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(54) Title: INJECTION STRETCH BLOW MOLDING PROCESS USING POLYLACTIDE RESINS

(57) Abstract: Containers are manufactured in an injection stretch molding process using a PLA resin having a specified ratio of lactic acid stereoisomers and stretch ratios. The process permits good quality containers to be made at good operating rates.

1  
2       **INJECTION STRETCH BLOW MOLDING PROCESS USING POLYLACTIDE**  
3       **RESINS**

4  
5  
6       This invention was made with United States Government support under  
7       Contract No. DE-FC36-00GO10598 awarded by the United States Department of  
8       Energy. The United States Government has certain rights in this invention.

9       This application claims priority from United States Provisional Patent  
10      Application No. 60/582,155, filed June 23, 2004.

11      This invention relates to injection stretch blow molding processes for  
12      making containers.

13      Containers such as bottles are often molded from thermoplastic resins in  
14      an injection stretch blow molding process. Poly(ethylene terephthalate) (PET)  
15      bottles are made in very large quantities in this manner. The containers are  
16      often desirably clear and are commonly used to package drinks such as water and  
17      carbonated beverages. PET performs very well in this application, but has the  
18      drawbacks of being derived from oil-based materials and of not being  
19      biodegradable or compostable. There is an increasing interest in developing  
20      substitute polymeric materials that are derived from annually-renewable  
21      resources. Biodegradable or compostable materials are also of interest, because  
22      they break down relatively quickly if landfilled or composted under proper  
23      conditions. The containers can be disposed of as well as recycled, and thus  
24      provide a wider range of disposal/reuse options.

25      Polylactide resins (also known as polylactic acid or PLA) are now available  
26      commercially. These resins can be produced from annually renewable resources  
27      such as corn, rice or other sugar- or starch-producing plants. In addition, PLA  
28      resins are compostable. For these reasons there is significant interest in  
29      substituting PLA into applications in which oil-based thermoplastic materials  
30      have conventionally been used. To this end, it has been attempted to use PLA  
31      resins in an injection stretch blow molding process to produce containers. See,  
32      e.g., U. S. Patent No. 5,409,751. However, PLA resins are difficult to process in  
33      injection stretch blow molding processes, as the PLA resins tend to have  
34      significantly different crystalline properties and much smaller processing  
35      windows than PET. PLA resins have so far proven to be difficult to process at  
36      high operating rates into good quality bottles. In some instances, the resin

1 cannot be blown well at all. In other cases, the resin tends to stress whiten  
2 during the molding process, forming opaque rather than clear containers. In yet  
3 other cases, the PLA resin forms containers having a considerable lack of  
4 uniformity in the container wall thickness or forms a container having poor  
5 impact strength. As a result, the processing window that can be used to make  
6 injection stretch molded containers from PLA resins has been so narrow that  
7 PLA resins have not been used successfully in injection stretch blow molding  
8 processes. Other types of resins that are used in injection stretch molding  
9 processes have sometimes encountered similar problems. These can be overcome  
10 in some instances by making structural changes to the polymer, such as by  
11 incorporating a comonomer into the polymer backbone. However, modifications  
12 such as these also tend to change other polymer properties, such as the glass  
13 transition temperature, melt viscosity, solubility, permeability, chemical  
14 resistance or toxicity. For this reason, it is usually preferable to avoid making  
15 changes in the chemical structure of the polymer.

16 It would be desirable to provide a method by which PLA resins can be  
17 used to produce containers in an injection stretch blow molding process at good  
18 operating rates to produce good quality containers.

19 This invention is in one aspect an injection stretch blow molding process  
20 for making containers of a thermoplastic resin, in which a thermoplastic resin is  
21 molded to form a preform which is mechanically stretched and blown into a  
22 container mold to stretch the preform axially and radially and form a container,  
23 wherein (1) the thermoplastic is a polylactic acid (PLA) resin which is a  
24 copolymer having repeating L and D lactic acid units, in which either the L or D  
25 lactic acid units are the predominant repeating units, and the predominant  
26 repeating units constitute 90 to 99.5% of the lactic acid repeating units and (2)  
27 the product of axial and radial stretch ratios is from about 3 to about 17.5.

28 The injection stretch blow molding process of the invention may be either  
29 a one-step or two-step process, as described more fully below.

