段共聚物，和含这些尼龙作为主要组分的共聚物。制备聚酰胺，例如尼龙 6/6 的方法是公知的。参见例如美国专利 Nos. 6,197,855；4,981,906；4,320,213；4,346,200；4,713,415；4,031,164；2,071,250；2,071,251；2,130,523；2,130,948；2,241,322；2,312,966；2,512,606；和 3,393,210。

[0010] 在本发明的一个方面中，尼龙是尼龙 6/6（在本文也称为尼龙 66 或尼龙 66 或聚酰胺 66 或 PA 66 或 PA66）。

[0011] 在本发明的一个方面中，配混的聚酰胺是均聚物。

[0012] 在本发明的一个方面中，配混的聚酰胺是共聚物。

[0013]　在本发明的一个方面中，熔融的聚酰胺原料在进入聚合物配混装置内时的温度为约 200℃ -400℃，例如 250℃ -375℃，例如 275℃ -300℃。

[0014]　在本发明的一个方面中，聚合物配混装置是挤出机。

[0015]　在本发明的一个方面中，挤出机独立地为双螺杆挤出机或单螺杆挤出机。

[0016]　在本发明的一个方面中，双螺杆挤出机同步旋转或反向旋转。

[0017]　在本发明的一个方面中，挤出机独立地含有至少两个排气口。

[0018]　在本发明的一个方面中，挤出机独立地含有至少 3 个排气口，例如 4，5，6，7，8，9 或 10 个排气口。

[0019]　在本发明的一个方面中，挤出机排气口处于大气压下（即不经受真空条件），或者备选地，经受真空条件。在多个排气口的情况下，一部分排气口可以处于大气压下，和一部分排气口可以经受真空条件。

[0020]　在本发明的一个方面中，双螺杆挤出机的螺旋轴具有范围为 24:1 至 56:1 的长度直径比。

[0021]　在本发明的一个方面中，双螺杆挤出机的螺旋轴具有范围为 36:1 至 48:1 的长度直径比。

[0022]　在本发明的一个方面中，将一种或多种添加剂，填料，增强剂或改性剂引入到配混挤出机内。

[0023]　在本发明的一个方面中，玻璃纤维以约 5％ - 约 60wt％，例如约 10％ -55％，例如 15％ -50％，例如 20％ -50％，例如 25％ -50％，例如 35％ -45％的范围与尼龙 66 配混。

[0024]　在本发明的一个方面中，排气口用于除去来自配混的聚酰胺中的水分或杂质。

[0025]　在本发明的一个方面中，仅仅一部分（例如，大于 0％到最多约 99％，例如约 5％到最多约 95％，例如约 15％到最多约 85％）熔融或基本上熔融的聚酰胺原料被直接输送到一个或多个聚合物配混装置中。

[0026]　在本发明的一个方面中，该聚合方法位于离该聚合物配混装置小于约 500 英尺处。

[0027]　在本发明的一个方面中，该配混的聚酰胺的相对粘度 (RV) 范围为约 35 至约 120，例如约 40 至约 100，例如约 40 至约 80，例如约 45 至约 60。

[0028]　本发明的一个方面是通过本文描述的方法制备的聚酰胺。

[0029]　本发明的一个方面是积垢值小于约 3mg/1，000 次注射，例如小于约 2.5mg/1，000 次注射，例如小于约 1.5mg/1，000 次注射，例如小于约 1.0mg/1，000 次注射，例如小于约 0.5mg/1，000 次注射，例如小于约 0.3mg/1，000 次注射的配混聚酰胺，且最低值为 0 或者大于 0 的数值，诸如，例如 0.01mg/1，000 次注射或 0.05mg/1，000 次注射或 0.1mg/1，000 次注射。

[0030]　本发明的一个方面是在注射模具中检测到燃烧材料之前呈现大于约 200 次注射，例如大于约 300 次注射，例如大于约 400 次注射，例如大于约 500 次注射，例如大于约 600 次注射，例如大于约 700 次注射，例如大于约 800 次注射，且包括在检测到燃烧材料之前诸如约 400 至约 800 次注射，例如约 500 至约 800 次注射，例如约 600 至约 800 次注射的配混聚酰胺。

[0031]　在本发明的一个方面中，配混聚酰胺样品之间的相对粘度 (RV) 范围为小于约 3 个

单位，例如小于约 2 个单位，例如小于约 1 单位，例如小于约 0.8 个单位，例如小于约 0.5 个单位。

附图说明

[0032] 附图代表例举的实施方案且并不意欲限制本发明的范围，除非本文中另外描述。

[0033] 图 1 代表适合于在本发明中使用的熔融物流进料配混操作的示意图。将包含己二胺 (HMD)，己二酸，水，催化剂，改性剂，稳定剂和添加剂的原材料进料到常规的连续聚合方法中，在此包含 PA66 的尼龙聚合物以介于约 35 至约 200 的 RV 水平生产。出于形成颗粒或任何其他固体生产方法的目的，不使这一熔融聚合物凝结 - 亦即，不使该熔融聚合物在连续聚合与后续配混方法之间发生显著凝固。而是将该熔融物流直接进料到邻近的配混设备中，在该配混设备中，将许多类型的添加剂，矿物，增强剂，改性剂，填料等任何物质混合到该聚合物中，形成新的配混产品。这一新的配混产品通过粒化系统加工，储存，传输并在工业中常用的容器的任何组合中包装。

[0034] 图 2 代表使用双螺杆挤出机作为配混装置的熔融物流进料配混操作的示意图。使来自连续聚合方法的熔融聚合物直接流入到该配混双螺杆挤出机中。提供多个排气口以供用于进行排气区中的绝对压力的逐渐降低。使用复合型机筒 (Combi-barrel)，引入固体类型的添加剂，改性剂，填料，增强剂等，并使用注射口引入最适合以液体形式引入的相同组分。在配混单元之后，典型地将该熔融产物物流进料到本领域技术人员已知的具有干燥和水分控制能力的捻股和粒化单元中。在粒化之后，将该配混产物传输，储存并包装在可用于配混塑料产物的任何标准包装容器中。

[0035] 图 3 代表适合于在本发明中用作配混工艺的多机筒挤出机的示意图。尽管任何若干种机筒和螺杆设计均可用于生产能通过所描述的系统生产的各种配混产品，但已发现所描绘的组合可高效地产生优异的积垢结果，其中用 50%玻璃填充的尼龙 PA66 具有 48 目的目标 RV 和 0.15wt%的水分含量。

