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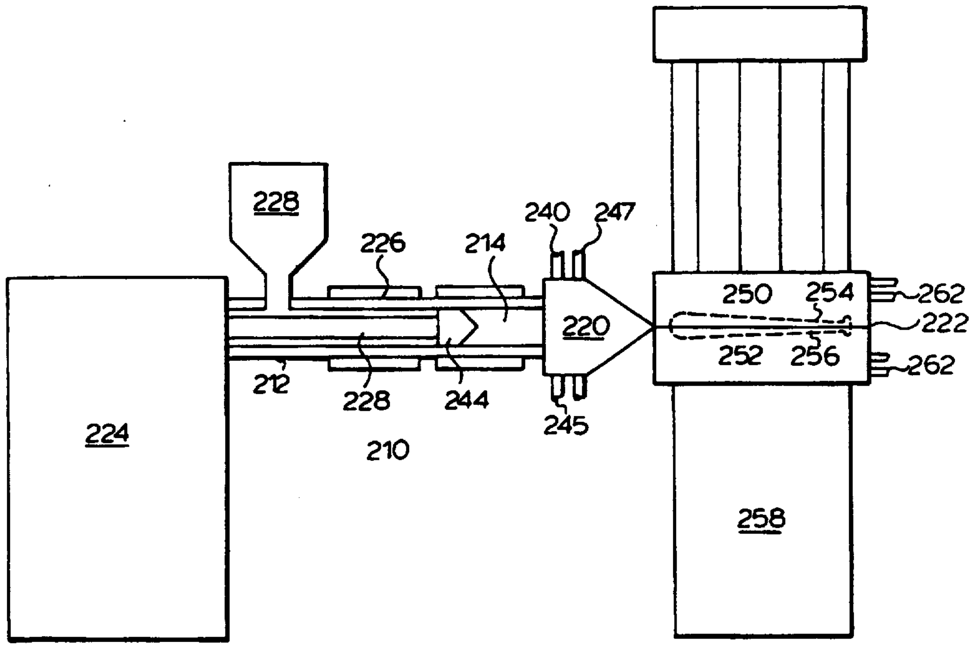
(54) Title: INJECTION MOLDING PROCESS FOR THE PRODUCTION OF ORIENTED THERMOPLASTIC AND PARTICULATE MATTER COMPOSITE ARTICLES

(57) Abstract

Improved injection molding apparatus for the manufacture of an article formed of a thermoplastics material having a melt index selected from the range 50 °C - 350 °C, comprising an article-shaping mold in communication with a melted feed means for intermittently feeding said thermoplastics material under pressure and at a temperature above said melt index in a first mold-filling and article-shaping amount to said mold; said mold having (i) cooling means within said mold for cooling said melted thermoplastics material below said melt index to form a cooled, said article; (ii) means for opening said mold to allow removal of said cooled article; (iii) means for sealably closing said mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of said melted thermoplastics material; (iv) an extrudate receiving aperture; (v) an inner surface defining an article-shaped inner cavity; the improvement wherein said melted feed means comprises (a) a converging die having a converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produce an extrudate for said mold, and (b) means to control the temperature of said method thermoplastics material or close to said melt index in said converging die. The articles are formed of oriented thermoplastics materials which may further comprise an oriented particulate material and may be hollow, foamed or unfoamed. The articles have strength, modulus and density values comparable to typical hardwoods or softwoods.



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INJECTION MOLDING PROCESS FOR THE PRODUCTION OF ORIENTED THERMOPLASTIC AND PARTICULATE MATTER COMPOSITE ARTICLES

FIELD OF THE INVENTION

This invention relates to articles formed of thermoplastic materials and composites thereof such as fiber or flake reinforced thermoplastic composite materials and their manufacture by injection molding processes. In particular, it relates to articles formed of cellulose fiber reinforced thermoplastic compositions and, more particularly, to foam compositions which have strength, modulus and density values comparable to typical hardwoods or softwoods; and injection molding processes for their manufacture.

BACKGROUND TO THE INVENTION

United States Patent Nos. 5234652, 5399308 and 5474722 to Woodhams, issued August 10, 1993, March 21, 1995 and December 12, 1995, respectively, describes processes for the melt phase extrusion of high molecular weight polyethylenes and composites to produce extrudates having substantially both an increased modulus and increased strength in the flow direction. In the process described therein, the high molecular weight plastic material, at or near its melt temperature, is forced through a die having a converging passage so as to produce a highly oriented extrudate. The plastic material at the die interface is in substantially extensional flow through the converging die passage.

The invention described in United States Patent No. 5,234,652 is based upon the proposition that polymer chains, when fully extended and oriented in parallel fashion, confer greatly increased strength and modulus to the resulting oriented extrudate. Although this concept has been extensively applied to fibers and films, attempts to apply this concept to thicker sections have been limited by the natural tendency of polymer chains to quickly recover their unstretched equilibrium conformations at elevated temperatures. This strain recovery often manifests itself in a phenomenon called die swell, in which the molten extrudate elastically retracts and expands as it exits the heated die. In United States Patent No. 5,234,652, a process is described wherein a polymer is extruded in the semi-solid state, viz. melt phase extrusion under conditions that forcibly extrude and extend the flexible polymer chains in the flow direction and retain such imparted orientation in the extrudate. In the three above cited patents, thermoplastics or their composites are purposely extruded at reduced temperatures, near their softening points, under conditions that forcibly extend and orient the plastic mass so that the flexible polymer chains contained therein are at least partially uncoiled and aligned in the flow direction, and then the extruded profile rapidly quenched in order to permanently retain such imparted orientation. Under such melt state extrusion conditions at low extrusion temperatures, sufficiently high molecular weight and plug flow, the molecular relaxation times are sufficiently long that product orientation is largely retained during and after cooling to ambient temperatures. High molecular weight polyethylenes were identified as particularly suitable for this process. When the thermoplastic contains fibrous or flake type fillers, the orientation process also aligns such anisotropic fillers in the flow direction, adding significantly to the mechanical properties in the flow direction. Cellulosic fillers, such as wood fibers, were found to be particularly effective in this process for the purpose of making artificial wood substitutes. The process of flow orientation in a lubricated convergent die was extended to integral structural foams, wherein the skin was highly oriented in the flow direction to impart increased bending strength and increased flexural stiffness comparable to wood at substantially the same overall density.

Various extrusion processes are known for the continuous production of integral structural foam products. Of particular relevance is United States patent Nos. 3,764,642 - P.E. Boutillier, issued October 9, 1973. These processes use the so-called "Celuka die" and provide a high-density, rigid skin extruded product of desired size having an inner foamed core.

Whereas hydrostatic extrusion of polymers has been known for some time (N. Inoue, M. Nishihara, HYDROSTATIC EXTRUSION, Theory and Applications, Section 4, Polymers, Elsevier Applied Science Publishers, pp. 333-362, 1985) the process is normally restricted to ram extrusion which entails deformation of a billet under conditions similar to the hydrostatic extrusion of metals. The prior art with respect to extrusion dies is extensive, as will be understood from the published text by W. Michaeli (EXTRUSION DIES, Design and Engineering Computations, Hanser Publishers, 1984). However, the precise conditions for achieving steady smooth extrusion of highly oriented polymers without melt fracture or die swell are not generally known by those in the extrusion industry.

Aforesaid USP 5474722 describes a process for the continuous production of a high modulus article comprising a composite of an oriented plastic material and an oriented particulate material, said process including the steps of: (a) continuously forcing an orientable plastics material, while it is close to or at its softening temperature and in admixture with an orientable particulate material, through a lubricated converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow, thereby to produce an extrudate; (b) deforming the extrudate, while it is maintained at or close to its melt temperature, to produce an oriented, deformed extrudate; and (c) cooling the deformed extrudate to preserve the orientation and provide said composite. The integral structural foam articles so produced have strength, modulus and density values comparable to typical hardwoods or softwoods.

However, such an extrusion process does not readily lend itself to the manufacture of non-uniformally shaped articles such as baseball bats, tennis rackets and the like which cannot be made by continuous extrusion processes wherein the thermoplastics composite material is maintained under tension. There is a need therefore for a comparable manufacturing process whereby irregularly shaped articles can be formed of a highly oriented thermoplastic material.

Injection molding processes are known for the manufacture of thermoplastic articles wherein a molten thermoplastic material is injected under pressure into a suitably-shaped mold, the material cooled and the cooled thermoplastic article removed after the short cooling period. In contrast to extrusion molding which is carried out under continuous, steady state conditions, injection molding is intermittent and discontinuous. Further, the physical size dimensions of an extrudate section are generally constant and uniform whereas injection molding allows of significant dimensional variations in the three dimensional shape of the molded article.

Due to the shortage of high quality hardwood lumber and escalating prices of certain types of hardwood species, there have been attempts to manufacture furniture components and baseball bats having the performance characteristics, physical properties, and aesthetic quality of traditional hardwood furniture and bats derived from ash, oak, maple or hickory and the like. Today, it is possible to purchase hollow aluminum bats but these have not yet met with favour in professional sports. Hence there is a desire to find a substitute material for hardwood that would duplicate the desirable features of a hardwood bat. These desired material characteristics include a density of hardwood near 0.64 g/cm^3, a modulus of elasticity near 12 GPa, a flexural strength of 100 MPa and possess a substantial impact resistance in order to resist fracture in repeated use over a prolonged period of time under adverse conditions of weather and abuse. The obvious solution is to simply mold a hollow bat from any one of several reinforced engineering plastic materials. However an examination of the technical literature reveals that there are few compounds having modulus values greater than 10 GPa even when reinforced with expensive graphite fibers. Moreover these molded composites tend to be brittle and easily fracture on impact. Therefore there has been no cost effective solution to the problem of designing a bat having hardwood-like properties.