30 The selection of PLA resin having the stated enantiomer ratios provides  
31 significant benefits to the ISBM process, allowing for containers to be prepared  
32 with short cycle times, controlled crystallinity, good clarity, good toughness and  
33 impact resistance and uniform wall thicknesses. Processing windows are

1 increased with the PLA resins having the stated isomer ratios, making it easier  
2 to produce good quality containers at high operating rates.

3 Containers are made in accordance with the invention using an injection  
4 stretch blow molding (ISBM) process. ISBM processes are known, being  
5 described, for example, in U. S. Patent No. 5,409,751. The process involves first  
6 forming a preform, or "plug", which is hollow and has dimensions a fraction of  
7 those of the final container. The preform is molded into a container by inserting  
8 it into a mold, and stretching it both axially (i.e. along its length) and radially.  
9 The axial stretching is done mechanically by inserting a pusher rod into the  
10 preform and mechanically extending it towards the bottom of the mold. Radial  
11 stretching is accomplished by injecting a compressed gas into the plug, thereby  
12 forcing the resin outward to contact the interior surface of the mold. Typically, a  
13 preliminary radial stretch is preformed by injecting a first increment of gas. This  
14 makes room for the stretcher rod, which can then be inserted. The preform is  
15 then stretched and immediately afterward is blown with more gas to complete  
16 the blow molding operation.

17 The axial strain (or axial stretch ratio) is typically about 1.5 to about 3.5,  
18 especially about 2 to about 3. The axial strain is considered to be the ratio of the  
19 container length to preform length. The radial, or "hoop" strain (or hoop stretch  
20 ratio) is typically from about 2 to about 5, especially 3 to about 5, and is  
21 considered to be the ratio of the preform circumference to that of the container.  
22 Hoop strain is generally not constant for any particular container, as the  
23 container generally does not have a constant circumference. Unless specified  
24 otherwise, hoop ratio, for purposes of this invention, refers to the average hoop  
25 ratio for the side walls of the container.

26 Areal strain (or areal stretch ratio) is the product of axial strain times  
27 hoop strain, and is typically in the range of about 3 to about 17.5, such as from  
28 about 3 to about 15, about 5 to about 12 or about 8 to about 11.

29 ISBM processes are divided into two main types. One type is a one-step  
30 process, in which the preform is molded, conditioned, and then transferred to the  
31 stretch blow molding operation before the preform is cooled below its softening  
32 temperature. The other main type of ISBM process is a two-step process in  
33 which the preform is prepared ahead of time. In this case, the preform is  
34 reheated to conduct the stretch blow molding step. The two-step process has the

1 advantage of faster cycle times, as the stretch blow molding step does not depend  
2 on the slower injection molding operation to be completed. However, the two-step  
3 process presents the problem of reheating the preform to the stretch blow  
4 molding temperature. This is usually done using infrared heating, which  
5 provides radiant energy to the outside of the preform. It is sometimes difficult to  
6 heat the preform uniformly using this technique and unless done carefully, a  
7 large temperature gradient can exist from the outside of the preform to the  
8 center. Conditions usually must be selected carefully to heat the interior of the  
9 preform to a suitable molding temperature without overheating the outside. The  
10 result is that the two-step process usually has a smaller operating window than  
11 the one-step process. The selection of a PLA resin as described herein has been  
12 found to broaden this processing window.

13 In the two-step process, the preform is generally heated to a temperature  
14 at which the preform becomes soft enough to be stretched and blown. This  
15 temperature is generally above the glass transition temperature ( $T_g$ ) of the PLA  
16 resin. A preferred temperature is from about 70 to about 120°C and a more  
17 preferred temperature is from about 80 to about 100°C. In order to help obtain a  
18 more uniform temperature gradient across the preform, the preform may be  
19 maintained at the aforementioned temperatures for a short period to allow the  
20 temperature to equilibrate.

21 Mold temperatures in the two-step process are generally below the glass  
22 transition temperature of the PLA resin, such as from about 30 to about 60°C,  
23 especially from about 35 to about 55°C. Sections of the mold such as the base  
24 where a greater wall thickness is desired may be maintained at even lower  
25 temperatures, such as from about 0 to about 35°C, especially from about 5 to  
26 about 20°C.