具体实施方式

[0036] 定义

[0037] 除非另有定义，否则本文中描述的所有技术和科学术语均具有如本发明公开内容所属技术领域的普通技术人员通常理解的相同含义。

[0038] 本文中所描述的“熔化”或“熔化的”是指从固相转化为液相。

[0039] 本文中所描述的“熔融的”是指材料从不以固相存在。

[0040] 本文中所描述的“基本上熔化的”是指至少 70%熔化，例如至少 75%熔化，例如至少 80%熔化，例如至少 85%熔化，例如至少 90%熔化，例如至少 95%熔化，例如至少 97%熔化，例如至少 99%熔化。

[0041] 本文中所描述的“基本上熔融的”是指至少 70%熔融，例如至少 75%熔融，例如至少 80%熔融，例如至少 85%熔融，例如至少 90%熔融，例如至少 95%熔融，例如至少 97%熔融，例如至少 99%熔融。

[0042] 本文中所描述的“聚合物配混装置”是指内部发生聚合物配混的装置。若该聚合物配混装置包含适合于在配混方法之前、期间和 / 或之后使该聚合物脱挥发的设置，则该

聚合物配混装置中可视情况任选地发生脱挥发作用。

[0043] 本文中所描述的“相对粘度”或“RV”是指聚合物的甲酸溶液的粘度与甲酸本身粘度的比较，且根据ASTM D789，利用90％甲酸和玻璃毛细管Ubbelohde粘度计测定。对于含有玻璃纤维或其他填料的样品来说，根据填料的含量调整待溶解的样品的重量，以提供所需的11.0g纯树脂/100ml甲酸。在负载至该粘度计中前，过滤含有这种填料的溶液。

[0044] 本文中所描述的“尺寸稳定性”是模塑方法中注射量之间尺寸一致性的量度。

[0045] 本文中所描述的“重量稳定性”是模塑方法中注射量之间质量一致性的量度。

[0046] 本文中所定义的“翘曲”是模制部件相对于模具尺寸偏差的量度。

[0047] 本文中所定义的“不良率”是根据模塑方法所生产的不合格部件的数量的量度。

[0048] 本发明提供一种生产改进的配混聚合物的方法，使得该配混聚合物呈现较小的粘度可变性，和当在模塑或挤出操作中使用时，导致较少的注塑沉积物（“积垢”），从而产生品质较高的模塑部件并延长模具（亦即，机器）在移除该沉积物所要求的检修间的工作寿命。在常规的配混操作中，将呈固体形式的聚合物（例如，聚酰胺）原料提供到挤出机中。相反，本发明在本文中称为直接插入配混（"ILC"）的方法中，将呈熔融形式的聚酰胺原料（例如，来自连续或间歇聚合方法）直接引入到聚合物配混设备中。在例举的实施方案中，连续或间歇聚合方法邻近于该聚合物配混设备（例如挤出机），例如在1,000英尺以内，例如在相同的建筑物内，例如在500英尺以内，例如在300英尺以内，例如在200英尺以内，例如在100英尺以内，例如在50英尺以内，例如在20英尺以内。通过将聚酰胺进料引入到聚合物配混设备（其中该聚酰胺进料已经呈熔融形式）中，常用于使树脂熔化的额外挤出机机筒也可用于增加真空曝露。这一增加的真空曝露进而移除更多的杂质，并得到更清洁的产物。在聚合物配混设备（例如，挤出机）中的更多区段中施加真空所产生的额外益处在于，最终的真空区段可利用常用真空设备在较低压力下（亦即，以减少的设备成本）操作，因为大量移除了已经出现于在先区段中的杂质。

[0049] 另外，到达聚合物配混设备的连续聚合或间歇聚合熔融进料物流导致具有改进的粘度和/或水分稳定性的配混聚合物。在例举的实施方案中，待挤出的呈熔化物的聚酰胺进料借助传输管传输至挤出机需要小于1小时（例如，1至50分钟，例如1至40分钟，例如1至30分钟，例如1至20分钟，例如1至10分钟）。这一熔融物流具有低的熔化历史和热循环，因为它在用于配混操作之前并未凝固（相比之下，当聚合物进料原料以固体形式存在时）。在聚合与配混操作间减少至少一个产物加工系统可减少污染或包含杂质的概率。通过本发明也可实现产率改进和劳动成本降低。

[0050] 连续聚合方法，例如本发明所使用的那些是公知的。参见例如美国专利Nos.3,113,843；3,947,424；4,851,466；5,674,974；和Handbook of Fiber Chemistry(2007)第3版，CRC Press，第35-77页。

[0051] 间歇（也称为“釜式(clave)”或“高压釜式(autoclave)”）聚合方法也适合于在本发明中使用，例如作为熔融进料直接引入到聚合配混装置中。间歇聚合方法是公知的。参见例如美国专利Nos.4,851,466；5,245,005；和4,032,517。

[0052] 常规的注塑、挤塑、吹塑、模压成型、压缩成型和气体辅助的模塑技术通常适合于模塑配混聚酰胺。参见例如美国专利No.8,658,757；4,707,513；7,858,172；和8,192,664。

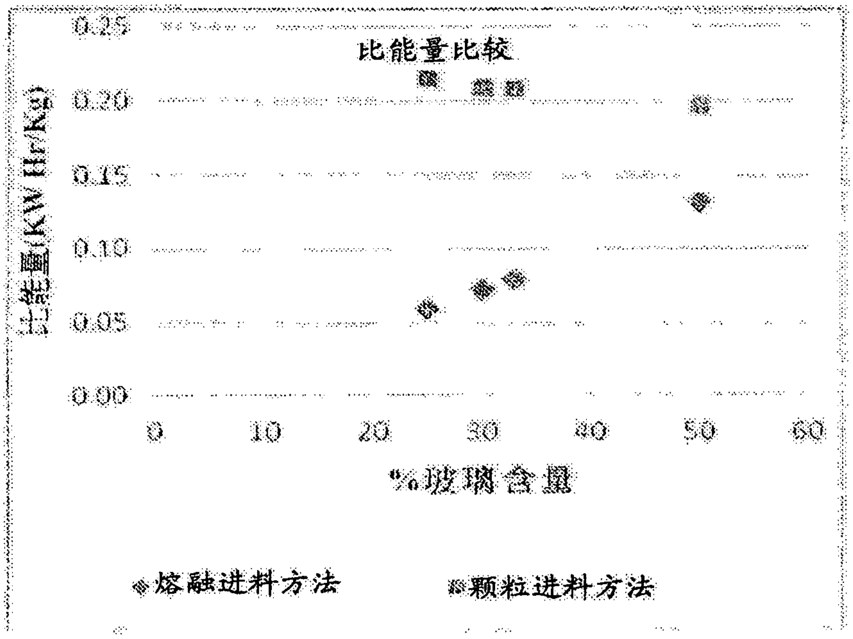
[0053] 与常规地制备的配混聚合物（其中原料以固体形式引入到聚合物配混设备中）相

