FURANOATE POLYESTER COMPOSITIONS INCORPORATING GLYCOLS YIELDING ESTER STERIC HINDERANCE

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ABSTRACT

This disclosure provides a novel container, poly(neopentyl-2,5-furandicarboxylate) (PNPGF) and for methods of use thereof.
FURANOATE POLYESTER COMPOSITIONS INCORPORATING GLYCOLS YIELDING ESTER STERIC HINDRANCE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of PCT patent application PCT/US16/017458, filed Feb. 11, 2016, which claims the benefit of priority to U.S. Provisional Application No. 62/116,226, filed Feb. 13, 2015, both of which are incorporated by reference herein in their entirety.

TECHNICAL FIELD

[0002] This disclosure relates to polyester beverage bottles such as PET carbonated soft drink bottles having improved barrier enhancement properties, and associated preforms and methods.

BACKGROUND

[0003] Polyethylene terephthalate (PET) containers have been widely used for packaging carbonated soft drinks (CSD), juice, water, and other beverages due to its combination of clarity and good mechanical properties. However, the relative susceptibility of PET to permeation by oxygen and carbon dioxide limits its application in smaller sized packages, as well as for the packaging of oxygen sensitive products. Consequently, there is a need in the packaging industry for further improvement of the gas barrier properties of PET.

[0004] Various technologies have been developed to enhance the barrier of PET against the permeation of small gas molecules. For example, gas barrier enhancement additives can be incorporated into PET in a monolayer configuration, to increase its modulus and gas barrier properties through an anti-plasticization mechanism. However, high levels of incorporation can degrade the PET and deteriorate its intrinsic viscosity (I.V.), especially when the additive contains functional groups that may react with PET.

[0005] Another approach to enhance the gas barrier properties of PET is to incorporate co-monomers in preparing the resin or blending the resin with other components. Examples include PET modified with isophthalate (IPA) co-monomer, blends or copolymers of polyethylene naphthalate (PEN) and PET, and the like. To achieve a moderate barrier enhancement (at least 2-fold), the modification typically requires a high percentage of co-monomers, which can adversely affect stretching properties of the PET and require new preform designs.

[0006] Early patent applications by Avantium (Furanix Technologies U. S. Patent Application 20110282020) and DuPont (U.S. Patent Application 2014020578) have employed 2,5-furan dicarboxylic acid to produce poly(ethylene-2,5-furan dicarboxylate) or PEF, and poly(trimethylene-2,5-furan dicarboxylic acid) or PTF, respectively, to improve barrier enhancement properties. Although both of these polyesters exhibit excellent gas barrier properties relative to commercial polyester resins such as poly(ethylene terephthalate) or PET, they crystallize slowly and do not exhibit the crystalline development characteristic of PET and its related compositions. Additionally, these polyesters, including PET, possess ester linkages that are prone to hydrolytic attack. In the presence of environmental stress cracking (ESC) agents such as aqueous caustic solutions and alkaline lubricants, these agents induce chain scission at the ester linkages, leading to a decrease in average chain molecular weight and lower mechanical resistance to creep and strength in the formed part.

[0007] It is believed the furan dicarboxylic acids such as 2,5- and 2,4-substituted diacids represent a novel platform on which to build the next generation of high performance polyester packaging resins which have excellent gas barrier characteristics that surpass PET. However, it is also believed that a glaring deficiency of PET, PEF, and PTF is the relatively low resistance to environmental stress cracking in the solid state and low hydrolytic stability in the melt state. The present invention preferably utilizes glycols that create steric hindrance about the ester linkage in the polyester chain to effectively block nucleophilic attack by water in the melt or the ESC agent in the solid polyester. Preferably, these glycols are symmetrically substituted to enhance the regularity and symmetry of chain structure to promote crystallization, which also benefits ESC performance. However, asymmetric glycols may be used to improve ESC performance without loss of loss generality in this invention.