The solution to this problem requires a substantial increase in strength, modulus and impact resistance of a thermoplastic resin while at the same time reducing the effective density to that of wood. I have discovered that under certain conditions of temperature and pressure, ordinary thermoplastics may be elongated and deformed to produce highly oriented structures having substantially improved mechanical properties. Furthermore, I have devised a means for providing flow orientation to produce elongate objects by a modified injection molding process by injection molding thermoplastics and wood fiber composites under conditions that simultaneously orient the wood fibers and also the polymeric chains comprising the binder matrix to effect the necessary increase in strength and stiffness. Furthermore, the oriented structure resists impact and is exceptionally tough due to the longitudinal orientation of the entire composite structure. To meet the density requirement, the composite is made hollow or internally foamed while retaining the orientation in the outer surface. By these methods, the color, texture, weight, density, appearance and feel of the molded composite closely resembles that of hardwood. Using an automated injection molding process as herein described, wood substitutes may be employed for the economic manufacture of hardwood baseball bats and other like wood articles such as furniture components (e.g. table legs). Using an automated injection molding process as herein described, thermoplastics can be injected under conditions that provide linear orientation in the special case of elongate objects, such as hardwood baseball bats and furniture components. Furthermore, the lubrication device attached thereto has been found most useful for injection molding in general, since it reduces surface friction in the nozzle and injection flow passages. This permits facile flow of the melt into the mold cavity. Thus, less energy is required to inject the plastic melt and complete mold filling takes place with less injection pressure. The lubricant also aids part removal and imparts a smooth, glossy surface to the molded article. The same benefits also apply to extrusion, wherein the lubrication injection device provides reduced friction in the die and facilitates faster extrusions without melt fracture. In the example of a baseball bat the die is designed to yield a composite having a solid section in the grip region where the greatest stress occurs. In the thicker outer section of the bat, the core is either hollow or foamed (according to preference) to maintain the overall density limitation. The solid oriented outer skin is sufficiently tough to resist normal abrasive wear and impact, so that the bat should possess extreme durability unlike wood, which has a tendency to split, the surface is easily damaged, and wood is affected by moisture and humidity. If desired the surface of the bat may be texturized or decorated according to methods known in the industry.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for the manufacture of thermoplastic articles by injection molding wherein the thermoplastic melt is lubricated at or near the mold entry region in order to reduce surface friction and increase the flow rate of the resin.

It is a further object to provide lubricated melt flow during injection so that the injection pressure is reduced.

It is a further object to provide lubricated flow under conditions of high viscosity so that complete mode filling can be achieved without excessive injection pressures being required.

It is a further object to provide melt lubrication in the nozzle region for the purpose of reducing viscous energy dissipation and thermal overheating of the resin.

It is a further object to provide lubricants containing additives for the purpose of surface modification of the molded article.

It is a further object of the invention to provide a lubricated converging passage that promotes elastic deformation by flow orientation of the melt as it enters the mold cavity, the said elastic deformation being permanently retained in the molded product after cooling.

It is a further object to provide in-line lubrication for extrusion processes wherein polymer melt friction is specifically reduced in the nozzle zone by lubricant injection.

It is a further object of the present invention to provide a process for the manufacture of an oriented thermoplastic article by injection molding.

It is a further object of the present invention to provide a process for the manufacture of an oriented thermoplastic composite article by injection molding.

It is a further object to provide aforesaid oriented composite articles made by injection molding.

A novel feature of the method is a means for in-line lubrication of the melt which enables flow orientation and retention of elastic deformation of the thermoplastic melt or composites thereof, after passage through a convergent zone.

We have found that in-line lubrication is of value for injection molding processes since it provides greater ease of injection combined with more favourable economical use of lubricant additives. In-line lubrication as herein described is also of advantage in extrusion processes.

Accordingly, in one aspect the invention provides an injection molding apparatus for the manufacture of an article formed of a thermoplastic material chosen from a broad Melt Flow Index range from 0.1 to 60 g/10 min (according the ASTM D1238), comprising an article-shaping mold in communication with a melted feed means for intermittently feeding said heated molten thermoplastic material under pressure in a first mold filling and article shaping amount to said mold; said injection molding machine having

i. lubricant injecting means for injecting a controlled amount of lubricant into the flow passage near the end of the injection barrel near the nozzle;

ii. streamline nozzle means to maximize flow rate and/or orientation;

iii. cooling means for cooling the nozzle and flow passages to control flow orientation;

iv. cooling means within said mold for cooling said heated plastic material to form a cooled, said article;

v. means for opening said mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of said heated thermoplastic material;

vi. an extrudate receiving aperture;

vii. an inner surface defining an article-shaping cavity; the improvement wherein said melted feed means comprises

a. a means for injecting lubricant directly into the flow passage following the melt plastification stage;

b. a lubricated converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produces an oriented extrudate for said mold; and

c. means to control the pre-form temperature of said thermoplastic material prior to flow orientation in said converging passage.

In a further aspect the invention provides an improved injection molding apparatus for the manufacture of an article formed of a thermoplastics material having a melt index at a suitable temperature selected from the range 0.1 to 60 dg/min, comprising an article-shaping mold in communication with a melted feed means for intermittently feeding said thermoplastics material under pressure and in a first mold-filling and article-shaping amount to said mold; said mold having (i) cooling means within said mold for cooling said melted thermoplastic material to form a cooled, said article; (ii) means for opening said mold to allow removal of said cooled article; (iii) means for sealably closing said mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of said melted thermoplastics material; (iv) an extrudate receiving aperture; (v) an inner surface defining an article-shaped inner cavity; the improvement wherein said melted feed means comprises (a) a die having a converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produces an extrudate for said mold, and (b) means to control the preform temperature of said thermoplastics material prior to passage into said converging die.

In yet a further aspect the invention provides an improved injection molding apparatus for the manufacture of thermoplastic materials comprising a means for selectively lubricating the molten thermoplastic near the nozzle entry region in order to reduce surface friction and promote slippage at the melt interface, thereby reducing the injection pressure and energy required to fill the mold cavity. The lubricating device comprises a reciprocating metering pump synchronized to the injection cycle of the molding machine that injects a known quantity of lubricant into the nozzle region on each return cycle. A non-return valve is situated to prevent the ingress of molten plastic into lubricant feed lines during the injection cycle. A heated lubricant reservoir is provided so that virtually all solid or liquid lubricant types may be employed in the system according to preference. In one application the melt is precooled near its softening temperture and extruded through an oversize convergent valve-gated nozzle equipped with a streamline valve stem in order to promote elastic or plastic deformation of the injected melt, whereby oriented articles may be produced. An oversize nozzle is preferrably employed since the injected slug is semi-solid (as in the case of jetting) and the formed slug is allowed to advance into the mold cavity by essentially plug flow. Use of the apparatus according to the invention in one aspect is applied to composite materials such as resins containing fibrous cellulose particles wherein both the fibers and the polymeric matrix are simultaneously aligned in the direction of flow to produce parallel orientation of the fibers in a partially oriented matrix. The properties of the highly oriented composite are further enhanced by the elastic deformation step which also aligns the polymer chains in the flow direction and thereby contributes to significantly increased mechanical properties. In another variation of the molding process, the injected melt, cooled to the elastic condition, is forcibly extended inside a convergent mold cavity and quickly chilled to form a highly oriented solid structure. The method of in-line lubrication may be also applied to foam injection molding or assisted gas injection molding to produce integral structural foams or hollow articles respectively, having substantially the same mechanical properties and overall densities as that of hardwoods or softwoods. Without in-line lubrication the pressures for achieving such dual orientation would be excessive and dual orientation would not be achievable. In-line lubrication as described is applicable to all thermoplastics and composites thereof, thereby improving the efficiency of injection molding in general. In-line lubrication according to the invention in a further aspect is applicable to extrusion processes, wherein the die is selectively lubricated by continuous injection of an appropriate lubricant.

When heated above their softening points molded oriented products according to the invention will spontaneously retract to their equilibrium states. By such means the degree of orientation can be easily ascertained. The present invention embraces products having greater than a 2-fold orientation, i.e. original oriented length divided by heat relaxed length. By such means the degree or extent of molecular orientation may be readily observed.

I have found that certain thermoplastic materials containing reinforcing fillers, the latter being substantially in flake or fibrous form, when injection molded under conditions that promote molecular orientation as well as particulate orientation, produce articles having greatly increased strength and modulus, rivalling the structural performance of softwoods and hardwoods. These injection molding processes include the step of orienting both the thermoplastic polymeric chains comprising the matrix and the dispersed particulate material, in the longitudinal flow direction, and which solidifies the molded article in that preferred orientation, while substantially preventing relaxation of the polymeric chains during the subsequent rapid cooling period in the mold to ambient temperatures.

Flow orientation of the thermoplastic elastic melt deforms the equilibrium conformations of the chain molecules in the converging die and imparts a preferential orientation of the chain segments in the flow direction. Such chain orientation increases the strength and modulus of the solid oriented structure in the direction of orientation. The term "orientable particulate" applies to anisotropic particles in which one dimension is much larger than another and which may be substantially oriented in one direction - parallel or planar arrangement. Such overlapping particles, typified by flakes and fibers, and embedded in a polymeric matrix are, thus, normally considered "reinforcing fillers".

The observed mechanical properties are a result of additive, or synergistic effects of these two mechanisms of reinforcement. The theory of such filler reinforcement is well understood in practice (short glass fibers, asbestos, mica, talc, wollastonite, wood fibers).

By the term "orientable particulate material" is meant material in the form of fibres, flakes and the like, which can substantially orient in parallel or planar arrangement as hereinbefore described. Preferably, the orientable particulate material is derived from a cellulosic material.

By the term "softening temperature" is meant that temperature near the melting point of a crystalline type polymer, or in the case of an amorphous polymer, the temperature near the glass transition temperature where there is an abrupt change in viscosity.

Thus, in a preferred aspect the invention provides a process of making by injection molding an article formed of a high strength and high modulus cellulosic-thermoplastic composite, which process comprises:

intimately admixing shredded cellulosic fibers or cellulosic particles with a thermoplastic polymeric material which has a softening point below about 220°C;

passing the mixture through a die having a converging passage and of which the cross-sectional area diminishes in the forward direction of plastic flow; forcing the molten mass through the converging die passage under conditions that impart longitudinal orientation to both the cellulosic particles and the thermoplastic polymer molecules in the direction of flow to produce an elongated segment;

feeding a said article-forming amount of said elongated segment to a mold having cooling means, while rapidly cooling said oriented segment to preserve said orientation and provide a cooled solidified article.

The invention preferably provides a process as hereinabove defined in which the converging passage is provided in a streamline die which converging passage has a geometry which provides a constant or decreasing strain rate of the elastic melt in the flow direction.

In a more preferred aspect, the invention provides a process for the batchwise production by injection molding of an integral structural foam composite article of a plastic composite material comprising a solid oriented skin said process including the steps of

intimately admixing suitably orientable particulate material with a thermoplastic material which thermoplastic has a softening point below about 220°C;

forcing the admixture through a converging die by injection pressure at a temperature near the softening point of the thermoplastic material, so as to impart predominantly longitudinal orientation to both the particulate material and the thermoplastic polymer chains throughout the extruded segment;

feeding a said article-forming amount of the oriented melted extrudate to a mold having cooling means and under conditions which permit foaming to take place in the core of the melt extrudate while rapidly cooling the article and maintaining a highly oriented, essentially solid outer skin on its surface.

The mean density of the product is most easily controlled by the use of a foaming agent in which the preferred orientation of the solid outer skin is maintained. Preferably the admixture is passed through a lubricated die which has been lubricated adjacent thereto so as to provide substantially elongational flow (slippage). The lubricating agent may be provided also in admixture with the thermoplastic-particulate feed materials.