比，通过ILC方法制备的配混聚合物显示出改进的模塑性能和显著更低的积垢和清洁间的更长模具寿命。这种产品的粘度和品质控制范围也比由常规的颗粒进料配混所产生的产品具有更低的可变性。与由利用固体形式的原料从常规的配混操作所制备的产品相比，这种品质方面的相应改进直接为客户提供具有改进的性能和更低成本的优越产品。

[0054] 还由于原料以熔融状态传输到聚合物配混设备，因此可降低该聚合物配混设备的马达尺寸，因为使原料熔化所需的最初能量得以避免。这种优势意味着制备配混产物期间，每磅产物的低投资成本和低的能量消耗。在其中聚酰胺PA66经配混以提供含35％玻璃纤维的产物的例举实施方案中，挤出机的马达尺寸减少了约62％。在例举的实施方案中，将熔融的聚酰胺进料物流从连续或间歇聚合方法直接引入到双螺杆挤出机的第一部分中，在引入到挤出机内之前，没有凝固处理步骤。通过将熔融进料引入到挤出机内，相对于接收并配混固体原料的挤出机，挤出机的能量消耗下降。在特别的实施方案中，已确定，为了生产33％玻璃纤维填充的尼龙，挤出机在使用熔融原料时需要0.071kw-hr/kg的比能量，与之相比，用常规的颗粒原料时所需的比能量明显更高，为0.21kw-hr/kg。这种能量上的显著差别主要可归因于使输入的固体尼龙原料最初熔化所需的能量。将熔融原料直接引入挤出机中会带来其他方面的节约，因为不会带来原料粒化，包装，储存和加工方面的累计成本。一般地，通过实施由数量上比常规技术更少的步骤组成的本发明，每磅可节省约5至约10个百分点。更低的原料工作量和更低的劳动力需求也包括在这种节约项中。在其中聚酰胺PA66被配混以提供含50％玻璃纤维的产物的例举的实施方案中，挤出机的马达尺寸减少了约35％。表1示出了例举的能量比较。

[0055] 表1

[0056]



[0057] 由于基于来自连续或间歇聚合方法的原料呈熔融状态而不再需要使提供至聚合物配混设备的固体原料的熔化步骤，因此增强了该聚合物配混设备的性能以供混合添加

剂，填料，增强剂和改性剂，从而导致例如挤出机的螺杆更具有灵活性。对于与典型的粒料进料配混挤出机相同的投资成本来说，本发明的熔融进料挤出机在生产更大量不同产物方面可实现更强的灵活性，因为可用于添加剂进料和混合的机筒数量有所增加。因此，利用本发明的熔融进料配混设备可制造数量更多且多样性更多的配混产物。

[0058] 尽管利用尼龙 66 阐述了本发明的特定实施方案，但预期其他尼龙，其他聚酰胺（例如聚（胺基十一烷酸酰胺），聚（胺基十二烷酸酰胺），聚亚己基癸二酰胺，聚（对二甲苯壬二酰胺），聚（间二甲苯壬二酰胺），和来自双（对氨基环己基）甲烷和壬二酸、癸二酸和同源脂族二羧酸的聚酰胺）等也可受益于本发明的方法。聚酰胺的共聚物也适合于本发明的方法。参见例如美国专利 Nos. 3,236,914 ;3,472,916 ;3,373,223 ;3,984,497 ;和 3,546,319。

[0059] 本发明的例举实施方案包括挤出机，熔融聚酰胺进料物流（其中熔融的进料物流从连续聚合方法进料到挤出机中），位于熔体入口下游的在该挤出机区段内的一种或多种添加剂进料，用于去除水分或杂质的一个或多个排气口，和提供真空的真空设备。在例举的实施方案中，在配混过程中通过使用夹带剂，例如氮气，氩气或二氧化碳来促进脱气。在例举的实施方案中，挤出机包括至少两个脱气（真空）区（即，至少两个排气口或入口），至少一个混合区（例如，2, 3, 4 或更多个），一个或多个计量区和任选地熔化区。

[0060] 在特定的实施方案中，在配混期间，真空系统是液环真空泵，它可在进行或不进行部分密封流体循环下使用。任选地，取决于所要求的真空水平，该真空溢流纹系统（vacuum skid system）中可包括增压压缩机。在例举的实施方案中，包括用于防止固体在排气区累积的小型反向排气式挤出机。这种排气式挤出机（也称为排气式填充机）使真空蒸汽流至下游真空设备，同时迫使任何冷凝物材料返回到挤出机中，并以足以使该材料不会因长时间曝露于高温而经历明显降解或变色的快速速率流动。

[0061] 本文中所定义的挤出机包括，但不限于，单轴或双轴或多轴螺杆挤出机，例如双轴螺杆挤出机。在例举的实施方案中，挤出机是双轴螺杆挤出机。在另一例举的实施方案中，挤出机是具有同步旋转轴的双轴螺杆挤出机。在例举的实施方案中，挤出机为排气式。在例举的实施方案中，挤出机的螺旋轴的长度直径比范围为 30:1 至 50:1，例如 32:1，例如 34:1，例如 36:1，例如 38:1，例如 40:1，例如 42:1，例如 44:1，例如 46:1，例如 48:1，以及所有范围的组合，例如 32:1 至 50:1，或 32:1 至 34:1，或 42:1 至 46:1 等。在特别的实施方案中，挤出机是 Werner&Pfleider 同步旋转的双螺杆挤出机 Model ZSK40。44:1 的长度直径比在本申请中是有效的。直径为 40mm 的 11- 机筒的挤出机代表用 PA66 熔融进料生产玻璃填充的产物的一种特定实施方案。

[0062] 在例举的实施方案中，利用范围为约 5 微米 - 约 120 微米，例如约 7 微米至约 100 微米，例如约 20 微米至约 50 微米的过滤器（例如，筛网或羊毛过滤器）来实现该熔融原料的聚合物过滤。

