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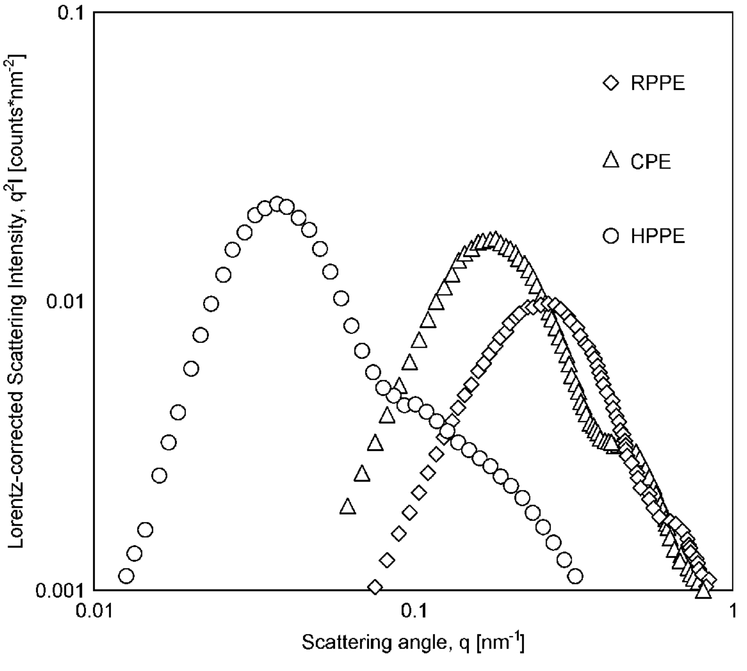
Figure 5



(57) **Abstract:** The invention provides methods of inducing crystallization in crystallizable polymers, and articles made therefrom. In one aspect, the method comprises bringing a preform to a first temperature to form a melted polymer preform and pressurizing the melted polymer preform to form a pressurized polymer and induce crystallization. Pressurization is at a pressurization rate ranging from about 1 MPa/s to about 1000 MPa/s. In another aspect, the invention provides a method of forming an article from the crystallisable polymer by first inducing crystallization as described herein, followed by cooling and depressurizing, either simultaneously or sequentially. The method of forming the article may further include steps of heating to a second temperature and a third temperature. The methods described herein provide a facile manner of controlling crystallization extents in an article formed from crystallizable polymers.

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METHODS FOR INDUCING CRYSTALLIZATION IN CRYSTALLIZABLE POLYMERS, AND ARTICLES THEREFROM

FIELD

[0001] This invention relates to articles of crystallizable polymers whose crystals are formed under rapid pressurization and methods of making the same.

BACKGROUND

[0002] Crystallizable polymers are usually semicrystalline and are characterized by two major transition temperatures- the peak melting temperature (or melting point) and glass transition temperature. They form a melt above the melting point, crystallize into a lamellar morphology as they are cooled below the melting temperature and finally, their amorphous phase present between adjacent crystalline lamellae becomes glassy as the temperature is reduced below the glass transition temperature. If a semicrystalline polymer is cooled from the melt state to room temperature and its glass transition temperature is lower than room temperature, then the amorphous phase present between crystalline lamellae remains liquid-like or rubber-like.

[0003] The fraction or degree of crystallinity as well as the rate of crystallization varies depending upon the type of crystallizable polymer, rate of cooling from the melt state, degree of undercooling, which is defined as the difference between melting point and the peak crystallization temperature, presence of nucleating agents in the polymer and other factors. If the crystallizable polymer is cooled at a fixed cooling rate from the melt state, the polymer usually does not crystallize immediately as the temperature decreases to a value below the melting point but rather a certain degree of undercooling is required to provide sufficient driving force for nucleation and crystal growth. Thus, polymers that are cooled from the melt state have a peak crystallization temperature that has a lower value than the melting point (Figure 1). For rapidly crystallizing polymers such as polyethylene, poly(ether ether ketone) and poly(tetra fluoro ethylene), the polymer crystallizes at a high rate at the peak crystallization temperature. Further crystallization continues to occur to a small degree below the peak crystallization temperature to until the maximum achievable crystallinity is attained under such a thermal history. Both melting point and peak crystallization temperatures are associated with a broad range of temperatures with a peak value rather than a single temperature when they are measured using thermal analysis methods such as differential scanning calorimeter, as depicted in Figure 1.

[0004] The control of overall crystallinity of crystallizable polymers has attracted much attention since the degree of crystallinity strongly affects the mechanical properties of crystallizable polymers in the semi-crystalline state. A high degree of crystallinity can increase the modulus, yield stress, impact strength, resistance to creep deformation and resistance to fatigue crack propagation of articles fabricated with crystallizable polymer, which are attractive for several load bearing applications. Secondly, high crystallinity makes crystallizable polymers more resistance to chemical attack and less permeable to gases, which is attractive for packaging applications and for medical devices. Thirdly, the presence of randomly oriented crystals in polymers which are crystallized without any applied strain makes the polymeric preform comprising the crystallizable polymer opaque, which is also desirable for some applications. In contrast, a low degree of crystallinity can decrease yield stress, impact strength and resistance to fatigue crack propagation but can also induce beneficial properties such as enhanced ductility, low brittleness and lower contact stress when contacted with a hard object. Furthermore, a low crystallinity makes the crystallizable polymer less opaque.

[0005] The degree of crystallinity of crystallizable polymers can be increased using several processing methods. Firstly, the preform comprising the crystallizable polymer can be slowly cooled from the melt, allowing more time for the polymer to crystallize, which induces a higher crystallinity compared to rapid cooling from the melt. Secondly, the polymer can be isothermally crystallized at a fixed temperature close to but below the melting point [1]. At such a low degree of undercooling, the nucleation density is low, which makes it possible for the formation of thick crystalline lamellae to grow from the nuclei. More importantly, the driving force for crystallization is also low, thereby decreasing the rate of growth of crystalline lamellae as the chains of the polymer slowly disentangle and chain fold into the crystalline lamellae. For example, polyethylene with a melting temperature of 133°C can be crystallized at 130°C, which takes approximately two days for the nucleation step and two weeks for the crystallization to be complete [1]. Thirdly, it is generally known that crystallization of several crystallizable polymers under elevated hydrostatic pressure enables the growth of thick lamellae, producing high crystallinity [2]. Lastly, crystallinity of a polymer can be enhanced by crystallization from the solution or gel state, which allows the chains to disentangle easily from each other and become incorporated into the crystalline lamellae to form chain-folded lamellae [3].

[0006] The degree of crystallinity can also be decreased using several approaches. Firstly, the polymeric preform can be rapidly cooled from the melt state so that there is rapid nucleation and growth but the nucleation density is so large that the crystalline lamellae that form are usually thinner than those formed by slow cooling, isothermal crystallization at low undercooling temperatures, high pressure crystallization or gel/solution crystallization. However, a major limitation of rapid cooling of rapidly crystallizing polymers is that it is only effective in small diameter particulates, fibers and thin films. Thus, in order to measure the peak melting temperature for rapidly crystallizing polymers such as polyethylene at very high cooling rates, the measurement has required the use of nanograms of polyethylene to minimize the effects of low thermal conductivity inherent in polyethylene [4, 5]. Like polyethylene, most polymers have a low thermal conductivity compared to metals. As a result, if rapid cooling is performed in a polyethylene preform whose smallest dimension exceeds about 500 micrometers, the surface regions of the preform rapidly crystallize to form a low crystallinity region or a skin layer, whereas the interior or bulk regions continue to crystallize slowly and have a higher crystallinity. Furthermore, when a large size preform is rapidly cooled from the melt state, the skin layer on the surface crystallizes first while the interior crystallizes slowly inside the crystallized skin layer and proceeds further into the core. This mismatch in the time at which different sub-surface regions of a preform crystallize can create residual stress as the preform shrinks in the skin layer and proceeds to shrink further into the interior.

[0007] A method to decrease crystallinity of a preform irrespective of its dimensions is by polymerization of crystallizable polymers from monomers that include co-monomers or chemicals with multiple reactive sites in order to create small chain or large chain branching. Examples of small chain branching are linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) and ultra-low density polyethylene (ULDPE). Examples of large chain branching are low density polyethylene (LDPE). Also, polymerization to a very high or ultra-high molecular weight can be conducted in order to have a high entanglement density in the melt state so that crystallization is hindered. For example, high density polyethylene has a high crystallinity of 60-80% whereas low density polyethylene, linear low density polyethylene, ultra-low density polyethylene and their analogs have a degree of crystallinity often less than 30% due to long chain or short chain branching. Ultra-high molecular weight polyethylene (UHMWPE), which are a class of linear polyethylenes whose molecular weight falls in a range of 500,000-10,000,000 g/mole, usually has an intermediate degree of crystallinity of 40-60%. Altering the chemical makeup of crystallizable polymers has several disadvantages such as high cost, the presence of residual, unreacted co-monomers and processing difficulties in the case of high molecular weight polymer resins, to name a few.

Until now, it has not been possible to produce bulk preforms with large dimensions from rapidly crystallizable polymers, such as polyethylene to crystallize at high undercooling temperatures, i.e. at low peak crystallization temperatures, such as is possible in thin films and fibers when contacted with a cold solid, liquid or gas.

SUMMARY

[0008] This invention relates to articles of crystallizable polymers whose crystals are formed under rapid pressurization and methods of making the same.

