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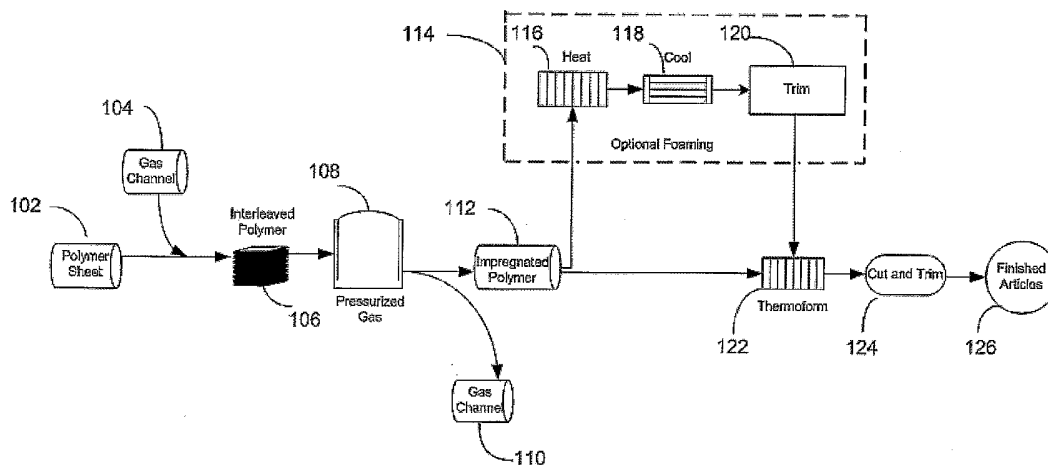
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(54) Title: METHOD OF PRODUCING THERMOFORMED ARTICLES FROM GAS IMPREGNATED POLYMER



(57) Abstract: A solid state process utilizes gas impregnation to enhance thermoforming of thermoplastic material. If the gas is plasticizing, the article is thereby plasticized for thermoforming. In some embodiments, the invention provides foaming the polymer prior to or during thermoforming by creating high levels of dissolved gas during gas exposure. Foaming may proceed spontaneously upon decompression from gas pressure, or foaming may be enhanced by heating the polymer sheet (112) near to or above the polymer's glass transition temperature, thereby producing plasticized foamed polymer for thermoforming. When objects of unfoamed polymer are desired, foaming may be suppressed by thermoforming gas saturated articles under gas pressure. This process may be used to enhance the thermoforming performance of articles that have been previously foamed, including articles foamed by prior processes. In some embodiments, polymer is sufficiently plasticized so that it may be foamed without heating. Plasticization of the polymer is reversible.



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METHOD OF PRODUCING THERMOFORMED ARTICLES FROM GAS IMPREGNATED POLYMER

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims priority from U.S. provisional application number 60/471,477, filed 05/17/2003, titled THERMOFORMED FOAMED THERMOPLASTIC PACKAGING.

BACKGROUND OF THE INVENTION

Field of the Invention.

10 This invention relates to a process of producing articles of thermoformed thermoplastic polymer. More specifically, this invention relates to improved thermoforming processes enabled by impregnating polymer with gas prior to thermoforming.

Description of the Related Art

15 Thermoforming processes are used to produce a wide array of shaped articles in modern life. Products made from thermoformed sheets of thermoplastic include trays, bowls, beakers, signs, briefcase shells, refrigerator door liners, and packages.

 Thermoplastic materials used in thermoforming include acrylic, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and
20 polyethylene terephthalate (PET), the latter both in crystalline form as crystalline polyester (CPET) as well as glycolised polyester (PETG). Foamed materials are also thermoformed, in particular polystyrene foam.

 Thermoforming processes entail applying heat, often in the form of infrared radiation, to thermoplastic sheeting or film, to raise the material to the temperature at
25 which the thermoplastic becomes soft and pliable, generally between 120 and 180 deg. C in the prior art. Thereafter, depending upon the specific thermoforming process, the softened thermoplastic material is shaped and allowed to cool to a point where it retains the desired shape. The molded sheet is then cut and trimmed to yield molded thermoformed articles.

30 As is understood by those of skill in the art, thermoforming in general refers to a set of related processes for producing shaped articles of thermoplastic. Included in

thermoforming are the processes of vacuum forming, pressure assisted thermoforming, high definition thermoforming, drape forming, press forming and line bending.

In vacuum forming, the heated sheet is sucked into shape on a male or female tool by applying a vacuum. Principal limitations of this thermoforming process are that, of necessity, edges and corners of objects are always rounded to an extent, and significant undercuts or reentries are not possible. Vacuum forming is a simple technique allowing economical, high production volumes.

In pressure assisted thermoforming, unlike conventional vacuum forming, the tool used is generally female. The plastic sheet is forced into the mold using air pressure. While not generally suited for very high speed production, crisp detail, 90 degree corners and complex features may be rendered in objects produced by this technique.

High definition thermoforming employs specially adapted forming machines. Utilizing pressure boxes and female tooling with advanced molding materials such as micro-porous, air-permeable aluminum composite, this process gives component definition close to that achieved in pressure assisted thermoforming while retaining higher production rates and lower costs associated with conventional vacuum forming.

Drape forming simply drapes a heated sheet over a male mold or into a female former, without the use of pressure. Only single curvature objects may be formed. As no pressure is applied and simple curves are used, the sheet does not thin during the forming process. This process is particularly useful for shaping polycarbonate sheet where impact strength is essential.

Press forming is one of the earliest forming techniques. The heated sheet is literally pressed into shape using direct pressure from a molded tool. Originally developed to shape cast acrylic sheet, it is now used to process PVC, polycarbonates and PET. Component shapes have to be less complex than vacuum forming, but the process produces less distortion. It is a preferred technique when optical clarity is required in a transparent or translucent finish.