27 In the one-step process, the preform from the injection molding process is  
28 transferred to the stretch blow molding step, while the preform is at a  
29 temperature at which the preform becomes soft enough to be stretched and  
30 blown, again preferably above the  $T_g$  of the resin, such as from about 80 to about  
31 120°C, especially from about 80 to about 110°C. The preform may be held at that  
32 temperature for a short period prior to molding to allow it to equilibrate at that  
33 temperature. The mold temperature in the one-step process may be above or  
34 below the  $T_g$  of the PLA resin. In the so-called "cold mold" process, mold

1   temperatures are similar to those used in the two-step process. In the "hot mold"  
2   process, the mold temperature is maintained somewhat above the  $T_g$  of the resin,  
3   such as from about 65 to about 100°C. In the "hot mold" process, the molded part  
4   may be held in the mold under pressure for a short period after the molding is  
5   completed to allow the resin to develop additional crystallinity (heat setting).  
6   The heat setting tends to improve the dimensional stability and heat resistance  
7   of the molded container while still maintaining good clarity. Heat setting  
8   processes may also be used in the two-step process, but are used less often in that  
9   case because the heat setting process tends to increase cycle times.

10   Blowing gas pressures in either the one-step or two-step processes  
11   typically range from about 5 to about 50 bar (about 0.5 to about 5 MPa), such as  
12   from about 8 to about 45 bar (about 0.8 to about 4.5 MPa). It is common to use a  
13   lower pressure injection of gas in the preliminary radial stretch, followed by a  
14   higher pressure injection to complete the blowing process.

15   For the purposes of this invention, the terms "polylactide", "polylactic  
16   acid" and "PLA" are used interchangeably to denote polymers having repeating  
17   units of the structure  $-\text{OC}(\text{O})\text{CH}(\text{CH}_3)-$ , irrespective of how those repeating units  
18   are formed into the polymer. The PLA resin preferably contains at least 90%,  
19   such as at least 95% or at least 98%, by weight of those repeating units. The PLA  
20   resin used in this invention is typically a random polymer containing both D and  
21   L enantiomer repeating units. When a single-step ISBM process is used, the  
22   predominant enantiomer constitutes from 90-99.5% of the polymerized lactic acid  
23   units and the other enantiomer constitutes from 0.5 to 10% of the polymerized  
24   lactic acid units. Suitable enantiomer ratios for the single-step process include,  
25   for example, 92-98% of the predominant enantiomer and 2-8% of the other  
26   enantiomer, 94-98% of the predominant enantiomer and 2-6% of the other  
27   enantiomer or 95-97% of the predominant enantiomer and 3-5% of the other  
28   enantiomer. It is most preferred that the PLA resin contains predominantly  
29   polymerized L lactic acid units, but it is equally within the scope of the invention  
30   to use a PLA resin containing predominantly D lactic acid units.

31   The PLA resin may be a blend of PLA resins, in which the average  
32   enantiomer ratios are within the aforementioned ranges. In particular, blends of  
33   one resin having an enantiomer ratio of 70:30 to 95:5, especially from 80:20 to  
34   90:10, and another resin having an enantiomer ratio of 95:5 or greater, especially

1    97:3 or greater, are useful. The proportions of the constituent resins are selected  
2    to produce an average enantiomer ratio for the blend as a whole within the  
3    ranges described before. In some instances, the use of such a polymer blend is  
4    found to lead to improvements in properties such as reduced shrinkage and  
5    reduced strain whitening.

6       A preferred PLA resin is a polymer or copolymer of lactide.  $\alpha$ -hydroxy  
7    acids such as lactic acid, exist as two optical enantiomers, which are generally  
8    referred to as the "D" and "L" enantiomers. Either D- or L-lactic acid can be  
9    produced in synthetic processes, whereas fermentation processes usually (but not  
10   always) tend to favor production of the L enantiomer. Lactide similarly exists in  
11   a variety of enantiomeric forms, i.e., "L-lactide", which is a dimer of two L-lactic  
12   acid molecules, "D-lactide", which is a dimer of two D-lactic acid molecules and  
13   "meso-lactide", which is a dimer formed from one L-lactic acid molecule and one  
14   D-lactic acid molecule. In addition, 50/50 mixtures of L-lactide and D-lactide that  
15   have a melting temperature of about 126°C are often referred to as "D,L-lactide".  
16   Polymers of any of these forms of lactide, or mixtures thereof, are useful in this  
17   invention, provided that the PLA resin has the isomer ratio described above.