[0009] Generally described herein are methods to decrease the thickness of the crystalline lamellae of large preforms of crystallizable polymers compared to that of slow cooled preforms. It is well known that rapid cooling or quenching of a crystallizable polymeric film or fiber from the melt state results in a high nucleation density and the formation of a large number of thin crystalline lamellae. Rapid cooling of a crystallizable polymer from the melt state is only effective for polymeric preforms wherein their smallest dimension, such as thickness or diameter, is less than approximately 500 micrometers. Figure 2 depicts the increase in undercooling, (the difference in the melting and crystallization temperature) as a function of cooling rate. The undercooling increases with an increase in cooling rate since the peak crystallization temperature decreases with an increase in cooling rate. However, when the cooling rate exceeds the thermal conductivity of the polymer, it confines the effects of crystallization at high undercooling to the surface regions for rapidly crystallizing polymers, such as polyethylene. This “skin layer” is quenched to form thin crystalline lamellae by contacting with a cold solid, liquid or gas, but the interior or bulk regions remain at a high temperature and cool at a much lower rate than the surface regions, thereby inducing a higher crystallinity associated with thicker crystalline lamellae.

[0010] This invention features processes which induce a crystallization at high undercooling in both the surface and bulk regions of polymeric preforms of crystallizable polymers. This is particularly advantageous for rapidly crystallizing polymers such as polyethylene, whose bulk properties would be different from their slow cooled counterparts and would increase their range of applications or enhance certain desirable properties, such as ductility and toughness. This invention also features large articles whose crystallinity and crystalline lamellar morphology are relatively uniform from the surface to the interior. Furthermore, this invention features processes, which can create a gradient in crystallinity.

[0011] Unlike rapid thermal cooling, in which the undercooling is increased by a decrease in peak crystallization temperature, this invention takes advantage of the increase in melting temperature of crystallizable polymers, such as polyethylene, with increase in applied pressure. Figure 3 shows a typical process, in which the temperature of the polymer preform is increased to a temperature higher than the melting point. Then the pressure is increased rapidly to a pressure at which the melting point of the polymer is high. Thus, in contrast to thermal cooling where the melting temperature of the polymer is constant at a constant pressure and the peak crystallization temperature decreases with rapid cooling thereby increasing undercooling, in the case of rapid pressurization at constant temperature, the peak crystallization temperature remains constant and the melting temperature increases with pressure, thereby increasing the undercooling. To those skilled in the art, it is known that rapid pressurization is not strictly an isothermal process and that pressurization without intentionally changing the temperature is adiabatic with a small change in the temperature [6]. However, for practical purposes, when the temperature is not intentionally increased and controlled by a temperature controller, the temperature of the polymer in the melt state is taken to be identical to the temperature of the crystallized polymer, especially when the temperature controller maintains a constant temperature. The advantage of pressure as a means to increase undercooling is that it is not limited by the thickness of large articles whereas cooling is limited by the thermal conductivity of the polymer. For polyethylene the slope of the melting curve of the phase diagram depicted in Figures 3 and 4 is approximately 0.25 [4]. This implies that if the rate of pressurization is 4 times the rate of cooling, the undercooling will be approximately the same for these two processes. It must be noted that the melting curve in the phase diagram is depicted as linear but in reality it is slightly non-linear. But approximating it to a linear curve enables a quantitative estimation of the equivalence of pressurization rate to cooling rate to obtain the same degree of undercooling. For polyethylene at atmospheric pressures, the rate of nucleation and crystallization is relatively low at low undercooling, until a temperature of 125°C is attained whereas it is rapid at its peak crystallization temperature (approximately 120°C) [1]. Thus, rapid pressurization of polyethylene can crystallize the polymer at high undercooling even if the polyethylene is below the melting temperature of 133°C (in the range of 133°C-120°C), as depicted in Figure 4. For the case of rapid pressurization of the polyethylene preform above the melting temperature or between the melting temperature and peak crystallization temperature, the preform can be further maintained at the high pressure for a time duration of ranging from 1 minute to 1 week, preferably ranging from 5 minutes to 48 hours, to anneal the preform and to thicken the formed crystalline lamellae.

[0012] Thus, in one aspect, the invention provides a method of inducing crystallization in a crystallizable polymer. The method comprises providing a polymer preform of the crystallizable polymer, which is then heated to a first temperature to form a melted polymer preform. In one embodiment, the first temperature is greater than the peak melting temperature of the polymer preform. In another embodiment, the first temperature ranges between the melting point and the peak melting temperature of the polymer preform, and in yet another embodiment, the first temperature ranges between the peak crystallization temperature and the melting point of the polymer preform. The method then includes a step of pressurizing the melted polymer preform to induce crystallization in the crystallizable polymer.

[0013] The preform can optionally also be increased in temperature under pressure to a temperature below the melting temperature at that applied pressure and maintained for a time duration to facilitate annealing and lamellar thickening. In another aspect, the preform can be under an applied pressure prior to rapid pressurization so long as the preform is in the melt state. The melt state is defined as a state wherein x-ray diffraction or thermal methods such as differential scanning calorimeter is unable to detect any crystal present in the crystallizable polymer.

[0014] If a gradient in crystallinity from the surface to the bulk of the preform is desired, the temperature of the preform is first increased to a first temperature exceeding the melt temperature until the entire preform has a uniform temperature to form a melted polymer preform, then rapidly cooled to a temperature exceeding the peak crystallization temperature so that the interior of the preform remains at a higher temperature than the surface regions, and then rapidly pressurized to a pressure at which the entire preform crystallizes and then cooled under pressure, thereby providing a preform with a low crystallinity at the surface and a high crystallinity at the interior since there is a difference in the undercooling between the surface regions and the bulk regions of the preform. Alternatively if a gradient in crystallinity is desired wherein the crystallinity of the interior or bulk regions is lower than the crystallinity of the surface, the temperature of the polymer preform is first rapidly increased to a temperature exceeding the melt temperature and the interior remains at a lower temperature, which also exceeds the melting temperature, the polymer preform is then rapidly pressurized to a pressure at which the polymeric preform crystallizes to form the pressurized polymer after which the pressurized polymer is cooled and pressure released. An alternate method to create such a gradient in crystallinity is to select a polymeric preform of a crystallizable polymer with a uniform low crystallinity induced by the first process mentioned above, heating the surface rapidly to an elevated temperature for a period of time and cooling it rapidly before the entire preform achieves a uniform elevated temperature, which would lead to an increase in crystallinity of the surface regions due to annealing. In all of these processes, the preform is finally cooled to a temperature below the peak crystallization temperature of the polymer at atmospheric pressure, prior to release of the pressure to return the preform to atmospheric pressure or the temperature and pressure may be simultaneously decreased so long as the difference between the peak crystallization temperature and the temperature of the polymeric preform do not exceed the difference between peak crystallization temperature and room temperature at atmospheric pressure.

[0015] Thus, in another embodiment, the invention provides a method of forming an article from crystallisable polymers, wherein the method comprises heating the polymer preform to a first temperature to form the melted polymer preform and pressurizing the melted polymer preform to form a pressurized polymer, followed by cooling the pressurized polymer to a second temperature to form a crystallized melt. The crystallized melt is then depressurized to form the article. The second temperature is a temperature below the peak crystallization temperature of the polymer at atmospheric pressure. Alternately, the second temperature is a temperature selected to be such that the difference between the peak crystallization temperature and the temperature of the polymeric preform do not exceed the difference between peak crystallization temperature and room temperature at atmospheric pressure.

[0016] To those skilled in the art, it is known that the bulk crystallinity for different types of polyethylenes is not identical and some polyethylenes do not crystallize from the melt state to as high a crystallinity as HDPE. This invention pertains to polyethylenes, including UHMWPE and HDPE, and mixtures thereof, both of which are largely unbranched, linear macromolecules. This processing methodology of this invention can also be applied to LDPE, LLDPE, VLDPE and ULDPE, and a mixture thereof. However, each of these polyethylenes have a substantially different melting temperature and peak crystallization temperature at atmospheric pressure and it is expected that the dependence of melting temperature on the applied pressure differs substantially from those of HDPE and UHMWPE. It must also be noted that this invention provides a pathway to crystallize other polymers under rapid pressurization using the slope of the melting curve in a temperature versus pressure diagram as a guide to determine how rapidly to pressurize a bulk crystallizable polymer that is equivalent to rapid cooling in that it provides the same degree of undercooling.

[0017] Rapid pressurization for polyethylene preforms may be conducted hydrostatically by immersing the preform within an incompressible fluid and then rapidly pressurizing the fluid and the preform to a desired pressure. In a typical hydrostatic application of pressure, the polymer preform is contained (or enveloped) within a flexible barrier film that allows pressure transfer between the fluid and the polymer preform but prevents direct contact between the fluid and preform. Rapid pressurization for polyethylene preforms may also be conducted by applying a uniaxial load to a mechanically constrained preform. A typical application of this method involves inserting a cylindrically-shaped polymer preform into a close fit cylindrical cavity within a rigid cell and then rapidly applying a load perpendicular to the free face and along the length of the cylindrically-shaped polymer preform. For each of these pressurization approaches, the polymer preform may be equilibrated at a fixed temperature prior to, during and/or after pressurization or may be subjected to a varying temperature profile prior to, during and/or after pressurization.

[0018] The term rapid pressurization for polyethylene preforms is taken to be a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s.