Line bending is used for shaping sheet thermoplastic by bending and folding. A strip heater is used to apply heat locally to part of a pre-cut plastic sheet. This

produces a 'hot hinge', allowing the sheet to be formed to the required shape. A jig is used to support the plastic while it cools.

Regardless of process used, all thermoforming is based upon the principle that thermoplastic materials are relatively rigid at lower temperatures owing to van der
5 Waal forces retaining thermoplastic polymer molecules in solid structural form. For a given thermoplastic, as the temperature rises, the kinetic energy of the polymer molecules increases until, at a temperature referred to as the glass transition temperature, T_g , the kinetic energy of the molecules generally overcome the relatively weak van der Waals forces and the polymeric material becomes plasticized. In the
10 plasticized state, the polymer molecules, while not in a fully liquid state, are able to slide over one another, allowing the material to flex without retaining a fixed shape. Thermoforming, then, is simply heating the polymer until it is plasticized, forming it, and then allowing it to cool while physically retaining its form, until the polymer is below the glass transition temperature and will retain the form on its own.

15 Plasticization is the result of aggregate molecular behavior, and to an extent is a phenomenon of degree. At the glass transition temperature, a significant number of polymer molecules become loosened from solid state retention by the weak van der Waals forces and the viscosity of the polymeric material drops dramatically although the material is not yet liquid. Significantly, though, as the temperature of the material
20 is raised above its glass transition point, a higher percentage still of the polymer molecules overcomes weak van der Waals forces, and the viscosity drops yet lower with increasing temperature. When the temperature reaches the melt temperature of the polymer, T_m , the kinetic energy of substantially all the polymer molecules dramatically overcomes intermolecular forces to the extent that the material flows
25 freely.

In thermoforming, the rheological behavior of the plasticized thermoplastic is of critical importance in forming high quality articles. As is well appreciated by those of skill in the art, in many cases it is desired that the plasticized material have a very low viscosity, enabling the softened polymer to assume maximum detail, sharp
30 corners and, when required for the object and enabled by the process employed, raised features, recesses and re-entrants. Accordingly, in thermoforming the general practice

is to obtain a low plastic viscosity prior to forming by heating the thermoplastic well above its glass transition temperature, but below its melt point.

Prior art thermoforming has a number of drawbacks. Higher temperatures required for low plastic viscosity require greater energy input and thus add to thermoforming costs. Plastic viscosity that is inadequate for rendering of detail by less expensive and/or higher production processes requires employing more expensive and/or lower production thermoforming processes to achieve results. As polymeric materials are subjected to higher temperatures, they are subject to thermo-oxidative degradation, wherein the polymer chains break and the polymer becomes more difficult to recycle, diminishing its value. In addition, the viscosity of some polymeric material in the prior art simply cannot be lowered sufficiently by heating, no matter how high the temperature, for some thermoforming applications.

Prior art thermoforming of foamed polymeric materials presents additional problems. In the prior art, foamed polymers are created by foaming extrusion, which entails producing or forcing a non-reactive foaming gas into a molten polymer mixture or alternately creating gas with chemical reactions within the molten polymer, thereby forming bubbles in the melt. The mixture is allowed to cool and harden around the bubbles, which become small, gas-filled cells in the now solid foam material.

Prior art foamed polymer is not suitable for thermoforming immediately after foaming extrusion, however, requiring a period of "curing", in which the foamed polymer is exposed to the atmosphere for several days after extrusion. The curing process is generally necessary, for the following reasons. On cooling after foaming extrusion, because of thermal contraction of the foaming gas, the now rigid cells in the newly cooled foamed polymer contain the foaming gas at a pressure considerably less than atmospheric pressure, on the order of 0.5 atmospheres. Forming at this low absolute pressure may well cause buckling of cell walls and collapse of cells. Because the cell walls are more permeable to atmospheric gases than to the various gasses used in foaming gas, during curing the atmospheric gases osmotically penetrate the cells in the foamed polymer, initially actually increasing the pressure in the cells to above atmospheric pressure, on the order of 1.5 atmospheres. When prior art foamed polymer has cured to the point that the cells are at a higher than atmospheric pressure,

thermoforming is facilitated principally because the additional pressure in the foamed polymer results in secondary expansion of the polymer on heating. Pressurized cells resist collapse and distortion during thermoforming, thereby resulting in superior thermoformed foamed products.

5 When prior art foamed polymer is exposed to the atmosphere for longer periods before thermoforming, however, the trapped foaming gas gradually dissipates from the cells in the polymer foam, and the pressure of the cells approaches atmospheric pressure. Accordingly, on thermoforming polymer foam that has been stored beyond optimal periods for curing, a substantial percentage of the microcells in
10 the foam collapse or distort during thermoforming, resulting in material that may tear or distort during forming or otherwise produce inferior thermoformed foamed products. Since prior art foamed polymer is reused only with difficulty, repeating the process of foamed extrusion and curing of such exhausted foamed polymer is generally not an economically viable option.

15 Yet another limitation of prior art thermoforming is related to the rheological properties of heated prior art foamed materials, which limits the geometry of products that can be formed with such materials. In the prior art, inadequate plasticity, strength and ductility at thermoforming temperatures limits both the steepness of object walls, whereby wall angles of less than 35 degrees from vertical are not possible, as well as
20 the relative height of objects, whereby a depth to width ratio exceeding 1:1 cannot be achieved.

 Yet another limitation of prior art foam thermoforming is the lack of a continuous smooth skin in untreated prior art foamed materials, resulting in thermoformed objects having poor appearance, low durability, lack of stain resistance,
25 and other undesirable qualities. Lack of skin may result in blistering or tearing of prior art foamed material during heating and thermoforming, limiting the suitability of such material for thermoforming. In the prior art, a separate skin of unfoamed material may be laminated or otherwise attached to the foamed material in an effort to address these shortcomings, but at an economic and environmental cost, the latter
30 because the attached skin may render the material and objects formed from it less suitable for recycling. Attempts to address these shortcomings of prior art

thermoformed foamed materials further include the use of closed or two sided molding, requiring considerably higher tooling expense and resulting in decreased production line efficiency, as is well understood by those of skill in the art.