SUMMARY

[0008] In its broadest concept, the present invention describes semi-crystalline polyesters, especially 2,4- and 2,5-furan dicarboxylic acid-based polyesters, comprising sterically hindered glycols such as 2-methyl propanediol, and most preferably symmetric sterically hindered glycols such as but not limited 2,2-dimethyl propanediol, 1,4-dihydroxybenzene, 1,4-benzene dimethanol, etc. offering an optimum range of steric hindrance to yield improved hydrolysis resistance compared to PET, with a glass transition temperature greater than about 60 degrees C., yet provide substantially economical esterification rates during the polyester synthesis reaction. Compared to terephthalic acid, the rate of esterification of furan-2,5-dicarboxylate will be faster due to its higher acidity and greater catalysis effect. The combination and polymerization of furanate diacids with sterically hindered glycols, especially symmetric sterically hindered glycols that express nucleation and crystallization on the forming process time scale described in this invention offer several key benefits that are highlighted below across a broad range of commercial applications.

[0009] This invention also describes formed articles produced from the aforementioned resin compositions, namely fibers, films (oriented and unoriented), and containers which may benefit from the enhanced functional barrier and hydrolysis resistance provided by the furanate polyesters described herein.

[0011] Water bottles comprised of bio-based PEF may not be lightweight to the extent of a semi-crystalline resin such as PET due to the lack of a reinforcing crystalline phase the enhances the mechanical performance properties of the bottle such as drop impact. Relative to PEF, the increased crystallinity provided by PNPGF will give rise to better drop impact performance.

[0012] Bottles for packaging still beverages and juices are expected to provide novel applications for the unique furanate polyester resin compositions described herein due to the lower O2 permeability and heat setting capabilities these resins provide. The isothermal crystallization kinetics shown in FIG. 1 for PNPF indicate that heat setting in the mold following heating from the glass can be accomplished under
stress at maximum rate at or below about 150°C. may yield a maximum rate of crystallization and some dimensional stabilization by annealing. It is believe an optimum range of in-mold thermal treatment for the stretch blow molded bottles will range between about 110°C to about 150 degrees C.

[0013] Carbonated soft drink (CSD) bottles ranging from about 100 mL to over 4.0 L using resins in the solution intrinsic viscosity (SIV) range of about 0.63 dL/g to over 1.0 dL/g using unmodified or reactivity modified (long-chain branched resins). Bottles in the middle and lower end of the volume range are especially applicable to this invention where the higher surface area to volume ratio of the package can benefit from the longer shelf life provided by the excellent CO2 gas barrier properties and low volumetric creep due to the enhanced crystallinity of bottles produced using the novel furanoate polyester resin compositions proposed herein. It is anticipated that by choosing appropriate preform injection or compression molding and stretch blow molding conditions (reheat or single-stage), polyester crystallinites may be controlled between 1 wt. % and up to 50 wt. % or more, with crystallinity distributions that may be tailored within the finish, neck, body sidewall, and base/gate regions of the bottle for specific optimization of package performance. For refillable bottle, the increase hydrolysis resistance afforded by the invention resin compositions should provide more refill cycles relative to PET, exceeding 25 or more trips or more depending upon the base bottle topological design (champagne, petaloid, etc.), thickness, thickness distribution, crystallinity, and crystallinity distribution.

[0014] The packaging of fermented beverages including wine, wine coolers, beers, and meads in the same size range as CSD bottles carbonated soft drinks where the low O2 and CO2 permeabilities and increased crystallinity provided by the disclosed furanoate polyesters of this invention could improve product shelf life and mechanical performance over similarly constructed packaging for PEF and PET.

[0015] 2. Cast, Blown and Solid-State Oriented Films

[0016] Amorphous and semi-crystalline furanicoxylate polyesters of this invention may be substituted for PEF in conventional and metallized barrier laminate films, especially where the furanicoxylate polyester has been biaxially oriented and metallized to provide significant shelf life enhancement due to greatly improved O2 barrier over standard PET-based laminate films. Monolayer or multilayer sheet or tubular cast or coextruded films that are subsequently monoxially oriented via machine-direction orientation (MDO processes) or biaxially oriented via tentering, or double bubble orientation of tubular films out of hot water, or following coextrude or infrared heating are potential processes for orienting the furanoate polyesters of the materials and films comprising this invention. Such orientation under high stress will impart high toughness, tensile strength, and improved gas barrier properties that are advantageous to flexible plastic packaging applications.