In a preferred embodiment, the particulate material is a cellulosic material obtained by the grinding, coating and fiberizing of suitable cellulosic fillers derived from wood, paper or agricultural residues.

The combined influence of fiber orientation and polymer matrix orientation greatly increases the resultant strength and modulus in the direction of flow so that the integral foam having a highly oriented skin compares favourably with the mechanical properties of wood. The average density of the injection molded composite may be readily adjusted by controlled foam expansion. In the case of "damp" cellulosic material, the moisture content of the wood filler can act as the "blowing agent". The endothermic cooling action of the water during vaporization and expansion helps to reduce the interior temperature of the molded article in thicker sections, thereby reducing the external cooling requirements. The cooled article is characterized by a solid skin and a finely textured foam core wherein the overall density is determined by the density of the core and the thickness of the outer skin. Thus, the final product density may be controlled within certain limits to that of various wood species. The maximum die head pressures reached are generally 145 MPa (21,000 psig) and permit cycle times of 30 seconds using a conventional reciprocating single screw injection molding machine.

In conventional extrusion processes it is common practise to minimize elastic deformations which cause die swell. One purpose of the present invention is to maximize elastic deformations during passage through the converging die and permanently retain such deformations in the mold by rapid quenching. This is achieved by deforming the melt near its softening point where the relaxation times of the polymer chains are sufficiently long to permit mold cooling before substantial elastic recovery is able to take place. Using conventional reciprocating screw injection molding methods, for example, the injection pressure could be very large, perhaps excessive, at such low temperatures near the softening point of the mixture where the viscosity is also very large. Accordingly it has been found necessary to employ die lubrication to facilitate the injection process, and allow the use of reduced injection pressures and temperatures, at least within the limit of conventional operating conditions. The injection of a lubricant adjacent to the converging die reduces surface friction at the metal interface so that an increased flow rate is favoured, with the result that the process can be operated at much lower temperatures and pressures. Injection molding at reduced temperatures is essential for preserving the orientation after passage through the converging die. After startup, the melt temperature is gradually reduced until the preferred temperature profile is attained. "Solid state" injection conditions are approached gradually to avoid excessive pressures during startup.

The cellulosic component may be derived from any number of available sources such as ground wood, sawdust, wood flour, ground newsprint, magazines, books, cardboard, wood pulps (mechanical, stone ground, chemical, mechanical-chemical, bleached or unbleached, sludge, waste fines), laminated foils and various agricultural wastes (rice hulls, wheat, oat, barley and oat chaff, coconut shells, peanut shells, walnut shells, straw, corn husks, corn stalks, jute, hemp, bagasse, bamboo). The resin component may comprise virgin or recycled (waste) thermoplastics derived from the polyolefin family (polyethylenes, polypropylenes and copolymers thereof), vinyls (chiefly copolymers of vinyl chloride), and styrenics (including ABS and maleic anhydride copolymers thereof) and in some cases, mixtures of such polymers. Since wood, or cellulosic, fibres tend to decompose at temperatures above 220°C, resins which must be processed above this limiting temperature are generally excluded. Thus, a majority of the so-called engineering resins may not be employed in the process of the invention when cellulosic fibres are present, since their softening temperatures are too high and would require processing temperatures greater than the cellulose decomposition temperature of 220°C. However, when inorganic fillers are present, there need be no temperature limitation. The process of the invention is of less value with thermosetting resins such as phenolics, urea-formaldehyde resins, polyesters and epoxy resins, since these liquid resins are normally processed in a different manner.

Preferably, the plastic material is one of the four classes comprising the polyethylenes, polypropylenes, vinyls and polystyrenes. Typically, the viscosities of these resins are characterized by the melt flow index, or simply the melt index (MI). Injection grade resins typically posses melt index values between 1 and 20 dg/min or g/10 min. After mixing with a cellulosic filler the melt index may be substantially below 1 dg/min which would be difficult to process by conventional injection molding means. Accordingly the use of die lubrication to facilitate flow and maintain the peak injection pressure within practical limits becomes necessary. Moreover, the application of extreme pressures can induce unfavourable changes in the plastic flow properties of the thermoplastic resin leading to embrittlement, scorching and increased resistance to plastic deformation during injection.

In order to utilize waste paper, newsprint, cardboard materials and the like, it is necessary to first shred the paper and then pass it through a hammer mill to open and at least partially fiberize the shredded paper according to end use. Wood waste may be passed through a hog mill before subjecting it to fine grinding with a hammer mill, Wiley Mill or Szego Mill. Minor contaminants such as sizing, paper additives, inorganic fillers, adhesives, paper glazes, wax coatings, pigments, food residues, and inks are normally tolerated without appreciable detriment to the extruded composite. However, the tolerance of such impurities or contaminants is largely determined by the intended application. Polar waxes, such as maleated polyolefins or fatty acids, may be advantageously employed during grinding to aid the grinding process and provide a pretreated fibrous material which is rendered hydrophobic, densified and made free-flowing for use in gravity fed machinery. The surface treatment of the cellulosic fillers during grinding eliminates fine dust which can cause explosive mixtures with air or health hazards due to inhalation. The wax pretreatment not only renders the wood fibres hydrophobic, but also facilitates subsequent dispersion in thermoplastic resins whenever conventional single or twin screw compounding machines are employed. The wax coating on the fibers becomes liquid at elevated temperatures and accelerates the release and dispersion of fibers into the molten thermoplastic matrix. Thus less mixing energy is required to achieve a satisfactory dispersion.

A weighed quantity of the cellulosic filler, thus fiberized and surface treated, is admixed with an appropriate resin and subjected to intensive mixing in a thermokinetic mixer such as a Gelimat (Werner and Pfleiderer Inc.) or K-Mixer (Synergistics Group Inc.) or Henschel Mixer. The intensive mixing not only separates the loosely bonded wood fibres from each other, but further disintegrates the individual wood fibres into much smaller wood fragments, with some wood fibres being reduced to a tenth of their original size. Despite this aggressive action, the resulting cellulosic fragments impart high strength and stiffness to the composite. Tests have shown that these composites may be reground and remolded numerous times (about 20) without significant loss of their mechanical properties. This remarkable durability is attributed to the extraordinary toughness of the cellulosic fragments which resist further breakage during reprocessing. It is usually necessary to employ dispersing agents or coupling agents in order to effectively mix wood or paper fibres with the thermoplastic resin, particularly with non-polar polyolefin resins, such as polyethylene and polypropylene which do not spontaneously wet cellulosic surfaces. In such cases, it has been found advantageous to add certain polar polymers or waxes such as carboxylic polyolefins, maleated polyolefins, or fatty acids. These additives can have a profound effect on the mechanical properties of the resulting composites in some cases. They may be added during the grinding and fiberization stage as described above or simply added to the resin mixture prior to intensive mixing according to preference. Pretreatment of the cellulosic fibres during the grinding stage is particularly desirable in order to increase the bulk density of the fibrous filler and provide a reinforcing filler which is acceptable for use in other types of compounders such as twin screw mixers, single screw mixers and Banburys. Various other additives may be incorporated during the compounding stage such as antioxidants, ultraviolet stabilizers, lubricants, fire retardants, pigments, blowing agents, or crosslinking agents.

The wood fibre concentration may be varied but the mixture becomes more difficult to injection mold at concentrations of wood fiber greater than about 80% by weight. In order to maximize the orientation of the wood fibres, the die preferably employs a converging flow with surface lubrication. The lubrication helps to promote extensional flow and slippage of the molten extrudate (as opposed to conventional shear flow) so that all the wood fibres throughout the cross section are preferentially oriented in the direction of extrusion, i.e. the flow orientation imparts a parallel wood-like grain throughout. This uniform parallel orientation maximizes the strength and stiffness in the longitudinal direction.

Preferential orientation of the wood fibres partially contributes to the strength and stiffness of the composite. Added stiffness and strength is imparted by passage through the converging nozzle of the composite under conditions that extend and orient the polymer chains (or crystalline fibrils) such that the molecular orientation is, subsequently, "frozen in" by the rapid cooling in the mold before the melted composite has an opportunity to relax. The orientation is conducted near the softening point of the resin (whether crystalline or amorphous) such that the relaxation times of the polymer chains are very long ie. it requires a long time to recover equilibrium chain conformations after elastic deformation in the converging die region, relative to the total time of cooling in the mold. Consequently, the lowest practical extrusion temperature is, preferably, elected in order to prolong polymer relaxation times, thereby preserving most of the orientation imparted by the converging nozzle in the finished product. To minimize the applied pressure and promote extensional flow in the die zone, surface lubrication is employed. Suitable lubricants include silicone oils (Dow Corning Inc.), liquid paraffins, ACuflow (Allied-Signal Inc.), glycerine, castor oil, fatty amides and titanates (Kenrich Chemical Co.).

In in-line lubrication of injection and extrusion processes, any substance that can reduce friction is a lubricant but in instant application the choice of lubricant is restricted by practical considerations, such as toxicity, volatility, solubility, and corrosiveness. Lubricants may be gaseous, liquid, plastic or solid. Solid lubricants are often combined with liquid lubricants for greater efficiencies. Preferably, the lubricant is in liquid form so that it can be metered by pumps into the barrel near the injection port (or in the case of extrusion, upstream of the die section). Solid lubricants may be pre-melted prior to injection by the use of a heated reservoir or other melting device. The lubricant may comprise one or more compounds in order to effect maximum reduction of friction at the melt interface, in which one component of the lubricant may be surface active i.e. contain a polar moiety, or even react chemically with the metal surfaces of the nozzle, flow passages or nozzle cavities.

Liquid lubricants include mineral oils (from petroleum), fixed oils (eg. glycerides, animal fats, vegetable oils, fish oils), and synthetic fluids (eg. silicones, silicate esters, polyglycols, dibasic acid esters, fluoro compounds, chlorofluorocarbon polymers, neopentyl polyol esters, polyphenyl ethers). Plastic lubricants include greases (eg. soap thickened oils, silicone greases). Gaseous lubricants include air, nitrogen, helium, hydrogen, carbon dioxide and water vapour. Solid lubricants include waxes, organic salts, esters, organophosphorus compounds, graphite, molybdenum disulfide, metallic phosphates, metallic stearates, metallic oleates, metallic naphenates, and certain polymers (eg. Teflon). These may be suspended or dissolved in liquid lubricants. Gases may also be mixed with liquid lubricants to produce a stable lubricating foam.