Accordingly, as is clear to those of skill in the art, the process for thermoforming foamed polymer in the prior art is subject to several significant drawbacks. First, because a curing period is necessary, the processes of foaming and thermoforming polymer are necessarily discontinuous, resulting in industrial inefficiency. Second, foamed polymer that has been cured for overly protracted periods loses value for thermoforming, a loss for which the prior art provides no satisfactory remedy. Third, the geometry of thermoformed foamed objects with prior art materials is considerably limited. Fourth a lack of integral skin may necessitate adhesion of a layer of unfoamed material and/or using expensive tooling entailing decreased production line efficiency.

What is needed is a process for treating thermoplastic material for thermoforming in which the plasticity of the thermoplastic may be reversibly enhanced at lower temperatures. What is needed further is method for processing thermoplastic material whereby the viscosity of the material at a given temperature between the material's glass transition temperature and melt temperature is lower than the viscosity of material in the prior art. What is needed further is a process for treating thermoplastic material so that it may be thermoformed at lower temperatures, allowing more economical production and enhancing recyclibility of thermoformed polymer. Yet further, what is needed is a process for thermoforming foamed polymer that does not require a curing period. Still further, what is needed is a way to inhibit the formation of blisters on the foam surface while thermoforming. What is needed further still is a process for thermoforming foamed polymer that is continuous from foaming through thermoforming. In addition, what is needed is an economical, industrial scale process for treating conventionally foamed polymer that has been cured for protracted periods so that it is again suitable for optimal thermoforming. Also needed is a method permitting formed objects with wider ranges of geometry including (1) foamed objects with steep or almost vertical walls and (2) tall foamed objects, with depth to width ratios exceeding 1:1. What is needed still further are such

processes adapted to continuous or semi-continuous industrial production requirements. It is also desirable that such processes have minimal negative environmental impact.

It has been discovered that dissolving a non-reacting gas, such as carbon dioxide, in polymer results in a "*plasticization effect*", affecting the rheological and thermal properties of the polymer (see, for example, *Effects of CO₂ on Polymer Properties*, by Surat Areerat et al., presented at the Regional Meeting on Polymer Processing, Taipei, 2002, available at <http://www.cheme.kyoto-u.ac.jp/6koza/pdf/H14/ID059.pdf>). Surprisingly, a polymer with dissolved gas undergoes glass transition at a dramatically lower temperature than it does without dissolved gas. For example, when PET is exposed to CO₂ as a plasticizing gas at 21 deg. C and 5 MPa for a period of time so that the concentration of CO₂ is about 8-9% by weight, the glass transition temperature of the exposed material depressed by fully 20 deg. C. Furthermore, at a given temperature above normal glass transition, polymeric material with dissolved gas has a lower viscosity than the polymer without dissolved gas. Yet further, because dissolved gas desolvates from polymer over time at atmospheric pressure, the plasticization effect is temporary and reversible.

Based upon these discoveries, it will be clear to those of skill in the art that improved thermoforming may be practiced by utilizing thermoplastic polymers in which sufficient non-reacting gas is dissolved to produce a plasticization effect. However, for such thermoforming to be of practical value, a means is needed for producing gas impregnated polymer exhibiting the plasticization effect on an industrial scale by continuous or semi-continuous process.

U.S. patent number 5,684,055 to Kumar et al., incorporated herein by reference in its entirety, discloses a process for producing foamed material from gas-impregnated polymer in the solid state. In that process, a roll of polymer sheet is provided with a gas channeling means interleaved between the layers of polymer. The roll is exposed to a non-reacting gas at elevated pressure for a period of time sufficient to achieve a desired concentration of gas within the polymer. The saturated polymer sheet is then separated from the gas channeling means. In '055, the polymer sheet is next foamed by initiating bubble nucleation and growth by heating the polymer sheet.

However, advantageously, the technique of using a gas channeling means to facilitate gas impregnation of polymer sheet under gas pressure may be utilized as an industrial method for the general impregnation of gas in polymer for plasticization, regardless of whether the polymer is later to be foamed.

5 Gas impregnation of polymer is additionally advantageous, however, when it is used to foam polymer that is to be thermoformed. Regardless of whether the impregnating gas is plasticizing, immediately after foaming the solid state foamed polymer at room temperature has microcells containing gas above atmospheric pressure. It has been found, therefore, that such polymer possesses the superior
10 thermoforming qualities of prior art foamed polymer that has been cured, without the need for a curing period.

It has been further discovered that, when prior art foamed polymer which has been cured for overly protracted periods of time is then exposed to non-reactive gas so that its cells become saturated with gas at elevated pressure, the thermoformability of
15 such material is greatly improved.

It is an object of this invention to provide a process for treating thermoplastic material for thermoforming in which the plasticity of the thermoplastic is reversibly enhanced at lower temperatures. It is a further object of this invention to provide a process for lowering the viscosity of a thermoplastic for thermoforming at a given
20 temperature. It is a further object of this invention to enable thermoforming a thermoplastic material at a lower temperature than is possible in the prior art, if indeed thermoforming the material is possible at all in the prior art, including enabling the use of thermoforming processes to shape objects without a need to heat the thermoplastic material. Further objects of this invention include: providing a process
25 for thermoforming foamed polymer that does not require a curing period; providing a process for thermoforming foamed polymer that is continuous from foaming through thermoforming; providing an economical, industrial scale process for treating conventionally foamed polymer that has been cured for protracted periods so that it is again suitable for optimal thermoforming; and providing a process for improving
30 material for thermoforming that is adaptable to industrial scale continuous or semi-continuous process and is environmentally acceptable.