18       A preferred lactide is produced by polymerizing lactic acid to form a  
19   prepolymer, and then depolymerizing the prepolymer and simultaneously  
20   distilling off the lactide that is generated. Such a process is described in U. S.  
21   Patent No. 5,274,073 to Gruber *et al.*, which is incorporated herein by reference.

22       The PLA resin may further contain repeating units derived from other  
23   monomers that are copolymerizable with lactide or lactic acid, such as alkylene  
24   oxides (including ethylene oxide, propylene oxide, butylene oxide, tetramethylene  
25   oxide, and the like), cyclic lactones or cyclic carbonates. Repeating units derived  
26   from these other monomers can be present in block and/or random arrangements.  
27   Such other repeating units preferably constitute from 0 to 10%, especially from 0  
28   to 5%, by weight of the PLA resin. The PLA resin is generally devoid of such  
29   other repeating units.

30       The PLA resin may also contain residues of an initiator compound, which  
31   is often used during the polymerization process to provide control over molecular  
32   weight. Suitable such initiators include, for example, water, alcohols, glycol  
33   ethers, polyhydroxy compounds of various types (such as ethylene glycol,  
34   propylene glycol, polyethylene glycol, polypropylene glycol, glycerine,

1 trimethylolpropane, pentaerythritol, hydroxyl-terminated butadiene polymers  
2 and the like).

3 The PLA resin advantageously has a number average molecular weight of  
4 from about 80,000-150,000, especially about 95,000 to about 120,000, as  
5 measured by GPC against a polystyrene standard. The PLA resin  
6 advantageously exhibits a relative viscosity of about 3.4 to about 4.5, especially  
7 from 3.6 to about 4.2, as measured in methylene chloride at 30°C.

8 A particularly suitable process for preparing PLA by polymerizing lactide  
9 is described in U. S. Patent Nos. 5,247,059, 5,258,488 and 5,274,073. This  
10 preferred polymerization process typically includes a devolatilization step during  
11 which the free lactide content of the polymer is reduced, preferably to less than  
12 1% by weight, and more preferably less than 0.5% by weight. In order to produce  
13 a melt-stable lactide polymer, it is preferred to remove or deactivate the catalyst  
14 at the end of the polymerization process. This can be done by precipitating the  
15 catalyst or preferably by adding an effective amount of a deactivating agent to  
16 the polymer. Catalyst deactivation is suitably performed by adding a  
17 deactivating agent to the polymerization vessel, preferably prior to the  
18 devolatilization step. Suitable deactivating agents include carboxylic acids, of  
19 which polyacrylic acid is preferred; hindered alkyl, aryl and phenolic hydrazides;  
20 amides of aliphatic and aromatic mono-and dicarboxylic acids; cyclic amides,  
21 hydrazones and bis-hydrazone of aliphatic and aromatic aldehydes, hydrazides  
22 of aliphatic and aromatic mono- and dicarboxylic acids, bis-acylated hydrazine  
23 derivatives, phosphite compounds and heterocyclic compounds.

24 The PLA resin may be modified to introduce long-chain branching. This  
25 long-chain branching has been found to improve the melt rheology of the  
26 polymer, and in particular to improve melt strength. Various methods of  
27 introducing long-chain branching have been described, including copolymerizing  
28 lactide with an epoxidized fat or oil, as described in U. S. Patent No. 5,359,026, or  
29 with a bicyclic lactone comonomer, as described in WO 02/100921A1; treating the  
30 PLA resin with peroxide, as described in U. S. Patent Nos. 5,594,095 and  
31 5,798,435, and to use certain polyfunctional initiators in its polymerization as  
32 described in US Patent Nos. 5,210,108 and 5,225,521 to Spinu, GB 2277324 and  
33 EP 632 081. Recently, acrylic polymers and copolymers containing multiple  
34 epoxy groups have been found to be useful branching agents for PLA resins.

1 Examples of such polymers and copolymers are commercially available from  
2 Johnson Polymers, Inc. under the trade names Joncrys® 4368 and Joncrys® 4369.

3 The PLA resin can be compounded with additives of various types,  
4 including antioxidants, preservatives, catalyst deactivators, stabilizers,  
5 plasticizers, fillers, nucleating agents, colorants of all types and blowing agents.