A lubricant mixture may comprise a solid lubricant such as a Teflon oligomer (PTFE) in a volatile carrier. It will be apparent to those in the art that certain other soluble or colloidal materials may be injected with the lubricant in order to apply various surface modifiers, such as paint primers, antioxidants, UV stabilizers, dyes, colorants, pigments, antimicrobials, crosslinking agents, plasticizers, mold release agents, flame retardants, or mixtures thereof, onto the surface of the molded part. By such means, additives can be preferentially applied to the molded surface where they are most effective.

A principle requirement of the lubricant is that it be insoluble in the molten polymer which is being injected. Polar surface active lubricants such as phosphate esters or fatty acids may be dissolved in other less surface active lubricants to form a fluid lubricating interfacial layer and attached boundary layer having the desired thickness and viscosity characteristics under the preferred operating conditions. Water may be employed to dilute certain glycol lubricants in order to control the viscosity. Similarly, organic solvents may be used to dilute highly viscous organic lubricants for viscosity control.

There are advantages of in-line lubrication over precompounded lubricants. There are numerous solid and liquid lubricants commercially available for polymer processing. In the majority of cases the recommended lubricant is precompounded with the resin prior to injection molding or extrusion. Precompounded lubricants will reduce friction in the mixing zone of screw type machines so that drag flow, pumping efficiency, and mixing efficiency are all reduced. Thus both flow rate and back pressure are reduced when lubricants are added to the feed, adversely affecting the maximum production rate and economic operation of the machinery. Conversely, injection of lubricant near the end of the mixing or plasticating section provides lubrication where it is most effective and thereby minimizes the force needed to fill a mold or extrude a profile.

The lubricant of choice will depend upon cost, compatibility with the finished product, viscosity, long and short term toxic effects (with respect to production workers and product liability), and general lubricant efficiency. Solid lubricants may be preheated until liquified and then metered in liquid form. Fatty amides and polyolefin waxes are typical of this solid class of lubricants. Although hydrocarbon oils are widely used as lubricants, the selection must consider the solubility of the lubricant in the polymer melt. Ideally, the lubricant must be incompatible with the polymer in order to maintain a liquid film at the interface. Silicone oils and fluorocarbons are virtually incompatible with all hydrocarbon based polymers and find universal use for such purpose. Castor oil is particularly effective with polyolefins and is more economical to use than silicone or fluorocarbon lubricants. Glycols and glycerine are potential candidates if the lubricant needs to be removed after molding or extrusion since these liquids are water soluble. However waste water disposal restrictions and volatility need to be considered. Since polymers and metals have different surface energies, surface friction characteristics, solubility behaviour, and chemical reactivity, lubricant selection requires careful evaluation for each system. Mixed lubricants may include a surface active agent which has a strong affinity for metal surfaces (boundary lubricant) and a second viscous lubricant to maintain a liquid interface of finite thickness. Thus the lubricant mixture may contain two or more components designed to provide minimum friction for a particular resin system at a designated temperature. The natural wetting tendency of surface active lubricants help to provide spontaneous and uniform distribution of the lubricant at the melt interface.

The nozzle assembly may be fitted with a porous metal lubrication insert ring to promote even distribution of the lubricant before it enters the nozzle. The lubricants are metered at controlled rates using high pressure pumps. Vapours or gases may be introduced under pressure by such means to essentially reduce the interfacial friction to zero (Brzoskowski et al, Rubber Chemistry and Technology 60(5), 945-956, 1987). Water may be injected at such ports in order to provide simultaneous lubrication and cooling of the interface. In certain cases it may be desirable to admix liquid and gaseous lubricants for minimizing friction in the converging zone. It will be evident that any friction encountered by the semi solid compound as it passes through the die assembly will limit the mold-filling rate. Although both internal and external lubricants as such are commonly employed as additives in plastics processing, their effectiveness is often limited by their dispersion throughout the resin so that only a fraction of the additive is available to reduce the surface friction, and therefore is not quite as effective as the method herein described which deposits the lubricant selectively at the die interface where it is required. The conditions for maximum lubricity are complex although well known in the art (i.e. tribology) particularly with respect to frictional behaviour in mechanical devices e.g. automotive engines.

For a particular nozzle, the flow efficiency is governed by the flow rate at a particular pressure. I have obtained test results with use of a spiral mold. The Spiral Flow Test (ASTM D 3123-72) is employed by plastics processors as a means of measuring the combined effect of melt viscosity and rate of solidification on the flow properties during injection. The injected melt is forced to travel in an outward spiral until the flow ceases. This test is appropriate for estimating hydrodynamic lubricant efficiency, the distance travelled by the melt at a set pressure and mold temperature being a measure of the relative lubricant effectiveness. The test is conducted under conditions that inject a small amount of lubricant between the barrel and the nozzle. Lubrication efficiency is influenced by composition, solubility, shear rate, temperature, pressure, viscosity, and surface energy.

During injection the lubricant film thickness in the exit region varied from 100 to 500 nm depending upon the operating conditions under the smooth, highly polished surface employed. Under conditions of strain hardening in a converging die or nozzle, extreme pressures were encountered which limited or prevented flow. However, under most conditions the pressure was greatest near the beginning of the injection stroke and decreased rapidly with increasing strain and strain rate as the resin was injected. A temperature rise due to viscous heating or plastic working in a convergent zone also affected the injection pressure.

The lubricant was selected so that it did not interfere with post-finishing operations such as painting or decorating. Although lubricants may be selected primarily for their surface friction effectiveness, the introduction of a liquid film at the interface provides simultaneously modification of the surface of the injection molded article. By suitable application of a primer, durable, weather resistant coatings having scratch resistance, were applied. Enamel finishes commonly used for plastic automobile parts were suitable for this purpose although any type of paint or varnish may be applied. The oriented objects may be further processed by cutting, shaping, drilling, welding, bending, branding, or forging. Veneers or decals may be applied as is known in the art. Surface modification by flame, corona or plasma treatment is frequently employed with some polymers to promote better adhesion for applying surface finishes or printing. In-mold coating techniques are commercially available. Metal inserts and bushings may be incorporated by known methods (Modern Plastics Encyclopedia).

Surface modification was accomplished by using lubricants having polar substituents, such as maleated polyolefin waxes, fatty amides, or monoglycerides. These low melting waxes solidified on cooling to ambient temperature and provided a high energy adhesive surface for subsequent application of paints and finishes. These polar surfaces also adhere to printing inks and decals.

There are several methods described herein of providing lubrication at the end of the screw plasticating barrel before it entered the nozzle section. By suitable design of the convergent section so that the critical elongational velocity was not exceeded, more uniform elongation was achieved throughout the entire cross section of the profile.

In the practice of the solid phase injection molding process of the invention the temperature was gradually reduced within a reservoir to a preferred temperature, where the relaxation times of the polymer chains was of such long duration that the elastic deformation imparted by a converging die was retained. In order to avoid excessive pressures at such low injection temperatures, the die was lubricated to facilitate slippage and promote streamline flow through the converging passage. By such lubrication the pressure was reduced to about 1/5 of the corresponding unlubricated flow with the same polymer. Thus, it was possible to injection mold or extrude polymers under such conditions that the orientation is fully retained and without excessive pressures being generated. Such in-line lubrication has direct benefits in terms of a more favourable orientation near the molded surface where orientation was more effective for increasing flexural strength and stiffness. Additionally, cooling times were reduced since the molded part was at least partially solidified when it was formed. Such reduced injection moding temperatures have the benefit of reducing cycle times which favorably aid the rate of production. Thus, in-line lubrication is desirable for the economic production of thick objects or products of large cross section having retained orientation.

In regards die design features, the preferred lubricant will vary according to the choice of polymer and operating conditions. Ideally the lubricant shall be chosen to provide a low viscosity film at the melt-polymer interface with an optimum film thickness. The internal flow passage must be highly polished to maintain the lowest possible friction. The metal components must be corrosion and abrasion resistant in order to retain a smooth surface during prolonged use. These conditions will be apparent to those skilled in the art of lubrication and tribology which art is applicable. Although additive polymer lubricants are known, the high degree of lubrication which is required for solid phase injection would adversely affect the plastication and metering action int he barrel section which depends upon drag flow for proper operation of the screw. That is, the polymer would slip inside the barrel and would be unable to generate forward motion and melt pressure. Hence standard lubricant additives are not as effective for solid phase injection molding. It is necessary that the lubricant be introduced into the barrel or nozzle region as described for the purpose of imparting flow orientation. However, it was found that in-line lubrication can greatly improve the operating efficiency of an injection molding machine in the majority of applications, whether or not flow orientation is desired. Mold release is facilitated and the use of separate mold lubricants is thereby eliminated.

For flow orientation it is preferred to employ vertical injection molding presses which allow vertical opening of the mold (Ludwig Engel Ltd.) This design allows linear flow of the resin directly into the cavity. Using this type of injection molding machine, elongate articles can be readily fabricated.

In a further aspect, the invention provides a high modulus article comprising a composite of an oriented plastics material and an oriented particulate material made by a process according to the invention as hereinbefore defined.

Thus, I have surprisingly discovered that suitably induced orientation characteristics may be retained in (a) thermoplastic materials and (b) thermoplastic composite materials whether integral structural foams or otherwise solid or hollow articles, by the process of the present invention as conducted under non-steady state conditions. Thus, the intermittent and discontinuous process steps inherent in injection molding operations have been found conducive to the production of oriented thermoplastic articles.

I have surprisingly found that the injection pressures necessary to pass the oriented thermoplastic out of the nozzle into the mold at reduced melt temperatures fall within practical values for commercial use. Further, I have found that the desired temperature can be achieved and suitably maintained in the reservoir and die to enable orientation to be obtained and retained in the final molded and solidified article.

Yet further, notwithstanding the intermittent variable pressure changes to which to the melt plastic material is subjected in the converging nozzle passage, as the thermoplastic material is forced through the converging passage into the mold, orientation is produced and maintained. It is desirable that laminar, extensional flow be induced in order to effect maximum orientation throughout the section and thereby provide a high strength and high modulus product. Temperature uniformity is a requirement in the reservoir in order to minimize channelling of the melt rather than a constant velocity throughout the cross section of flow. Such temperature uniformity is induced by properly positioned static mixers equipped with a cooling feature that partially overcomes the low thermal conductivities of such viscous melts. Ideally, a two-stage hydraulic injection molding machine (Husky Injection Molding Systems, Inc.) is employed with a separate reservoir. Further, I have found that sufficient foam expansion can be obtained to result in an integral structural foam. I have also found that no significant warping or distortion of elongate article products has been observed.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be better understood, preferred embodiments will now be described by way of example only with reference to the accompanying drawings, in which:

Fig. 1 is a schematic representation of the major components of an apparatus for carrying out the relatively low temperature plastic and melt phase feeding and injection molding process of the invention;

Fig. 2 is a schematic representation of an alternative injection molding assembly of use in the practice of the invention; and

Fig. 3 is a schematic representation of an injection molding apparatus comprising a vertical hydraulic press assembly.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

With reference to Fig. 1, the apparatus for carrying out the injection molding within the process of the present invention is shown generally as 10 and comprises four main components consisting of an injection molding drive and feed screw assembly unit 12, a reservoir 14, a converging nozzle 20 and a split mold 22 arranged in co-axial lengthwise serial communication. Mold 22 is suitably shaped in the embodiment shown to form a baseball bat 24.