BRIEF SUMMARY OF THE INVENTION

The present invention utilizes a solid state process of gas impregnation to enhance the performance of thermoplastic material used in thermoforming. A roll of polymer sheet is provided with a gas channeling means interleaved between the layers of polymer. The roll is exposed to a non-reacting gas at elevated pressure for a period of time sufficient to achieve an elevated concentration of high-pressure gas within the polymer. If the gas is a plasticizing gas, exposure is for a period of time required to bring about a plasticizing effect of the polymer. The saturated polymer sheet is then separated from the gas channeling means and decompressed and subsequently thermoformed. In embodiments utilizing plasticizing gas, the glass transition temperature of the exposed polymer is reduced, and therefore thermoforming may take place at a lower temperature than used for thermoforming unexposed polymer.

In some applications, the invention provides foaming the polymer prior to thermoforming by creating high levels of dissolved gas during gas exposure. In some embodiments practicing foaming, bubble nucleation and growth proceeds spontaneously upon decompression, while in other foamed embodiments bubble nucleation and growth is initiated and enhanced by heating the polymer sheet near to or above the polymer's glass transition temperature, thereby producing foamed polymer for ready for immediate thermoforming. In embodiments practicing foaming, the processes of foaming and thermoforming may be continuous. In preferred embodiments practicing continuous foaming and thermoforming, foaming is performed by heating just prior to forming. It should be noted, in addition, that thermoforming of conventionally foamed polymers may be enhanced by solid state gas impregnation.

In some other embodiments in which foaming is not desired, the invention provides thermoforming the saturated polymer under pressure, cooling the polymer below the glass transition temperature for the saturated polymer, and then depressurizing the polymer to yield a thermoformed article of unfoamed polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects, advantages, features and characteristics of the present invention, as well as methods, operation and function of related elements of structure, and the combination of parts and economies of deployment, will become apparent upon
5 consideration of the following description and claims with reference to the accompanying drawings, all of which form a part of this specification, wherein:

Fig. 1 is a process flow chart for plasticizing polymer and thermoforming articles therefrom according to the present invention; and

10 Fig. 2 is a graph illustrating CO₂ gas concentration over time elapsed since foaming in polymer foamed by the solid state process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for reversibly enhancing the plasticity of thermoplastics for thermoforming. It is applicable in general to the class of glassy amorphous, non-glassy elastomeric, or semi-crystalline thermoplastic polymers or copolymers. While many descriptions are herein exemplified with PET, it should be recognized that other polymers or mixtures of polymers may be used in place of or in addition to PET. Suitable gas-polymer systems include CO₂ and Polypropylene, as disclosed in *CO₂-Assisted Crystallization of Polypropylene for Increased Melting Temperature and Crystallinity* by Mitsuko Takada et al, Proceedings of Polymer Processing Society meeting, Hertogenbosh, Netherland, May 31, 1999. Other gases and pressures may be used (for example, CO₂ may be used with polyethylene, polyvinyl chloride, acrylonitrile butadiene styrene, polycarbonate, polyethylene terephthalate, and polypropylene; and N₂ gas may be used with polystyrene). It is intended that these teachings should encompass reversibly enhancing plasticity for thermoforming of any and all such polymers.

Turning now to FIG. 1, depicted is a general process for reversibly enhancing the plasticity of polymeric material which is then thermoformed. In this process, a polymer sheet 102 is interleaved with a gas channeling means 104 to form an interleaved roll, stack of sheets, or festoon 108 of polymer and gas channel. Gas channeling means 104 preferably consists of a layer of flexible gas permeable material. While porous paper sheet is a preferred material, other gas permeable materials, such as particulate material, gauze, mesh, and woven or non-woven fabrics, may also be successfully employed in the present invention.

Alternatively, a gas channeling means may be provided mechanically rather than in the form of a gas permeable material. Such mechanical gas channeling means may comprise raised portions such as bumps or ridges attached to or integral in the polymer material. The material may thus be interleaved with itself, the raised portions serving to separate layers of the material for gas penetration.

In any case, interleaved material 106 is next exposed 108 under elevated pressure to a non-reacting gas which is soluble in the polymer for a time sufficient to achieve a desired concentration of gas within the polymer, typically at least 0.5% by

weight for PET-CO₂ systems. The solvated gas concentration must at a minimum be the amount required to bring about the plasticizing effect in the polymer, but need not be high enough for the gas-impregnated polymer to become nascent foam.

Exposure to pressure 108 is generally carried out at room temperature (around 21 degrees C.). Higher temperatures may be employed to accelerate the rate of diffusion of the gas within the polymer, while lower temperatures may result in higher levels of gas saturation over time. The pressure can be varied above tank supply pressure with booster pumps. For example, the preferred tank pressure range when employing CO₂ is about 0.345 to 5.2 MPa. This can be increased to over 8.27 MPa with a suitable booster pump. Pressures as high as 17.2 MPa or higher (supercritical CO₂) are usable.

The preferred gas can depend upon the polymer being treated. For example, carbon dioxide is the preferred gas for use in foaming PET, PVC and polycarbonate, while nitrogen is the preferred gas for use in foaming polystyrene. "Modified air", which is atmospheric air in which the percentage oxygen has been reduced to 1% to 20% by reverse osmosis under pressure, as well as pure atmospheric air, may alternatively be employed in some embodiments.

The amount of time during which the polymer roll is exposed to gas varies with the thickness of the solid polymer sheet, the specific polymer-gas system, the saturation pressure, and the diffusion rate into the polymer, and is generally determined experimentally. However, periods of between 3 and 100 hours are typically employed for sheet thicknesses of .25mm to 2mm. For example, when saturating a 0.5 mm. thick sheet of PET with CO₂, a saturation time of between about 15 to 30 hours is preferred.

Following saturation of the polymer-gas permeable material sheet, the sheet is returned to normal pressure and the gas channeling means removed 110, yielding a sheet of gas impregnated polymer 112 exhibiting the plasticizing effect, which gradually reverses as the gas dissipates from the impregnated polymer 112.