[0063] 待与聚合物混合 / 共混的材料包括，但不限于，玻璃纤维（例如，呈短切或粗纺形式的玻璃纤维），蜡，矿物质，碳纤维，芳族聚酰胺纤维，纤维增强材料，链终止剂，粘度改性剂，增塑剂，热稳定剂，UV 稳定剂，着色剂，催化剂，其他聚合物和抗冲改性剂，阻燃剂，去光剂，填料，抗微生物剂，抗静电剂，光学增亮剂，增量剂，加工助剂，滑石，云母，石膏，硅灰石和本领域技术人员已知的其他常用的添加剂。优选地，添加剂是抗水解的短切玻璃，

铜热稳定剂，成核剂，苯胺黑（Nigrosine）和炭黑。其他合适的添加剂可以见于 Geoffrey Pritchard 编辑的 Plastics Additives，An A-Z reference（1998）中。在例举的实施方案中，任选地添加到添加剂分散体内的稳定剂以约 0.75％至约 7.5％存在，基于分散体总重量。适合于添加剂分散体的稳定剂包括，但不限于，聚乙氧基化物（例如，聚乙氧基化烷基苯酚 Triton X-100），聚丙氧基化物，嵌段共聚聚醚，长链醇，多元醇，烷基硫酸盐，烷基磺酸盐，烷基－苯磺酸盐，烷基－磷酸盐，烷基－膦酸盐，烷基－萘磺酸盐，羧酸和全氟化物。

[0064] 合适的真空设备包括，但不限于，液环真空泵，干式真空泵和真空喷射器。优选液环真空泵。为了实现杂质的充分移除和因此获得充分的积垢模塑性能的足够低的真空，期望低于约 1013mbar 绝对压力，例如低于约 500mbar，例如低于约 300mbar，例如低于约 150mbar，例如低于约 65mba，其中下限值为约 20mbar。取决于系统泄露和真空负荷，该液环真空泵体系可辅以干式真空增压压缩机。在例举的实施方案中，在对尼龙 PA66 进行常规玻璃配混挤出时，不要求增压压缩机。

[0065] 在例举的实施方案中，将熔融聚酰胺进料物流从连续或间歇聚合方法直接引入到双螺杆挤出机的第一部分中，在引入该挤出机中前没有凝固处理步骤。通过将熔融进料引入到该挤出机中，该挤出机的能量消耗相对于接收并配混固体原料的挤出机有所减少。

[0066] 在例举的实施方案中，通过增加熔融原料曝露于聚合物配混设备的真空区而延长真空时间，实现了产物的低模具积垢的益处，从而导致更大程度的杂质移除和水分移除。通过使用熔融聚合物进料物流（例如熔融聚酰胺进料物流）而不是固体形式的聚合物，更大份额的挤出机长度或空间可用于施加真空条件而不是用于使固体原料熔化。从连续或间歇聚合方法直接进料的熔融原料物流还赋予真空系统较低的水分负载，由此进一步提高真空系统有效移除产物的水分和杂质的能力。

[0067] 在例举的实施方案中，通过消除聚合物进料树脂的粒化，储存和运输，并组合较小的配混马达，实现了配混产物的最低资本和操作成本，因为无需使该进料树脂粒化和熔化的步骤。此外，因无需储存颗粒进料贮存，原料加工劳力，计量设备，且没有高成本的树脂操作量，因此可减少成本。由于设备较少，因此可最小化总操作量和维护劳务。由于设备数量较少，因此只需要较少构件，且可靠度较高。典型地，粒化单元需要大量维护保养，构件，离线校准和高额的修理成本。还由于配混操作直接偶合熔融操作，因此要求较少的实验室样品来维持优良的工艺和产品品质控制。因与不熔化进料树脂颗粒有关的配混操作的较低能量消耗，实现了另一方面的成本减少。综合资本和操作成本优势与品质改进（例如，较低的可变性，较低的挥发物含量，较好的积垢性能）提供高度有利的商业结构。

[0068] 将受益于本文描述的直接插入方法改进的应用实例将包括通过注塑方法，型材挤塑方法，片材挤塑方法和本领域技术人员已知的其他成形方法制备的制品。这些制品可用于电气和电子应用（例如，但不限于，断路器，接线板，连接器等），汽车应用（例如，但不限于，空调系统，散热器端槽，风扇，导流罩等）和家具与电器部件。

[0069] 实施例 1：用于评估积垢性能的注塑树脂方法

[0070] 这一方法测定注塑树脂中的积垢残渣量。积垢由单体、润滑油和添加剂在注塑方法期间溢流至表面而形成。客户期望生产长度与积垢的产品品质存在关联。

[0071] 工序

[0072] 1. 将积垢工具安装在注塑机中。根据 ISO 294，构建用于这一测试的模具，其存

在以下偏差：将模具排气口变为 0.0005 英寸深和 0.125 英寸长的区域，然后使其恢复为 0.005 英寸深和 1.0 英寸长。

[0073] 2. 利用纸巾和甲醇彻底清洁整个模具表面。

[0074] a. 当表面上没有残留的残余物时，模具表面是清洁的。

[0075] 3. 根据 ISO 294，模塑 600 次注射，差异在于注射速率为 50mm/s 和模塑温度为 30℃，这些变化的目的是加速积垢沉积物的累积。

[0076] 实施例 2：测量聚丙烯擦拭物上收集的模具沉积物（积垢）的方法

[0077] 使用预清洁的非织造聚丙烯擦拭物，收集在已知数量的注射周期之后残留在注射模具表面上的积垢沉积物。在控制条件下用热甲醇从该擦拭物上移除沉积物，干燥并称重。用沉积物重量减去从清洁擦拭物中获得的背景可萃取物的重量。将这一校正的重量针对 1000 次注射归一化，并报道为 mg 可萃取积垢 /1000 次注射。