[0017] Protective packaging films are broadly classified and may range from laminated trapped bubble film (Bubble Wrap®) to biaxially oriented, super-tough heat shrinkable and/or heat set packaging films for overwrapping and protecting consumer goods, produced by the methods described in the preceding paragraph. In the case of cast or blown film sheet where orientation and heat shrinkability are limited by low stress melt processing, the improved gas barrier properties (relative to PET) inherent to the resins of this invention will still be expressed in the particular flexible packaging application produced via these processes.


[0019] The low spinning speed of carpet fibers and monofilaments (10 m/min to 2,000 m/min), and medium to high spinning speed apparel and specialty fibers (2,000 m/min to about 3,500 m/min) for PET generally do not exhibit appreciable stress-induced crystallization in the spinline at the low uniaxial stress levels characteristic of these commercial melt spinning processes. It is believed that for PNPF melt spun fiber will be primarily amorphous with developed orientation commensurate with strain rates and stresses developed upon cooling to the glass transition temperature of the resin (Tg=73 degrees C.). Crystalline development in the melt spun yarns will primarily be developed under high stress in subsequent drawing operations, where crystallinity development will proceed upon heating from the glass. According to FIG. 1, PNPF appears to crystallize slightly faster than PET in the temperature range between Tg and about 120 degrees C. For high-speed partially-oriented filaments and yarns (POY) exceeding about 3,500 m/min, crystallization in both resins may proceed via a stress-induced mechanism that is dependent upon both stress, cooling rate and supercooling. In any event, PNPF should provide a hydrolytically stable melt and resulting melt spun filaments for a variety of end uses such as monofilament, carpets, apparel, and specialty textile fabric applications where environmental stress cracking and breakdown must be avoided.

[0020] Spin-draw processed fibers. For spin draw yarn, multifilament yarns are spun from one or more spinnerettes in a manner similar to POY manufacturing processes except that the yarn is produced at higher spinning speeds coupled with intermediate drawing stage integrated in the process before take-up. This process facilitates increase stabilization of the filaments through controlled orientation and crystallization in a heated environment that may or may not employ process water or humidity to enhance polyester plasticization and stress development/crystallization during drawing. A comparison of crystallization rates for PNPFG and PET as shown in FIG. 1 suggest that upon heating from the glass in the spin draw process, the faster crystallization kinetics indicated for PNPFG may provide an advantage over PET.

[0021] Moreover, polyesters with increased hydrolysis resistance would lessen resin drying requirements prior to melt processing operations. For example, PET is typically dried for about 6-8 hours with 150 degrees C. air (dew point temperature of -40 degrees C.) and an air flow rate of about 1.0 cfm/lbm/hr to reach a preferred maximum residual moisture content of 50 ppm. For the furanoate-based polyesters, the drying conditions are essentially the same, but due to higher moisture diffusivities, drying times are extend to as long as 4-5 days to reach a preferred maximum moisture content of 35 ppm. A polyester resin such as PNPFG may offer the ability to increase the maximum residual moisture content in the resin prior to melt processing to take advantage of the lower hydrolysis rate in the melt provided by sterically-hindered, substituted glycol structure.

[0022] Additionally, greater hydrolytic stability of the resin in the melt will decrease IV loss in molded preforms, thereby leading to better stretch blow molding performance and final bottle mechanical properties such as reduced volumetric creep and better shelf life. Higher developed crystallinity in the bottle coupled with enhanced ESC per-
DetaIed DIsCriscriPtion

The procedures for the synthesis and subsequent analytical characterization of the novel polyester poly(neopentylene-2,5-furandicarboxylate) or PNPF and shaped articles (monolayer and multilayer films, fibers, and containers) produced therefrom are summarized below for a non-limiting example of the invention. Other compositions and embodiments may be considered for polyesters based upon 2,4-furandicarboxylic acid, its monoesters, or diesters without loss of generality of scope for this invention.