Injection molding unit 12 has a housing 24 containing drive motor, gears, hydraulics and electrical controls (not shown). Unit 12 has a longitudinal aligned heated barrel 26 which supports a feed hopper 28 by which thermoplastic resin and, optionally combined with cellulosic fibre materials, are introduced into barrel 26 containing a rotating and reciprocating screw 28. The resin composite may be, for example, a mixture of polyethylene and wood fibres which is gravity fed into the heated barrel 26 where it is advanced by screw 28 and simultaneously heated and plasticated. Barrel 26 connects with a tubular cooling reservoir 30 having a cylindrical body 32 having a cooling jacket 34 and an inner circumferential annular lubrication channel 36 operably fed with a lubricant (not shown) via an annular porous metal ring 38 connected with a lubricant port 40. Reservoir 30 contains a static mixer 42 to promote thermal cooling and homogenization of the melt.

Screw 28 injects the molten plastic composite mixture into reservoir 30 where it is cooled to a desired lower temperature. Static mixer 42 uniformly cools and equilibrates the desired melt temperature as the mixed composite material advances. Lubricant is introduced through port 40 and is chosen so as to minimize interfacial friction and promote plug flow (wall slippage) of the composite. Lubricant port 40 may optionally comprise a single aperture or a plurality of apertures defined by portions of body 32 of reservoir 30.

A non-return valve 44 between barrel 26 and reservoir 30 allows molten thermoplastic material to enter reservoir 30 and prevents return to barrel 26.

Reservoir 30 connects with a die 46 having a converging passage with respect to the longitudinal axis and of which the cross-sectional area diminishes in the forward direction of plastic flow to produce an oriented extrudate as it enters the cavity mold 22.

Mold 22 in the embodiment shown is a split mold formed of two mating members 50 and 52 in the closed position. Mold 22 in its closed position has an inner surface 54 defining an article-shaped cavity 56 which receives the injected and oriented plastic composite. In the embodiment shown, the article is a typically-shaped baseball bat 24 of a substantially elongate form having a central longitudinal axis co-axial with the longitudinal axis of cavity 56, and also the longitudinal axis of the converging passage of die 46.

Mold 22 is supported by stand 58 and has opposing side hydraulic clamps 60 which actuate side mold members 50, 52 to intermittently open and close mold 22. Mold 22 further has cooling lines 62 which receive cooling fluid, generally, cold water to effect rapid cooling of the plastic composite to well below the solidification temperature of the plastic to prevent spontaneous relaxation from its oriented form.

In the case of polyethylene mixtures the exit temperature from injection molding unit 12 may be as high as 200°C before it enters reservoir 30. The melt is then cooled to a temperature near the softening point (i.e. near 130°C) where the plastic exhibits its greatest elasticity. Under these conditions the elastic melt is forcibly injected into split mold 22 where it is rapidly cooled to preserve the orientation imparted to the melt after it passes through converging nozzle 46. The lubricant facilitates the sliding of the melt so that shear flow is minimized and maximum elongation of the melt is obtained throughout its cross section. The lubricant also reduces the pressure needed to inject the melt into the split mold despite the high viscosity of the melt near its softening point. Injection pressures will depend upon the resistance to flow but commonly are less than 30,000 psi and may be less than 10,000 psi depending upon the area reduction ratio and rate of filling. The elongational flow aids longitudinal orientation of fibrous fillers such as wood fibres, thereby maximizing the mechanical strength of the molded part. After a short residence time in the water cooled mold, the molded part is ejected into a water bath to ensure complete cooling of the part, particularly the interior region which may remain molten for an extended period due to the low thermal conductivities of most polymeric resins. The injection molding machine is adjusted to inject just the correct amount of plastic needed to fill cavity 56.

Split mold 22 is designed to facilitate smooth laminar flow of the resin as it enters cavity 56. An automated cut-off device 64 located at the exit of nozzle 46 is positioned to sever molded article 24 from nozzle 46 during ejection from mold 22. After ejection, hydraulic actuators 60 are reactivated whereby mold 22 is closed and the cycle repeated.

Under the action of reciprocating screw 28 the oriented composite melt is forced into elongated mold cavity 56. Cavity 56 is, in the case where an integral structural foam composite is required, maintained at atmospheric pressure whereby moisture contained in the wood fibre filler vaporizes and causes the molten interior of the composite material to foam and expand as it proceeds along elongate cavity 56. In the example of a baseball bat, a blowing agent may be employed, causing the semi-solid resin mass to increase in diameter as it expands into the mold, thereby forming an integral foam with a solid skin. The expansion of the resin as it enters mold cavity 56 occurs spontaneously due to the pressure exerted by the blowing agent. The highly oriented solid skin contributes most of the strength and stiffness to the composite, whereas the foam core reduces the average density of the article. Thus, baseball bat 24 is formed inside the mold cavity and has a foam core 66 surrounded by a solid skin 68 with a variable thickness of 1-3 mm. The length of bat 24 is of normal size, being about 33 inches in length and 2 inches in diameter at its outer end.

Mold cavity 56 may be so shaped as to suitably define the outline of other articles such as cricket bats and furniture legs, and, indeed, many other articles generally formed of wood. Other suitable resins for use with wood fibres include polypropylenes, vinyl resins and polystyrenes.

As depicted in Fig. 2, the injection process may alternatively use an assembly, shown generally as 100, which comprises a reciprocating extruder unit 102 coupled with a heavy duty hydraulic injection unit 108. The injection assembly 100 comprises extruder unit 102 with reciprocating screw 104 which feeds reservoir 106 of hydraulic injection unit 108. The thermoplastics material is fed into extruder 102 through hopper 122 where the resin is heated and plasticated before ejection from extruder into injection chamber 106. Units 102 and 108 are interconnected with barrel head passageway 110 containing a three way shuttle valve 112. After filling the temperature controlled chamber of injection unit 106, injection plunger 114 forces the thermoplastic resin through converging nozzle 116 into mold cavity 118. Reservoir 116 is lubricated as in Fig. 1 in order to minimize friction and promote extensional flow in the converging passageway. Lubrication port 124 is inserted in injection reservoir 116 to provide said lubrication. The mold cavity is contained in split mold 120 which is designed to cool the injected rein and eject the molded article therein after solidification. Three-way shuttle valve 112 automatically directs the cooled resin from hydraulic injection unit 108 into mold cavity 118. This design enables the temperature gradient in the cooled injector unit 108 to be programmed separately for achieving maximum orientation during injection without exceeding the peak pressure limit. Moreover the diameter of the melt reservoir is independent of the dimensions of the extruder and allows for greater flexibility in design and operation.

Fig. 3 describes an arrangement for the injection molding of elongate objects using a vertical type hydraulic press. To accommodate the in-line shot of the reciprocating screw, the mold is split horizontally. The conditions of injection may be adjusted to produce integral structural foams, hollow objects or solid objects according to design. The following features are identified in the drawings:

With reference to Fig. 3 the apparatus for carrying out the injection molding within the process of the present invention is shown generally as 200 and comprises four main components consisting of an injection molding drive and feed screw assembly unit 212, a reservoir 214, a converging nozzle 220 and a split mold 222 arranged in co-axial lengthwise serial communication. Mold 222 is suitably shaped in the embodiment shown to form a composite integral structural foam baseball abt 224.

Injection molding unit 212 has a housing 224 containing a drive motor, gears, hydraulics and electric controls (not shown). Unit 212 has a longitudinal aligned heated barrel 226 which supports a feed hopper 228 by which thermoplastic resin and, optionally combined with cellulosic fiber materials, are introduced into barrel 226 containing a rotating and reciprocating screw 228. The resin composite may be, for example, a mixture of polyethylene and wood fibers which is gravity fed into the heated barrel 226 where it is advanced by screw 228 and simultaneously heated and plasticated. Barrel 226 connects with a converging nozzle which is internally lubricated by means of part 240 and cooled by suitable heat transfer fluid via ports 245. The die is preferably instrumented to provide continuous readout of pressure and temperature from inserts located at position 247.

Screw 228 injects the molten plastic composite mixture into a converging die where it is cooled to a lower temperature. Lubricant is introduced through port 240 and is chosen so as to minimize interfacial friction and promote wall slippage of the molten resin or composite. Lubricant port 240 may optionally comprise a single aperture or a plurality of apertures defined by portions of the converging die 220. Further the internal surface of the die may comprise a porous insert to more efficiently distribute the lubricant at the melt interface. The nozzle region may contain a reservoir to permit melt homogenization and thermal conditioning of the melt before it enters the converging zone. Due to the small thermal conductivities of most polymers, a temperature gradient will affect the degree of orientation throughout the thickness of the injected profile unless uniform temperature is attained prior to flow orientation.

A non-return check value 244 between barrel 226 and die 220 allows molten plastic to enter the converging valve gated nozzle into the mold and prevents return of melt into the barrel 226 during the injection cycle.

The barrel 212 connects with a converging nozzle 220 having a converging passage with respect to the longitudinal axis and of which the cross sectional area diminishes in the forward direction of plastic flow to produce an oriented extrudate as it enters the mold cavity 256. The convergent zone is tapered according to a mathematical formula which maximizes the strain rate at each position along the converging zone such that the ultimate strain of the melt is not exceeded during the injection cycle i.e. causing melt fracture to occur. The valve gated nozzle is purposely designed with a large opening to minimize the peak pressure and promote parallel flow directly into the mold cavity.

The vertical mold 222 in the embodiment shown in Fig. 3 is a split mold formed of two mating members 250 and 252 in the closed position. Mold 222 in its closed position has an inner surface 254 defining the article shaped cavity 256 which receives the injected and oriented plastic composite. The injected melt is allowed to expand and fill the mold, wherein an integral structural foam is formed having a partially oriented skin.

Mold 222 is supported by stand 258 and has a vertical hydraulic press to actuate the upper platen 250 while the lower platen 252 remains stationary. Mold 222 further has cooling lines 262 which receive cooling fluid, generally cold water, to effect rapid cooling of the plastic composite to well below the solidification temperature of the plastic in order to prevent spontaneous relaxation from its oriented form.