[0078] I. 制备清洁擦拭物

[0079] a. 利用锋利的剪刀将非织造聚丙烯布片剪成 3x3 英寸的正方形，以避免产生毛糙边缘。

[0080] b. 将约 20 片 3x3 英寸的擦拭物置于带有磨口玻璃塞的 500mL 锥形烧瓶中并添加 200mL 甲醇。

[0081] c. 将锥形烧瓶置于含有约 2 英寸近沸腾的水的大型结晶皿中；将锥形烧瓶和结晶皿置于设定为低热的热板上，并使甲醇温和地回流 30 分钟。

[0082] d. 倒出甲醇，换上新鲜甲醇，并另外加热 30 分钟。

[0083] e. 倒出甲醇；利用金属镊子将擦拭物置于通风橱中的清洁结晶皿中，直到擦拭物看起来干燥。

[0084] f. 通过在 90℃的烘箱内干燥 30 分钟，移除最后少量的甲醇。

[0085] g. 将每一擦拭物置于两侧已用丙酮清洁的折叠铝箔片内。

[0086] h. 将铝箔包裹的擦拭物置于塑料压锁袋中并标上清洁日期和该批次的背景可萃取物 mg（如以下所述测定）。

[0087] II. 测量清洁擦拭物的背景可萃取物（包括任何溶剂残余贡献）

[0088] a. 将所有重量记录至 0.00000g(0.00mg)。

[0089] b. 用丙酮清洁铝盘并用甲醇彻底冲洗，在 90℃烘箱中干燥，冷却并称重。

[0090] c. 用甲醇冲洗酸性消化瓶，并用金属镊子将清洁擦拭物置于其中。

[0091] d. 添加约 7mL 甲醇，盖上盖子，并振荡或涡流式混合 15 秒。

[0092] e. 将瓶子置于设定为 80℃的铝加热块中 30 分钟。

[0093] f. 利用皮革手套或其他耐热手套，将瓶子从加热块中移出，并振荡或涡流式混合 15 秒。

[0094] g. 使瓶子在流动的蒸馏水中冷却约 1 分钟，以使甲醇温度低于沸点。

[0095] h. 打开瓶子，并将甲醇倾倒至来自步骤 IIb 的已称重的铝盘中。

[0096] i. 将约 3mL 甲醇添加到瓶子中，盖上盖子，并振荡 15 秒，将其倾倒在铝盘中。

[0097] j. 将铝盘置于表面温度为 90-110℃的热板上，并蒸发掉甲醇，一旦干燥，则移除铝盘。

[0098] k. 重复步骤 IId-IIj。

[0099] l. 将铝盘置于约 90℃的空气烘箱中达 5 分钟。

[0100] m. 从烘箱中移除，在干燥器中冷却 5 分钟，并称重。

[0101] n. 重复步骤 IIl 和 IIm。若重量相差超过 0.00005g，则将铝盘置于经研磨的金属表面上达 5 分钟以排出静电，并再次称重。

[0102] o. 计算背景可萃取物，方法为：步骤 IIn 的干燥铝盘重量的平均值减去步骤 IIb 的清洁铝盘重量。

[0103] p. 核对所制备的每 40 片擦拭物中至少两片擦拭物的可萃取物，并使用这两片擦拭物的可萃取物平均值作为该批次的背景可萃取物的水平。

[0104] q. 典型的背景可萃取物水平为约 0.5mg/ 擦拭物或更小。若背景较高，则重复清洁工艺并再次测量背景。

[0105] III. 测量用过的擦拭物上的可萃取沉积物

[0106] a. 擦拭干净模具后，将擦拭物放回铝箔包覆材料和塑料袋中，并标出进行注塑周期的数（“次注射”）。

[0107] b. 对用过的擦拭物进行步骤 IIa-IIn。

[0108] c. 计算出可萃取物净值，方法为用过的擦拭物的平均可萃取物重量减去该批次的擦拭物的背景可萃取物重量。

[0109] d. 利用 IIIa 中所记下的模塑“注射量”的次数，将可萃取物净值针对 1000 次注射归一化，并将结果记录至小数点后一位，记为：“可萃取积垢量＝ x.x mg/1000 次注射”。

[0110] IV. 化学品和可消耗材料

[0111] a. 非织造聚丙烯纤维清洁布 Berkshire **Pro-Wipe®** 880 或等同物 12″x 12″。

[0112] b. Fisher Scientific HPLC 品级甲醇或等同物，其中蒸发残余物小于或等于 0.5ppm。

[0113] c. 酸性消化小瓶，其具有惰性衬里的旋合式酚醛树脂盖的硼硅酸盐玻璃；瓶子尺寸为约 19cm 长 ×1.6cm 直径，12mL 体积。

[0114] d. 铝制称量皿，约 70mm 宽 ×15mm 高，重约 2g；VWR 科学产品目录号 25433-085 或等同物。

[0115] 表 2 示出了增加熔化物曝露和真空对配混尼龙树脂的模塑性能积垢性的影响。从该结果明显看出，与常规的方法相比，本发明实现了优异的性能。根据以下运算，测定熔化物真空曝露时间：

[0116] 变量：

[0117] N ＝螺杆数量

[0118] ID ＝螺杆内径 (mm)

[0119] OD ＝螺杆外径 (mm)

[0120] F ＝真空部分的填充％

[0121] L ＝处于真空下的长度 (mm)

[0122] R ＝通过挤出机的流速 (kg/hr)

[0123] D ＝配混物的密度 (g/cm^3)

[0124] Vf ＝体积流速＝ (R*1000)/(D*3600)