In some embodiments, the impregnated plasticized polymer 112 may be foamed 114 prior to thermoforming 122, while in other embodiments unfoamed plasticized polymer 112 is thermoformed 122 directly. In the other embodiments, the

plasticized polymer may or may not be foamed during the heating step of thermoforming depending on gas saturation pressure, absorbed gas concentration level, and thermoforming temperature.

For optional foaming 114 in some embodiments, on unwinding from the gas channel 110, the polymer sheet 112 is heated above its glass transition temperature by drawing under tension through a heating station 116. The polymer sheet is thereby foamed in a continuous manner. After passing through the heating station 116, the polymer sheet may be drawn through a cooling station 118, such as a cold water bath, a set of chilled rollers or simply air, to cool the polymer and stop bubble nucleation and growth. In such embodiments, the temperature of the heating station 116 as well as the rate at which the polymer sheet is drawn through the heating station 116 and cooling station 118 can be varied to provide sheets of varying bubble size and density. After foaming, the polymer sheet is trimmed 120, yielding finished foamed polymer material which may then be thermoformed 122.

While embodiments may practice foaming simultaneously with forming, such embodiments require additional forming time to allow the material to foam, and may therefore be less adaptable to high throughput production requirements. Preferred embodiments for high throughput production requirements employ a heating station 116 to heat the saturated polymer to a temperature suitable for both foaming and thermoforming, and then immediately thermoform the material 122 without need of a cooling station 118.

Surprisingly, it has been found that, while the gas employed is non-reacting and does not alter the polymer chemically, because gas saturation reversibly plasticizes the polymer, its glass transition temperature is effectively reduced, enabling some foaming to take place at a temperature that is lower than the polymer's nominal glass transition temperature. In fact, if exposure to gas pressure is takes place at a sufficiently low temperature or at a sufficiently high pressure, the solvated gas pressure in the polymer is sufficient that, upon decompression to atmospheric pressure, desolvation of the gas may overcome the polymer's yield strength at room temperature, causing bubble nucleation and formation, thereby foaming the polymer. In such a case, depending upon degree of foaming desired, it is possible to create the

foamed polymeric material entirely without the need for heating 116 and consequent cooling 118 of the material.

A surprising and significant result of foaming gas impregnated polymer according to the processes described above is that the micro-cells in the resulting polymer foam contain gas pressurized above atmospheric pressure. At thermoforming temperatures, the effect of the pressurized gas trapped in micro-cells is to create secondary expansion of the microcells, thereby keeping the cells from buckling or collapsing. Further, when the gas is plasticizing, the polymer at the cell walls is highly plasticized, enhancing the effective plasticization of the polymer yet further, thereby resulting in foamed polymers of lower viscosity than expected at a given temperature.

A similar result obtains when polymer already foamed by prior art processes is then impregnated with gas. The microcells in the foamed polymer accumulate gas under pressure, retaining pressurized gas after exposure. If such gas impregnated, prior art foamed polymer is then thermoformed, the cell walls similarly resist buckling and collapsing, and, if the gas is plasticizing, the viscosity of the polymer is lower at thermoforming temperatures than the viscosity of untreated prior art foamed polymer.

In any case, either unfoamed impregnated polymer 112 or gas impregnated foamed polymer 114 may be thermoformed 122. As discussed earlier, the temperature required for thermoforming articles from plasticized gas impregnated material is generally lower and often significantly lower than for the same material without the plasticizing effect. Astoundingly, for some gas/polymer systems in which the polymer is highly saturated with plasticizing gas, the polymer may be sufficiently plasticized that the material may be "thermoformed" at room temperature. Furthermore, because the viscosity of the polymer is lowered by the plasticizing effect, for a given thermoforming process, greater detail and deeper "draws" are possible when thermoforming the plasticized material than is possible with material that has not been plasticized. In some cases, such as vacuum forming with PET foam, articles may be thermoformed that cannot be thermoformed with polymer that has not been plasticized.

When an unfoamed article is desired but the saturated polymer to be used would otherwise foam when thermoformed at atmospheric pressure, thermoforming may take place under pressure. Referring back to FIG. 1, for such unfoamed articles, after saturating with gas under pressure 108, the gas channeling means is removed 110
5 and the saturated polymer 112 is thermoformed 122 while it remains under pressure. As will be understood by those in the art, the thermoformed article will then be allowed to cool below its glass transition temperature or the temperature at which it would foam at atmospheric pressure, and then it is depressurized to yield a thermoformed unfoamed article.

10 In any case, after thermoforming 122, articles are then cut and trimmed as needed 124 to form finished articles 126 according to processes with which persons skilled in the art are well acquainted. Significantly, because the processes involved have little or no irreversible effect upon the chemistry of the polymer, and because thermo-oxidative degeneration is minimized due to lowered heat requirements, scrap
15 from this process is more recyclable and hence more valuable than scrap from prior art processes for thermoforming articles. Furthermore, since only non-reacting gasses are used in the process, it is environmentally sound.

EXAMPLES:

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Example 1 Trials. In each of the following examples, 0.762 mm thick virgin PET was saturated with CO₂ at 4 MPa pressure for 67.25 hours at 21 deg. C. Within 10 minutes after depressurization, the saturated material was foamed at 100 deg. C, yielding foamed polymer with little or no noticeable surface skin and rough surface
25 texture. Thermoforming ovens were held at a constant temperature (about 550 deg. C). The temperature of plastic that was thermoformed therefore increased with duration of heating. A one-sided male mold was employed, having a 2.4 areal draw ratio, height 11.11 cm, top opening 8.636 cm, height to width ratio of 1.29, bottom diameter of 5.842 cm, average wall angle of 6.5 degrees from vertical. The degassing
30 time after foaming was varied to observe the effect of degassing on thermoforming at different temperatures of foamed objects having no significant surface skins. As the

elapsed degassing time after foaming increases prior to thermoforming, the gas concentration in the polymer decreases, as illustrated in FIG. 2.