Fig. 1, 2 and 3 thus illustrate two injection molding assemblies and methods of modifying conventional injection molding machines to permit low temperature lubricated injection molding in the manufacture of highly oriented thermoplastics materials and composites thereof. It will be apparent that there are many variations of this process and apparatus that can achieve the desired result.

MECHANICAL PROPERTIES OF WOOD FIBER COMPOSITES

Flexural properties were measured using the ASTM D-790 procedure . For circular extruded rods the supporting jig was modified as in ASTM D-4476 to accommodate the curvature of the test specimens. The Izod fracture toughness measurements followed the ASTM D-25 procedure.

The mechanical properties of extruded polyethylene wood fiber composites (WFC), polypropylene WFC and polystyrene WFC are summarized in Tables 1, 2, 3, and 4, respectively. At 50 percent wood fibre content, the flexural modulus values for these three polymeric composites were between 3 and 5 GPa.

The following examples will illustrate the method of manufacture.

EXAMPLE 1

In a typical experiment, 184.5 grams polypropylene (Himont 6301S) having a melt flow index of 10 g/10 min is mixed with 62.5 grams of thermomechanical pulp (Abitibi-Price Spruce), 3.1 g of a dispersing agent (Eastman Chemical Products Epolene E43 wax) and variable amounts of blowing agent (Uniroyal Celogen AZNP 130). Mixing was carried out in a laboratory scale one liter Gelimat mixer (Werner-Pfleiderer Inc., New Jersey) set at 3300 rpm and dump temperature 170°C. The mixing times were about 30 seconds. The molten discharge was cooled and granulated in a Brabender granulator prior to injection molding.

The above composition was injection molded using an Engel ES 80/20 machine equipped with an accumulator. The results are summarized in Tables 1 and 2.

Table 1. Injection Molding Conditions (Non-lubricated)

Injection pressure				4.84 MPa
Clamp pressure				14.5 MPa
Cycle times	-	injection		9.1 s
	-	cooling period		50 s
		mold open time		2.0 s
Temperature profile in barrel		-	zone 1	177°C
		-	zone 2	199°C
		-	zone 3	221°C
		-	nozzle	210°C
Mold temperature				50°C
Shot size				28 g

Table 2. Mechanical Properties of Polypropylene Composites

Property	Unfilled Foam	25% Wood Fibres
Tensile strength (MPa)	21.4	37.0
Flexural strength (MPa)	42.9	67.2
Notched Izod (J/m)	18.9	18.0
Reverse Notched Izod (J/m)	369	128

Unnotched Izod (J/m)	486	212
Heat deflection temperature at 264 psi (°C)	49.0	84.5
Melt flow index (g/10 min)	17.3	3.1
Density (g/cm^3)	0.78	0.95

Tables 1 and 2 illustrate the difficulty of injection molding wood fibre composites using conventional injection molding machinery. Due to small gates and sprues the Melt Flow Index, which is a measure of the melt viscosity, must be maintained above 1 g/10 min or the mold cavity will not fill even with the maximum injection pressure. The ASTM test specimens were 3 mm thick which produced molded parts having a skin thickness of one millimeter on each surface with a one millimeter foam core. Flexural modulus values were less than 3 GPa depending upon the extent of foaming, which is not an adequate substitute for hardwoods (which generally possess flexural modulus values greater than 10 GPa). The low strength (37 MPa) and low unnotched Izod values (212 J/m) indicate the possibility of brittle fracture at low impact energies. hence conventional injection molding does not satisfy the requirements for a hardwood replacement for which flexural strength values greater than 100 Pa would be required as well as an increased stiffness at the designated density of wood. Thus molecular orientation by the methods described above have been employed to increase the mechanical properties of the composite.

EXAMPLE 2

The following experiment was conducted to determine the effectiveness of in-line lubrication in coating a molded part.

An injection molding machine was fitted with a positive displacement pump for the addition of a metered amount of lubricant through a non-return valve at the nozzle. A vented spiral cavity mold (ASTM D3123-72) was installed on the machine to evaluate the performance of the lubricant. White polystyrene plastic sellets were fed from a hopper, melted and injected through the nozzle into the spiral cavity mold unit it would no longer flow. The shot size of the polystyrene was determined to be greater than the volume of the mold cavity. The various temperatures of the barrel, nozzle and mold were held constant at 470°F. The injection pressure was held constant at 1000 psi (6.9 M Pa). Clear silicone fluid (Dow Corning 200) was injected into the mold between cycles of the injection molding machine. Lubricant shot sizes ranged between .035cc and .07 cc/cycle and fed at a rate of 1.4% of the plastic shot size. The molded parts were visually examined for evidence of lubrication (shiny slippery surface). It was noted that prior to the introduction of lubricant the parts stuck in the mold and would not eject properly. After the introduction of lubricant, even at the .035 cc level, the parts released easily from the mold. There was a long term residual effect 20 - 30 parts after the lubrication ceased and the parts continued to come off the mode easily. At the lowest (.035cc) additive level there was no readily apparent evidence of any lubricant on the part. At the upper (.07cc) additive level there the parts were coated. Sections of the parts were uniformly shiny or slippery.

The average mass of the lubricated parts was 5.26g representing an increase of 11% over non-lubricated parts produced under the same conditions of temperature and pressure. These injected parts exhibited considerable flash, an indication of the greatly increased flow characteristics of lubricated melts. It was observed that in-line lubrication increased the mass of the injected part in all experiments.

After lubrication was terminated, there was a short lived residual effect that lasted for about 10 shots, after which the size of the injected parts became smaller and the parts began sticking in the mold again.

This experiment shows a correlation between in-line lubrication and improved flow conditions for polypropylene melts during conventional injection molding.

A larger amount, .35cc was then injected into the nozzle. The resultant part was covered with pigmented silicone fluid. The pigments were not uniformly distributed over the part but the silicone lubricant was. There were definite concentrations of pigment. The part was shiny and slippery all over with darkly and lightly pigmented sections.

The results showed that the coating of the part by a lubricant injected in-line at the nozzle was uniformly distributed over the surface of the molded part. The improved mold release characteristics shows that lubricant was present all throughout the melt/mold interface.

EXAMPLE 3

The following experiment relates to in-line lubrication with peanut oil to improved flow conditions and mold release for polypropylene.

Polypropylene resin was melted in an injection molding machine and injected through a nozzle into a vented spiral cavity mold until it would no longer flow. The potential shot size was determined to be greater than the volume of the spiral cavity. The injection pressure and barrel temperature were held constant from shot to shot. The temperature of the nozzle and mold were held constant. The mold was clean and unlubricated.

A series of 76 shots were taken. The mass of the molded part, its ease of release from the mold and its general appearance were documented. The average nozzle temperature was 255.66°C and the average mold temperature was 29.02°C. The average mass of the molded part was 4.68 grams. The molded parts were well defined without flash and did not come free from the mold automatically. Peanut oil was fed under pressure into a positive displacement metering pump. A metered shot of peanut oil which was approximately 1.4% of the mass of the part to be molded was injected into the nozzle through a non-return valve. The injection molding machine was then cycled with all the parameters held constant as they were in the control samples. The resultant part was examined for ease of release from the mold, its mass and general visual characteristics.

It was found that the mass of the parts molded under lubricated conditions was on average 5.19 grams. An increase of 10.9% over the mass of the non-lubricated parts. The parts molded under in-line lubrication did not stick in the mold and came free, automatically. It was also noted that the parts made under in-line lubrication were covered with flash, indicating much enhanced flow characteristics of the melt.

It was found that each time lubrication was injected in-line, there was an increase in mass. It was also found that there was a short lived residual effect, once in-line lubrication was stopped. The subsequent parts were larger than average, but returned to average size within 9 or 10 shots and began sticking in the mold again.

This investigation shows there is a definite correlation between in-line lubrication with peanut oil and improved flow conditions of melted polypropylene. Also, there is a definite correlation between in-line lubrication with peanut oil and improved mold release qualities.

The examples herein provided illustrate a new method of forming oriented objects by injection molding using flow convergence at low temperatures to forcibly align and solidify polymer molecules in their extended configurations, thereby producing articles with enhanced physical and mechanical properties. The process is applicable to thermoplastics possessing long stress relaxation times under the temperatures and conditions of molding. The process is also applicable to thermoplastic composites containing organic or inorganic fillers. In one example, a means for producing an oriented composite with a foam core is illustrated, eg. a baseball bat. Similarly, oriented hollow objects may be formed by gas injection molding. The novel features of the injection molding machine include a cooled reservoir with means for uniform cooling of the melt, a converging lubricated passage, and a laterally opening mold. The process is conducted under conditions that maximize the extensional elongation of the elastic melt and retain such forced elongation in the solidified product. A means is described for forming a baseball bat using foam expansion and having mechanical properties and densities comparable to hardwood bats.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope of the invention as described and claimed.

Claims:

1. Improved injection molding apparatus for the manufacture of an article formed of a thermoplastics material having a melt index at a suitable temperature selected from the range 0.1 to 60g/10min, comprising an article-shaping mold in communication with a melted feed means for intermittently feeding said thermoplastics material under pressure and at a temperature above said melt index in a first mold-filling and article-shaping amount to said mold; said mold having (i) cooling means within said mold for cooling said melted thermoplastics material below said melt index to form a cooled, said article; (ii) means for opening said mold to allow removal of said cooled article; (iii) means for sealably closing said mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of said melted thermoplastics material; (iv) an extrudate receiving aperture; (v) an inner surface defining an article-shaped inner cavity; the improvement wherein said melted feed means comprises (a) a converging die having a converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produce an extrudate for said mold, and (b) means to control the temperature of said method thermoplastics material or close to said melt index in said converging die.

2. Improved injection molding apparatus for the manufacture of an article formed of a thermoplastic material having a melt index selected from the range 1-10 dg/min, comprising an article-shaping mold in communication with a molten feed reservoir for intermittently injecting said thermoplastic material under pressure and at a reduced temperature to effect mold-filling and article-shaping inside said mold; said mold having (i) cooling means within said mold for cooling said melted thermoplastics material to form a solid oriented article; (ii) means for opening said mold to allow removal of said oriented article; (iii) means for sealably closing mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of melted thermoplastic material; (iv) an aperture with device for

severing molded article after molding; (v) an inner surface defining an article-shaped inner cavity; the improvement wherein said melted feed means comprises (a) a die having a converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produces an oriented extrudate for said mold, and (b) means to control the temperature of said thermoplastics material in a reservoir prior to entry into the converging die.

3. Apparatus as defined in Claim 1 wherein said melted feed means has lubricant entry means by which said melted thermoplastics material in said converging die may be operably lubricated.

4. Apparatus as defined in Claim 1 wherein said converging die has a longitudinal axis central of said die, and said mold cavity is of a substantially elongate shape having a longitudinal axis substantially co-axial with said longitudinal axis of said die.