[0019] In one aspect, this invention features methods of selecting a polyethylene preform, increasing the temperature of the preform to a first temperature in the range between the melting point of the polyethylene and 180°C, rapidly pressurizing the preform to an elevated pressure in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0020] In another aspect, this invention features methods of providing a polyethylene preform, increasing the temperature of the preform to a first temperature in the range between 120°C and the melting point of the polyethylene, rapidly pressurizing the preform to a pressure in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0021] In another aspect, this invention features methods of providing a polyethylene preform, increasing the temperature of the preform to a first temperature in the range of 180°C to 320°C, decreasing the temperature of the preform until it reaches a third temperature in the range between the melting point of the polyethylene and 180°C, rapidly pressurizing the preform to a pressure in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the preform does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0022] In another aspect, this invention features methods of providing a polyethylene preform, increasing the temperature of the preform to a first temperature in the range of 180°C to 320°C to provide a melted polymer preform, decreasing the temperature of the melted polymer preform until it reaches a third temperature in the range between 120°C and the melting point of the polyethylene, rapidly pressurizing the melted polymer preform to a pressure in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0023] In another aspect, this invention features methods of making a polyethylene preform, increasing the temperature of the preform to a first temperature in the range of 180°C to 320°C to form a melted polymer preform, decreasing the temperature of the melted polymer preform until it reaches a third temperature in the range between 120°C and the melting point of the polyethylene, rapidly pressurizing the melted polymer preform to a pressure in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0024] In another aspect, this invention features methods of making a polyethylene preform comprising a crystallizable polymer with a gradient in crystallinity whose surface crystallinity is higher than its bulk crystallinity. The method includes heating the preform to a temperature above the melting temperature rapidly so that the surface regions have melted but the bulk regions remain semicrystalline and then rapidly pressurizing in the range of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced.

[0025] In another aspect, this invention features methods of fabricating a polyethylene preform with a gradient in crystallinity whose surface crystallinity is higher than its bulk crystallinity. The method includes heating the preform to a first temperature above the melting point to form melted preform, decreasing the temperature of the melted preform to a second temperature between the melting point and peak melting temperature, then further rapidly heating the surface to a third temperature exceeding the melting point, rapidly pressurizing the preform to a pressure of 10-1000 MPa to form a pressurized polymer, wherein crystallization is induced, whereupon the preform is cooled under pressure to room temperature and the pressure released.

[0026] In another aspect, the polyethylene featured in this invention is high density polyethylene.

[0027] In another aspect, the polyethylene featured in this invention is ultra-high molecular weight polyethylene.

[0028] In another aspect, the polyethylene featured in this invention is medical grade ultra-high molecular weight polyethylene.

[0029] In another aspect, the polyethylene preform further comprises an additive, including but not limited to antioxidants, stabilizers, chemical crosslinking agents plasticizing agents, processing agents, foaming agents, porogens, or a mixture thereof.

[0030] In another aspect, the polyethylene preform comprises a chemical crosslinking agent is a peroxide or silane.

[0031] In another aspect, the antioxidant additive is a 0.05-1% weight fraction of a hindered phenol.

[0032] In another aspect, the antioxidant additive is a 0.05-1% weight fraction of alpha-tocopherol.

[0033] In another aspect, the polyethylene is gamma or electron beam irradiated to a dose in the range of 25-1000 kGy, more preferably in a dose range of 50-250 kGy, prior to rapid pressurization.

[0034] In another aspect, the polyethylene preform is gamma or electron beam irradiated to a dose in the range of 25-1000 kGy, more preferably in a dose range of 50-250 kGy, after rapid pressurization.

[0035] In another aspect, the polyethylene preform is sterilized using 25-40 kGy dose of gamma or electron beam radiation or optionally by ethylene oxide or gas plasma sterilization.

[0036] In another aspect, the invention features a polyethylene preform that is a medical device including but not limited to an acetabular component, tibial component, intervertebral disc replacement component, glenoid component, ankle component, meniscus implant, elbow component, stent, heart valve, ophthalmic lens, dental implant, and maxillofacial implant.

[0037] In another aspect, the invention features a polyethylene preform comprising a solid, liquid or gaseous filler with a characteristic size of 0.1 nanometers to 500 micrometers, or a mixture thereof.

[0038] In another aspect, the polyethylene preform comprises a powder, flakes, film, fiber, bar, sheet or a net-shaped medical device

[0039] In another aspect, the invention features a polyethylene preform comprising fillers in particulate form, platelets, fibers, spheres, lamellae, sheets, single wall carbon nanotubes, multiwall carbon nanotubes, graphene, graphene oxide, clay or a mixture thereof.

[0040] In another aspect, the invention features a polymeric preform including but not limited to a material for building construction, windows and automotive parts.

[0041] It is recognized to those skilled in the art that a polymeric preform may be fabricated comprising a combination of the various aspects of the invention outlined above. In addition, the materials, methods and examples are illustrative only and not intended to be limiting.

BRIEF DESCRIPTION OF THE FIGURES

[0042] Further description of the invention summarized above can be found in the embodiments illustrated in the figures. It must be noted that the figures are only provided as illustrative embodiments of this invention and are not to be considered limiting of its scope since the invention may admit to other embodiments that are equally effective. It must also be noted that in Figures 2-5 the increase in the melting temperature, peak crystallization temperature and glass transition temperature with pressure has been shown to be a linear dependence but actually can be slightly non-linear.

[0043] Figure 1. A schematic showing a differential scanning calorimeter (DSC) thermogram, which comprises a plot of heat flow on the y-axis and temperature on the x-axis of a temperature scan of a crystallizable polymer. It illustrates the heat flow at a constant rate heating of the polymer, whose baseline shifts upon encountering the glass transition temperature, Tg, onset of melting at a temperature, Tonset, with a broad exothermic melting curve with a peak melting temperature or melting point, Tm, until melting is completed and the heat flow returns to a baseline level. The figure also illustrates cooling and illustrates a crystallization endothermic curve with a peak crystallization temperature, Tc, occurring at a temperature below the peak melting temperature, Tm. Undercooling is defined as the difference between the melting temperature, Tm, and the crystallization temperature, Tc.

[0044] Figure 2. A schematic of a plot of peak crystallization temperature, Tc, versus logarithm of the cooling rate. The schematic shows that as cooling rate increases the peak crystallization temperature decreases (Tc1 > Tc2 > Tc3 > Tc4) and since the melting temperature remains the same, Tm, the undercooling increases with increase in cooling rate so that (Tm-Tc4) > (Tm-Tc3) > (Tm-Tc2) > (Tm-Tc1).

[0045] Figure 3. A schematic of a phase diagram of a polyethylene with temperature on the y-axis and pressure on the x-axis showing the melting curve above which polyethylene is in the melt state. It must be noted that the melting curve is shown to be linear for simplicity whereas in reality it is slightly non-linear. Polyethylene is in a semicrystalline state below the melting curve and its crystalline lamellae have an orthorhombic unit cell except for a region above the triple point, defined by a temperature of 230°C and a pressure of 360 MPa, where the crystalline lamellae have a hexagonal unit cell. The schematic further shows polyethylene at atmospheric pressure, P_0, and a temperature, T_0, above its melting temperature, T_{m0}, pressurized isothermally to pressures of P_1, P_2, P_3 and P_4 at which the melting temperature increases to T_{m1}, T_{m2}, T_{m3} and T_{m4}, respectively, and for which the undercooling is (T_{m1}-T_c), (T_{m2}-T_c), (T_{m3}-T_c) and (T_{m4}-T_c), respectively.

[0046] **Figure 4.** A schematic of a phase diagram of a polyethylene with temperature on the y-axis and pressure on the x-axis showing the melting curve above which polyethylene is in the melt state. It must be noted that the melting curve is shown to be linear for simplicity whereas in reality it is slightly non-linear. Polyethylene is in the solid state below the melting curve and its crystalline lamellae have an orthorhombic unit cell except for a region above the triple point, defined by a temperature of 230°C and a pressure of 360 MPa, where the crystalline lamellae have a hexagonal unit cell. The schematic further shows polyethylene at atmospheric pressure, P_0, and a temperature, T_0, below its melting temperature, T_{m0}, but above its peak crystallization temperature, T_{c0}, pressurized isothermally to pressures of P_1, P_2, P_3 and P_4 at which the melting temperature increases to T_{m1}, T_{m2}, T_{m3} and T_{m4}, respectively, and for which the undercooling is $(T_{m1}-T_c)$, $(T_{m2}-T_c)$, $(T_{m3}-T_c)$ and $(T_{m4}-T_c)$, respectively.

[0047] Figure 5. A plot of Lorentz-corrected scattering intensity, q^2I [counts*nm^{-2}] versus scattering angle, q[nm^{-1}] where $q=4\pi(\sin\theta)/\lambda$, where q is one-half the scattering angle of the x-ray and λ is its wavelength. The plot shows scattering curves for RPPE. CPE and HPPE, respectively.

DETAILED DESCRIPTION

[0048] Described herein are novel processing methods to induce crystallization in polymer preforms of crystallizable polymers, and articles made therefrom. These novel processing methods can be used to produce preforms with a gradient in crystallinity and crystalline lamellar morphology.

[0049] High density polyethylene (HDPE) and ultra-high molecular weight polyethylene (UHMWPE) are commercial, thermoplastics that find a wide application in a variety of articles. HDPE is widely used as bottles, toys, containers, ropes, grocery bags, recycling bins and a variety of other common applications due to its ease of processing. UHMWPE is a tough, wear-resistant polymer used in gears, ski soles, conveyer belts, cutting boards, dock fenders and as bearing components in total joint replacement prostheses. Examples of suitable medical grade UHMWPE polymers include GUR 1020 and GUR 1050 available from Celanese Corporation. These polymers are usually provided as powders that are ram-extruded or compression molded into bulk preforms from which components of joint replacement prostheses are manufactured. In the late, 1990s, it was discovered that irradiating UHMWPE with ionizing radiation, such as gamma radiation or electron beam radiation, to a dose of 50-200 kGy followed by post-radiation melting and cooling increased their wear resistance substantially with radiation dose

[7-9]. The post-radiation melting step was performed in order to extinguish free radicals trapped in the crystalline lamellae, which would otherwise result in long-term oxidation, thus providing a wear-resistant, oxidation-resistant radiation crosslinked UHMWPE. This was highly desirable for the durability of UHMWPE components of joint replacements. However, the result of radiation crosslinking and post-radiation melting was that the tensile properties, such as ultimate tensile stress and maximum strain-to-failure decreased with an increase in radiation dose [7-9]. It became unnecessary for post-radiation melting when an antioxidant, such as Vitamin E, was added to the UHMWPE since the antioxidant was available in the amorphous regions to quench free radicals that diffused out of the crystalline lamellar regions before they could oxidize from the dissolved oxygen present in the amorphous regions. The elimination of post-radiation melting preserved the ultimate tensile stress of unirradiated UHMWPE containing Vitamin E but it led to a decrease in the maximum strain-to-failure.