A. Synthesis of Poly(neopentylene-2,5-furandicarboxylate)

0.5 liter autoclave reactor was charged with 173.45 g of 2,5-furandicarboxylic acid (1.115 moles, internally prepared, 99% purity), 162.56 g neopentyl glycol (1.561 moles, Sigma-Aldrich, 99% purity), 0.157 g of a 25 wt. % aqueous solution of tetramethylammonium hydroxide (Sigma-Aldrich), 0.041 g of a an 85 wt. % aqueous solution of phosphoric acid (H3PO4), and 0.043 g of titanium tetrabutoxide [Ti(Obu)4, Sigma-Aldrich, 99% purity]. The temperature was raised to 200 degrees C. to commence esterification and was removed with a nitrogen flush by distillation as a liquid condensate.

B. Properties of Poly(neopentylene-2,5-furandicarboxylate)

Results from the thermal analysis of the PNPF polyester resin composition produced for this invention are summarized in Table 1 (attached), and are compared and contrasted against PET, PEI, and PTF.

The surprising result that is first noted from the data summary in Table 1 is the observation of a cold crystallization exotherm in the 10 degrees C./min second heat DSC scan for PNPF, which is not present in the thermal scans of the other furanate-based polyesters such as PEF and PTF. In fact, the thermal transitions observed in a 10 degrees C./min second heating scan for a commercial grade PET (Formula 1001) and PNPF indicates the two resins are reasonably close: glass transition temperature (80 degrees C. versus 72 degrees C.), cold crystallization enthalpy (31 J/g versus 33 J/g), cold crystallization peak temperature (166 degrees C. versus 152 degrees C.), melting enthalpy (32 J/g versus 31 J/g). With regard to the peak melting temperatures observed, PNPFG exhibits a 46 degrees C. lower temperature than PET. This lower temperature is surprising, and provides an advantage to melt processing and thermal stability that PET cannot provide.

Another surprising result for PNPFG was manifest in the resin's significantly broader molecular weight distribution. PET and PEF clearly demonstrate polydispersity indices characteristic of a most-probable distribution (PDI~2). The polydispersity index for PTF is close at 1.67, and was synthesized in the same reactor apparatus as the PNPFG polyester. The polydispersity index of PNPF was substantially higher: PDI~2.78. This higher PDI value indicates that rapid ester interchange may not be occurring in the PNPF polyester at the higher rate it is occurring in the other listed polyesters, and may provide evidence of the superior hydrolysis resistance of the PNPF polyester. This observation may also indicate that PNPF may not show the characteristic 0.03-0.08 dl/g drop in intrinsic viscosity that is typically experienced during the injection molding of performances, and may not require the same low level of moisture in the resin feed. PET is typically dried to 50 ppm moisture prior to injection molding, whereas PEF is typically dried to about 35 ppm to avoid excessive intrinsic viscosity decrease in the injection molded part. Though more testing is required to validate the impact of this result with regard to melt processing performance, it indicates that PNPF may not require the intensive drying to reach the low moisture levels require for PEF, especially if the melt time scale is not sufficient to allow significant ester hydrolysis to deplete the intrinsic viscosity of the molded part.
Monosodium salts of the respective comprising dicarboxylic acid have also been employed as efficient nucleating agents for polyesters. While not intending to be limited by the foregoing list, it is believed that any of the nucleating agents commonly employed for polyesters processed at melt temperatures exceeding 150 degrees C, but below about 300 degrees C. and are thermally stable within this range are suitable for the polyesters of the present invention, provided their critical nucleation size adequately accommodates and accelerates the nucleation rate for the polyesters of this invention. It is also believed that such nucleating agents may provide a more stable nucleus for PNPF to reduce the required supercooling for crystallization from the melt.