6 In the preferred embodiment, in which clear bottles are produced, the PLA resin  
7 is preferably devoid of additives that cause the resin to whiten (due to  
8 crystallization) or become opaque. A preferred additive is a particulate material  
9 such as carbon black, which if used in very small quantities does not cause  
10 whitening or opacity, while aiding the ISBM (in particular the two-step) process  
11 by absorbing infrared radiation and increasing preform heating rates.

12 The PLA resin may be co-injected with a polymer that has barrier  
13 properties, in order to make a preform and resultant container having a barrier  
14 polymer layer that makes the container more resistant to moisture and other  
15 vapor transmission. Examples of polymers having suitable barrier properties  
16 include polyethylene or copolymers of ethylene, polypropylene or copolymers of  
17 propylene, polyvinylidene chloride or copolymers of vinylidene chloride, ethylene-  
18 vinyl alcohol copolymers, polyethylene terephthalate, polycarbonates, polyamides  
19 and similar polymers.

20 It is of particular interest to produce clear bottles using the invention.  
21 Clarity is conveniently expressed in terms of % haze, which can be measured  
22 according to ASTM D-1003. Bottles produced in accordance with the invention  
23 preferably have a haze of no greater than 20%, more preferably no greater than  
24 15% and even more preferably no more than 10%.

25 The following examples are provided to illustrate the invention but are  
26 not intended to limit the scope thereof. All parts and percentages are by weight  
27 unless otherwise indicated. Molecular weights are determined by GPC in  
28 tetrahydrofuran against a polystyrene standard.

29

30 **Example 1**

31 1.5 L bottles are prepared from various PLA resins in a two-step ISBM  
32 process as follows. Preforms having a length of 129 mm, an average diameter of  
33 23 mm and weights of 42-44 grams are injection molded by heating the resin to a  
34 temperature of 200-210°C and injecting it into a preform mold. The molding

1 conditions are optimized to produce minimal part stress and to produce clear  
2 parts free of haze. The molded preforms are cooled to room temperature before  
3 stretch blow molding in a separate step.

4 Stretch blow molding is performed on a laboratory scale machine capable  
5 of producing approximately 2400 bottles/hour at full rates. The preforms are  
6 heated with infrared lamps to a temperature of about 98-110°C, inserted into the  
7 mold, pre-blown at a pressure of about 10 bar (1 MPa), and then stretched and  
8 blown at a pressure of 38 bar (3.8 MPa). The mold temperature is 100°F (38°C),  
9 except at the base of the mold which is chilled to 40°F (4°C). Stretch ratios are:  
10 axial stretch ratio = 2.1; hoop stretch ratio=4.0; areal stretch ratio=8.4.

11 The PLA resins used are:

12 1. Resin 1, a copolymer of 96.5% L- and 3.5% D- lactide having a number  
13 average molecular weight of about 105,000.

14 2. Resin 2, a copolymer of 96% L- and 4% D-lactide having a number  
15 average molecular weight of about 105,000.

16 Under these conditions, Resins 1 and 2 process well at rates of 2300-2400  
17 bottles/hour to make good quality, clear bottles.

18

19 **Example 2**

20 Sixteen ounce carbonated soft drink bottles are prepared from various  
21 PLA resins in a two-step IBSN process as follows. Preforms having a length of  
22 68.2 mm, a reference inside diameter of 15.7 mm, a reference outside diameter of  
23 22.4 mm and a weight of ~24 grams are injection molded by heating the resin to a  
24 temperature of 205-225°C and injecting it into the preform mold.

25 Stretch blow molding is performed on a laboratory scale machine capable  
26 of producing approximately 1200 bottles/hour at full rates. The preforms are  
27 heated with infrared lamps to a temperature of about 85-90°C, inserted into the  
28 mold, pre-blown at a pressure of about 20 bar (2MPa), and then stretched and  
29 blown at a pressure of 38 bar (3.8 MPa). The mold temperature is 120°F (49°C),  
30 except at the base of the mold which is chilled to 40°F (4°C). Stretch ratios are:  
31 axial stretch ratio = 2.2; hoop stretch ratio=3.7; areal stretch ratio=8.1.

32 Preform temperatures are then varied to determine for each resin the  
33 range of preform temperatures at which good quality bottles can be prepared at  
34 the stated production rate. Bottle quality is evaluated by examining the bottles

1 for the appearance of stress whitening, thin walls at the base, thin side walls and  
2 the development of a resin slug at the center of the base.