[0050] Described herein are novel processes that can produce a UHMWPE morphology that is more ductile, and associated with a higher maximum strain-to-failure. Such a UHMWPE preform would have the advantage of increasing the maximum strain-to-failure of radiation crosslinked UHMWPE containing an antioxidant, such as Vitamin E. It was shown that rapid cooling of 1 mm thick UHMWPE sheets from the melt state by immersion in liquid nitrogen followed by annealing led to an increase in maximum strain-to-failure and the work-of-fracture, a measure of toughness, defined by the area under the tensile stress-strain curve [10]. However, rapid cooling is not a viable option for large articles such as total joint replacement prostheses since the low thermal conductivity of UHMWPE does not enable rapidly crystallized lamellar morphology to be induced in the bulk regions and consequently, the effects are confined to a surface layer. This invention takes advantage of rapid pressurization to circumvent this problem since pressure transmits rapidly and results in an increase in melting temperature with an increase in pressure. Thus, if the large article is in the fully melted state it can crystallized during rapid pressurization at large undercooling, which is equivalent to rapid cooling wherein the polymer also crystallizes at large undercooling. In the case of rapid cooling of UHMWPE or HDPE from the melt state, the peak crystallization temperature decreases with an increase in cooling rate thereby increasing the undercooling with increasing cooling rate. In contrast, rapid pressurization of UHMWPE or HDPE from the melt state increases the melting temperature rapidly while maintaining the peak crystallization temperature, thus increasing the undercooling with an increase in pressurization rate. However, since pressure transmits instantaneously throughout a large article, such as a bar, sheet or a net-shaped medical device, its effect is throughout the article whereas in the case of rapid cooling, it remains a surface effect since the rapid decrease in surface temperature does not transmit rapidly into the bulk material due to the low thermal conductivity of UHMWPE and HDPE. Thus, this invention takes advantage of the rapid undercooling of large articles due to rapid pressurization to induce lamellar morphology in UHMWPE or HDPE or a mixture thereof that will increase its tensile properties, such as ductility and work-of-fracture.

[0051] In one embodiment, this invention includes selecting a UHMWPE preform in the form of a film, fiber, sheet, bar, rod, ball, or a shaped article, increasing the temperature of the preform to a first temperature above the melting temperature in the range between 180°C and 320°C for a duration in the range of 1-600 minutes, decreasing the temperature to a second temperature in the range between 120°C and 180°C to form a melted polymer preform, pressurizing the preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer, thus inducing crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0052] In another embodiment, this invention includes selecting a UHMWPE preform in the form of a film, fiber, sheet, bar, rod, ball, or a shaped article, increasing the temperature of the preform to a first temperature above the melting temperature in the range between the melting point of the polyethylene and 180°C, pressurizing the preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer, wherein crystallization is induced. The preform is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the preform does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0053] In another embodiment, this invention includes selecting a UHMWPE preform in the form of a film, fiber, sheet, bar, rod, ball, or a shaped article, irradiating the preform using ionizing radiation to a radiation dose in the range of 50-500 kGy, increasing the temperature of the preform to a first temperature above the melting temperature in the range between 180°C and 320°C for a duration in the range of 1-600 minutes, decreasing the temperature to a second temperature in the range between 120°C and 180°C, pressurizing the preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and inducing crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the preform does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%.

[0054] In another embodiment, this invention includes selecting a UHMWPE preform in the form of a film, fiber, sheet, bar, rod, ball, or a shaped article, irradiating the preform using ionizing radiation to a radiation dose in the range of 50-500 kGy, increasing the temperature of the preform to a first temperature above the melting temperature in the range between the melting point of the polyethylene and 180°C, pressurizing the preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0055] In another embodiment, this invention includes providing a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form or a mixture thereof, irradiating the preform using ionizing radiation to a radiation dose in the range of 50-500 kGy, increasing the temperature of the preform to a first temperature above the melting temperature in the range between 180°C and 320°C for a duration in the range of 1-600 minutes, decreasing the temperature to a second temperature in the range between 120°C and 180°C to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%.

[0056] In another embodiment, this invention includes providing a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form, irradiating the preform using ionizing radiation to a radiation dose in the range of 50-500 kGy, increasing the temperature of the preform to a first temperature above the melting temperature in the range between the melting point of the polyethylene and 180°C to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0057] In another embodiment, this invention includes providing a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form, increasing the temperature of the preform to a first temperature above the melting temperature in the range between 180°C and 320°C for a duration in the range of 1-600 minutes, decreasing the temperature to a second temperature in the range between 120°C and 180°C, pressurizing the preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induces crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0058] In another embodiment, this invention includes providing a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form, increasing the temperature of the preform to a first temperature above the melting temperature in the range between the melting point of the polyethylene and 180°C to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0059] In another embodiment, this invention includes providing a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form or a mixture thereof. The preform further comprises a 0.1-5 weight percent of a chemical crosslinking agent such as a peroxide or silane. The method comprises increasing the temperature of the preform to a first temperature above the melting temperature in the range between 180°C and 320°C for a duration in the range of 1-600 minutes, pressurizing the UHMWPE preform to a about 1-10 MPa, decreasing the temperature to a second temperature in the range between 120°C and 180°C to remain in a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%.

[0060] In another embodiment, this invention includes selecting a UHMWPE preform in the form of a powder, resin, flakes in loose or compacted form. The preform further comprises a 0.1-5 weight percent of a chemical crosslinking agent such as a peroxide or silane. The method comprises increasing the temperature of the preform to a first temperature above the melting temperature in the range between the melting point of the polyethylene and 180°C to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized melt does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The UHMWPE preform further optionally comprises an antioxidant in a weight percentage of 0.05-1%. The preform is further irradiated using ionizing radiation to a radiation dose in the range of 50-500 kGy.

[0061] In all of the embodiments above, the temperature of the UHMWPE preform can be increased to a first temperature under a pressure in the range of 0.1-1000 MPa as long as the first temperature is sufficiently high for the UHMWPE to be in the melt state.

[0062] In another embodiment, the method comprises providing a UHMWPE preform, increasing the pressure to a pressure of 10-1000 MPa, increasing the temperature under pressure to a first temperature below the melt state, decreasing the pressure until the preform enters the melt state and form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0063] In another embodiment, the method comprises providing a UHMWPE preform, increasing the pressure to a pressure of 10-1000 MPa, increasing the temperature under pressure to a first temperature below the melt state, decreasing the pressure until the preform enters the melt state to form a melted polymer preform, decreasing the temperature to a second temperature wherein the melted polymer preform remains in the melt state, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0064] In another embodiment, the method comprises providing a UHMWPE preform, increasing the pressure to a pressure of 10-1000 MPa, increasing the temperature under pressure to a first temperature below the melt state, decreasing the pressure until the preform enters the melt state, increasing the temperature to a second temperature wherein the preform remains in the melt state but below 320°C to form the melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C.

[0065] In another embodiment, the method comprises selecting a UHMWPE preform, increasing the temperature to a first temperature in a range of 120-180°C for a duration wherein the surface attains the target temperature but the bulk remains at a lower temperature to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the pressurized polymer does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The method induces a gradient in crystallinity and crystalline lamellar morphology in UHMWPE.

[0066] In another embodiment, the method comprises selecting a UHMWPE preform, increasing the temperature to a first temperature in a range of 180-320°C, decreasing the temperature to a second temperature of 120-180°C, wherein the surface attains the second target temperature but the bulk remains at a higher temperature to form a melted polymer preform, pressurizing the melted polymer preform to an elevated pressure in the range of 10-1000 MPa at a pressurization rate in the range of 1 MPa/s to 1,000 MPa/s, more preferably in the range of 10 MPa/s to 1,000 MPa/s, most preferably in the range of 10 MPa/s to 100 MPa/s to form a pressurized polymer and induce crystallization. The pressurized polymer is then cooled to room temperature under pressure and then the pressure released. The cooling and pressure release may optionally be performed simultaneously so long as the preform does not reenter the melt state during the simultaneous cooling and depressurization and preferably maintains the degree of undercooling until the temperature is below 120°C. The method induces a gradient in crystallinity and crystalline lamellar morphology in UHMWPE.

[0067] In another embodiment, this invention features a polymeric preform comprising a blend of HDPE and UHMWPE.