[0125] C ＝总横截面面积＝ N*PI*(OD/2)^2-PI*(ID/2)^2

[0126] Cp ＝用给定聚合物填充的总横截面面积＝ C*F

[0127] Vv ＝真空部分的总体积＝ Cp*L/1000

[0128] 真空曝露时间＝ Vv/Vf（秒）

[0129] 对于这些计算来说，使用下述常数：

[0130] # 螺杆 :2

[0131] ID:70mm

[0132] OD:96mm

[0133] 密度 :1.6g/cm^3

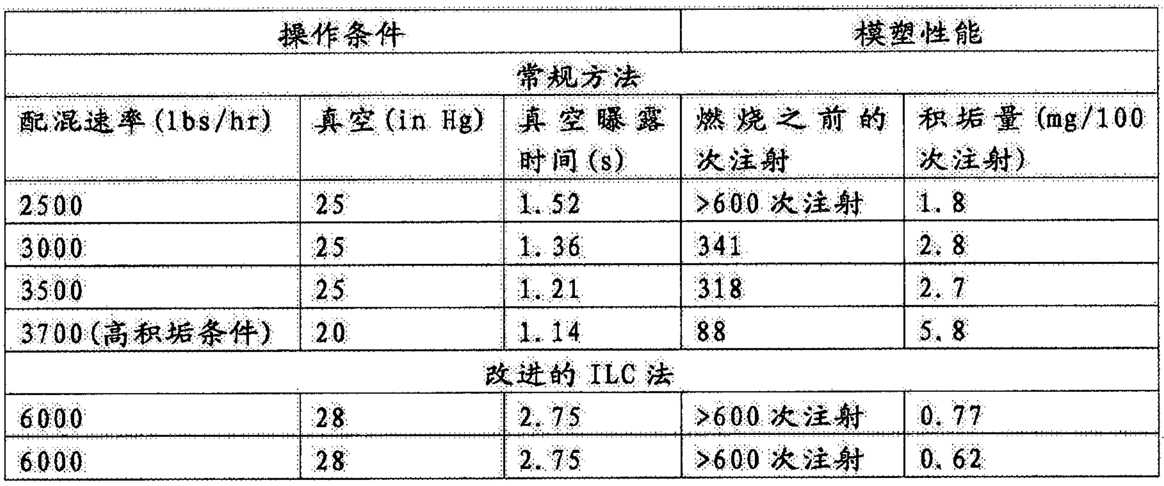
[0134] %填充 (F):25%

[0135] 处于真空下的长度 (L):768mm

[0136] 其他关于双螺杆挤出机的脱挥发性能的信息可见于例如 Chris Rauwendaal 的 Polymer Extrusion，(2001) 第 4 版，第 618-622 页。挤出机中高的表面更新和薄膜生成以低的总停留时间有效地增强脱挥发。

[0137] 表 2

[0138]



操作条件			模塑性能	
常规方法				
配混速率 (lbs/hr)	真空 (in Hg)	真空曝露时间 (s)	燃烧之前的次注射	积垢量 (mg/100 次注射)
2500	25	1.52	>600 次注射	1.8
3000	25	1.36	341	2.8
3500	25	1.21	318	2.7
3700(高积垢条件)	20	1.14	88	5.8
改进的 ILC 法				
6000	28	2.75	>600 次注射	0.77
6000	28	2.75	>600 次注射	0.62

[0139] 回顾表 2 的结果，明显看出，与其中尼龙原料以颗粒（亦即，固体）形式引入的条件（常规方法）相比，本发明得到显著改进的成型性能。例如，曝露至最小量真空时间的固体原料呈现最小数值的燃烧前注射量 (88) 和最高积垢值 (5.8)。相比之下，熔融尼龙原料 (ILC 法）的模塑性能显示在模具中无燃烧，且更显著地，与所有使用固体原料的测试相比显示出最小积垢量 (0.7 或更少）。对于客户而言，这种改进意味着显著延长设备正常运行时间，因为模具的检修较少，从而允许该设备以相同资本成本和较低操作成本生产出更多部件。产品品质也随着较少积垢量而得到改进，因为沉积物可污染产品，并给所制备的模制部件带来表面缺陷。在显示复杂或繁杂的模具排气歧管的客户模塑应用中，这一益处对改进产品品质和工艺产量或产率具有甚至更大影响。考虑到较低积垢的潜能，这些工厂的节省成本和收益可增加多达 50%或更多。在特别的实施方案中，客户典型地通过常规方式利用配混产物原料生产注塑部件，通常从周一运转至周五。然后，在两天周末期间必须安排清洁模塑设备。采用本发明的低积垢配混产物作为原料，这种模塑客户可在需要停工清洁设

备前连续运转至少两周，从而使 14 天中的生产率显著增加 2 天，增加约 15％。

[0140] 在表 3 中，对以常规方式制备的产物（标准颗粒进料结构）与以本发明的 ILC 方法制备的产物进行比较。显而易见地，积垢结果表明，直接插入熔融进料生产出实质上优于以标准颗粒进料操作获得的材料。与由颗粒进料操作制备的产品不同的是，ILC 产物具有可实现的实质上更低的积垢性能，因为使用该材料增加了客户的正常运行时间和生产率。

[0141] 表 3

[0142]

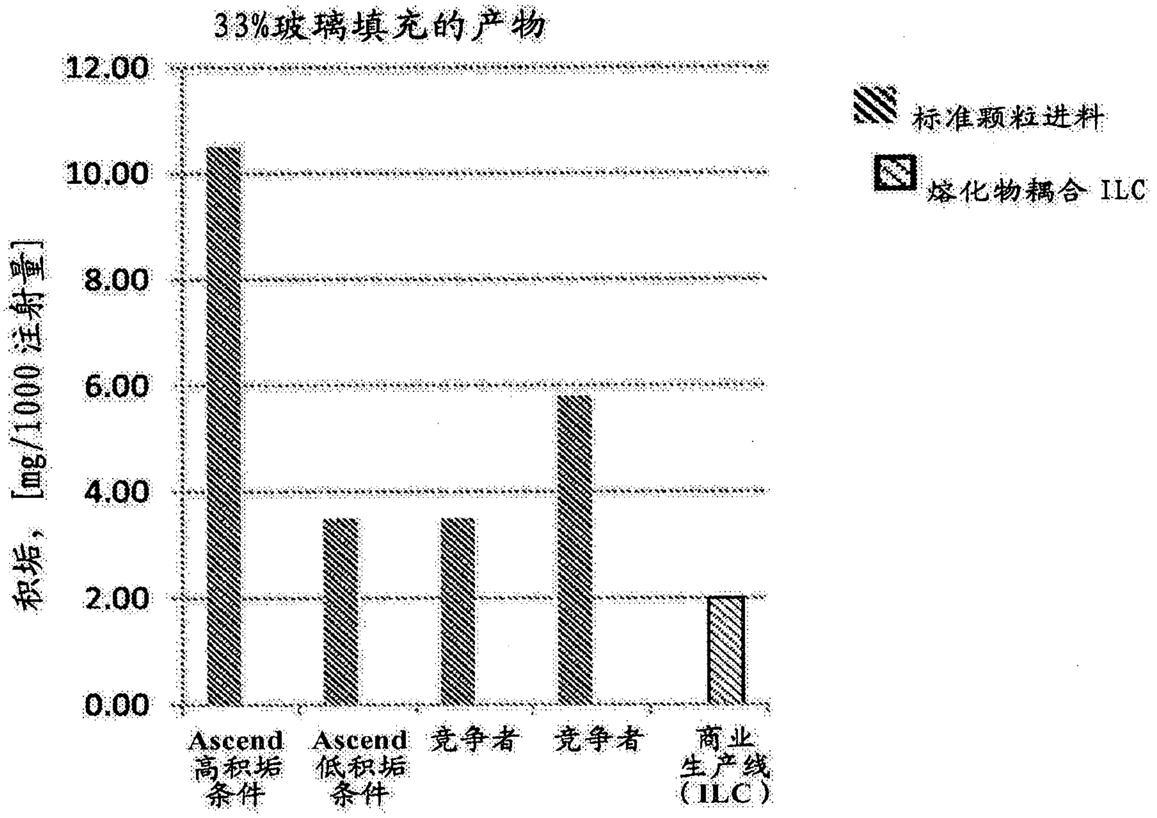
	玻璃	积垢量
来源	%FG	mg/1000 次注射
颗粒进料-高积垢条件	33	10.50
颗粒进料-低积垢条件	33	3.50
竞争者 A 尼龙产物	33	3.50
竞争者 B 尼龙产物	33	5.80
连续聚合 (ILC) 熔融进料商业生产线	33	2.00
颗粒进料标准条件	50	2.80
竞争者 A 尼龙产物	50	3.80
连续聚合 (ILC) 侧物流熔融进料试产级生产线	50	0.90
连续聚合 (ILC) 熔融进料商业生产线	50	0.90