5. An apparatus as defined in Claim 1 wherein said melted feed means comprises a pre-die reservoir adjacent said converging die and having cooling means by which the temperature of said melted thermoplastics material can be adjusted.

6. An apparatus as defined in Claim 2 wherein said molten feed is contained in a separate reservoir attached to the converging die and having cooling means by which the temperature of said melted thermoplastics material can be uniformly cooled to a lower temperature.

7. An apparatus as claimed in Claim 5 wherein said pre-die reservoir has lubricant addition means.

8. A process for the batchwise production by injection molding of a high modulus article formed of an oriented thermoplastics material, said process

comprising the steps of:

forcing under pressure an orientable plastics material, while it is close to or at its softening temperature, through a converging passage having a central longitudinal axis and of which the cross-sectional area diminishes in the forward direction of plastic flow, to produce an oriented extrudate;

feeding a said article-forming amount of said oriented extrudate to a mold having cooling means and an inner surface defining a said article-shaped cavity, while rapidly cooling said oriented extrudate to preserve said orientation and provide a cooled said article.

9. A process as defined in Claim 8 wherein said mold cavity is of a substantially elongate shape having a longitudinal axis substantially co-axial with said longitudinal axis of said converging passage.

10. A process as defined in Claim 8 wherein said orientable plastics material is in admixture with an orientable particulate material.

11. A process as defined in claim 10 wherein said orientable particulate material is a cellulosic material.

12. A process as defined in claim 10 further comprising lubricating said admixture adjacent said passage to obtain substantially plug flow of said admixture through said passage.

13. A process as defined in claim 10 in which said admixture further comprises a lubricating agent.

14. A process as defined in claim 10 wherein said admixture further comprises a blowing agent to provide said article comprising an integral structural foam.

15. A process as defined in claim 12 wherein said blowing agent is water.

16. A process as defined in claim 8 in which the plastic material has a weight average molecular weight of between 20,000 - 500,000 daltons.

17. A process as defined in Claim 16 wherein said plastic material is a polyethylene;

18. A process as defined in claim 8 in which the converging passage is provided in a die having a converging zone, which passage has a geometry which provides a decreasing strain rate of the elastic melt in the flow direction within the converging zone.

19. A process as defined in claim 8 in which the converging passage in the die has a geometry which provides a constant elongation rate of the elastic melt in the flow direction within the converging zone.

20. A process of making by injection molding an article formed of a high strength and high modulus cellulosic-thermoplastic composite, which process comprises:

intimately admixing shredded cellulosic fibers or cellulosic particles with a thermoplastic polymeric material which has a softening point below about 220°C;

passing the mixture with converging flow through a die having a converging passage having a central longitudinal axis and of which the cross-sectional area diminishes in the forward direction of plastic flow by melt phase extrusion at a temperature near the softening point of the thermoplastic material, to impart longitudinal orientation of both the cellulosic particles and the thermoplastic polymer molecules in the direction of flow to produce an oriented extrudate;

forcing a said article-forming amount of said oriented extrudate into a mold having cooling means, while rapidly cooling said oriented extrudate to preserve said orientation and provide a cooled solidified said article.

21. A process for the batchwise production by injection molding of an integral structural foam composite article of an oriented plastic material and an oriented particulate material, said process including the steps of

intimately admixing suitably orientable particulate material with a thermoplastic material which thermoplastic has a softening point below about 220°C;

extruding the admixture through a converging die by melt phase extrusion at a temperature near the softening point of the thermoplastic material, so as to impart predominantly longitudinal orientation to both the particulate material and the thermoplastic polymer chains throughout the melted extrudate;

forcing a said article-forming amount of the oriented melted extrudate into a mold having cooling means and under conditions which permit foaming to take place in the core of the melt extrudate while rapidly cooling the external surface of said article and maintaining a highly oriented, essentially solid outer skin on its surface.

22. Improved injection molding apparatus for the manufacture of an oriented article formed of a thermoplastic material wherein the molten thermoplastic resin is forcibly extruded through a converging die into a mold cavity under conditions that deform and orient the polymeric molecules prior to mold filling;

rapidly cooling said article in the mold while it is still oriented so as to permanently retain said orientation;

means for opening said mold and ejecting the solidified article;

means for reclosing said mold and to operably receive, intermittently, a second and subsequent amounts of thermoplastic material;

the inner surface of the mold cavity thus defines the shape of the molded article;

the improvement comprising (a) a cooling reservoir with a converging die assembly interposed between the injection molding machine and the mold wherein the melt temperature of the resin is lowered to its elastic region and (b) injection of a lubricant into the reservoir to promote frictionless flow of the polymer through the converging die passage and (c) thereafter rapidly cooling the injected material in the mold in order t fully retain said orientation.

23. Apparatus as defined in Claim 22 wherein said converging die mates with the mold cavity in uninterrupted streamline fashion to minimize turbulence (no gates or spruce).

24. Apparatus as in Claim 22 wherein the mold cavity is substantially elongate in form with said mold cavity having its longitudinal axis collinear with the axis of the converging die in order to promote minimum resistance to linear streamline flow.

25. A reservoir with means for cooling the polymer melt as defined in Claim 22 wherein the molten plastic is brought to the desired temperature prior to entering the converging die.

26. A process for the batchwise production by injection molding of a high modulus article formed of a thermoplastic material, said process comprising the steps of:

forcing under pressure an orientable plastics material through a lubricated converging passage, while it is close to its softening temperature, so as to elastically deform the melt;

injecting the elastically deformed segment into a chilled mold cavity to solidify the material and preserve said orientation.

27. A process as defined in Claim 26 in which the polymeric resin admixed with a cellulosic filler is selectively chosen from the family of

polyethylenes, the family of polypropylenes, the vinyl polymers, or the styrenic polymers.

28. A process as defined in Claim 26 wherein the orientable plastic material is in admixture with an orientable particulate filler material selected from talc, mica, short glass fibers, asbestos or Wollastonite.

29. A process as defined in Claim 26 wherein the lubricated converging passage has a horn shaped geometry, which provides a decreasing strain rate of the elastic melt in the flow direction within the converging zone.

30. A process as defined in Claim 26 wherein the lubricated converging passage provides a constant strain rate in the direction of flow within the converging zone.

31. A process of making by injection molding an article formed of a high strength, high modulus composite of a cellulosic filler admixed with a thermoplastic resin which process comprises;

intimately admixing cellulosic fibers or cellulosic particles with a thermoplastic which as a softening point below 220°C;

forcing the heated mixture through a lubricated converging die at a temperature near the softening point so as to impart longitudinal orientation of the cellulosic fibers and the polymeric matrix;

rapidly cooling said injected segment in a chilled mold to preserve the orientation;

32. A process for the batchwise production by injection molding of an integral structural foam composite article, said process including the steps of

intimately admixing an orientable particulate material with a thermoplastic material;

forcing the admixture through a lubricated converging die at a temperature near its softening point, so as to impart predominantly longitudinal orientation to both the particulate filler and the polymeric matrix;

injecting the elastically deformed segment into a chilled mold which mold permits the extruded segment to expand radially to form a foam core while the outer skin remains essentially solid and unfoamed.

33. A process for the batchwise production by injection molding of an oriented thermoplastic having a hollow section comprising the steps of

forcing said thermoplastic material through a converging die near its softening point;

injecting an inert gas under pressure within the lubricated converging passage during the injection cycle;

allowing the injected section which has been longitudinally oriented to expand and fill the chilled mold thereby producing a hollow article.

34. A process as defined in Claim 28 wherein the converging die has a gradual contour such that the angle of incidence of the melt does not exceed 10° and is preferably about 5°.

35. An injection molding apparatus for the manufacture of an article formed of a thermoplastic material chosen from a broad Melt Flow Index range from 0.1 to 60 g/10 min (according the ASTM D1238), comprising an article-shaping mold in communication with a melted feed means for intermittently feeding said heated molten thermoplastic material under pressure in a first mold filling and article shaping amount to said mold; said injection molding machine having

i. lubricant injecting means for injecting a controlled amount of lubricant into the flow passage near the end of the injection barrel near the nozzle;

ii. streamline nozzle means to maximize flow rate and/or orientation;

iii. cooling means for cooling the nozzle and flow passages to control flow orientation;

iv. cooling means within said mold for cooling said heated plastic material to form a cooled, said article;

v. means for opening said mold for said mold to operably receive, intermittently, a second and subsequent mold filling amount of said heated thermoplastic material;

vi. an extrudate receiving aperture;

vii. an inner surface defining an article-shaping cavity; the improvement wherein said melted feed means comprises

a. a means for injecting lubricant directly into the flow passage following the melt plastification stage;

b. a lubricated converging passage of which the cross-sectional area diminishes in the forward direction of plastic flow and produces an oriented extrudate for said mold; and

c. means to control the pre-form temperature of said thermoplastic material prior to flow orientation in said converging passage.

36. Injection molding apparatus having a barrel, an oversize convergent valve-gated streamline nozzle, a convergent mold cavity lubricant feed lines for the manufacture of thermoplastic materials from a melt comprising

i. injection means for intermittently injecting lubricant into said barrel adjacent said nozzle to reduce friction and promote increased flow rates;

ii. cooling means for cooling said melt to its elastic or plastic state near its softening point just prior to deforming it in a said oversize convergent valve-gated streamline nozzle or said convergent mold cavity;

iii. means for introducing a semi-solid oriented slug of material into said mold cavity;

iv. a heated reservoir to premelt solid lubricants for injection into said barrel adjacent said nozzle;

v. automatic switching means to synchronize the injection of lubricant into the nozzle region;

vi. a non-return valve means in the lubricant injection port to prevent the ingress of molten polymer into said lubricant feed lines during the injection pressure cycle;

vii. fluid means for introducing air or gas into said melt for the purpose of forming oriented integral structural foams or hollow articles.