[0068] In a further embodiment, the polymeric preform comprises a UHMWPE or HDPE polymer or a mixture thereof containing an additive, including but not limited to antioxidants, chemical crosslinking agents, stabilizers, plasticizing agents, processing agents, foaming agents, porogens, or a mixture thereof. Examples of antioxidants which can be used in any of the methods described herein include alpha- and delta-tocopherol; propyl, octyl, or dodecyl gallates; lactic, citric, and tartaric acids and salts thereof; as well as orthophosphates and sulfur based antioxidants. In some instances, a preferable antioxidant is vitamin E. Still other antioxidants are available form Eastman under the trade name TENOX. For example other antioxidants include tertiary-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), or mixtures of any of these or the prior-mentioned antioxidants. Antioxidants include Grape seed extracts, procyanidolic oligomers, ferulic acid, 4,4’ Butylidene-bis(6-tert-butyl-m-cresol, N-acetyl cysteinamide, 1-ergothioneine, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)s-triazine-2,4,6-(1H,3H,5H)-trione, 4,4'-methylene-bis(2,6-di-tert-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 4,4'-isopropylidene-diphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-p-cresol, 1,3,5-trimethyl-2,4,6-tris(3,5-di-di-tert-butyl-4-hydroxybenzyl)benzene, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butyl-phenyl)butane, 4,4-thio-bis(2-tert-butyl-m-cresol), tetrakis (methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)methane, 1,3,5-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1- H,3H,5G)-trione, bis-[3,3-bis-(4'-hydroxy-3'-tert-butyl-phenyl-butanoic acid]-glycol ester, 4,4'-thio-bis(6-tert-butyl-m-cresol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(2-tert-butyl-m-cresol), 2,6-di-tert-butyl-4-sec-butylphenol, 1,6-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid trimester, 2,2'-methylene-bis(4-ethyl-6-tert-butylphenol), 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, octadecyl-3-(3'5-di-tert-butyl-4-hydroxyphenyl)propionate, 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6-(1H,3H,5H)trione, ,2-Bis (3, 5-di-t-butyl-4-hydroxyhydrocinnamoyl) hydrazine, 4,4’-Bis (α, α--dimethylbenzyl) diphenylamine, 3,5-Di-t-butyl-4-hydroxyhydrocinnamic acid, 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6-(1H,3H,5H)-trione trimester, Dilauryl thiodipropionate, Distearyl pentaerythrityl diphosphite, Distearyl thiodipropionate, N,N’-Hexamethylene bis (3,5-di-t-butyl-4-hydroxyhydrocinnamamide), Irganox(® 1098; Lankromark ® LE 109; Naugard® 445; Nickel dibutyldithiocarbamate; Nickel dimethyldithiocarbamate; Pentaerythityl tetrakis [3-(3’,5’-di-t-butyl-4-hydroxyphenyl) propionate]; Phenol, styrenated; Tetramethylthiuram disulfide; Tris (2,4-di-t-butylphenyl) phosphate; 1,1,3-Tris (2-methyl-4-hydroxy-5-t-butylphenyl) butane; Tris (nonylphenyl) phosphate; Vanlube® PCX, Ethoxyquin, 1,2-dihydro-6-ethoxy-2,2,4-trimethylquinoline, Rosemary extract, carnosol, rosmanol, and epirosmanol, phenolic diterpenes or mixtures thereof.

[0069] A UV light stabilizer may also be included in the preform. The UV light stabilizer may be thermally stable up to a temperature of about 300° C. Suitable stabilizers are Hostavin, Chimassorb 2020, Chimassorb 944, Tinuvin 622, Tinuvin 791, SONGNOX 1010 and Tinuvin 770 available from Clariant Corporation, Charlotte, NC. The UV absorber may comprise one or more benzophenone compounds such as 2-hydroxy-4-methoxybenzophenone, 2,4-dihydroxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-benzyloxybenzophenone, 2-hydroxy-4-methoxy-5-sulfoxytrihydride benzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-5-sulfoxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxy-5-sodiumsulfoxybenzophenone, bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane, 2-hydroxy-4-n-dodecyloxybenzophenone or 2-hydroxy-4-methoxy-2'-carboxybenzophenone. The UV absorber may comprise benzotriazole compounds such as 2-(2-hydroxy-5-tert-octylphenyl)benzotriazole, 2-(2-hydroxy-5-methylphenyl)benzotriazole, , 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-(2N-benzotriazol-2-yl)phenol], 2-(2-hydroxy-3,5-dicumylphenyl) phenylbenzotriazole, 2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole2-(2-hydroxy-3,5-di-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-3,5-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-3,5-di-tert-amylphenyl)benzotriazole, 2-(2-hydroxy-4-octoxyphenyl)benzotriazole, 2,2'-methylenebis(4-cumyl-6-benzotriazolephenyl), 2-[2-hydroxy-3-(3,4,5,6-tetrahydrophthalimidomethyl)-5-methylphenyl]benzo- triazole, 2,2'-p-phenylenebis(1,3-benzooxazin-4-one) or a combination thereof.

[0070] Examples of common peroxide crosslinking agents for incorporation into the UHMWPE powder preforms include dicumyl peroxide, di-tert-butyl peroxide, di-(2-tert-butyl-peroxyisopropyl)-benzene, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane, 2,5-di(tertbutylperoxy)-2,5-dimethyl-3-hexyne, or a combination thereof. Examples of silane crosslinking agents are vinyltriethoxysilane, vinyltrimethoxysilane or a mixture thereof. Both peroxides and silanes can be incorporated into the UHMWPE or HDPE.

[0071] Any of the crystallizable polymers described herein can include microwave radiation active materials, which can aid in the heating of the polymeric preform in any step described herein. Generally, the microwave radiation active materials can be inorganic materials, such as ceramics (for example, nitrides, borides, carbides), metals and metal alloys, quantum dots, or organic materials, such as edible oils or solids, e.g., sunflower oils, corn oils, wheat germ oils, Vitamin E, fatty acids, or a mixture thereof.

[0072] In another embodiment, the invention features a polymeric preform that is a medical device including but not limited to an acetabular component, tibial component, intervertebral disc replacement component, glenoid component, ankle component, meniscus implant, elbow component, stent, heart valve, ophthalmic lens, dental implant, and maxillofacial implant. In another embodiment, the invention features a polymeric preform including but not limited to a material for building construction, windows and automotive parts.

[0073] In another embodiment, the invention features a polyethylene preform comprising a solid, liquid or gaseous filler with a characteristic size of 0.1 nanometers to 500 micrometers, or a mixture thereof. A few examples of solid fillers are hydroxyapatite, alumina, carbon black, carbon or graphite fibers. An example of liquid filler is alpha-tocopherol, and an example of gaseous filler is air. In further embodiments, the invention features a polymeric preform comprising a crystallizable polymer containing fillers in particulate form, platelets, fibers, spheres, lamellae, sheets, single wall carbon nanotubes, multiwall carbon nanotubes, graphene, clay or a mixture thereof.

[0074] Pressurization can be conducted by several methods, including but not limited to hot isostatic pressing, warm isostatic pressing, compression molding, ram-extrusion, sintering and high-pressure injection molding. Pressurization can be performed using hydrostatic pressure. In a typical process the polymeric preform is placed in a flexible barrier packaging, which is placed in a high-pressure cell and surrounded by oil. A pump is used to pressurize the oil contained in the sealed cell which transmits the pressure to the polymeric preform uniformly. Pressurization can alternatively be performed using a pseudo-hydrostatic method such as fitting a cylindrical polymeric preform snugly into a cell with a cylindrical cavity and then applying a compressive load until the desired pressure is attained.

CHARACTERIZATION

[0075] Differential scanning calorimeter (DSC) is a common method to measure the glass transition temperature, melting point, crystallization temperature and degree of crystallinity of a polymer. In this method, a known quantity of the polymer, usually, less than 10 mg, is encapsulated in a pan and is heated against a reference pan and the heat flow is measured as the polymer is heated at a constant rate of increase of temperature. Referring now to Figure 1, which shows a schematic of the heat flow with increase in temperature from a starting temperature below the glass transition temperature. The heat flow increases, decreases or remains constant at a baseline level until the glass transition temperature is attained whereupon there is a shift in the baseline. Then as the polymer begins to melt, a broad melting curve or endotherm is encountered until the sample is completely melted. The area enclosed by the melting curve and the baseline normalized by the weight of the sample and divided by the heat of fusion of the 100% crystalline polymer provides the fraction or degree of crystallinity. Upon cooling, the polymer does not crystallize just below the melting temperature but at a few degrees centigrade lower since a certain amount of undercooling, defined as the difference between the melting point (peak of the melting curve) and the sample temperature, is required for crystallization occurs, as shown in Figure 1. In most polymers, there is a difference between melting point and the peak crystallization temperature, which is referred to as undercooling or degree of undercooling. The crystallizable polymer crystallizes at its highest rate at the peak crystallization temperature. ASTM F2626-10(2016) provides guidance into the measurement of thermal properties of UHMWPE using DSC [11]. A DSC instrument equipped with a high-pressure cell with pressure and temperature control can be used to measure the melting temperature and peak crystallization at various pressures and temperatures to construct a temperature-pressure phase diagram. It can also be used to detect peak crystallization temperature during different pressurization rates.

Small angle x-ray scattering can be used to measure the inter-lamellar spacing. In this method, a sample of polyethylene of approximately 0.5-2mm thickness is placed in the path of a collimated x-ray beam and the scattered intensity is measured as a function of the scattering vector, q, where q is defined as $q=(4\pi/\lambda)\sin\theta$ where λ is the wavelength of x-ray used and θ is one-half the scattering angle. The inter-lamellar spacing, D, is measured using Bragg's law wherein $L=2\pi/q_{max}$ where q_{max} is the peak of a plot of q^2I versus q. Combined with DSC crystallinity, X, the lamellar thickness, L, can be calculated as L=D*X.

[0076] The swell ratio and gel content of crosslinked polyethylene can be measured by extraction of soluble fractions in xylene using ASTM 2765-95 as guidance [12].

[0077] The degree of crosslinking and molecular weight between crosslinks for crosslinked UHMWPE can be measured by measuring the equilibrium swelling of crosslinked samples in hot xylene at 130°C using ASTM-F2214 as guidance [13].

TENSILE PROPERTIES

[0078] The tensile properties of UHMWPE can be measured using guidance from ASTM F648 [14] and ASTM D638 [15], which describe the specimen geometry, gauge length, crosshead speed and all the parameters required to measure tensile properties such as tensile modulus, yield stress, ultimate tensile stress and strain-to-failure.