1. Trials with 10-19 minutes degas time after foaming:

5 Forming pressure: 0.31 MPa. Secondary expansion in thermoform observed in all trials.

 Trial 1: .7 sec. heat time: foam broke through, no cup,

 Trial 2: 10 sec. heat time: formed cup, some creases, good mold detail definition

10 Trial 3: 15 sec. heat time: blisters and bubbling – not enough skin to keep contain secondary expansion of bubbles.

2. Trials with 2.5 hrs degas time after foaming:

 Forming pressure: 0.31 MPa. Secondary expansion in thermoform observed in
15 all trials.

 Trial 1: 8 sec. heat time: foam broke through, no cup indicating not enough ductility

 Trial 2: 12 sec. heat time: cup formed, good mold detail definition, some creases

20

3. Trials with 23 hrs. degas time after foaming:

 Forming pressure: 0.31 MPa. No secondary expansion in thermoformer noted in any trials.

 Trial 1: 4 sec. heat time: cup formed, poor definition, no creases,

25 Trial 2: 8 sec. heat time: cup formed, poor definition, no creases

 Trial 3: 10 sec. heat time: cup formed, poor mold detail definition, no creases

4. Trials with 51 hrs. degas time after foaming

 0.758 MPa forming pressure required for forming. No secondary expansion in
30 thermoformer noted in any trials.

Trial 1: 4 sec. heat time: plastic pulled out of clamp frame when object reached a depth of about 5 cm.

Trial 2: 8 sec. heat time: plastic pulled out of clamp frame at full depth, partial cup

5 Trial 3: 14 sec. heat time: cup partially formed, plastic clamp frame not holding plastic sheet against stretching

Example 1 Conclusions: When thermoforming foams without thick or noticeable skin:

- 10 a. Short degas times after foaming limited heat time (foam temperature) to too low a temperature for thermoforming – longer times caused blistering;
- b. The best compromise of gas concentration versus formability (ductility) was at a few hours desorb time;
- c. Longer degas times decreased formability. At 51 hours, a cup could not be
- 15 formed with 14 seconds of heat time due to low ductility, even at 110 psi forming pressure, where at 23 hrs degas time, a cup was made with four seconds of heat time at 45 psi pressure;
- d. Secondary expansion in thermoformer increases detail-

20 Example 2 Trials. In each of the following examples, 0.762 mm thick virgin PET was saturated with CO₂ at 5 MPa pressure for 26 hours at 21 deg. C. A skin of variable thickness was created by varying desorb time after depressurization prior to foaming. The saturated and partially desorbed material was foamed at 105 deg. C for two minutes, yielding foamed polymer with a density of 21% relative to unfoamed

25 polymer. Thermoforming ovens were held at a constant temperature (about 550 deg. C). The temperature of plastic that was thermoformed was therefore proportional to duration of heating. A one-sided male mold was employed, having a 1.7 areal draw ratio, height 8.73 cm, top opening 7.62 cm, height to width ratio of 1.31, bottom diameter of 5.08 cm, average wall angle of 6.5 degrees from vertical.

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Trial set 1: Foaming within 10-20 minutes of depressurization: Thermoforming was attempted within ten minutes of foaming. The cups would not form adequately with 10-15 sec. heat time. Increasing the heating time caused the cups to warp and blister. These cups failed through tearing of the plastic during attempt to form. Skin did not
5 form that was obvious to naked eye.

Trial set 2: Desorb prior to foaming of 1.5 hours. A smooth glossy skin observed on foamed material. All cups had 2.1 areal draw ratio.

- 10 a. Degassed 38 min after foaming, 9 sec. thermoforming heat time: cup with good surface detail. Clamp frame held plastic.
- b. Degassed 19 hrs, 50 min after foaming, 10 sec. thermoforming heat time.: cup poorly defined; Plastic slipped out of clamp frame.
- c. Degassed 99 hrs, 30 minutes after foaming, over 30 seconds thermoforming heat time: poor cup definition. Clamp frame could not hold plastic against
15 higher stiffness of plastic.
- d. Degassed 135 hours after foaming, over 30 seconds thermoforming heat time: very poor cup definition. Clamp frame could not hold plastic against higher stiffness of plastic.
- e. Degassed 135hours after foaming, 40 seconds thermoforming heat time: cup
20 foam walls melted through creating a spider web effect. No useful result.

Example 2 Conclusions:

- a. Longer degas time required higher temperatures for forming objects.
- b. With more than 6.0-7.0 % gas concentration, a significant increase in
25 formability was noted, allowing deeper draws.
- c. With gas concentration around 0.5% by weight, little ductility is imparted to PET.

Example 3 Trials. A number of trials were conducted with 0.889 mm thick recycled
30 PET that was saturated with CO₂ at 5 MPa pressure for 40 hours at 21 deg. C. In order to form a noticeable skin, the polymer was depressurized and allowed to desorb

CO₂ for approximately 390 minutes. Then it was foamed for various times of 10 to 30 seconds in infrared heaters at 550 deg. C and immediately thermoformed thereafter. A one-sided female mold was employed with a plug assist, having a 1.97 areal draw ratio, height 11.11 cm, top opening 8.26 cm, height to width ratio of 1.31, 5 bottom diameter of 5.72 cm, average wall angle of 7.0 degrees from vertical. The relative density of the resulting foamed objects averaged 20% relative to the unfoamed polymer.

Example 3 Conclusion: Continuous processing from foaming to thermoforming is 10 possible using gas impregnated polymer, resulting in objects of relatively low density, having steep walls and height to width ratios over 1:1.

Comparing Example 1 to Examples 2 and 3, it is clear that solid integral skin adds strength, thereby allowing deeper draws, and contains secondary expansion, thereby 15 inhibiting blister formation even at higher gas concentrations. Integral skin allows use of open one sided tooling rather than the closed tooling commonly employed in prior art foam thermoforming.

Although the detailed descriptions above contain many specifics, these should 20 not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of this invention. Various other embodiments and ramifications are possible within its scope, a number of which are discussed in general terms above.