[0038] 2. Reactively Modified Compositions

[0039] Polyfunctional (F-3) reactive chain modification agents such as trimethyl propane (F-3), pentaerythritol (F-4), pyromellitie dihydride (F-4) are common examples of reactive, multifunctional chain extension and long chain branching agents used to modify polyester chain structure to induce changes to the rheological behavior and flow performance in the melt and rubbery plateau regimes of viscoelastic response. It is anticipated that reactive multifunctional reagents having a hydroxyl (carboxylic acid, ester, and epoxy reactive), carboxylic or anhydride (hydroxyl or amine reactive) are particularly favored chain modifying agents for the polyester resins declared herein.

[0040] Reactively modified polyester compositions involving the polyester resins described herein may crystallize to a slower and lesser extent than unmodified polyesters of similar base monomer composition. It is anticipated that such reactivity modified polyesters may have improved melt rheological characteristics (higher shear viscosity and melt strength, longer average relaxation times, broader relaxation spectra, etc.) that lead to enhanced processing characteristics in extrusion blow molding; preform injection molding; single-stage stretch blow molding; cast, blown and double bubble biaxially oriented films; machine-direction cast and oriented, and tenner oriented polyester films; and melt-spun fibers (low speed carpet to high-speed partially oriented polyester filaments), where rheological behavior and crystallization kinetics must be carefully tailored for optimal processing performance.

[0041] 3. Polyester Blends and Alloys

[0042] While it is anticipated that sterically hindered glycols may slow the esterification if located proximate to the ester group, but once reacted, it is believed these ester-flanking substituents, especially methyl groups, may provide increased hydrolysis resistance and slow ester interchange reactions in the melt. It is well-known that PET maintains a most-probable molecular weight distribution (MWD) in the melt due to rapid ester interchange reactions. It is further believed that sterically hindered glycols, especially with symmetric glycol substituents, as proposed in this invention will impede the rate of ester interchange reactions leading to molecular weight distributions which remain broader (PDI>2) in the polyester melt for a longer period of time than for those polyesters characterized by a most-probable MWD.

[0043] Consequently, the surprising molecular weight distribution results obtained with this novel polyester composition leads the inventors to the belief that the polyester compositions proposed herein may enable the formation of polyester block copolymers that are able to preserve a stable block structure for longer times in the melt, especially if the chain ends of the symmetrically substituted glycol-based polyester are substantially end-capped with carboxylic acid end groups. A preferred method to accomplish raising the carboxylic end group concentration for the symmetrically-substituted glycol based polyester would be to convert hydroxy chain ends in the polymer by condensing into the polymer melt a suitable anhydride, e.g. succinic anhydride.

[0044] Formed diblock or multiblock copolymers could be used as interfacial phase compatibilizers for polyester blends and multilayer coextruded and laminated films, fibers, and other multilayer formed articles. It is anticipated the polyester compositions described herein will contain glycol units that exhibit enough steric hindrance to block hydrolysis in the solid state, but not so much as to substantially inhibit the polycondensation rate in either the melt of solid states. Accordingly, other prior art polyesters, such as PET, PEN, PEF, PTF, and PBF could benefit from a blending strategy utilizing the more hydrolysis resistant polyesters described by this invention. Blend compositions ranges for the polyesters described herein would range between 100.0 wt % and 0.1 wt %.

[0045] 4. Moisture Conditioning of Formed Articles in the Solid State

[0046] In two-stage stretch blow molding processes, moisture conditioning may be used to plasticize the polymer to improve stress self-leveling and to promote crystallization during stretch blow molding. Conditioning the injection molded preforms in a controlled moisture-laden environment at a prescribed temperature prior to stretch blow molding will enhance chain mobility and nucleation rate during heating and stretch blow molding processing above the polymer glass transition.

[0047] E. Bottle Production

[0048] Containers or bottles may be produced using single-stage injection or compression molded preforms stretch blow molded on the cooling trajectory, as well as two-stage processes involving compression molded preforms. Injection molded preforms followed by reheat stretch blow molding of the preforms, or various processing combinations thereof. Bottle inflation may employ axial stretch ratios between 1.5 and 6.0, hoop stretch ratios between 1.5 and 8.0, yielding areal stretch ratios in the range of 2.2 to 48.0, with stretching/molding temperatures situated between 74 degrees C. and 160 degrees C. Preform residual molded-in stresses should be maintained with a fringe order of less than 8, preferably less than 4, and most preferably less than about 2. Preforms may possess an end cap geometry varying from hemispherical to conical, including end cap geometries with inflected continuous surfaces transitioning from the preform body to the injection molding gate to effect proper heating of the preform end cap to obtain an optimal thickness distribution in the stretch blow molded bottle base.