[0079] It is recognized to those skilled in the art that a polymeric preform may be fabricated comprising a combination of the various embodiments of the invention outlined above. In addition, the embodiments, crystallizable polymers, additives, fillers, type of high pressure process and examples are illustrative only and not intended to be limiting.

EXAMPLES

[0080] EXAMPLE 1**:** Ram extruded GUR 1050 UHMWPE (Celanese, Oberhausen, Germany) bars served as controls (CPE) and machined into 75 mm long cylinders of 12.5 mm diameter to snugly fit into a high pressure cell. These polyethylene (PE) cylindrical preforms were then subjected to the following thermal and pressurization profiles. Conventional high-pressure crystallization was conducted by heating the PE to 180°C, applying 500 MPa pressure in a pseudo-hydrostatic fashion and slowly over 5 minutes, cooling to room temperature under pressure followed by pressure release. Rapid pressurization was conducted by heating the PE to 200°C to erase previous thermal history, cooled to 140°C and then rapidly pressurizing the cylindrical preform to 500 MPa via a compressive load at a rate of 50 MPa/s. The cylindrical preform was then slow cooled under pressure followed by pressure release (RPPE). ASTM standard tensile tests using ASTM 638-Type V specimens were conducted to measure the ultimate tensile stress (UTS) and maximum strain (MS). A Q1000 (TA instruments, New Castle, DE) differential scanning calorimeter (DSC) was used to measure the degree of crystallinity. Percentage crystallinity was obtained as $X= 100*\square H/\square H_f$, where □H is the area under the endotherm and $\square H_f$ is the heat of fusion of PE (293 J/g). Small angle x-ray scattering (SAXS) was performed to measure the inter-lamellar spacing and lamellar thickness was calculated using a combination of SAXS and DSC

[0081] Figure 5. A plot of Lorentz-corrected scattering intensity, q^2I [counts*nm^{-2}] versus scattering angle, q[nm^{-1}] where $q=4\square(\sin\theta)/\lambda\square$ □where q is one-half the scattering angle of the x-ray and λ is its wavelength. The plot shows scattering curves for RPPE. CPE and HPPE, respectively.

[0082] SAXS plots showed that RPPE had the highest scattering angle followed by CPE and HPPE, indicating that the RPPE had the smallest inter-lamellar spacing (Figure A). Combined with DSC, lamellar thickness was calculated showing that RPPE had the thinnest lamellae and lowest crystallinity (Table 1) compared to CPE while HPPE had the thickest lamellae and highest crystallinity. As expected, HPPE had the lowest UTS and MS while there was no statistical difference between the UTS of CPE and PQPE. However, the MS of RPPE was much higher than for both CPE and HPPE.

Table 1. Crystallinity (X), Lamellar thickness (L), Ultimate tensile stress (UTS) and maximum strain (MS)(mm/mm) for CPE, HPPE and RPPE, respectively.

ID	X(%)	L(nm)	UTS(MPa)	MS
CPE	51.8±0.8	23.8±0.3	50.5±4.3	9.9±0.4
HPPE	69.4±1.4	125.6±2.4	24.5±1.4	4.0±0.7
RPPE	44.7±3.1	20.6±0.7	50.2±1.7	21.9±0.8

EXAMPLE 2: Ram-extruded rod stock of GUR 1050 UHMWPE (Celanese, Oberhausen, Germany) was purchased and machined into cylinders of 25mm length and 12.5mmm diameter to snugly fit into a custom-built high-pressure cell. The cylindrical preform was heated to a temperature of 160C and then pressurized to 500 MPa at a rate of 50 MPa/s. Then it was slowly cooled to room temperature while maintaining the pressure followed by pressure release. A Q1000 (TA instruments, New Castle, DE) differential scanning calorimeter (DSC) was used to measure the degree of crystallinity. Percentage crystallinity was obtained as $X = 100*\delta H/\delta H_f$, where δH is the area under the endotherm and δH_f is the heat of fusion of PE (293 J/g). Small angle x-ray scattering (SAXS) was performed to measure the inter-lamellar spacing and lamellar thickness was calculated using a combination of SAXS and DSC. The crystallinity and lamellar thickness of control UHMWPE was 51.8 ± 0.8 and 23.8 ± 0.3, respectively but for the cylinder heated to 160°C and rapidly pressurized was 48.3 ± 0.3 and 21.7 ± 0.1, respectively.

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[11] ASTM-F2625-10(2016), Standard Test Method for Measurement of Enthalpy of Fusion, Percent Crystallinity, and Melting Point of Ultra-High-Molecular Weight Polyethylene by Means of Differential Scanning Calorimetry.

[12] ASTM-D2765-95(1995), Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics.

[13] ASTM-F2214-16(2016), Standard Test Method for In Situ Determination of Network Parameters of Crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE).

[14] ASTM-F648-21(2021), Standard Specification for Ultra-High-Molecular-Weight Polyethylene Powder and Fabricated Form for Surgical Implants.

[15] ASTM-D638-14(2014), Standard Test Method for Tensile Properties of Plastics.

The invention claimed is:

1. A method of making a polyethylene material comprising the steps of:
    a) providing a preform of the polyethylene;
    b) irradiating the preform at a temperature that is below the melting point of polyethylene, wherein the polyethylene is irradiated at a dose level between about 1 and 1000 kGy;
    c) heating the preform to a first temperature to form a melted polyethylene preform;
    d) rapidly pressurizing the melted polymer preform to induce crystallization;
    e) cooling the preform under pressure to room temperature;
    f) depressurizing the preform.

2. A method of making a polyethylene material comprising the steps of:
    a) providing a preform of the polyethylene;
    b) heating the preform to a first temperature to form a melted polyethylene preform;
    c) rapidly pressurizing the melted polymer preform to induce crystallization;
    d) cooling the preform under pressure to room temperature;
    e) depressurizing the preform;
    f) irradiating the preform at a temperature that is below the melting point of polyethylene, wherein the polyethylene is irradiated at a dose level between about 1 and 1000 kGy.

3. A method of making a polyethylene material comprising the steps of:
    a) blending a chemical crosslinking agent into a polyethylene preform;
    b) heating the preform to a first temperature to form a melted polyethylene preform;
    c) rapidly pressurizing the melted polymer preform to induce crystallization;
    d) cooling the preform under pressure to room temperature;
    e) depressurizing the preform.

4. A method of making a polyethylene material comprising the steps of:
    a) blending a chemical crosslinking agent into polyethylene resin;
    b) heating the polyethylene to a first temperature to form a melted polyethylene preform;
    c) pressurizing the melted polyethylene to a pressure range of about 1-10 MPa to sinter the resin;
    d) cooling the polyethylene to a second temperature above the peak crystallization temperature;
    e) rapidly pressurizing the melted polymer preform to induce crystallization;
    f) cooling the preform under pressure to room temperature;
    g) depressurizing the preform.

5. A method of making a polyethylene material comprising the steps of:
    a) providing a preform of the polyethylene;
    b) heating the preform to a first temperature to form a melted polyethylene preform;
    c) rapidly pressurizing the melted polymer preform to induce crystallization;
    d) cooling the preform under pressure to room temperature;
    e) depressurizing the preform.

6. The method of claim 1, 2, 3, 4 or 5, wherein the rapid pressure is applied to about 10-1000 MPa.

7. The method of claim 1, 2, 3, 4 or 5, wherein the pressurizing is at a pressurization rate that ranges from about 1 MPa/s to about 1,000 MPa/s.

8. The method of claim 1, 2, 3, 4 or 5, wherein the pressurizing is at a pressurization rate that ranges from about 10 MPa/s to about 1,000 MPa/s.

9. The method of claim 1, 2, 3, 4 or 5, wherein the pressurizing is at a pressurization rate that ranges from about 10 MPa/s to about 100 MPa/s.

10. The method of claim 1, 2, 3, 4 or 5, wherein pressurizing is conducted by using at least one of hydrostatic pressure, hot isostatic pressing, warm isostatic pressing, compression molding, ram-extrusion, sintering or high-pressure injection molding.

11. The method of claim 1, 2, 3, 4 or 5, wherein the polymer preform comprises at least one of high- density polyethylene, low density polyethylene, linear low-density polyethylene, very low-density polyethylene, ultra-low-density polyethylene, ultra-high molecular weight polyethylene, or combinations thereof.

12. The method of claim 11, wherein the polymer preform comprises one or more additives.

13. The method of claim 12, wherein the additive is at least one of antioxidants, stabilizers, chemical crosslinking agents, UV light stabilizers, microwave radiation active materials, plasticizing agents, processing agents, foaming agents, porogens, or a mixture thereof.

14. A method of claim 13, wherein the antioxidant is a hindered phenol.

15. A method of claim 13, wherein the antioxidant is alpha-tocopherol.

16. The method of claim 1, 2, 3, 4 or 5, wherein the preform is a powder, flakes, film, fiber, bar, sheet or a net-shaped device.

17. A medical device comprising the preform of claim 16 that is formed into an acetabular component, a tibial component, an intervertebral disc replacement component, a glenoid component, an ankle component, a meniscus implant, an elbow component, a stent, a heart valve, a dental implant, or a maxillofacial implant.

18. The net-shaped device of claim 16 that is an acetabular component, a tibial component, an intervertebral disc replacement component, a glenoid component, an ankle component, a meniscus implant, an elbow component, a stent, a heart valve, a dental implant, or a maxillofacial implant.