[0143]

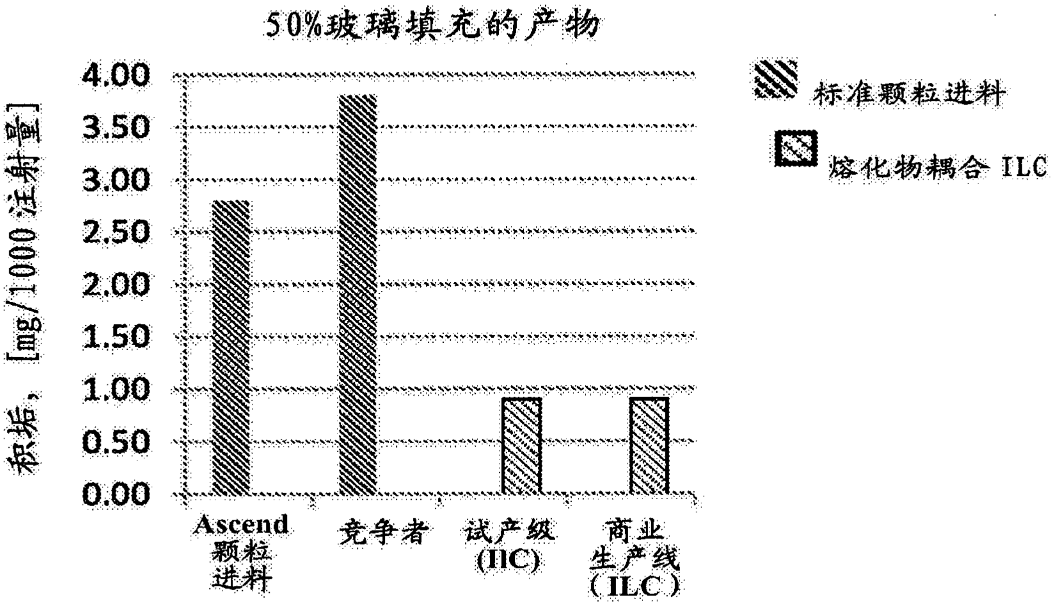
[0144] 在表 3 中，"ILC" 是指直接插入配混。竞争者 A 和 B 产物是指商业尼龙产物并被测试以显示利用本发明的 ILC 方法实现的关于积垢方面的优异性能。

[0145] 以下图表以柱状图格式显示了表 3 的数据。该图清楚地显示速率为每小时可生产 400 磅 50％玻璃产物的试产级单元与每小时可生产超过 6,000 磅 50％玻璃产物的商业规模 ILC 生产线二者中与直接熔融进料配混生产线 (ILC) 有关的显著积垢（模具排气口沉积物的量）。

[0146]



[0147]



[0148] 如本文所描述的，来自连续聚合方法的连续进料为配混提供更加稳定的原料。这种低可变性转化成配混产物的更低可变性。

[0149] 在本发明的例举实施方案中，通过本文描述的方法制备的聚酰胺的值小于约

2mg/1000 次注射，例如小于约 1.5mg/1000 次注射，例如小于约 1.0，例如小于约 0.5mg/1000 次注射，其中 0.1mg/1000 次注射被视为最小值。

[0150] 表 4 比较了典型颗粒进料配混产物和以 150kg/h 试产级操作所生产的本发明产物的粘度标准偏差。与常规的颗粒进料配混生产线不同，直接插入的熔融物经耦合配混生产线在连续聚合生产线内呈现低的可变性，没有由多种树脂来源、树脂的多种水分含量和树脂原料的多种使用期限所引起的可变性。这种一致的进料导致更低的可变性，如下文试产级生产线结果所证实的。熔融物经耦合配混可独一无二地提供测试的任何配混操作中可变性最小的产物。

[0151] 表 4

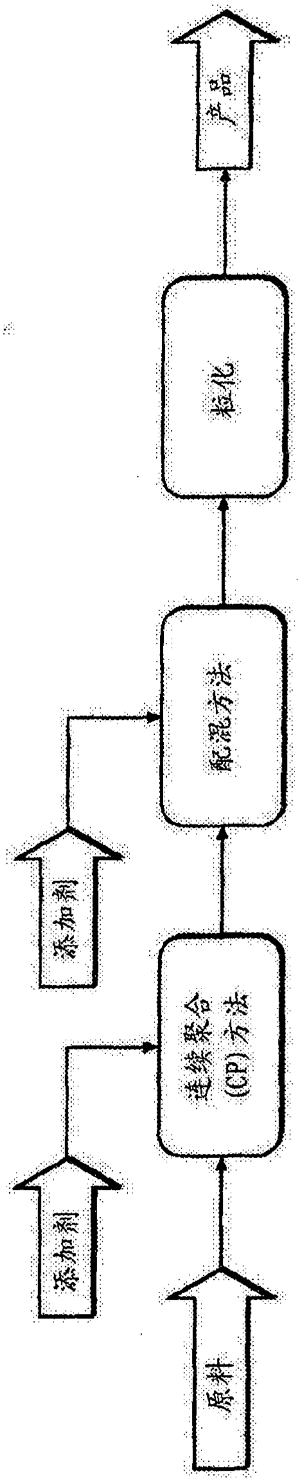
[0152]

	常规颗粒进料配混	熔融进料配混（ILC）	减少％
相对粘度的标准偏差	1.9	0.9	53％

[0153] 由于配混产物低的可变性，因此，预期客户在模塑操作中具有更好的射出一致性(shot to shot consistency)，从而导致更大的尺寸和重量稳定性，更少的翘曲和更低的不良率（亦即，更高产率）。在任何给定操作下，以注塑方法所生产的部件将具有尺寸分布，其中配混材料的粘度变化可引起分布变化。其他因素（环境条件，机器磨损等）也可引起分布变化。在任何给定操作下，以注塑方法所生产的部件将具有质量分布，其中配混材料的粘度变化可引起分布变化。其他因素（环境条件，机器磨损等）也可引起分布变化。