While the invention has been described with a certain degree of particularity, it 25 should be recognized that elements thereof may be altered by persons skilled in the art without departing from the spirit and scope of the invention. Accordingly, the present invention is not intended to be limited to the specific forms set forth herein, but on the contrary, it is intended to cover such alternatives, modifications and equivalents as can be reasonably included within the scope of the invention. The invention is limited 30 only by the claims appended hereto and their equivalents.

We claim:

1 1. A method of reversibly enhancing the plasticity of polymeric material for
2 thermoforming, comprising:

3 (a) interleaving an article of raw polymeric material with a gas channeling
4 means;

5 (b) exposing the interleaved article at elevated pressure to a plasticising gas
6 which is soluble in the polymer for a time sufficient to achieve a desired concentration
7 of gas within the polymer, thereby forming an exposed polymeric article which is at
8 least partially gas-saturated and plasticized; and

9 (c) decompressing the exposed polymeric article and separating the article
10 from the gas channeling means.

1 2. A method of thermoforming polymeric objects with high definition, comprising:

2 (a) interleaving an article of raw polymeric material with a gas channeling
3 means;

4 (b) exposing the interleaved article at elevated pressure to a non-reacting gas
5 which is soluble in the polymer for a time sufficient to achieve a desired concentration
6 of gas within the polymer, thereby forming an exposed polymeric article which is at
7 least partially gas-saturated;

8 (c) decompressing the exposed polymeric article and separating the article
9 from the gas channeling means; and

10 (d) thermoforming an object from the at least partially gas-saturated polymeric
11 article.

1 3. A method according to claim 2, further comprising foaming the article prior to
2 thermoforming.

1 4. A method according to claim 3, wherein the article is foamed by achieving a
2 suitable concentration of gas within the polymer while exposing it and by heating the

3 article after decompressing it to a temperature equal to or above the glass transition
4 temperature of the exposed article.

1 5. A method according to claim 4, wherein the temperature to which the article is
2 heated after decompressing it is below the glass transition temperature for the
3 unexposed polymer.

1 6. A method according to claim 4, wherein the article is heated to a temperature equal
2 to or above the glass transition temperature and below the melt temperature of the
3 exposed article.

1 7. A method according to claim 1 or claim 2, wherein the material or object
2 comprises previously foamed polymer.

1

1 8. A method according to claim 2, wherein thermoforming comprises heating the
2 article to a temperature between its glass transition temperature and its melting
3 temperature.

1 9. A method according to claim 8, wherein the thermoforming temperature is closer
2 to the glass transition temperature than to the melting temperature of the raw
3 polymeric material.

1 10. A method according to claim 2, wherein the article is foamed when it is
2 thermoformed.

1 11. A method according to claim 2, wherein the article is thermoformed by forming
2 the article without heating.

1 12. A method of forming unfoamed polymeric objects enabling high definition and
2 deep draw, comprising:

3 (a) interleaving an article of raw polymeric material with a gas channeling
4 means;

5 (b) exposing the interleaved article at elevated pressure to a plasticizing gas
6 which is soluble in the polymer for a time sufficient to achieve a desired concentration
7 of gas within the polymer, thereby forming an exposed polymeric article which is at
8 least partially gas-saturated;

9 (c) separating the article from the gas channeling means;

10 (d) thermoforming an object from the at least partially gas-saturated polymeric
11 article while under pressure; and

12 (e) decompressing the formed object and letting it desorb the plasticizing gas.

1 13. A method according to claim 12, wherein the step of forming an object is
2 performed without applying additional heat to the gas-saturated polymeric article.

1 14. A method according to claim 13, wherein the article has two sides and the object
2 is formed by using pressure differences between the two sides of the article.

1 15. A method according to claim 13, wherein the object is formed using mechanical
2 means.

1 16. A method according to claim 13, wherein the object is formed using pressure.

1 17. A method according to claim 13, wherein the object is formed using mechanical
2 means to force the article into the desired shape of the object.

1 18. A method according to claim 12, wherein the article comprises previously foamed
2 polymer.

1 19. A method of making thermoformed foamed objects having wall angles of less
2 than 35 degrees from vertical.

- 1 20. A method of making thermoformed foamed objects with a depth to width ratio
- 2 exceeding 1:1.