19. The medical device of claims 17 or 18 that is cleaned, packaged and sterilized.

20. The method of claim 19, wherein the sterilization is performed using gamma or electron beam radiation.

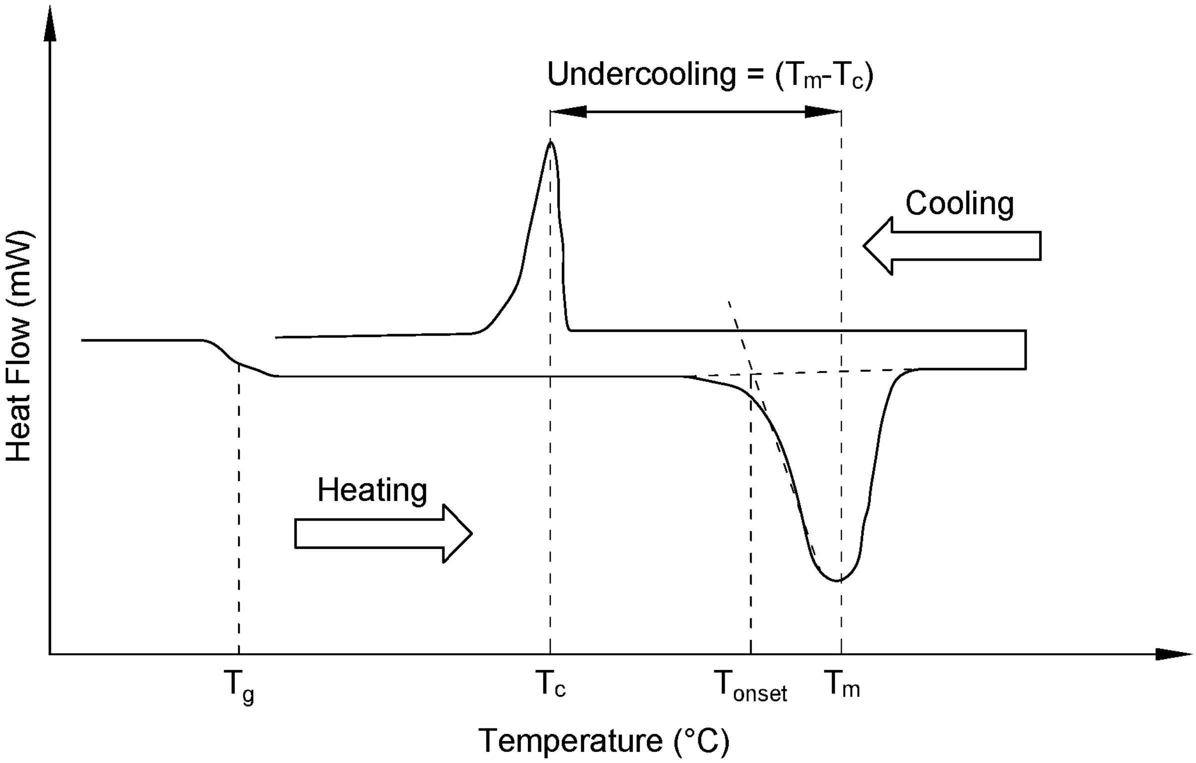
Heat Flow (mW)
Undercooling = (Tm-Tc)
Cooling
Heating
Tg
Tc
Tonset
Tm
Temperature (°C)

Figure 1

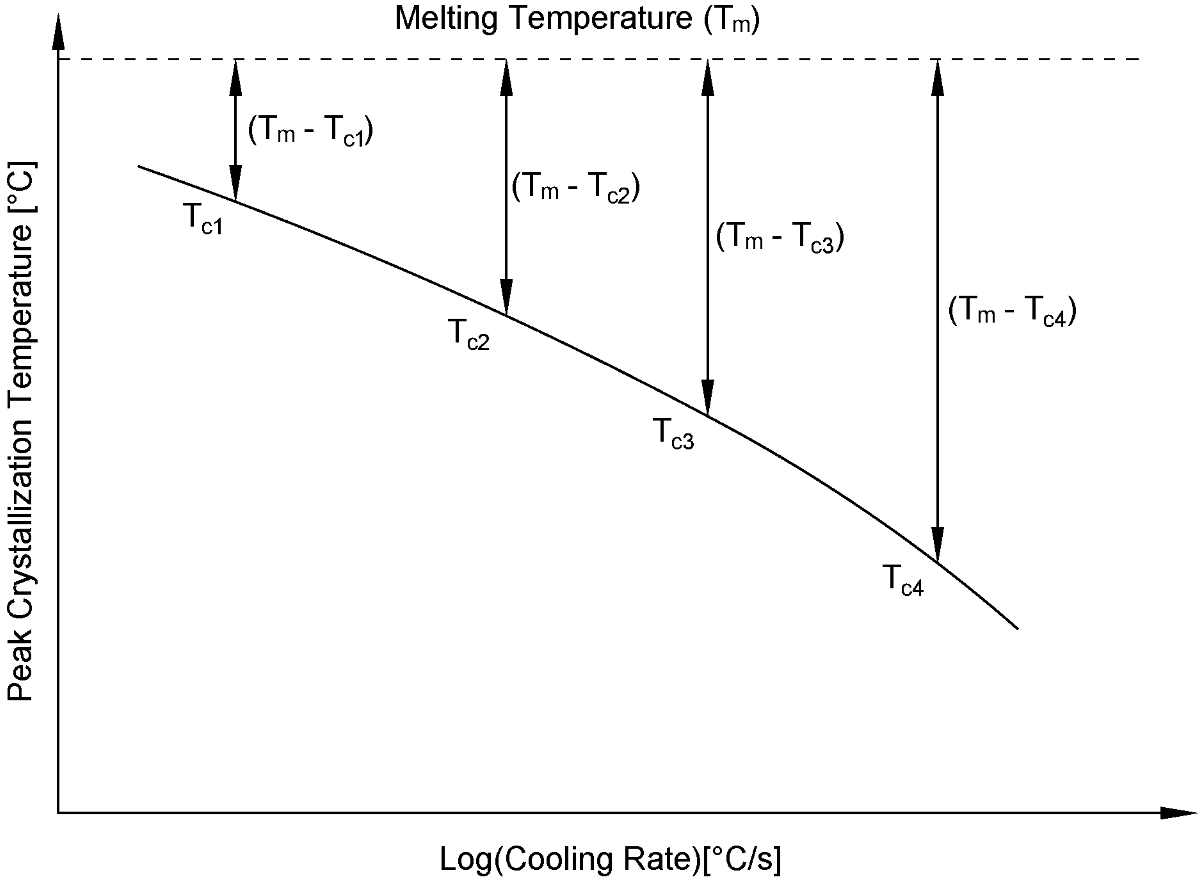
Melting Temperature (T_m)
(T_m - T_{c1})
(T_m - T_{c2})
(T_m - T_{c3})
(T_m - T_{c4})
T_{c1}
T_{c2}
T_{c3}
T_{c4}
Peak Crystallization Temperature [°C]
Log(Cooling Rate)[°C/s]

Figure 2

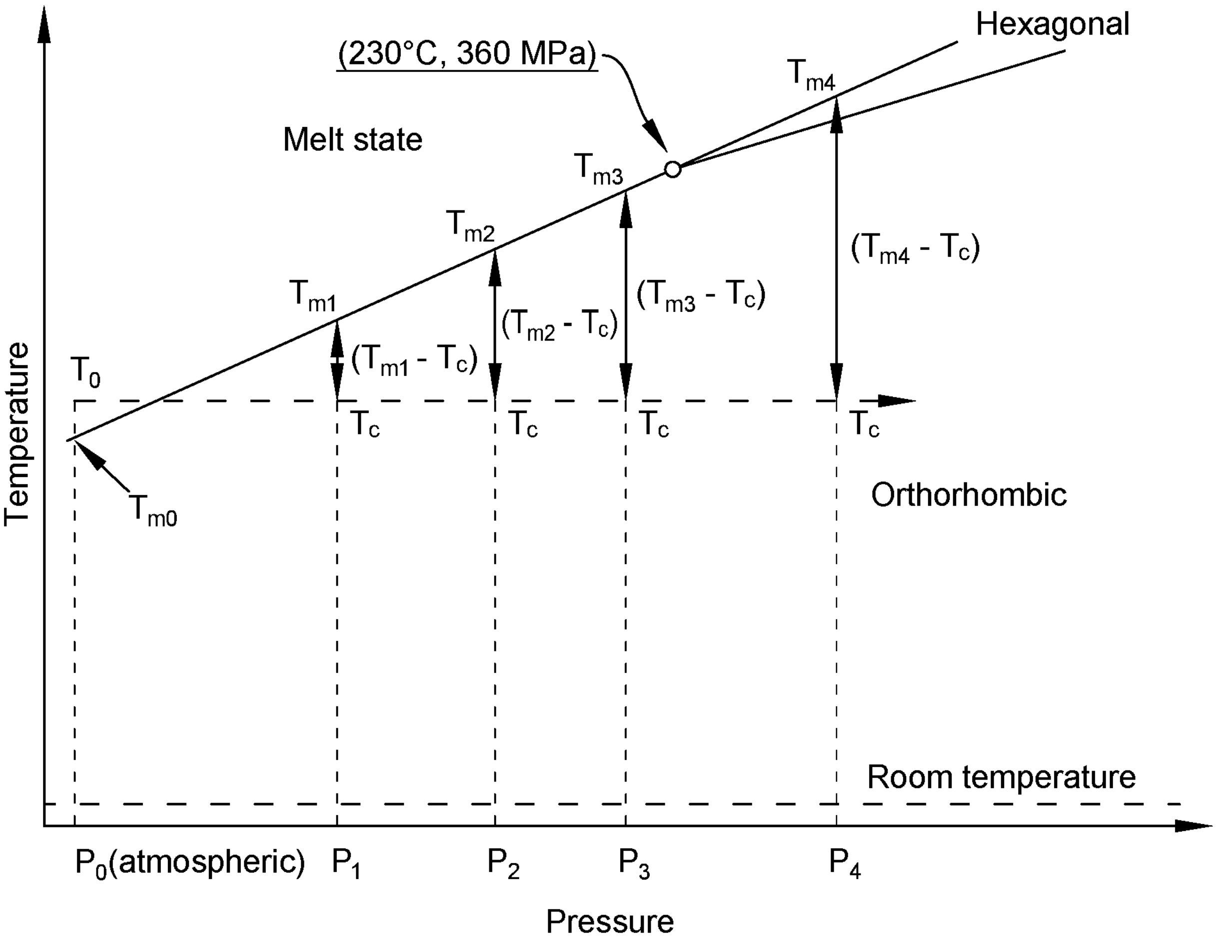
Hexagonal
(230°C, 360 MPa)
T_{m4}
Melt state
T_{m3}
T_{m2}
T_{m1}
$(T_{m4} - T_c)$
$(T_{m3} - T_c)$
$(T_{m2} - T_c)$
$(T_{m1} - T_c)$
T_0
T_c
T_c
T_c
T_c
Temperature
T_{m0}
Orthorhombic
Room temperature
P_0(atmospheric)
P_1
P_2
P_3
P_4
Pressure