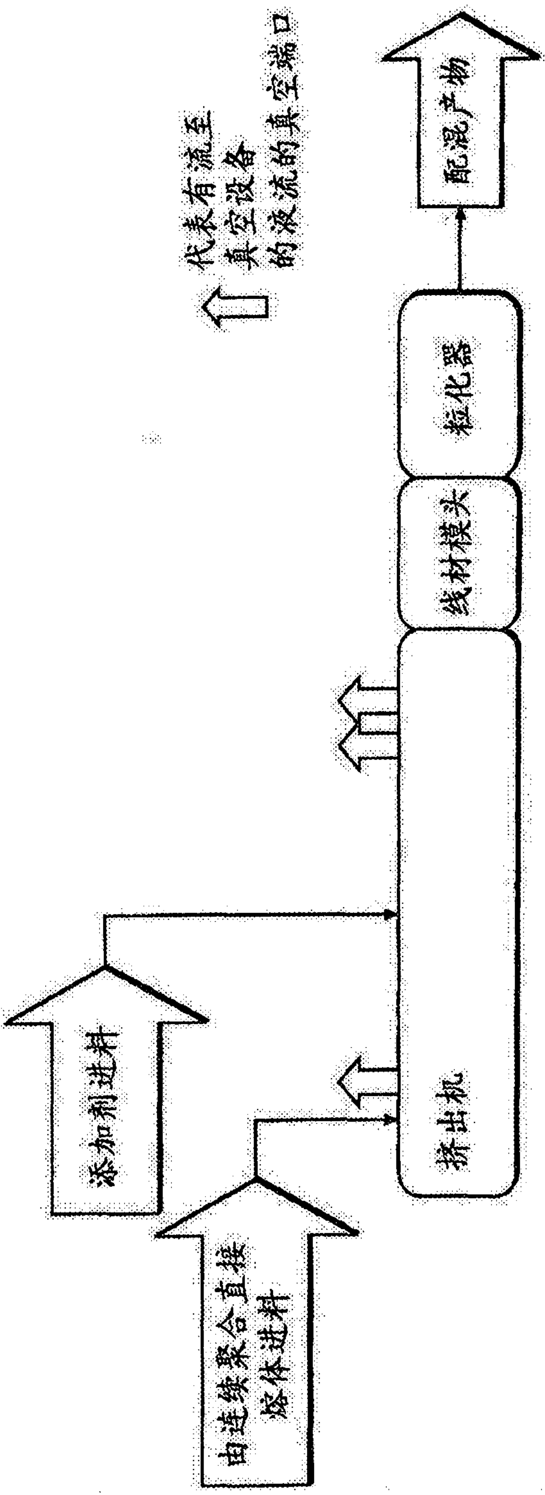
[0154] 另外，在客户的模塑方法中，预期较低可变性会导致较一致的压力和进料速率，这导致较低的不良率（亦即，较高产率）和较快循环时间，从而导致较高生产率或产量。因此，客户可以更低投资生产更多产物。还预期这种产物呈现改进的产物颜色，通常看起来没那么黄。预期这种产物还具有较高的抗张强度，这是因为较快循环时间造成较低的加热历史（例如，温度和停留时间因素）之故，较快循环时间可归因于较低进料可变性和在连续聚合与配混方法间没有熔化步骤。

[0155] 本文所引用的所有公开文献（例如专利，杂志文章，书籍）通过参考将其全文引入。除非另外指明，本发明公开内容的实施方案使用该技术领域内的化学和工程技术。文献中充分地阐明了这种技术。正如本领域技术人员所知晓的，本文描述的若干实施方案具有可容易地从其他实施方案的特征相分离或与之组合而不脱离本发明公开内容范围或精神的组分和特征。



工艺发明示意图

图 1



配混方法实例示意图

图 2

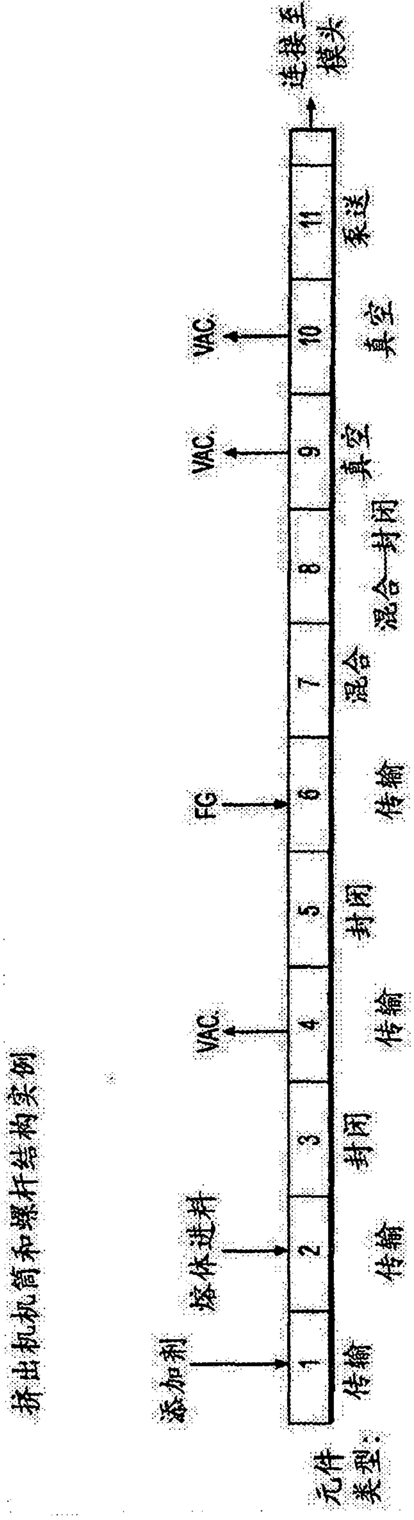

挤出机机筒和螺杆结构实例
添加剂
熔体进料
VAC.
FG
VAC.
VAC.
连接至模头
1
2
3
4
5
6
7
8
9
10
11
元件类型:
传输
传输
封闭
传输
封闭
传输
混合
混合—封闭
真空
真空
泵送

图 3