37. A high modulus article produced by a process as defined in Claim 8.

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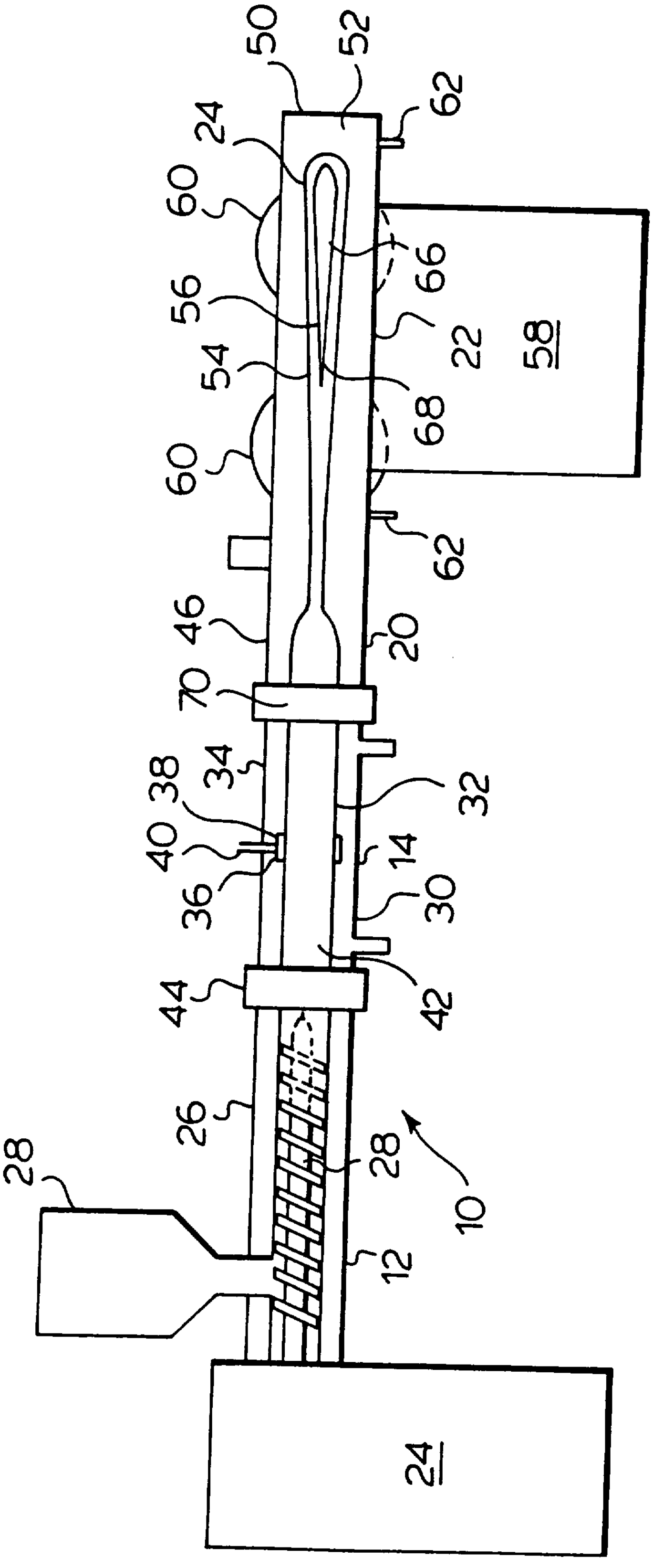
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FIG. 1.

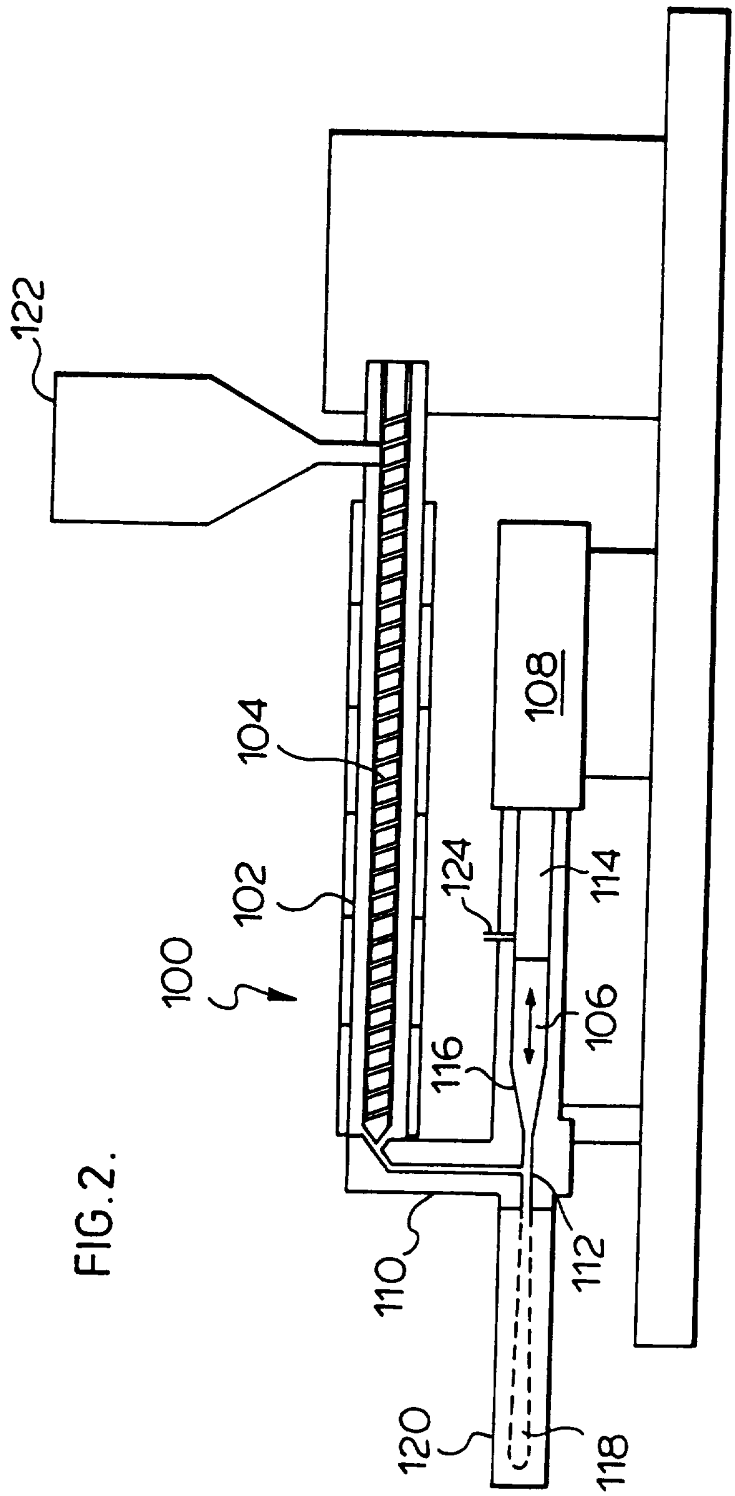

FIG. 2.

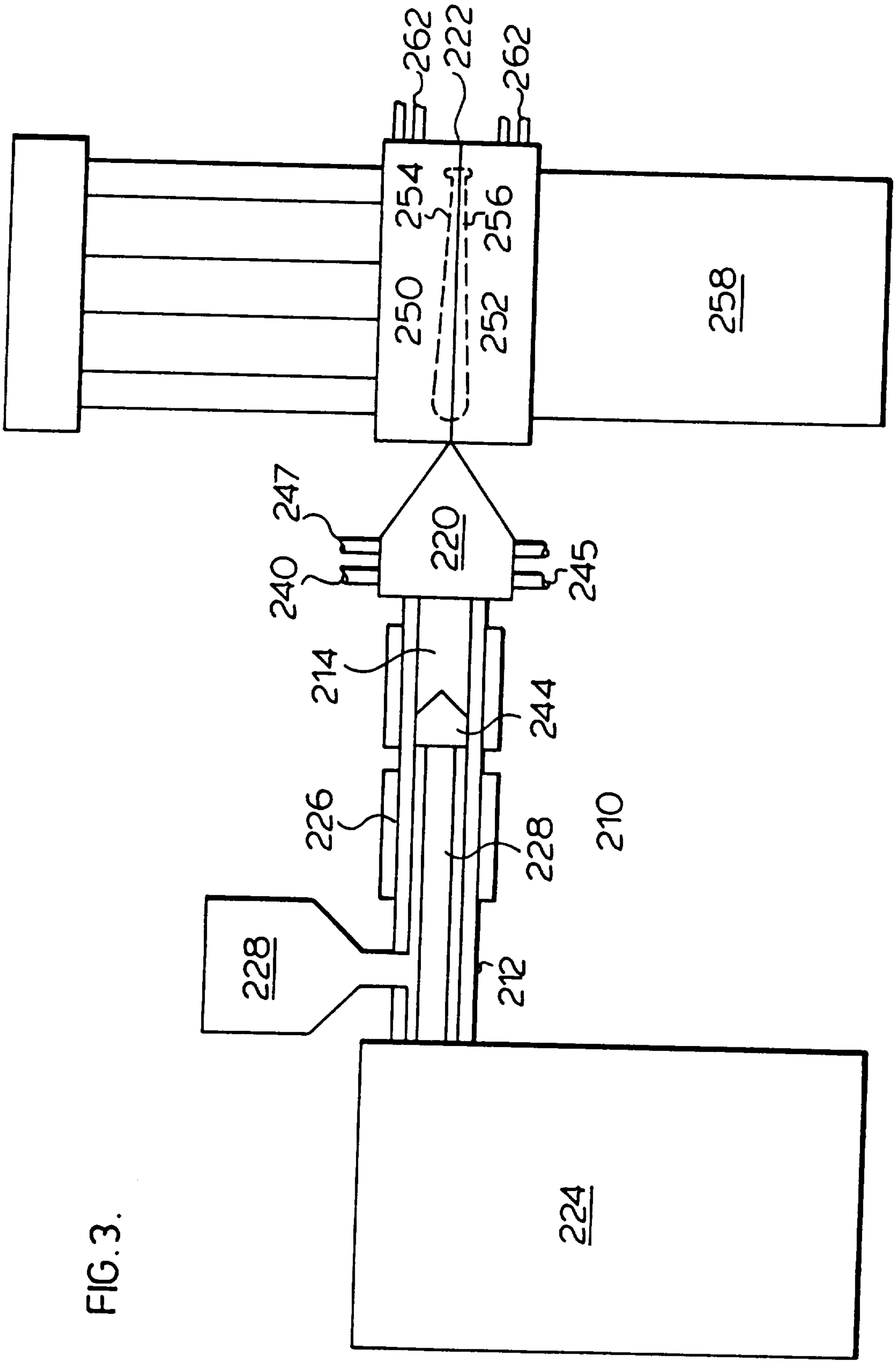
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FIG. 3.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 95/00614

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C45/00 B29C45/83 B29C44/42

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 6 B29C

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 629 751 (MANCEAU, CONSTRUCTIONS IND. D' ANJOU) 13 October 1989 see the whole document	1
Y		2-4, 8-10,13, 14,20, 21,37
A		22,25, 26,31,33

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 January 1996	23.01.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Bollen, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 10 no. 142 (M-481) [2199] ,24 May 1986 & JP,A,60 264237 (SEKISUI KAGAKU KOGYO KK) 27 December 1985, see abstract	2,4, 8-10,37
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A		22-24, 26,31-33
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