[0049] Flanking substituents on the glycol moiety leading to steric hindrance of hydrolysis may provide enhanced protection of the polyester from environmental stress attack, especially from contact with aqueous caustic solutions. It is believed that bottles produced using the polyesters described herein will provide increased caustic stress cracking resistance for non-returnable and refillable bottles, especially those bottles employed in the packaging of carbonated soft drinks and other pressurized beverage solutions.
Some of the embodiments of the present invention comprises of the following:

A container comprising poly(neopentylenylene-2,5-furandicarboxylate) or PNPGF.

A container according to claim 1, wherein an outer layer defining an exterior surface and an inner layer defining an interior surface and interior space, wherein the outer layer comprises PNPGF.

A container according to claims 1 and 2, wherein a multilayer co-polyester exists further wherein said co-polyester comprises: poly(neopentylenylene-2,5-furandicarboxylate) or PNP; poly(ethylene-2,5-furandicarboxylate) (PEF); poly(trimethylene-2,5-furandicarboxylate) (PTF); poly(butylene-2,5-furandicarboxylate) (PBF); poly(isosorbide-2,5-furandicarboxylate) (PISF); poly(isoidide-2,5-furandicarboxylate) (PIIT); poly(isomannide-2,5-furandicarboxylate) (PIMF); poly(neopentyl-2,5-furandicarboxylate) (PNPGF); poly(ethylene-2,5-furandicarboxylate) with 10 mol. % 1,8-naphthalene dicarboxylate (PEF-PEN); poly(1,4-phenylene-2,5-furandicarboxylate) (PCHF); poly(1,2-dimethylphenylene-2,5-furandicarboxylate) (PDMFF); and any combinations thereof, mixtures thereof, or copolymers thereof.

A container according to claims 1 and 2, wherein each of the outer layer and the inner layer independently has a thickness from about 0.01 mm to about 2.5 mm.

A container according to claims 1 and 2, wherein either one or both of the outer layer and the inner layer comprises PNPGF.

A container according to claims 1 and 2, wherein at least one of the outer layer, or the inner layer further comprises a colorant, a UV blocker, a lubricant, a slip agent, a processing aid, an antioxidant, an antimicrobial agent, a thermal stabilizer, or any combination thereof.

A packaged beverage comprising the container according to claims 1 and 2 and a beverage disposed in the interior space of the container.

A preform comprising:

a) an outer layer defining an exterior surface and an inner layer defining an interior surface, wherein the outer layer comprises a polyester and the inner layer comprises PNPGF.

A method of making a container, the method comprising:

b) providing a preform according to claim 9; and

c) stretch blow-molding the preform to provide the multilayer container.

A 2,5-furandicarboxylate polyester or co-polyester polymer selected from poly(neopentyl-2,5-furandicarboxylate) (PNPGF); poly(ethylene-2,5-furandicarboxylate) with 10 mol. % 1,8-naphthalene dicarboxylate (PEF-PEN); poly(1,4-phenylene-2,5-furandicarboxylate) (PCHF); and poly(1,2-dimethylphenylene-2,5-furandicarboxylate) (PDMFF).

Table 1 depicts Proton and Carbon-13 NMR Spectra for PNPF.

Values or ranges may be expressed herein as “about”, from “about” one particular value, and/or to “about” another particular value. When such values or ranges are expressed, other embodiments disclosed include the specific value recited, from the one particular value, and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. In another aspect, use of the term “about” means ±20% of the stated value, ±15% of the stated value, ±10% of the stated value, ±5% of the stated value, or ±3% of the stated value.