3 The resins are as follows:

4 Resin 3: a copolymer of 96.8% L- and 3.2% D- lactide having a number  
5 average molecular weight of about 102,000 and a relative viscosity of 3.99.

6 Resin 4: a copolymer of 95.9% L- and 4.1% D- lactide having a number  
7 average molecular weight of about 103,500 and a relative viscosity of ~4.00.

8 Resin 5: a copolymer of 95.1% L- and 4.9% D- lactide having a number  
9 average molecular weight of about 101,000 and a relative viscosity of 3.6.

10 Resin 6: a copolymer of 95.7% L- and 4.3% D- lactide having a number  
11 average molecular weight of about 83,000 and a relative viscosity of 3.29.

12 Resin 7: a copolymer of 95.3% L- and 4.7% D- lactide having a number  
13 average molecular weight of about 80,000 and a relative viscosity of 3.23.

14 Good quality bottles are prepared using each of Resins 3-7. However,  
15 significant differences in processing windows are seen. Resins 3 and 4 exhibit  
16 the widest processing windows, both producing good quality bottles at preform  
17 temperatures from about 88-95°C. Resin 5, having a higher content of D-isomer  
18 and slightly lower molecular weight and relative viscosity, has a processing  
19 window from about 87-91.5°C, a range of about 4.5°C. Resins 6 and 7, which  
20 have lower D-isomer contents but lower molecular weights than Resin 5, also  
21 have processing windows of about 4.5-5°C.

22

### 23 Example 3

24 A particulate copolymer of 82.5% L- and 17.5% D-lactide is dry blended  
25 with a particulate copolymer of 98.6% L- and 1.4% D-lactide. Ratios of the  
26 starting materials are selected so the blend has an average ratio of L:D-  
27 enantiomer of 96.8:3.2.

28 One-liter straightwall bottles are prepared from various PLA resins in a  
29 two-step ISBM process as follows. Preforms having weights of ~29 grams are  
30 injection molded. The molded preforms are cooled to room temperature before  
31 stretch blow molding in a separate step.

32 Stretch blow molding is performed on a laboratory scale machine at a rate  
33 of approximately 1200 bottles/hour. The preforms are heated with infrared  
34 lamps to a temperature of about 83°C, inserted into the mold, pre-blown at a

1 pressure of about 5 bar (0.5 MPa), and then stretched and blown at a pressure of  
2 40 bar (4 MPa). The mold temperature is 100°F (38°C). Stretch ratios are: axial  
3 stretch ratio = 2.3; hoop stretch ratio=4.35; areal stretch ratio=10.0.

4 Ten of the bottles are dimensionally measured for height, major diameters  
5 and overfill volume after aging for 24 hours at ambient conditions. The bottles  
6 are then subjected to 100°F (38°C) and 100% relative humidity for 24 hours, and  
7 the dimensions are remeasured. The bottles show an average shrinkage of  
8 1.03%.

9 Bottles made in the same manner, except that a single PLA resin  
10 containing 96.8% of the L-enantiomer and 3.2% of the D-enantiomer is used,  
11 exhibit a shrinkage of 1.19% on the same test.

12 More bottles are made, this time using a blend of the same starting resins  
13 at ratios that produce an average ratio of L:D-enantiomer of 96:4 in the blended  
14 resin. These bottles exhibit a shrinkage of 1.16%. Bottles made using a single  
15 PLA resin having an L:D-enantiomer ratio of 96:4 exhibit a shrinkage of 1.32%.

16

17 It will be appreciated that many modifications can be made to the  
18 invention as described herein without departing from the spirit of the invention,  
19 the scope of which is defined by the appended claims.

## 1    WHAT IS CLAIMED IS:

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3    1.    An injection stretch blow molding process for making containers of a  
4    thermoplastic resin, in which a thermoplastic resin is molded into a preform, and  
5    the preform is mechanically stretched and blown in a container mold to stretch  
6    the preform axially and radially to form a container, wherein (1) the  
7    thermoplastic is a polylactic acid (PLA) resin which is (a) a copolymer having  
8    repeating L and D lactic acid units, in which either the L or D lactic acid units  
9    are the predominant repeating units, or (b), a blend of such copolymers, wherein  
10   the predominant repeating units in the copolymer or blend constitute 90-99.5% of  
11   the lactic acid enantiomer repeating units in the PLA resin or blend and (2) the  
12   product of axial and radial stretch ratios is from about 3 to about 17.5.