Figure 3

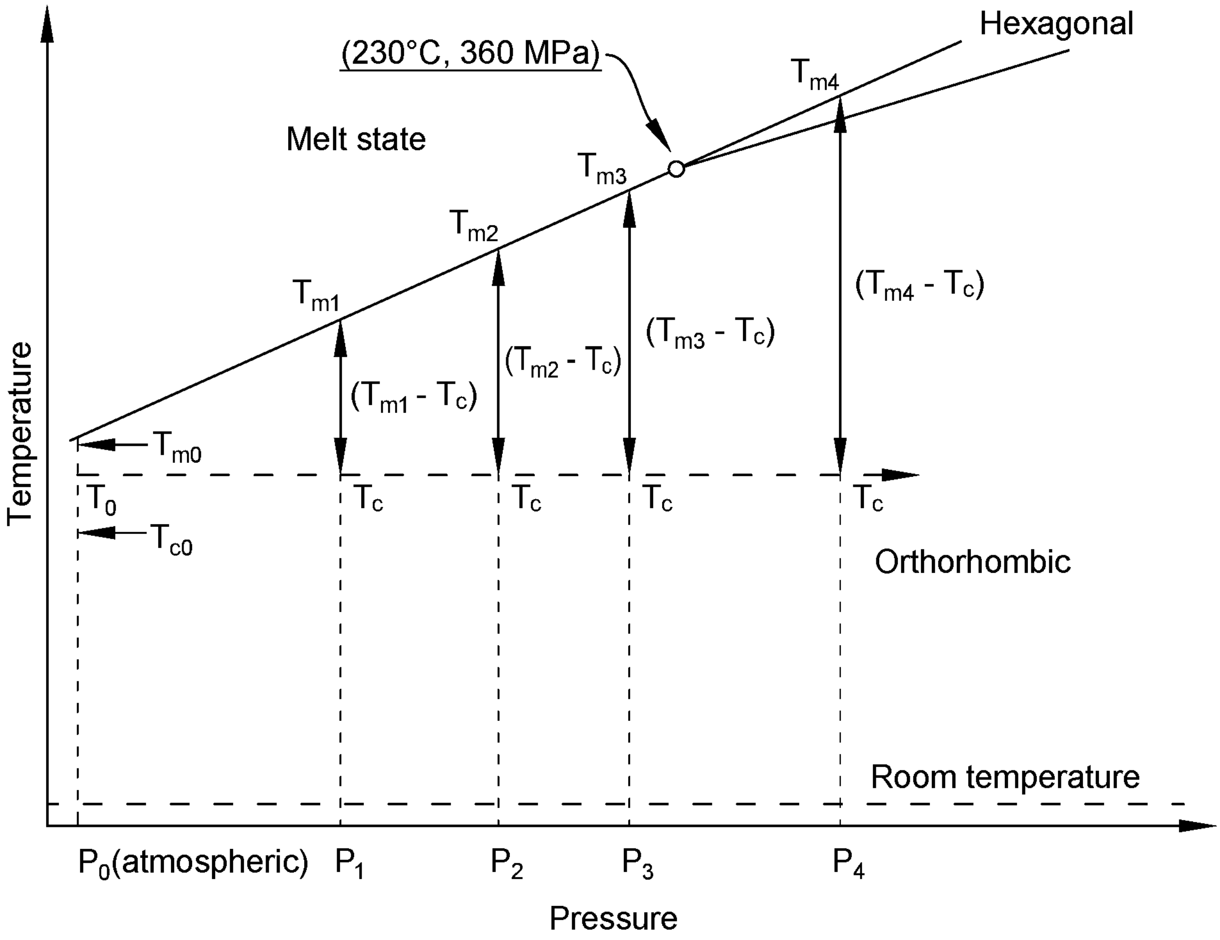
Hexagonal
(230°C, 360 MPa)
Melt state
T_{m4}
T_{m3}
T_{m2}
T_{m1}
T_{m0}
$(T_{m1} - T_c)$
$(T_{m2} - T_c)$
$(T_{m3} - T_c)$
$(T_{m4} - T_c)$
T_0
T_c
T_c
T_c
T_c
T_{c0}
Orthorhombic
Room temperature
Temperature
P_0(atmospheric)
P_1
P_2
P_3
P_4
Pressure

Figure 4

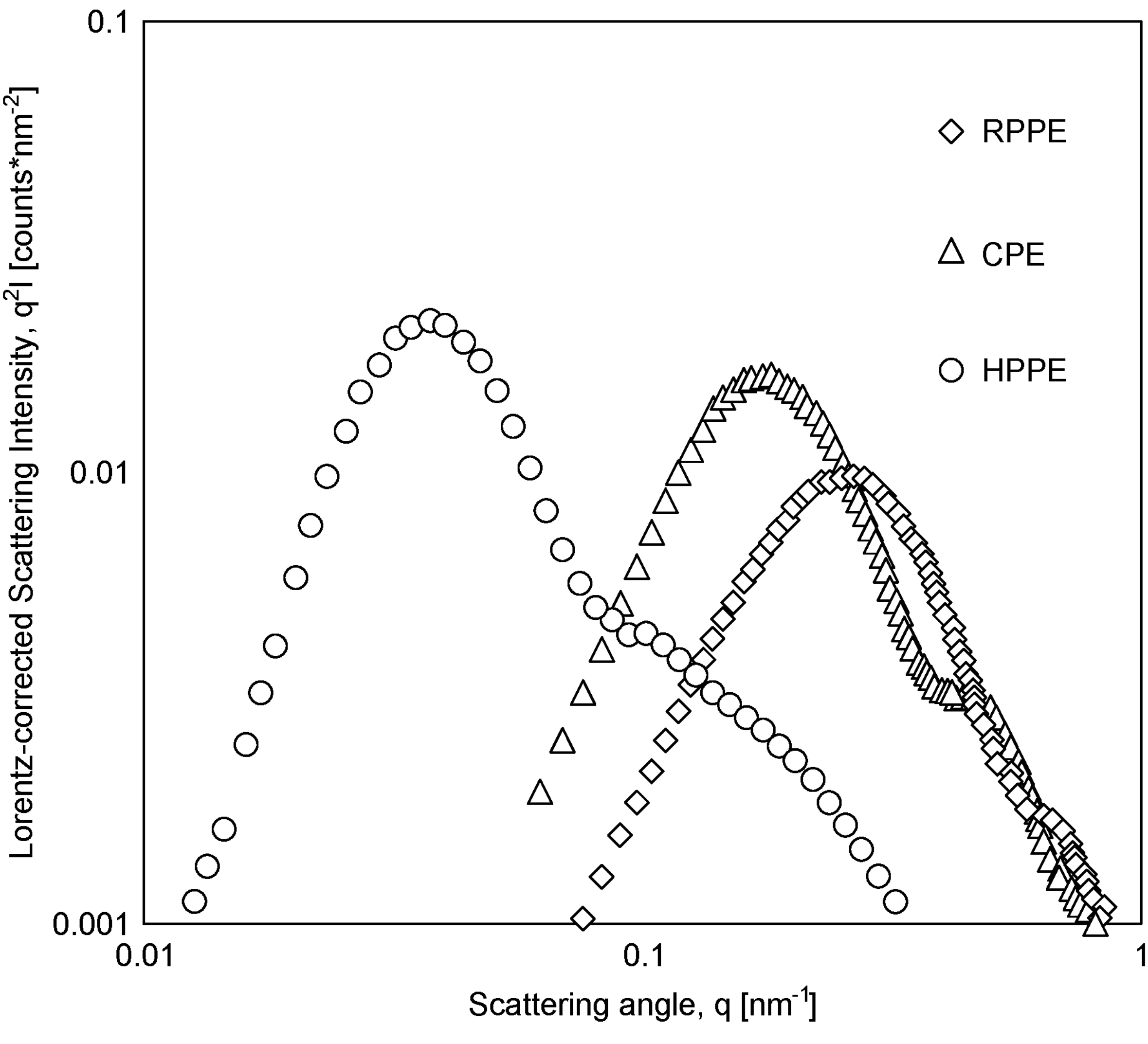
Lorentz-corrected Scattering Intensity, q^2I [counts*nm^{-2}]
0.1
0.01
0.001
0.01
0.1
1
Scattering angle, q [nm^{-1}]
◇ RPPE
△ CPE
○ HPPE

Figure 5