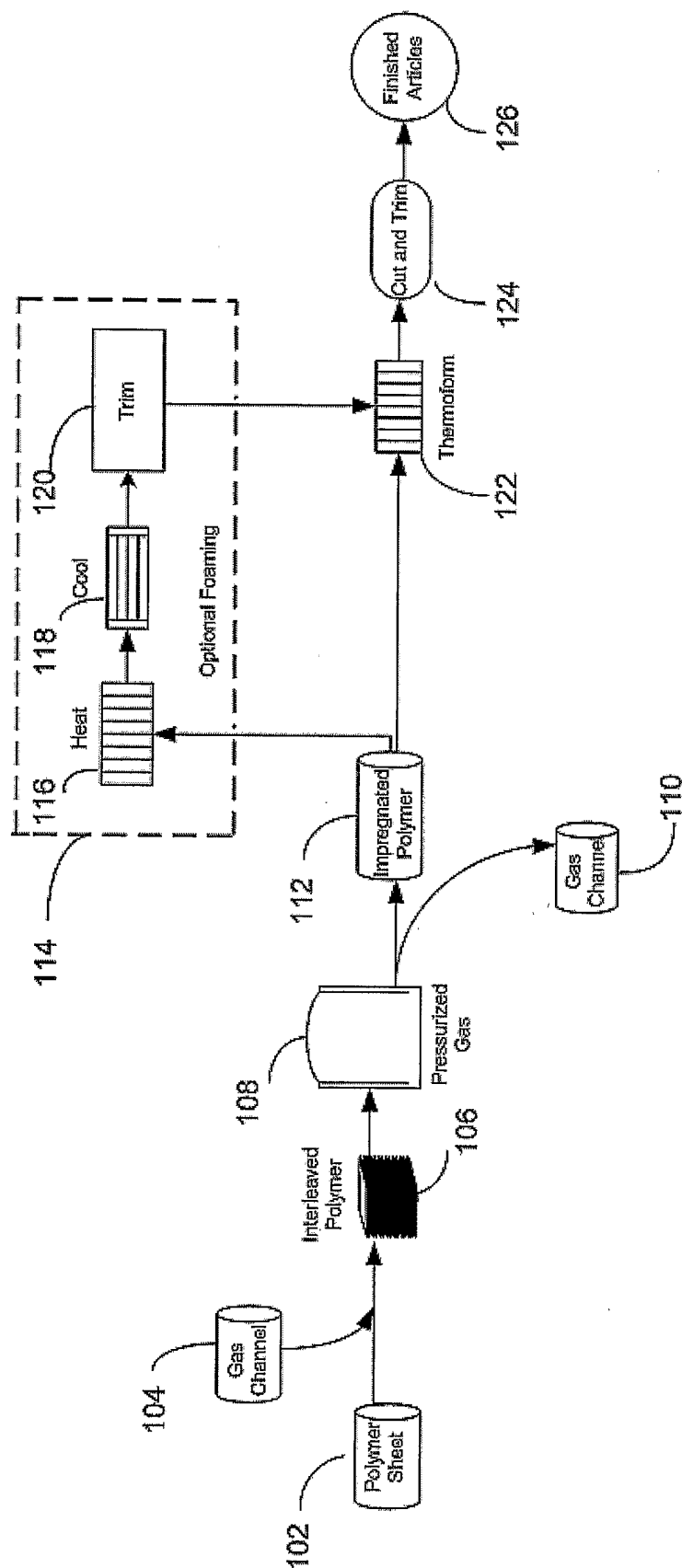


Fig. 1

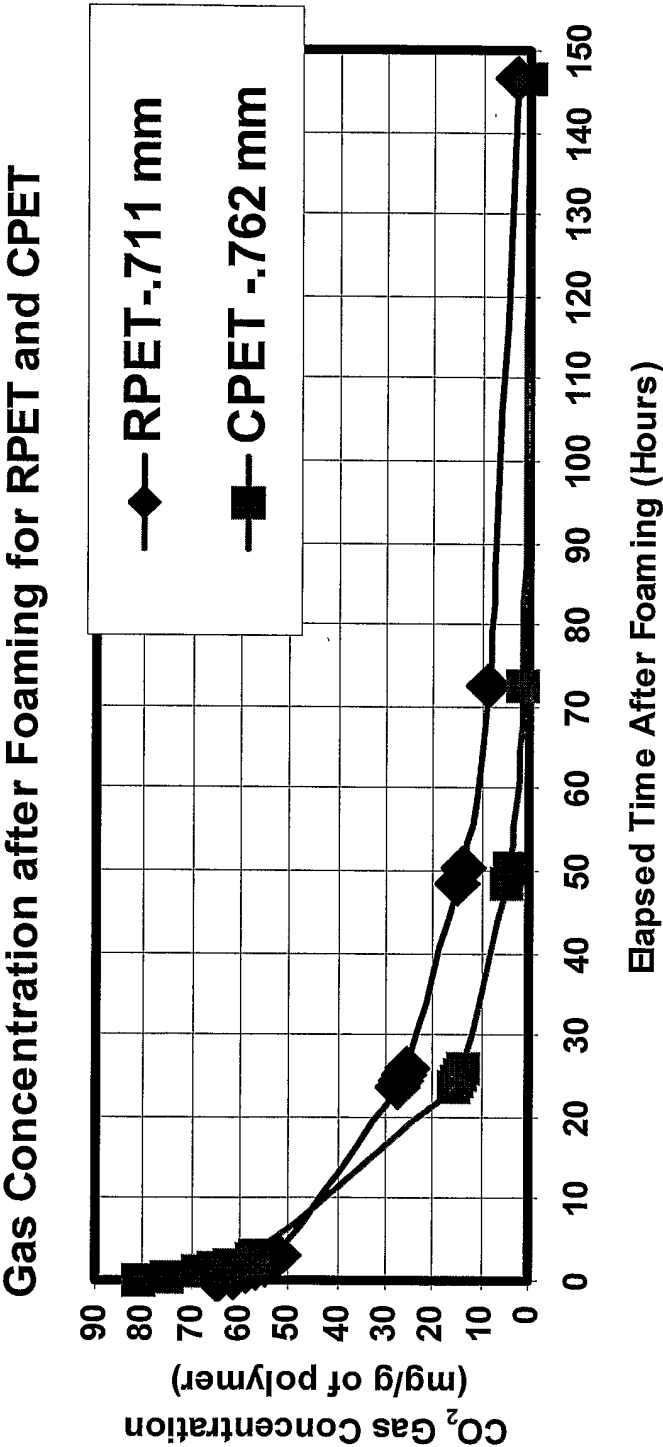


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/15246

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : B29C 44/02, 51/02, 67/20 US CL : 264/50, 320, 321, 544 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) U.S. : 264/50, 320, 321, 544 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,981,631 A (CHEUNG et al.) 01 January 1991 (01.01.1991), column 9, lines 15-24	2-18
X	US 5,364,696 A (WAGNER) 15 November 1994 (15.11.1994), the entire document	19-20
X	US 5,684,055 A (KUMAR et al.) 04 November 1997 (04.11.1997), column 4, line 42 to column 5, line 16	1

Y		2-18
A	US 5,723,510 A (KABUMOTO et al.) 03 March 1998 (03.03.1998)	
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 October 2004 (12.10.2004)		Date of mailing of the international search report 19 OCT 2004
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703)305-3230		Authorized officer Allan Kuhns Telephone No. (571) 272-1202 DEBORAH A. THOMAS PARALEGAL SPECIALIST GROUP 1500-Deft