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14   2.    The process of claim 1, after the resin is molded into a preform, the  
15   preform is mechanically stretched and blown in a container mold after the  
16   preform is molded but before the molded preform is cooled to below the softening  
17   temperature of the resin.

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19   3.    The process of claim 1, wherein the containers are clear containers.

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21   4.    The process of claim 3 wherein the PLA resin has a number average  
22   molecular weight of 80,000-150,000, as measured by gel permeation  
23   chromatography using a polystyrene standard.

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25   5.    The process of claim 4 wherein the PLA resin has a relative viscosity, in  
26   methylene chloride at 30°C, of from 3.4 to 4.5.

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28   6.    The process of claim 5, wherein 92-99.5% of the lactic acid enantiomer  
29   repeating units in the PLA resin are of the predominant lactic acid enantiomer.

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31   7.    The process of claim 6, wherein 94-99% of the lactic acid enantiomer  
32   repeating units in the PLA resin are of the predominant lactic acid enantiomer.

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1 8. The process of claim 2, wherein the container mold is at a temperature  
2 below the glass transition temperature of the PLA resin.

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4 9. The process of claim 2, wherein the container mold is at a temperature  
5 above the glass transition temperature and below the melting temperature of the  
6 PLA resin.

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8 10. The process of claim 9, wherein the container is heat set in the container  
9 mold.

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11 11. The process of claim 2, wherein the PLA resin is co-injected with a barrier  
12 polymer to form a preform having at least one layer of a barrier polymer, and the  
13 preform is stretch blow molded to form a container having at least one layer of  
14 the barrier polymer.

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16 12. The process of claim 11, wherein the barrier polymer is a polyethylene or  
17 copolymer of ethylene, polypropylene or a copolymer of propylene, polyvinylidene  
18 chloride or copolymer of vinylidene chloride, an ethylene-vinyl alcohol copolymer,  
19 polyethylene terephthalate, a polycarbonate or a polyamide.

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21 13. The process of claim 1 wherein the preform is heated from below to above  
22 the glass transition temperature of the thermoplastic resin and then  
23 mechanically stretched and blown in a container mold.

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25 14. The process of claim 13, wherein the containers are clear containers.

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27 15. The process of claim 14 wherein the PLA resin has a number average  
28 molecular weight of 80,000-150,000, as measured by gel permeation  
29 chromatography using a polystyrene standard.

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31 16. The process of claim 15 wherein the PLA resin has a relative viscosity, in  
32 methylene chloride at 30°C, of from 3.4 to 4.5.

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1 17. The process of claim 16, wherein 92-99.5% of the lactic acid enantiomer  
2 repeating units in the PLA resin are of the predominant lactic acid enantiomer.

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4 18. The process of claim 17, wherein 94-99% of the lactic acid enantiomer  
5 repeating units in the PLA resin are of the predominant lactic acid enantiomer.

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7 19. The process of claim 13, wherein the container mold is at a temperature  
8 below the glass transition temperature of the PLA resin.

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10 20. The process of claim 13, wherein the PLA resin is co-injected with a  
11 barrier polymer to form a preform having at least one layer of a barrier polymer,  
12 and the preform is stretch blow molded to form a container having at least one  
13 layer of the barrier polymer.

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15 21. The process of claim 20, wherein the barrier polymer is a polyethylene or  
16 copolymer of ethylene, polypropylene or a copolymer of propylene, polyvinylidene  
17 chloride or copolymer of vinylidene chloride, an ethylene-vinyl alcohol copolymer,  
18 polyethylene terephthalate, a polycarbonate or a polyamide.

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20 22. The process of claim 13, wherein the container mold is at a temperature  
21 above the glass transition temperature and below the melting temperature of the  
22 PLA resin.

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24 23. The process of claim 2, wherein the PLA resin contains from 0-10% by  
25 weight of repeating units derived from a monomer that is copolymerizable with  
26 lactide or lactic acid.

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28 24. The process of claim 13, wherein the PLA resin contains from 0-10% by  
29 weight of repeating units derived from a monomer that is copolymerizable with  
30 lactide or lactic acid.

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