In any application before the United States Patent and Trademark Office, the Abstract of this application is provided for the purpose of satisfying the requirements of 37 C.F.R. §1.72 and the purpose stated in 37 C.F.R. §1.72(b) “to enable the United States Patent and Trademark Office and the public generally to determine quickly from a cursory inspection the nature and gist of the technical disclosure.” Therefore, the Abstract of this application is not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Moreover, any headings that are employed herein are also not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Any use of the past tense to describe an example otherwise indicated as constructive or prophetic is not intended to reflect that the constructive or prophetic example has actually been carried out.

Those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments disclosed herein without materially departing from the novel teachings and advantages according to this disclosure. Accordingly, all such modifications and equivalents are intended to be included within the scope of this disclosure as defined in the following claims. Therefore, it is to be understood that resort can be had to various other aspects, embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to one of ordinary skill in the art without departing from the spirit of the present disclosure or the scope of the appended claims.

Applicants reserve the right to proviso out any selection, feature, range, element, or aspect, for example, to limit the scope of any claim to account for a prior disclosure of which Applicants may be unaware.
Table 1

Polymer of FDCA and NPG, RK-3645-50, 1D $^1$H---[TFA-d]

![Chemical Structure of Polymer 1H](image1)

Polymer of FDCA and NPG, RK-3645-50, 1D $^{13}$C---[TFA-d]

![Chemical Structure of Polymer 13C](image2)
What is claimed is:

1. A container comprising poly(neopentylene-2,5-furandicarboxylate) or PNPGF.

2. A container according to claim 1, wherein an outer layer defining an exterior surface and an inner layer defining an interior surface and interior space, wherein the outer layer comprises PNPGF.

3. A container according to claims 1 and 2, wherein a multilayer co-polyester exists further wherein said co-polyester comprises: poly(neopentylene-2,5-furandicarboxylate) or PNPGF; poly(ethylene-2,5-furandicarboxylate) (PEF); poly(trimethylene-2,5-furandicarboxylate) (PTF); poly(butylenedimethylene-2,5-furandicarboxylate) (PBDF); poly(isosorbide-2,5-furandicarboxylate) (PISF); poly(isosidode-2,5-furandicarboxylate) (PIIF); poly(isosaminate-2,5-furandicarboxylate) (PIMP); poly(neopentylene-2,5-furandicarboxylate) (PNNPGF); poly(ethylene-2,5-furandicarboxylate) with 10 mol. % 1,8-naphthalenedicarboxylate (PEF-PEN); poly(1,4-phenylene-2,5-furandicarboxylate) (PCHF); poly(1,2-dimethylphenoxylenedimethylene-2,5-furandicarboxylate) (PDMFF); and any combinations thereof, mixtures thereof, or copolymers thereof.

4. A container according to claims 1 and 2, wherein the container is stretch blow-molded.

5. A container according to claims 1 and 2, wherein each of the outer layer and the inner layer independently has a thickness from about 0.01 mm to about 2.5 mm.

6. A container according to claims 1 and 2, wherein either one or both of the outer layer and the inner layer comprises PNPGF.

7. A container according to claims 1 and 2, wherein at least one of the outer layer, or the inner layer further comprises a colorant, a UV blocker, a lubricant, a slip agent, a processing aid, an antioxidant, an antimicrobial agent, a thermal stabilizer, or any combination thereof.

8. A packaged beverage comprising the container according to claims 1 and 2 and a beverage disposed in the interior space of the container.

9. A preform comprising:
   a. an outer layer defining an exterior surface and an inner layer defining an interior surface, wherein the outer layer comprises a polyester and the inner layer comprises PNPGF.

10. A method of making a container, the method comprising:
   a. providing a preform according to claim 9; and
   b. stretch blow-molding the preform to provide the multilayer container.

11. A 2,5-furandicarboxylate polyester or co-polyester polymer selected from poly(neopentylene-2,5-furandicarboxylate) (PNPGF); poly(ethylene-2,5-furandicarboxylate) with 10 mol. % 1,8-naphthalenedicarboxylate (PEF-PEN); poly(1,4-phenylene-2,5-furandicarboxylate) (PCHF); and poly(1,2-dimethylphenylenedimethylene-2,5-furandicarboxylate) (PDMFF).

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